

UNIVERSITY OF PRETORIA

DOCTORAL THESIS

Analysis of biodiesel by SFC×GC

5

by

Daniel MALAN

Submitted in partial fulfilment of the requirements for the
degree

10

Doctor of Philosophy

In the Faculty of Natural & Agricultural Sciences
University of Pretoria
Pretoria

15 July 2019

¹⁵ **Declaration of Authorship**

I, Daniel MALAN, declare that the thesis, which I hereby submit for the degree PhD (Chemistry) at the University of Pretoria, is my own work and has not previously been submitted by for a degree at this or any other tertiary institution.

SIGNATURE:

²⁰

DATE:

"Learning is a peculiar compound of memory, imagination, scientific habit, accurate observation, all concentrated, through a prolonged period, on the analysis of the remains of literature.

²⁵ *The result of this sustained mental endeavour is not a book, but a man."*

Mark Pattison

UNIVERSITY OF PRETORIA

Abstract

Natural and Agricultural Sciences
30 Department of Chemistry

Doctor of Philosophy

Analysis of biodiesel by SFC×GC

by Daniel MALAN

The Thesis Abstract is written here (and usually kept to just this page). The page is
35 kept centered vertically so can expand into the blank space above the title too...

Acknowledgements

I gratefully acknowledge my supervisor, Prof Egmont Rohwer, who had the faith in me to invite me to take on the project, and the patience to wait for me to respond and the patience to wait for me to finish. I am extremely grateful for the funding he supplied at the beginning of the project, when funding was a real problem.

Dok Fanie (Dr SJ van der Walt) who was appointed as my co-supervisor, but was also my predecessor, was willing to lend an ear and encourage, supply new ideas.

The various Deans who allowed me to re-register every year.

I acknowledge my fellow students,

• Kobie Smit lent a kind ear to the laments, and helped me feel less alone.

• Marc Bouwer, whose youthful energy proved to be highly contagious, spent hours in front of the whiteboard with me, helping to clarify thoughts and understanding basic science.

• Elize Smit, who set me such a good example of academic performance. Thank goodness I didn't try to follow it.

• Linda Pretorius, whose PhD challenges made me grateful for the simplicity of my project.

• Nadine Broodryk for all the conversations.

• MY office mates, in no particular order: Sifiso Nsibande, Madelien Wooding, Kedibone Mashala, Portia Makhubela, Chiedza Munyeza, Amanda ..., Margaux Lim-a-Tock,

My father, Danie Malan, spent a lot of energy and time on being an instrument maker for me.

My mother, Retha Malan, made sure that feeding and dressing myself during this time was as simple as possible.

Of course the project would not have been possible without the assistance from the technical team at the University of Pretoria:

• Our instrument maker, Nico van Vuuren, whose excellent work inspired me to create designs worthy of that quality of work.

• My thanks to David Masemula, who maintained the supply of gas cylinders.

• Yvette Naudé has been a most kind and helpful lab manager.

• Naomi Steenkamp is the most quietly effective financial administrator known to man. Through her services purchasing supplies was a painless exercise.

• Annetjie Kok and Ria Swart were our kindest

• Antoinette ??insert surname of the Centre for Microscopy and Microanalysis at the University of Pretoria provided invaluable aid in performing the SEM images.

For Sunil Patel, who, in true hacker spirit, made the L^AT_EXtemplate this document is based on freely available.

Our commercial suppliers also need acknowledgement. Beyers at Chemetrix, who spent effort in keeping our outdated HP instrumentation running. For Agilent,

who supplied us with an excellent used instrument at a nominal cost. Restek, for free columns. Reynard Heymans from FLIR recorded thermal videos of the instrument in action without asking for a cent of money. For Neil Frame from D.C. Wort, who
80 supplied me with free material and offered valuable advice.

For Barbara Lotze, for whose support I will be eternally grateful.

My mental health team who kept me sane. Johan Erasmus, whose professional psychological help first guided me through clinical depression, and then was crucial in getting me unstuck. Maria Ramaahlo at the Disability Unit was the first person to
85 offer concrete help with ADHD. Dr GP Grobler, my competent psychiatrist, always offered interesting conversations, despite his limited time. whom I had . Dr Zuleikha Ahmed of Student Support treated me with the utmost kindness, even when I was extremely angry. Dr Erna Gerryts, whose conversations brought me back to reality. And of course the innumerable staff members of Virgin Active Health Clubs who
90 kept the gym going.

"Works well when under constant supervision and cornered like a rat in a trap."

Sasol Fuel, who saw the need for expertise, and started acting as a major funding source. This freed up so many resources.

The financial assistance of the South African National Energy Research Institute
95 towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to SANERI.

Contents

	Declaration of Authorship	iii
	Abstract	vii
100	Acknowledgements	ix
	1 Introduction: Climate, fuel, and biodiesel	1
	1.1 Energy, fuel and the atmosphere	1
	1.2 Carbon footprints and carbon neutrality	5
	1.3 Internal combustion engines.	7
105	1.3.1 Scaling and efficiency	7
	1.3.2 Engine design and thermodynamic cycles.	8
	Otto engine and Otto cycle	9
	Diesel Cycle	10
	Gas turbines and the Brayton Cycle	11
110	1.3.3 Noxious pollution from internal combustion engines.	12
	Unburnt fuel	12
	Contaminants and additives.	13
	Side-reactions	13
	1.3.4 Mitigating pollution from internal-combustion engines.	13
115	Fuel formulation	14
	Exhaust gas cleanup	14
	Engine management	14
	Efficiency implications	14
120	1.3.5 Avoiding pollution from internal-combustion engines	15
	Electrification	15
	Carbon-neutral fuels	16
	1.4 Biofuels	16
125	1.4.1 Bio-gas	17
	1.4.2 Bio-ethanol	17
	Brazilian ethanol	18
	US maize	19
	1.4.3 Fischer-Tropsch fuel from biomass	19
	1.4.4 Refined vegetable oil: "Green diesel"	19
	1.4.5 Biodiesel	19
130	1.5 The significance of biodiesel and its quality control.	20
	1.6 Conclusion: the role of chromatography.	21
	2 Introduction: Carbon dioxide and chromatography	23
135	2.1 The chemical industry	23
	2.1.1 "Green chemistry"	25
	2.1.2 Carbon dioxide as a green chemical	26

2.2	Extractions using carbon dioxide	27
140	2.2.1 Commercial extractions	27
	Plant oils	27
	Hops	27
	Coffee	27
145	2.2.2 Analytical Extractions	28
	2.2.3 Why carbon dioxide?	28
	Modifiers	30
	Practical extractions	30
145	2.3 Supercritical Fluid Chromatography	31
	2.3.1 SFC and FID	32
	2.3.2 SFC×GC	34
150	3 Literature survey	37
	3.1 SANS 1935	37
	3.1.1 Subsection 1	37
	3.1.2 Subsection 2	37
	3.2 SFC	37
	3.3 Fast Gas Chromatography	37
155	4 Instrumentation: Supercritical Fluid Chromatography	39
	4.1 SFC	39
	4.2 Mobile phase	39
	4.3 Pump	40
	4.3.1 Pressure control system	41
	4.3.2 Modifier Control	42
160	4.4 Sample injection	43
	4.4.1 Column	44
	4.4.2 Stopped-flow	45
	4.5 Pressure Relief	46
	4.6 Detector	49
165	5 Instrumentation: Fast temperature programmed gas chromatography	51
	5.1 Speed of analysis	51
	5.2 Fast gas chromatography theory	52
	5.3 Temperature programming	54
	5.4 Temperature ramp rates	54
170	5.4.1 Resistive heating	55
	5.5 Calibration	57
	5.5.1 Heating control and temperature programming	57
	5.5.2 Temperature uniformity	57
	Resistivity's dependence on temperature	57
175	Thermal conduction	57
	Radiation	58
	Convection	58
	Examining thermal uniformity by imaging	58
	5.5.3 Temperature calibration	60
180	5.5.4 Thermocouple Welding	61
	5.5.5 Termocouple probe construction	62
	5.5.6 Thermocouple interfacing	62
	5.5.7 Calibration procedure	65

	5.5.8 Cold spots	65
185	5.5.9 Cold column	67
	Cryogen supply	68
	5.5.10 Column mounting	71
	5.5.11 Heating control	71
	Temperature monitoring	77
190	PID tuning	77
	Heating rates	78
	Cooling rates	78
	5.6 Detector	78
	5.7 Data acquisition and control software	79
195	5.8 Data capture	79
	5.9 Data visualization	79
	6 Investigating biodiesel feedstock by SFC×GC	83
200	6.1 Main Section 1	83
	6.1.1 Subsection 1	83
	6.1.2 Subsection 2	83
	6.2 Main Section 2	83
	7 Application: Analysis of biodiesel	85
205	7.1 Main Section 1	85
	7.1.1 Subsection 1	85
	7.1.2 Subsection 2	85
	7.2 Main Section 2	85
	8 Conclusion	87
210	8.1 General	87
	8.2 Suggested design improvements	87
	8.2.1 Four-wire resistance measurement	87
	8.2.2 Legs heating and cooling integrated in detector and inlet	87
	8.2.3	87
	8.2.4 Subsection 1	87
	8.2.5 Subsection 2	87
215	8.3 Main Section 2	87
	Bibliography	89

List of Figures

	1.1 The Otto cycle	9
220	1.2 The Diesel cycle	10
	1.3 The Brayton cycle	12
	1.4 Transesterification	20
	2.1 Cyanocobalamin	24
225	2.2 The carbon dioxide phase diagram	29
	2.3 SFE system diagram	31
	2.4 SFC system diagram	32
	2.5 FID diagram	33
	4.1 Filling a CO ₂	40
230	4.2 A process control system	42
	4.3 A cutaway diagram of the mixing chamber	43
	4.4 Schematic diagram of the injection valve	44
	4.5 Schematic diagram of a continuous-flow valve	45
	4.6 A diagram of a integral restrictor	47
	4.7 A electron microscope photo of a restrictor orifice	47
	4.8 A electron microscope photo of a blocked restrictor orifice	48
235	5.1 Schematic diagram of a the chromatograher's trilemma	53
	5.2 A temperature-rate table from the Agilent7890B data sheet	54
	5.3 Coaxial heater resistance heater	56
	5.4 A photograph of the setup used to record the thermal video	59
	5.5 A thermograph of the coaxial heater at temperature	59
240	5.6 Welding process schematic	62
	5.7 Fine-wire welder	63
	5.8 A microphoto of a thermocouple twist ready to be welded	63
	5.9 A cartoon explaining how to construct a long, thin thermocouple probe	64
	5.10 Calibration curve of the coaxial heater	66
245	5.11 Measurement curve of the coaxial heater	66
	5.12 Manifold dimensions	69
	5.13 Manifold assembly	70
	5.14 Coolant reservoir	72
	5.15 Technical drawing of coaxial heater mounting rails	73
250	5.16 Technical drawing of coaxial heater mounting	74
	5.17 Technical drawing of coaxial heater mounting	75
	5.18 Technical drawing of coaxial heater mounting	76
	5.19 Effect of controller tuning	77
	5.20 Heating rate illustration	78
255	5.21 A 2D SFC×GC chromatogram	80

List of Tables

List of Abbreviations

EROEI	Energy returned on energy invested.
LCA	Life Cycle Analysis
LAH	List Abbreviations Here
WSF	What (it) Stands For
UNFCCC	United Nations Framework Convention on Climate Change
IPCC	Intergovernmental Panel on Climate Change
CCGT	Combined cycle gas turbine
HPLC	High performance liquid chromatography
GC	Gas chromatography
SFC	Supercritical fluid chromatography
CCGT	Combined cycle gas turbine
CCGT	Combined cycle gas turbine

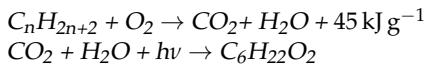
Physical Constants

Constant Name $Symbol = ConstantValue$ with units

List of Symbols

a	distance	m
P	power	$\text{W} (\text{J s}^{-1})$
ω	angular frequency	rad

For/Dedicated to/To my...



Hydrocarbons give heat and sunshine
makes sugar

1

Introduction: Climate, fuel, and biodiesel

1.1 Energy, fuel and the atmosphere

Industrialized societies depend on reliable sources of energy. For the purpose of 265 this discussion, the main types of energy can be counted as electricity and fuels, although they are interconvertible. Fuels for industrialized societies are predominantly found as underground mineral deposits, from where they are extracted by mining or drilling. They are found as solids, liquids and gases, which the energy industry refers to as *coal*, *crude oil*, and *natural gas*. Because these fuels are of biological origin, deposited during previous geological eras, and then metamorphosed and 270 preserved by geological processes, these fuels are commonly referred to as ‘fossil fuels’.

The large-scale exploitation of fossil fuels started in the middle of the 18th century, when the plentiful coal from the coalfields of Great Britain drove a development 275 that is known to history as the Industrial Revolution. This development is closely associated with steam engines (Rosen 2012). The use of crude oil started in the middle of the 19th century, and is associated with the development of the automobile (Watts 2005, p. 42). The use of natural gas started in the middle of the 20th century and is associated with the introduction of gas-fired central heating in 280 for homes in cold climates (Hanmer and Abram 2017) Fossil fuels also serve as feedstock to the chemical industry, but that topic lies outside the scope of this discussion.

There is no doubt that the use of fossil fuels as an energy source greatly improved the human lot. The mechanization of agriculture and the easy distribution of food by motorized transport have eliminated famine as a natural disaster (Angelis et al. 285 2007). The distribution of medical supplies by motorized transport and the rapid deployment of medical personnel have limited the impact and spread of epidemics (Ministere de la santé 2018). Heating and cooling of buildings have increased the habitable zone on earth. Artificial light has increased the hours available for mental activity, in particular extending the reach of entertainment, art and education.

However, in the context of chemistry, the uncontrolled use of fuels has at least 290 two major problems.

The first problem with fossil fuel is that it is finite. There is only a certain amount of fossil fuel on earth. If all of it is extracted it will no longer be a reliable source of energy, and the existence of industrialized societies and the complex civilizations

295 that depend on them will be in jeopardy. It is tempting to think that civilizations would have the foresight to prepare for such an eventuality, but the historical record shows that societies can collapse when at the height of their powers (Diamond 2006).

300 The second problem with fuels is that they produce pollution wherever they are produced, processed, transported and used. Pollution is injurious to the health and well-being of individuals, societies and nature. If pollution is serious enough, it not only degrades society and the environment, but also negates the benefits brought by the application of energy: modern hospitals are energy-intensive, but if they are filled with victims of pollution there is no nett benefit.

305 The first approach to pollution from fuels has been to ignore it. Pictures from the early industrial revolution shows English towns coated with soot and choked with smoke (Flick 1980), and rivers became toxic sewers (Halliday 2001).

310 The development of public health, social responsibility (Sreter 2003) and an embryonic environmental movement (Williams 1965) lead to political pressure for the implementation of pollution controls, which governments gradually introduced and increased in strictness.

The first generation of pollution control offered essentially two options: concentrate or dilute.

315 I will illustrate these two options using a typical South African coal-fired power station. In such a power station coal is burned to produce heat, which converts liquid water into high-pressure steam. The steam is allowed to expand through a turbine, which converts the energy in the steam into rotary motion, which is used to turn an alternator that produces an electric current by rotating a set of electrical conductors in a magnetic field. The furnaces of such a power station produce a flow of waste. This waste is an *aerosol*: finely divided solids suspended in a mixture of gases.

320 The solid part is typically separated from the gas-phase part by filter bags and electrostatic precipitators: the collected material is known as *fly ash*. The gas-phase part might be sent through scrubbers to remove some of the gas-phase pollutants, capturing it in a solid form. The solid part of the power station's furnace waste has now been concentrated. It is transported to a storage site, where it is stored indefinitely. It goes without saying that concentrated pollutants should be encapsulated during storage in some way, otherwise they just become more sources of pollution.

330 The gas-phase part of the pollutant is handled by diluting it. The outlet for the gas-phase stream of waste is through a tall stack, which ends high above ground level¹. At this altitude the wind is strong and steady, which rapidly carries the gases and remaining aerosols away and disperses them.

335 The dilution of pollutants might seem like an abdication of responsibility, but it is an reasonable response to pollution. At low enough concentrations pollutants that enter the biosphere are broken down by sunlight and microbes which render it harmless. This makes dilution a reasonable first attempt at controlling pollution.

340 The devil is, of course, in the detail. For example, mercury that find its way into the environment is eventually converted by microbes to methyl mercury, which concentrates in aquatic animals. All rivers in the continental USA are now polluted by airborne mercury that originate from coal-fired power stations (Wentz et al. 2014). Some persistent organic pollutants, which also concentrate in the food chain, originate in fuel combustion. So while dilution was a reasonable first attempt at controlling pollution, it it certainly not the final answer.

¹The chimneys of those sooty Victorian towns were not there to disperse the smoke, but to create a 'draft', a flow of air created by the buoyancy of hot air. The better the draft, the more efficient the fire.

The majority of fuels provide their energy as heat, which can be converted into useful work. This heat is obtained by combining the chemical compounds found in the fuel with atmospheric oxygen to form compounds with lower internal energy.
345 The maximum amount of work that can be extracted from a given fuel can be estimated by examining the Gibbs free energy equation:

$$\Delta G = \Delta H - T\Delta S \quad (1.1)$$

For a given compound fuel compound, ΔH is determined by the difference in enthalpy of formation of the product waste compounds and the enthalpy of formation
350 of the reactant fuel compounds. Since the reactant fuel compounds are given, ΔH is maximized by having product compounds with very low enthalpies of formations.

To maximize ΔS , the products should be as disordered as possible. This implies that *gas-phase* products composed of *small molecules* will yield more work.

The temperature T should also be as high as possible.

355 Because the industrial machinery in economically competitive, capital-intensive industries are highly efficient, the maximum amount of energy is extracted from their fuels for the lowest cost. Following Gibbs, the major compounds left over after extracting the energy from a fuel should have very low enthalpies of formation and be in the gas phase at the temperature of the process.

360 Because all fuels contain carbon as a major component, the extraction of energy yields compounds containing carbon. Most fuels also contain hydrogen. Reacting these fuels with the oxygen in air to extract maximal work will therefore yield water (H_2O) and carbon dioxide (CO_2).

(Of course the argument is not that Victorian engineers designed steam engines
365 using the Gibbs energy equation, but the variation-selection process (Vincenti 1990, Chapter 8) by which engineering improvements accrue would inevitably drive the development of heat engines fuelled by fossil fuels to emit large quantities of carbon dioxide gas.)

Water is of course not a pollutant at all, and carbon dioxide is only toxic at very
370 high concentrations, and therefore, for most of the industrial era, carbon dioxide was easily dealt with by diluting it in the atmosphere, where it is also naturally present at low levels. To the extent that carbon dioxide was considered a pollutant it was assumed that it would be absorbed by the biosphere.

Photosynthesis, the process by which green plants capture the energy from sun-
375 light to live and grow, does indeed remove carbon dioxide from the atmosphere, and an elementary model of the carbon cycle that assumes stability would seem to indicate that excess carbon dioxide in the atmosphere would be captured by photosynthesis and sequestered, leaving the carbon dioxide concentration in the atmosphere stable. Of course this model contains testable assumptions, which scientists could,
380 and did, test.

The most famous of these tests is probably the “Keeling Curve” (Harris 2010). This is a continuous record of measurements of concentration of atmospheric carbon dioxide in the pristine air of the Pacific Ocean. This record starts in 1958 and shows that the carbon dioxide concentration of the atmosphere is increasing.

385 Paleoclimatologists have studied the hypothesis that the carbon dioxide concentration is stable over time. Not only have they found that the carbon dioxide concentration is *not* stable, they have also determined that the pre-industrial concentration of atmospheric carbon dioxide was lower than it was in 1958 (Petit et al. 1999).

390 So it is clear that the carbon dioxide concentration in the atmosphere is rising because of the biosphere is not absorbing all the carbon dioxide produced by the combustion of fossil fuels.

The projected concentration of carbon dioxide in the atmosphere is, however, still not at or even near toxic levels, which might make the continued dilution of carbon dioxide in the atmosphere seem a viable disposal method.

395 Emitted gases, however, do not only have chemical properties and biological impacts, they also have physical properties. Of concern for the current discussion is carbon dioxide's absorbance of electromagnetic radiation, in particular the radiation arriving from the sun, and the radiation from the earth's surface out to space, both which must pass through the atmosphere. A molecule can absorb parts of this radiation by having its electrons excited, or by changing its vibration. Carbon dioxide is electronically very stable, and therefore absorbs only extreme ultraviolet radiation, just like the major gases in the atmosphere, molecular nitrogen and molecular oxygen. However it poorly absorbs near ultraviolet and visible light, in which is it also similar to the major gases. Because there is a dipole moment between the carbon atom and the oxygen atoms of carbon dioxide, it has vibrational modes which can absorb radiation in the infrared region of the electromagnetic spectrum. Oxygen and nitrogen do not have dipole moments, and therefore do not absorb infrared radiation strongly. This means that carbon dioxide will absorb infrared radiation in the atmosphere much more strongly than the major gases. The energy from the absorbed infrared radiation is of course turned into vibration, a form of kinetic energy, and this kinetic energy is randomly further distributed among the gases of in the atmosphere, appearing as an increase in temperature as the energy distribution moves towards equilibrium.

410 The most cursory understanding of the absorption of infrared radiation in the atmosphere by carbon dioxide therefore seems to say that an increase in the concentration of carbon dioxide in the atmosphere would lead to a higher average temperature in the atmosphere. This increase in temperature was first estimated by Svante Arrhenius in 1896 (Arrhenius 1897).

420 (The other major product of extracting energy from fuel is water. Its molecule also has a dipole moment, and it also absorbs infrared radiation strongly. However, its intermolecular properties sets an upper limit to its concentration: at high enough concentrations it will either condense into water or crystallize into ice and precipitate from the atmosphere to end up as surface water.)

425 Further research has only confirmed that industrial processes extracting energy from fuel is increasing the amount of carbon dioxide in the atmosphere by gigatons every year, and that this increase in concentration is leading to higher temperatures in the atmosphere. It had also become increasingly certain that this increase in temperature is inevitable and significant: it will change earth's climate². This projected increase in temperature and the accompanying change in global climate is bound to have impact on societies within the lifetime of people alive today, and a larger impact on future generations. Some of these projected changes are incompatible with the maintenance of the complex civilizations that are supported by industrialized societies (IPCC 2014).

435 Scientists do not inhabit ivory towers, and their research is funded by public money in the expectation that the resulting science will benefit their societies. As the

²The atmosphere is in contact with the hydrosphere, and the two exchange carbon dioxide. The carbon dioxide diluted in the atmosphere is therefore also diluted in the oceans. This leads to *ocean acidification*, a gigaton problem in it's own right, but one that falls outside the scope of this discussion.

understanding of carbon pollution grew, it became obvious to scientists that industrialized societies could not just continue diluting gigatons of carbon dioxide in the atmosphere, and they alerted policymakers. The iconic moment of this development was the testimony of Dr James E. Hansen, at the time director of NASA's Goddard Institute of Space Studies, before the Senate of the US Congress in 1988 (Shabecoff 1988). In the same year the scientists of the world came together and established the Intergovernmental Panel on Climate Change (IPCC) to create a coherent body of knowledge to inform decision-making. The IPCC has so far produced a series of five Assessment Reports, which assesses the science of climate change, its impacts, and ways to mitigate it (Allen et al. 2014).

(Carbon dioxide is not the only greenhouse gas and the IPCC reports consider each in detail, but because the other gases are not produced in significant quantities by fuels and the energy industry they fall outside the scope of this discussion.)

Industrialized societies currently depend on energy from fossil fuels. Huge investments have been made in infrastructure, large numbers of people find employment in this industry, and available alternative sources of energy are not nearly sufficient. The health and well-being of the greater part of the world's population depend on it. But the future health and well-being of those same societies also depend on ending that dependence. It would be in the best interest of industrialized societies to create plans to reduce the dependence on energy from fossil fuels and exploit alternative energy sources.

But industrialized societies are also in economical competition with each other. This means that any society that spends resources on risky, expensive alternative sources of energy risks falling into a competitive disadvantage, and there is a surfeit of short-sighted politicians who will take advantage of this risk to create fear and so prevent planning for and investment in changes in energy production and use³.

Fortunately there are enough leaders who have vision, and based on the recommendations of the IPCC the governments of the world have come together to create the UNFCCC. The United Nations Framework Convention On Climate Change is an international agreement that structures the response of nations to limit their emissions of greenhouse gases. Two international treaties have been agreed to so far: the Kyoto Protocol in 1997 (*Kyoto Protocol to the United Nations Framework Convention on Climate Change*. 1997) and the Paris Agreement in 2015 (*Paris Agreement* 2015).

These agreements attempt to reduce the amount of carbon dioxide released into the atmosphere by dividing the cost of reducing emissions fairly. While the Kyoto Protocol invoked a complex carbon credit trading scheme, in the Paris Agreement nations pledge to reduce emissions of carbon dioxide into the atmosphere, and each is free to do so in a way that suits them best.

The Republic of South Africa is a signatory to the Paris Agreement, and therefore the country is legally bound to limit and reduce its emissions of carbon dioxide and other greenhouse gases. The country has so far promised to stop increasing emissions between 2020 and 2025 (*South Africa's Intended Nationally Determined Contribution (INDC)* 2016).

1.2 Carbon footprints and carbon neutrality

Ending the emission of carbon dioxide by industrialized societies is an exercise in balancing effort with consequences. Every reduction in carbon dioxide emissions

³The impact of political corruption is not negligible, but I will abstain from commenting on it.

must necessarily have an effect on the economy, and conversely, every change in economic activity will have an effect on carbon dioxide emissions.

485 A rational, discerning society in searching for ways to carbon dioxide emissions will therefore attempt to change their economy in such a way that the emission of carbon dioxide is limited or reduced. But in most societies there are many ways to reduce carbon dioxide emissions, and decisions have to be made on which ones to implement. Such decisions must be based on sound information, and one way to generate that information is a discipline called *life cycle analysis* (LCA).

490 Life cycle analysis can yield rigorously-calculated data and comparisons, but it is a very general method. For analyses that are very similar and differ only in context, it is possible to develop simplified, standardized life-cycle analysis tools.

495 One such tool is the *carbon footprint*. Every economic activity in an industrialized society generates emissions of greenhouse gases. These emissions might be far removed from the activity in space and time. A most obvious example of this is the use of electricity: At the moment I'm using a computer to compose this paragraph and electric light illuminates the desk I'm working on here in my office in Pretoria. The electricity that powers the computer and the lamps are generated hundreds of 500 kilometres from here, most of it on the Mpumalanga Highveld, in coal-fired power stations which emits carbon dioxide in the process. So my activity is far removed from the associated emissions **in space**. But even before the coal was burned, the machines that mined it and transported it to the power station emitted carbon dioxide, so my activity is also removed from the emissions **in time**. The sum of all these emissions connected with my activity constitute the carbon footprint of my activity.

505 Although carbon footprinting is conceptually straightforward, it is analytically rigorous and computationally complex. But there are standard protocols (World Resource Institute 2004) that can be followed, so that carbon footprints from different activities and different organizations are transparent and comparable.

510 Once an organization's activities have been footprinted, the organization can examine its operations and look at ways to change activities that will reduce that footprint.

515 If my university, for example, decides to install photovoltaic panels on the roof of my building, and use the electricity to illuminate my office, the activity will now most likely have a reduced carbon footprint, because photovoltaic electricity usually has a lower carbon footprint than coal-derived electricity.

To prevent a climate disaster, at some point industrialized societies will have to change all their activities until they no longer emit any greenhouse gases. Such activities will have carbon footprints of zero, and will be known as 'carbon neutral activities'. There are also activities that are nett removers of carbon from the atmosphere, which would be 'carbon negative'.

520 In truth, in industrialized societies there are very few carbon neutral activities. Even if I'm just sitting quietly in a pristine nature reserve, the food I am digesting and metabolizing have a positive carbon footprint: carbon was emitted to fix nitrogen from the air, which was used as fertilizer to help grow the food I ate, and is now in the proteins of my body. The very calcium and phosphorus in my bones were sourced from mines that were powered by fossil fuels.

1.3 Internal combustion engines.

Carbon footprinting exercises quickly show that a major source for emissions is transport. Most transport in industrialized societies is powered by internal-combustion engines. They are called ‘internal-combustion’ engines because the chemical transformation that extracts the energy from the fuel is internal to the engine. This is in contrast to the power station steam turbines mentioned earlier, where the extraction of the chemical energy from the fuel happens outside of the engine. The engine is the device that produces the mechanical energy. These engines are usually powered by liquid fuels derived from crude oil, although some designs run on gas, and of course in South Africa Sasol and PetroSA supply us with liquid fuels derived from coal and natural gas.

This discussion will use the term *noxious pollution* to describe pollution that is directly harmful to humans and *carbon pollution* to describe pollution that leads to industrial climate disruption.

The simplest way to reduce an activity’s carbon footprint is to use the fuel that drives that activity more efficiently. Fortunately market forces are aligned with this, because more efficient use of a fuel also reduces running costs. Discussing engine designs therefore almost always invokes *efficiency*. Efficiency of an engine is calculated by taking the ratio output power:input power. The greek letter η is used as a symbol for efficiency:

$$\eta = \frac{P_{out}}{P_{in}} \quad (1.2)$$

Conservation of energy dictates that the output power cannot be more than the input power, and therefore $\eta \leq 1$. The power is ‘lost’ to two factors: firstly entropy, as dictated by the Second Law of Thermodynamics, and secondly losses, such as friction.

1.3.1 Scaling and efficiency

The efficiency of engines scales disproportionately with its linear dimensions, by which is meant that the larger an engine is, the more efficient it is. There are three factors that improve efficiency in larger engines (Brown, Menon, and Hagen 2015):

- 555 1. Longer residence time: In larger engines, the reacting fuel spends more time in the engine. This gives reactions more time to reach equilibrium, and hence more energy can be extracted.
- 560 2. Smaller surface area to volume ratio: The volume of an engine increases with the cube of its linear dimension, but the surface area increases with the square of its linear dimensions. This means that larger engines have a smaller surface-to-volume ratio than smaller engines. Since losses take place at the surface, the loss per unit volume is therefore larger for smaller engines than it would be for larger engines of the same type. If the losses in larger engines are comparatively smaller, we can expect larger engines to be more efficient than smaller ones.
- 565 3. Larger Reynolds number: The Reynolds number is a number that predicts the onset of turbulent flow, and is calculated from the viscosity, velocity and a characteristic linear dimension. The higher the Reynolds number, the higher the likelihood of turbulent flow. Turbulent flow promotes mixing, which leads

570 to improved combustion and hence higher efficiency. The larger the engine, the larger the characteristic linear dimension, and therefore the higher the likelihood of turbulent flow.

From the viewpoint of reducing carbon pollution, one should therefore aim to use a few large engines rather than a multitude of small engines.

575 **1.3.2 Engine design and thermodynamic cycles.**

The final design of a successful internal combustion engine is determined by the variation-selection process described by Vincenti (Vincenti 1990). Such a design sufficiently satisfies a wide range of requirements. These requirements might be explicitly expressed in documentation, or they may be implied, or they may be practical. 580 These requirements would include, but are not limited to, capital cost, running cost, maintenance cost, noise, sound, ease of maintenance, power output, emissions, surface finish, weight, mounting method, size, supply chain capability, shape, colour, fuel availability, operating temperature, altitude tolerance and torque.

From designers' attempts to fulfil these requirements arise the myriad of different engine designs, delivering anything from milliwatts to megawatts of power to anything from model aircraft to oil tankers. It is the good fortune of researchers who study engine efficiency that there are only a few conceptual systems that explain how the internal combustion engines convert the chemical energy of the fuel into mechanical work.

590 The principles on which the different engines operate are named 'cycles', because the way they convert heat into work can be described in terms of a series of events that are repeated endlessly. The concept of a cycle is further entrenched because it is customary to explain the thermodynamic processes involved using at pV diagram, showing the changes of state of the working fluid during engine operation.

595 Theoretical thermodynamic cycles are useful because they can predict the performance of heat engines, allowing for comparison. In particular, it allows for comparison with theoretical maxima. The maximum efficiency of a heat engine is delivered by an engine running on the Carnot cycle. This describes a hypothetical engine that uses only reversible processes to extract useful work from the temperature difference between two reservoirs of heat. It has been shown that the Carnot cycle offers the maximum possible heat extraction, and that the maximum efficiency (η_C) is determined solely by the temperature difference between the hot (T_h) and the cold (T_c) reservoirs.

$$\eta_C = 1 - \frac{T_c}{T_h} \quad (1.3)$$

605 The Carnot cycle, however, can only deliver an infinitesimal amount of work, because the heat transfer must be reversible, and therefore infinitesimal. A more realistic maximum efficiency is given by the Chambadal-Novikov efficiency (η_{CN}) (Hoffmann 2008):

$$\eta_{CN} = 1 - \sqrt{\frac{T_c}{T_h}} \quad (1.4)$$

This theoretical efficiency takes into account the irreversible processes that are inevitable in engines delivering finite amounts of power.

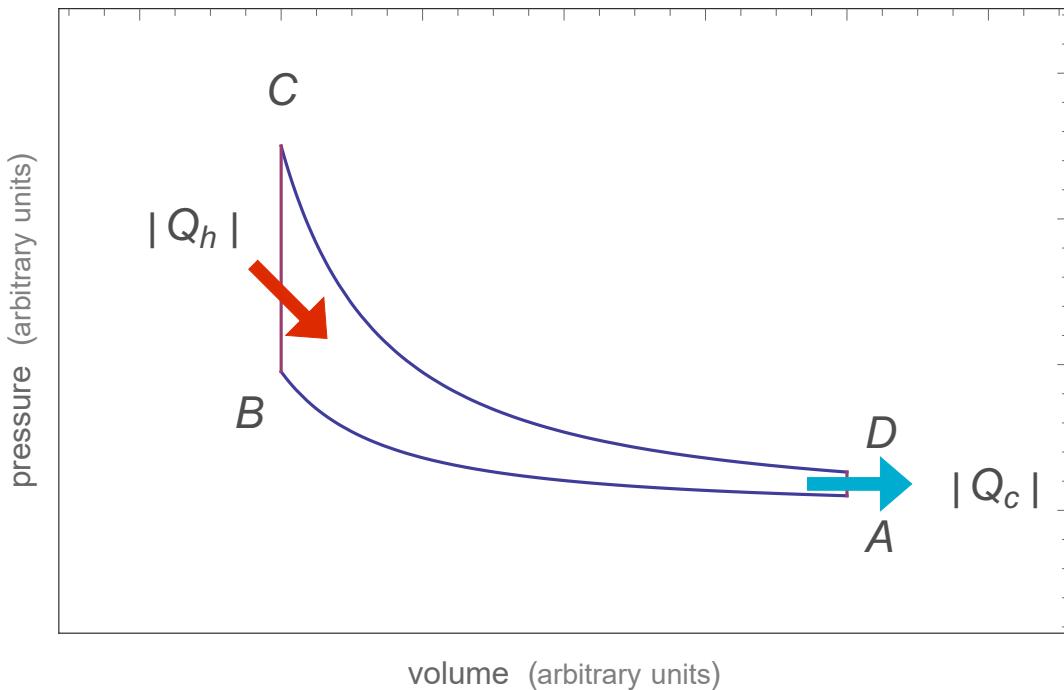


FIGURE 1.1: The pV diagram of the thermodynamic Otto cycle. The isochoric heat addition step (BC) corresponds to the burning of the homogeneous air-fuel mixture. Work is extracted from the engine during the adiabatic expansion CD (Wolfram | Alpha 2019a).

610 Barring revolutionary new discoveries and inventions, there will be only three thermodynamic cycles and their corresponding internal combustion engines on the market, as we enter the low-carbon era.

Otto engine and Otto cycle

615 The oldest of the internal combustion engines is the Otto engine. It is named after Nikolaus Otto, who developed the first working engine of this kind in 1876 (Cummins 1989, Chapter 9). In South Africa these engines are usually called ‘petrol engines’.

620 In the Otto engine, a homogeneous mixture of atmospheric air and vaporized fuel is compressed. This mixture is then ignited by an electric spark. The energy released by the chemical reaction between the oxygen in the air and the fuel vapour causes the temperature of the compressed air to rise, and consequently the pressure. If this, now hot, gas is allowed to expand in an expandable vessel, the motion of the vessel can be captured to perform useful work. Once the useful work is extracted, the vessel can be collapsed again to expel the exhausted air, and re-filled with a 625 compressed air/fuel vapour mixture. This completes the cycle. The expandable vessel is usually in the form of a cylinder and piston, with the piston connected to a crank that drives a shaft that transfers the work from the engine to the machine being powered.

630 (These legs of the cycle are only loosely related to the ‘strokes’ of a four-stroke engine, and should not be confused for them.)

The theoretical efficiency of the Otto Cycle is given by

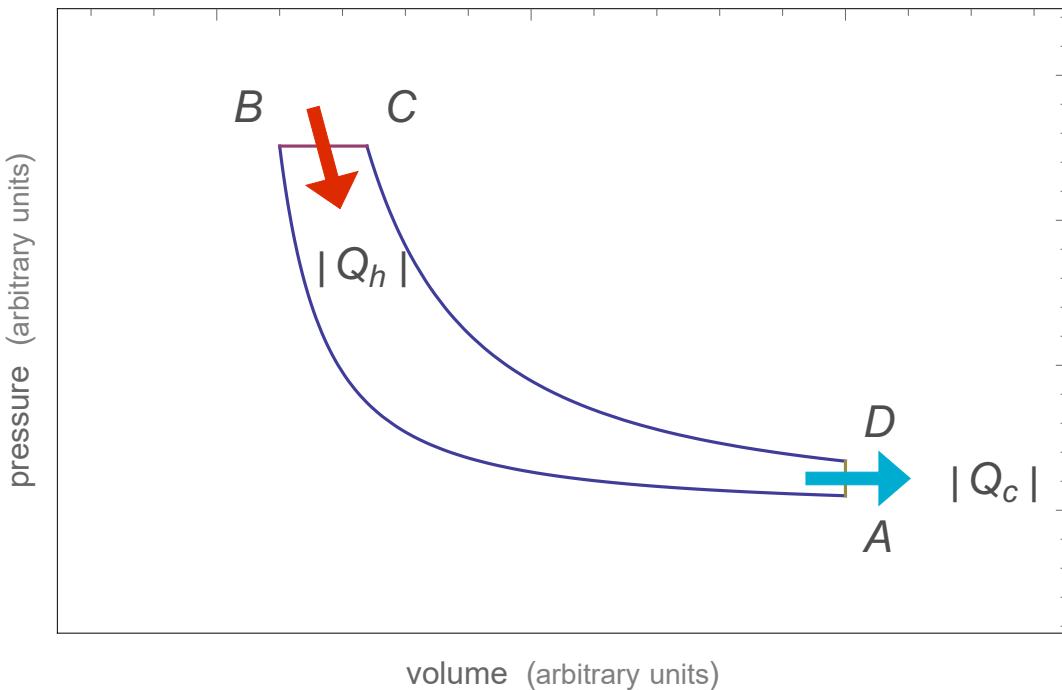


FIGURE 1.2: The pV diagram of the thermodynamic Diesel cycle. The isobaric process BC corresponds to the combustion of the finely divided fuel particles in air. Work is extracted from the engine both during this process and during the adiabatic process CD. (Wolfram | Alpha 2019b)

$$\eta = 1 - \left(\frac{1}{r^{\gamma-1}} \right) \quad (1.5)$$

where r is the *compression ratio*, $\frac{V_1}{V_2}$, and γ is the heat capacity ratio, which can be considered a constant for the purposes of this discussion (Wolfram | Alpha 2019a).

This means that the efficiency of an Otto engine can be improved by increasing the degree of compression of the intake air before combustion.

Diesel Cycle

In the Diesel engine, named after Rudolf Diesel who demonstrated the first engine of this type in 1897 (Cummins 1989, Chapter 14), air is compressed, and then a finely divided solid or liquid fuel is injected into the system. The fuel then reacts with the oxygen in the air. The energy released in the reaction appears as a higher temperature in the gas, and — following Gay-Lussac's Law — the pressure of the gas rises. If the gases expand in the confines of a collapsible vessel, useful work can be extracted from expansion of the vessel. Once the work has been extracted, the vessel can be collapsed again to remove the now inert ('exhausted') gas and prepare for receiving the next charge of air, completing the cycle.

The theoretical cycle used to analyse the performance of the Diesel Engine is called the Diesel Cycle. (See figure 1.2)

The Diesel cycle differs from the Otto cycle in the heat addition step. In the Otto engine, the heat addition takes place when the homogeneous air/fuel mixture combusts. This combustion takes place in a short space of time during which the

engine parts move only a negligible distance. Hence the pressure rises rapidly. In the Diesel engine, the fuel is injected into a volume of compressed air, where it combusts. (There is no separate ignition source: the temperature of the adiabatically compressed air is higher than the fuel's ignition temperature, so that the fuel ignites upon injection. While this is another difference between the two engines, it is of second-order importance when discussing thermodynamic cycles.) Because the combustion takes place at the surface of fuel particles, the combustion rate is lower than the combustion rate of the homogeneous mixture in the Otto cycle. Hence the rising temperature is balanced by the motion of the engine, and the heat addition is essentially isobaric.

The efficiency of the Diesel cycle is given by Equation 1.6

$$\eta = 1 - \frac{1}{r^{(\gamma-1)}} \left(\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right) \quad (1.6)$$

where α is the *cut-off ratio* and γ is the compression ratio.

The term $\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)}$ is always larger than 1, and therefore, when we compare equation 1.6 with equation 1.5 it is clear that for a given compression ratio the Diesel cycle is always less thermally efficient than the Otto cycle.

However, at high compression ratios Otto engines start suffering from 'knocking', when the homogenous air/fuel mixture detonates, instead of burning smoothly. The shock waves from this detonation will damage the engine and lead to faster wear. (The *octane number* of a fuel indicates the compression ratio it can accommodate.) Because Diesel engines do not suffer from this problem, they can, and usually are, designed to operate at higher compression ratios than Otto engines. Otto engines normally operate with a compression ration of up to 9:1, whereas Diesel engines have compression ratios of up to 25:1. This makes Diesel engines significantly more efficient than Otto engines.

675 Gas turbines and the Brayton Cycle

The third internal-combustion engine important to industrialized society is the *gas turbine*. Gas turbines are used rarely in road transport, more often in marine and stationary applications, but thousands take to the sky every day, propelling aircraft (Morris 2017) carrying billions of airline passengers every year.

680 The first gas turbines were developed during wartime urgency to deliver pure jet thrust for military aircraft, but this proved to be an inefficient use of the available energy. Most modern turbine engines drive a shaft to extract rotational work. This shaft might drive a bypass fan (as used in airliner engines), a propeller (as used in smaller, low-speed aircraft), or a shaft which might drive a helicopter rotor or an electrical generator.

In operation, a gas turbine compresses air with one or more compressor stages. The compressed air passes through a combustion chamber, where fuel is added and combusted. As the now hot gases expand they pass through one or more turbine stages, which is connected to drive the compressor and the output shaft, which extracts work from the system. After the gas has passed through the turbine it returns to atmospheric pressure, optionally doing work on the engine in the form of thrust.

695 The theoretical thermodynamic cycle that is customarily used to analyse the gas turbine is called the Brayton cycle, named after George Brayton, who successfully manufactured a reciprocating engine based on this cycle. (See figure 1.3) Such engines are no longer manufactured (Cummins 1989, Chapter 10).

The efficiency of the Brayton cycle is given by equation 1.7

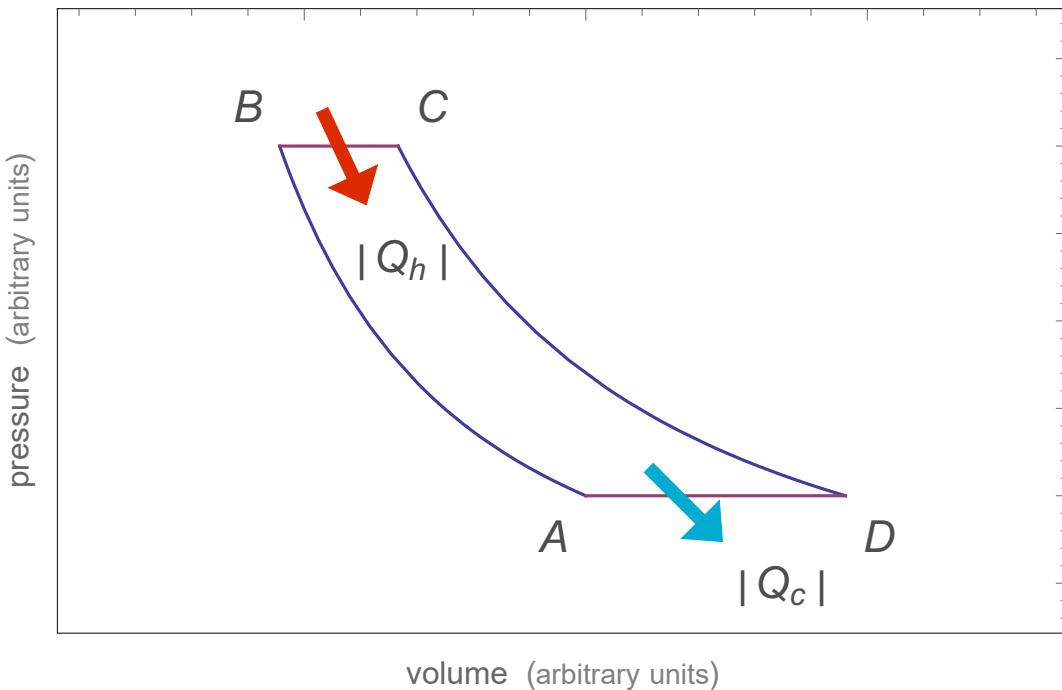


FIGURE 1.3: The pV diagram of the thermodynamic Brayton cycle. In the gas turbine the continuous combustion of the injected fuel and free expansion of the air through a turbine means that the heat addition (BC) is isobaric. Work is extracted during the adiabatic expansion process CD (Wolfram | Alpha 2019c).

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} \quad (1.7)$$

where γ is the compression ratio (Wolfram | Alpha 2019c).

Because the fuel is continuously added to the compressed air and the combustion takes place in a heterogeneous mixture, gas turbines do not suffer from ‘knocking’ and therefore there is no upper limit to the compression ratio. The main figure determining the efficiency of the engine is the turbine inlet temperature, (*i.e.* the outlet temperature of the combustion chamber) which reaches 1600 °C in modern engines.

1.3.3 Noxious pollution from internal combustion engines.

Carbon pollution is not the only pollution emitted by internal combustion engines. There is also noxious pollution, which affects the societies in which they are used. There are ways to reduce or eliminate such pollution, but the implementation of such measures affect the efficiency of the engine.

Noxious pollution from internal-combustion engines come from different sources and have different effects.

710 Unburnt fuel

The combustion reactions in internal-combustion engines are very fast, but they are never at equilibrium. This means that at the end of a cycle, the exhaust gases expelled from the engine contains, besides the carbon dioxide, also chemical intermediates and unreacted fuel molecules.

715 Unreacted fuel is a noxious pollutant, not only in its own right, but also, during the decomposition process in the environment, chemical reactions induced by sunlight produces ozone, a reactive oxygen species that leads to respiratory problems in victims of pollution (Davidson 1998).

720 Some of the fuel-like pollutants from internal-combustion engines are not present in the fuel. These compounds are formed in a process that might be called *pyro-synthesis*. They are themselves more stable than the compounds from which they originate, but not as stable as the combustion end products, carbon dioxide and water. Because they are themselves quite stable, they require high temperatures to combust, which might not be achieved before they leave the engine as waste.

725 Notable pollutants from this source are the polycyclic aromatic hydrocarbons (PAH) and, if trace amounts of chlorinated substances are present in the fuel, dioxins

730 One of the products of pyro-synthesis is particles of soot. These particles are agglomerations of nano-sized particles of pure, amorphous carbon. The agglomerations might include adsorbed PAHs and acids. Soot particles are very stable and only react at very high temperatures. Diesel engines in particular have a reputation for producing soot (Mohankumar and Senthilkumar 2017).

735 The final pollutant that can be classed as originating from partially combusted fuel is carbon monoxide. It forms readily when fuels are burned in oxygen-poor environments. Modern, well-maintained engines is a relatively rare cause of acute carbon monoxide poisoning (Reumuth et al. 2018), but chronic exposure to low levels of environmental carbon monoxide has harmful effects (Wright 2002).

Contaminants and additives.

740 Crude oil and coal contains not only carbon and hydrogen, but also other elements, most notably sulfur and nitrogen. Depending on the refining process, these elements might find their way into fuels. Organic nitrogen and sulfur will easily oxidize and form stable oxides, yielding energy. Once outside the engine, however, the volatile oxides will dissolve in any water in the air, forming acids. (Duncan et al. 2016)

745 Fuel manufacturers add additives to fuels for various reasons, such boosting octane rating or preventing corrosion. The prime example of additives as a source of noxious pollution was tetraethyllead, which was added to petrol as an octane booster. The emitted lead compounds was shown to be a pollutant that lead to neurological impairment in its victims, and its use was phased out (Needleman 2000).

Side-reactions

750 Most internal combustion engines use atmospheric air as oxidant. This air is 21% oxygen, and 78% nitrogen. Although nitrogen is very stable and inert, at high temperatures it can react with oxygen. These reactions produce the oxides of nitrogen: NO, NO₂, NO₃ and N₂O, and N₂O₅. They are collectively called NO_x.

755 These oxides can participate in the cycle that causes the photochemical smog. They will also dissolve in atmospheric water and form acids: this might happen far from the point of emission, resulting in *acid rain*.

1.3.4 Mitigating pollution from internal-combustion engines.

Pollution from internal combustion engines is a social ill, and most governments have regulations in place to limit and reduce this pollution. Engine and fuel manufacturers are working hard to reduce this pollution.

760 The noxious pollution from internal combustion engines can be reduced by various improvements, but there are three complementary approaches: fuel formulation (Gertler et al. 1999), cleanup (Braun et al. 2018) and engine management (Reif 2015).

Fuel formulation

Adding oxygenates improves the octane rating of fuel and reduces NO_x formation.

765 **Exhaust gas cleanup**

Exhaust gases from internal combustion engines can be “cleaned”, and there are basically two approaches. The first is catalytic conversion, in which the exhaust gases that contain the pollutants are passed over a catalyst bed. The catalyst (a proprietary formulation of platinum, palladium and/or rhodium), adsorbs the uncombusted volatile organic carbons, and oxidizes them. It simultaneously catalytically decomposes NO_x to molecular nitrogen and oxygen.

770 Secondly, filter systems can be used to remove particulate matter.

Engine management

775 As described above, the main source of noxious pollution from internal-combustion engines is uncompleted or undesired chemical reactions, and is not fundamental to the operation of the engine. By carefully managing the engine system, noxious pollution can be reduced.

780 The oldest engine management technology is the oxygen or ‘lambda’ sensor, which measures the oxygen in the exhaust gases. Such a sensor, coupled to an engine-management computer, allows the metering of the exact amount of fuel needed for optimum combustion (Frauhammer, Schweinsberg, and Winkler 2014).

A newer technology is known as exhaust gas recirculation. This mixes the intake air of the engine with exhaust gases, effectively diluting the oxygen. This reduces peak temperatures, and thereby NO_x formation.

785 In *stratified charge* engines the distribution of fuel in the volume of intake air is controlled by selective fuel injection. Carefully injecting the fuel at the right place at the right time can allow for higher compression ratios without inducing pinging. *Lean-burn* engines are Otto engines that use extremely high air:fuel ratios.

790 Electronic engine management systems result in much more efficient and less-polluting engines than non-managed ‘mechanical’ engines, but because engines for automotive applications endure such a wide range of operating conditions, they can at best achieve a compromise between power, efficiency and emissions. It was this unsatisfactory compromise that lead to the Volkswagen emissions scandal: manufacturers chose to cheat on emissions test rather than admit to the relatively poor 795 performance of a managed engine optimized for low emissions (Mansouri 2016).

Efficiency implications

Attempts to mitigate noxious pollution from internal-combustion engines mostly lead to losses in efficiency. For example:

- Exhaust gas flow through catalytic converters and filters consume energy.
- 800 • The engines cannot approach their theoretical maximum efficiencies, because reducing NO_x emissions is handled by limiting maximum combustion temperatures.

- NO_x reduction catalysts require the presence of hydrocarbons, *i.e.* incomplete reactions, which implies that not all energy is extracted from the fuel.
- Every treatment system added to the engine adds weight to the vehicle, which reduces payload and hence the total efficiency.

Before carbon dioxide pollution was a concern, it made sense to accept lower efficiencies as a necessary cost of reducing noxious pollution, but in a low-carbon future we cannot just keep on trading less noxious pollution for more carbon dioxide production.

1.3.5 Avoiding pollution from internal-combustion engines

The efficiency and cleanliness of internal-combustion engines have dramatically increased over the last century, and more improvements are being implemented. But these improvements have not been fundamental to the engines in any way, and have been driven mostly by government regulation, at the cost of increased complexity and a higher purchase price.

It would seem obvious that it would be a good idea to introduce alternative technologies.

Electrification

In principle, there is nothing special about internal-combustion engines: they are not an end in themselves. They merely deliver a source of torque, which can be coupled to machinery to do useful work. Before the industrial era such torque was available from windmills and waterwheels, and today an alternative is the electric motor.

Electric motors are engines that use the interaction between electric current and magnetic fields to deliver useful torque to drive machines. Because they use electricity as a source of energy, they have no noxious emissions where they operate. Because they are not heat engines, their efficiencies are not subject to the Carnot limit, and efficiencies exceeding 95% are standard (Li and Curiac 2012).

Electricity, of course, is not necessarily carbon-neutral. Most electricity is generated in power plants that use fossil fuels as a primary source of energy. But because these plants are huge, and efficiency scales disproportionately with size, the energy output by the electric motor has a similar or lower carbon footprint than an equivalent internal-combustion engine (Doucette and McCulloch 2011).

Electricity grids are also increasingly being fed by solar and wind power, which are carbon-neutral at source. These renewable plants are also smaller and more flexible than their behemoth fossil-fuel counterparts, with lower capital costs and extremely low running costs.

Hence, in a low-carbon future, there is every reason to support or mandate the use of electrical motors for stationary applications wherever possible.

In automotive applications, *i.e.* in cases where the engine is used to move itself in addition to some form of payload, the application of electric motors is more demanding. In this case it is not easy to bring the electricity to the motor, although electric trains and buses fed by overhead conductors are splendid examples of the electrification of transport. So for electric vehicles to use the existing road network, they need to carry a source of electricity with them.

This source of electricity can be either a chemical battery, or a fuel cell. In a chemical battery power from the grid is stored in the form of reversible electrochemical reaction, and in a fuel cell the chemical energy from a fuel is directly converted

into electricity. There are fuel cells that can use hydrogen as a fuel, and fuel cells
850 that can use methanol as a fuel. (It goes without saying that the hydrogen and the
methanol need to be sourced from low-carbon sources for fuel cells to count as low-
carbon energy sources.)

The storage and transport of hydrogen remain hurdles to the large-scale adoption
855 of hydrogen-fuelled automobiles, although a market seems to be developing for
hydrogen-fuelled electric trains (Agence France-Presse 2018). Hydrogen fuel cells
emit no carbon or noxious pollution at point of use.

Direct methanol fuel cells can react methanol with atmospheric oxygen in an
electrochemical cell to yield electricity, with carbon dioxide as a waste product. Little
is known about possible noxious pollution.

860 At this time it seems that the electrification of road transport will be by chemical
batteries. Lithium-ion batteries can now store enough energy and deliver enough
power to make electric motor vehicles practical and attractive (Hayes et al. 2011),
and some governments are considering plans to no longer allow the production of
passenger vehicles propelled by internal combustion engines (Burke-Kennedy 2018)
865 (Reuters 2018) (Gabbatiss 2018).

Carbon-neutral fuels

Another way to avoid the carbon pollution associated with internal-combustion engines is to change the fuel. Not all fuels are fossil fuels, and it is possible to use fuels that are carbon neutral, and in some cases carbon negative.

870 Apart from using hydrogen in a fuel cell, as described above, *hydrogen* can also be used as a fuel in Otto engines, because it will combust in air to yield heat. The emissions are water and NO_x. Presently there are no hydrogen-fuelled Otto engines on the market.

Methanol is a common product of the fossil fuel industry, but work is under-
875 way to produce methanol by reducing carbon dioxide using solar energy. Such *solar
methanol* might be used in direct conversion fuel cells, or in internal-combustion engines.

It is possible to harness the energy in contained in the reduced carbon in biological materials and use it as fuel. Such fuels are known as *biofuels*.

880 1.4 Biofuels

Biological processes are an integral part of the carbon cycle, because photosynthesis in plants reduces carbon dioxide in the atmosphere to sugars, which are converted by plant physiology into structural cellulose and other metabolites.

The prototypical biofuel is of course wood, used in all societies for cooking and heating.
885 This familiarity makes biofuels seem an obvious and viable source of energy, but details matter, and switching from fossil fuels to biofuels to reduce carbon footprints of human activities is not a simple choice.

Firstly, the efficiency of photosynthesis is notoriously low: not above a few per cent, whereas the efficiency of a mass-produced silicon-based solar panel is in excess of 20%. In general it is much more efficient to capture solar energy in a PV panel and use an electric motor to provide the necessary mechanical power than to create a biofuel and use it to drive an internal-combustion engine.

Second, increased biofuel production has numerous impacts on the environment and society, which cannot be ignored.

895 Discussing all the factors that need to be studied to make such a decision is outside the scope of this work, but as an example a report prepared for stakeholders in the Netherlands (Smeets et al. 2006) uses the following criteria:

- 900
- GHG [greenhouse gas] emissions – the use of biofuels should cause reductions of GHG emissions. The comparison should be done regarding the average use of fossil fuels, considering the life cycle of fossil and biofuels (i.e., well-to-wheel basis) and in case of biofuels reduction should be at least 30%
 - 905 • Impacts over food supply – the production of biomass for energy must not endanger the food supply and other local biomass applications. The analysis should be developed considering possible changes of land use in the region of biomass production.
 - Biodiversity – Biomass production must not affect protected or vulnerable biodiversity.
 - 910 • The basic criteria are that violation of national laws and regulations are unacceptable.
 - Local environmental effects – Principles include (a) soil and soil quality, that must be retained or even improved, (b) ground and surface water supply, that must not be polluted.
 - Local economic effects – The production of biomass must contribute towards local prosperity.
 - 915 • Social well-being – The production of biomass must not decrease the well-being of local societies.

Nevertheless, there are cases where using biofuels is a good option.

1.4.1 Bio-gas

920 Anaerobic bacteria can convert biogenic carbon compounds to methane. This methane is identical to the methane obtained from natural gas, and can be used for the same applications.

925 An excellent application for the use of bio-gas is waste remediation. Waste material from the agri-food industry can be highly polluting if not treated properly, emitting noxious chemicals into water and the potent greenhouse gas methane into the atmosphere. But when used as feedstock for bio-gas production, it reduces carbon pollution by capturing methane and displacing natural gas, and also prevents water pollution (I. Venter 2014).

Bio-gas can be used to fuel Otto engines or gas turbines.

1.4.2 Bio-ethanol

930 Yeast and other microbes can convert sugar or starch from plants into ethanol. This technology is as old as civilization. Archaeologists may be in disagreement where beer was brewed first, but it is clear that between 3200 and 3000 BCE in ancient Sumeria the brewing of beer was an activity regulated by the government (Damerow 2012). By 2000 BCE in ancient Egypt the technology of fermentation was harnessed well enough that bakeries and breweries were co-located (*Model Bakery and Brewery from the Tomb of Meketre* 1920).

940 Beer and wine can best be described chemically as aqueous solutions of sugars, ethanol, flavourants and colourants, with or without suspended solids. It was not until the 8th century CE that Persian and Arab scientists mastered the art of distillation and purified ethanol (Modanlou 2008), and it was not until Pasteur that yeast was seen as a living organism, and ethanol a product of its metabolism (Barnett 2000).

945 It is unclear when ethanol was firsted as a fuel, but its flammability must have been noticed by the first distillers. By 1838 ethanol was common enough to be used in alcohol lamps as a source of heat in the chemical laboratory (Griffin 1838), and by the 1850s it was a major component of lamp oil used for illumination in the USA (Abebe 2008).

950 Ethanol as a fuel for internal combustion engines has a clear start date: in 1826 Samuel Morley was granted a patent for an engine designed to use ethanol as fuel (Cummins 1989, p. 79).

The industrial production of ethanol is a technologically advanced process. It is an active research field. A paper (Cardona and Sánchez 2007) reviewing the process technology of producing bio-ethanol written in 2007 had garnered 644 citations by January 2019.

955 The industrial production of ethanol consists of three steps.

1. Fermentation
2. Distillation
3. Dehydration

960 The fermentation step is the biological process by which the yeast organism *Saccharomyces cerevisiae* convert the sugar and starch in the biological material to ethanol and carbon dioxide. This needs to be done in a sterile environment to prevent contamination by other micro-organism.

965 The distillation step is the physical process of separating the produced alcohol from the aqueous mixture in which it is produced. This generally produces an azeotropic mixture that contains 95.6 % ethanol (Kumar, Singh, and Prasad 2010).

970 While the processes of fermentation and distillation of ethanol for fuel is in principle the same as that of producing alcoholic beverages, the emphasis of the processes are very different. In the beverage industry the emphasis is on the development of complex flavours and a consistent, recognizable drinking experience. In the fuel industry the emphasis is on efficiency and throughput.

To produce fuel-grade ethanol from the distilled azeotrope, dehydration is a necessary third step. This step can be implemented by various distillation processes that add a third compound, but in most modern plants the water is removed by adsorption onto molecular sieves (Kumar, Singh, and Prasad 2010).

975 **Brazilian ethanol**

Brazilian sugar-cane ethanol is an integral part of the country's energy network. Most Otto-engine vehicles have 'flex-fuel' engines, which can be fuelled with any blend of ethanol and petrol. The industry is regarded as sustainable ((Smeets et al. 2006).

980 **US maize**

US maize ethanol is primarily blended with petrol to meet legislative requirements of oxygenates in fuels. The production of maize is water-intensive and the fermentation process is carbon-intensive. The US ethanol from maize has a poorer energy balance and larger carbon footprint than Brazilian ethanol from sugar cane, but has
985 a smaller water footprint (Mekonnen et al. 2018).

Ethanol can fuel Otto engines and gas turbines.

1.4.3 Fischer-Tropsch fuel from biomass

It is possible to heat woody biomass with steam in a low-oxygen environment to produce synthesis gas, which can be converted to a mix of fuel products in the
990 well-known Fischer-Tropsch catalytic process. Such a fuel could be called a bio-fuel, but its production would be difficult to reconcile with the principles of *green chemistry*, described in Section 2.1.1.

1.4.4 Refined vegetable oil: “Green diesel”

The petroleum industry has developed a collection of chemical processes, such as hydrogenation, oxygenation and cracking. This collection of processes can be applied to vegetable oils to produce a fuel for diesel engines and gas turbines. This path is being followed by the aviation industry (Chiaramonti et al. 2014).

1.4.5 Biodiesel

Oils and fats have been used as fuels since antiquity, most obviously as a fuel for
1000 lamps: olive oil has been identified as the fuel used in lamps dating from around 600 CE (Kimpe, P. A. Jacobs, and Waelkens 2001), and at the Paris World Fair in 1900 Rudolf Diesel demonstrated an engine that ran on peanut oil (Knothe 2010).

During the energy crisis of the 1970s, the South African government looked at alternative sources of fuel. Experiments were done with sunflower oil in tractors,
1005 but there was a problem with the formation of carbon deposits around the injector nozzles. Seeing that the clogging of the injectors might be caused by the high viscosity of the sunflower oil as a fuel, the transesterification of the oil was implemented, replacing the glycerol in the sunflower oil with methanol. This created an oily liquid with a lower viscosity, which proved to be a trouble-free replacement (Van Niekerk
1010 1980).

Such a transformed oil is termed *biodiesel*. It consists primarily of a mixture of fatty acid methyl esters, often abbreviated into the acronym FAMEs.

Compared to ethanol, biodiesel production is relatively simple, the main method sharing much with the ancient technology of making soap. This simplicity makes
1015 the production of biodiesel attractive to small and decentralized manufacturing, and consequently governments consider biodiesel production an attractive proposition: it can create job opportunities in rural population and it can create a stable market for farmers who produce vegetable oil crops.

Biodiesel is not yet carbon neutral: the methanol used to create the methyl esters is a product of the petroleum industry, and therefore biodiesel emissions contribute to global warming. But replacing fossil diesel fuel with biodiesel results in a nett reduction of carbon emissions, with the future possibility of replacing fossil-derived methanol with carbon-neutral bio-methanol (Shamsul et al. 2014).

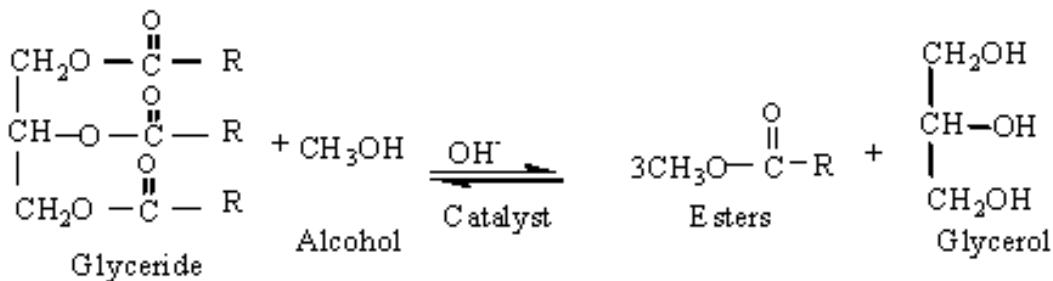


FIGURE 1.4: Transesterification

1.5 The significance of biodiesel and its quality control.

1025 In a complex technical, economic and social environment it is likely that there will always be a need that can be best met by internal combustion engines. The decision on the type of engine and the decision on the fuel for that engine are not independent, as Cummins reminds us (Cummins 1989):

1030 "Our generation faces a similar challenge in a real liquid fuel energy shortage that will come within the lifetime now living. As we plunge into the seeking of solutions to our dilemma, we must never forget that *an engine and the fuel it consumes are inseparable partners*; the one cannot progress without the full cooperation of the other. This precept is vital to the planning of future powerplants, since an engine's design determines 1035 its fuel and binds us to our future resource requirements."

1040 While the variation-selection process by which real engineering progress is 'blind', i.e. the combination of factors that make a design successful is not known at the start of a development (Vincenti 1990), scientific knowledge provides guidance in the form of insight into processes and theoretically achievable targets for performance. Using the scientific knowledge we have today, we can risk a forecast: if society is determined that its carbon footprint should be reduced with minimal noxious pollution the application of internal combustion engines would tend towards the following:

1. Larger: Because larger engines are more efficient than smaller engines, larger engines will be preferred. (See section 1.3.1)
2. Low-carbon: The preferred engine would be fuelled by carbon-neutral fuels. (Section 1.3.5)
3. Constant speed: Engines are most efficient when they can work at constant load. (Section 1.3.4)
4. Efficient: Engines with high efficiency should be preferred, which implies engines with high compression or pressure ratios. (Section 1.3.2)
5. Cleanup: The exhaust should be amenable to cleanup, i.e. the exhaust gases of the fuel-engine system should not contain compounds that are incompatible with available converter or filter technologies. (Section 1.3.4)

1055 From this it should be clear that the optimal engine of the future will not be an Otto engine, because it will always have a limited compression ratio and its catalytic exhaust cleanup will always require stoichiometric air:fuel ratios, which puts bounds to efficiency increases.

1060 Because it is the most efficient engine, the gas turbine will play an important role. However, its exhaust temperature is very high, which begs for energy recovery to increase the efficiency of the system. Such systems are already seen in the *combined cycle gas turbine* (CCGT). But energy recovery systems are not light and small, so their best application outside aerospace (where the excess heat is utilized as thrust) appears to be stationary electricity generation.

1065 For automotive applications the engine that will best contribute to reduce the carbon footprint of may be a large Diesel engine with exhaust cleanup to remove NO_x and soot, fuelled with a carbon-neutral fuel.

1070 In choosing between refined vegetable oil and biodiesel as a fuel, it is most likely that biodiesel will have a lower carbon footprint. Refinery operations are energy intensive, which might add to the carbon footprint of the fuel, and refineries are not usually near the point of use, so that transport will also add to its carbon footprint. The carbon emissions of biodiesel production are comparatively low. (At this point it is important to note that these observations are not definitive: carbon footprints are not predicted, they must be calculated.)

1075 Buying large, highly efficient diesel engines with sophisticated management systems and exhaust cleanup require high capital investment. In an economically competitive environment they therefore need to bring reliable returns, which implies high availability, as measured by frequency of breakdown and length of time between maintenance stops. Such high reliability can only be achieved if the manufacturer understands the fuel-engine system well and it behaves predictably.

1080 In a low-carbon future, therefore, well-characterized biodiesel might be expected to play a central role in non-electric ground transport and industrial application where electrification is not possible.

1.6 Conclusion: the role of chromatography.

1085 The development of the fuel-engine systems depends heavily on the chemical characterization of fuels and engine emissions, and chromatography has always played a central role: some of the earliest researchers developing gas chromatography were employees of a petrochemical company (Keulemans, Kwanten, and Zaal 1955).

1090 This thesis explores the possibility of applying comprehensive two-dimensional (supercritical fluid × gas) chromatography to the chemical analysis of biodiesel for the purpose of characterization and quality control.

$PV \neq nRT$

The ideal gas law does not apply to supercritical fluids.

2

Introduction: Carbon dioxide and chromatography

1095 2.1 The chemical industry

Industrialized societies depend on chemicals. (In this discussion I define chemicals as pure substances that are produced by industry for industry.) Chemicals might be used in the processing of products, or blended with other chemicals in formulations that might be sold to users as products. In a familiar example, sugar is a chemical produced by the sugar industry from sugar cane or sugar beet. It is a pure substance (sucrose) that is mostly used in the industry as an ingredient for processed food. Other uses of sugar include coatings for medication, and feedstock for engineered micro-organisms that produce pharmaceuticals. (Sugar is a rare example of a chemical that is also sold to consumers.)

1105 The chemical industry produces a huge variety of products, from compounds as simple as hydrochloric acid to compound as sophisticated as cyanocobalamin (Figure 2.1). All of these chemicals help produce the products indispensable to industrialized societies. Nevertheless, the chemical industry is not held in high regard by people outside the industry. A part of this negative perception comes from the 1110 chemical industry's reputation for fatal accidents and pollution (Gumm 2015).

1115 The list of incidents is long and examples easily spring to mind: In 1984 a leak at a chemical plant in Bhopal, India, caused the death of thousands of people and the injury of thousands more (R. Varma and D. R. Varma 2005). Stratospheric ozone is struggling to recover from depletion caused by the reckless emissions of chlorofluorocarbons (Ball et al. 2018). Plastics microparticles are now found everywhere in the oceans (Woodall et al. 2014), and the pesticide DDT is found in the breast milk of Inuit mothers (Gibson et al. 2016).

1120 The chemical industry is also a prodigious producer of greenhouse gases. Apart from the carbon dioxide emitted by the production of the energy that power chemical processes, some chemical processes emit carbon dioxide as a waste product. Most notable of these is the reduction of atmospheric nitrogen as the first step in the production of nitrogen fertilizers. Of all the greenhouse gases monitored by the IPCC, only carbon dioxide, methane and nitrous oxide are found in nature: the others are exclusively products of the chemical industry (IPCC 2014).

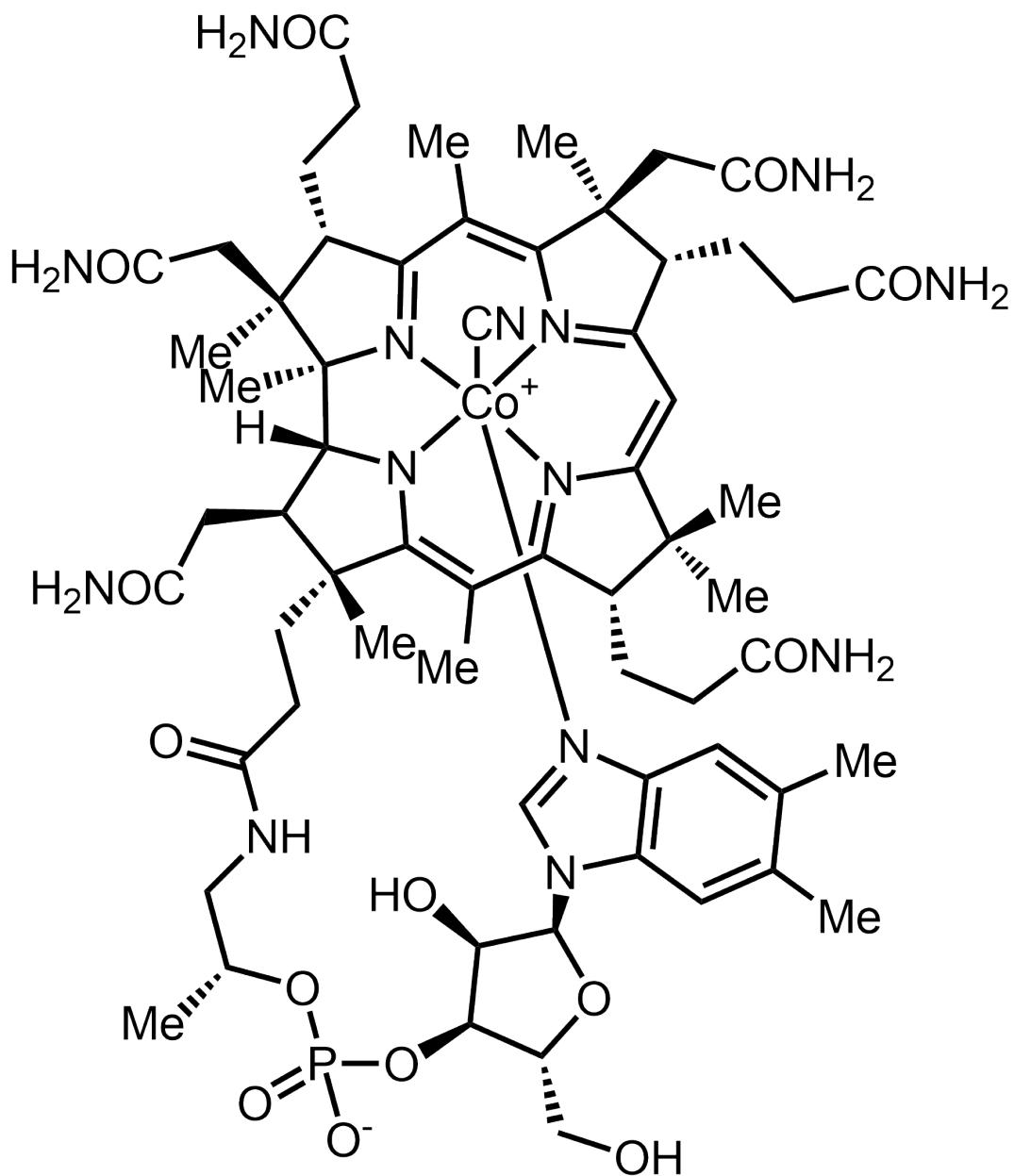


FIGURE 2.1: The chemical structure of cyanocobalamin, a form of vitamin B12. This compound is produced on the tonne scale by the chemical industry.

1125 No chemical has ever jumped out of a lab, multiplied uncontrollably, and spread into the environment to poison or pollute: they have all been introduced into the environment by human ignorance, negligence, or recklessness. All chemicals behave well when used in properly controlled environments, but human actions can let them escape and damage and pollute. But while we try to solve the intractable
1130 problem of human behaviour, we as chemists cannot just lay blame: we must pay attention to the intrinsic safety of chemicals and chemical processes.

2.1.1 “Green chemistry”

The date of the birth environmental movement is conventionally set to 1962, when
1135 the biologist Rachel Carson published the book *Silent Spring*, which pointed out the destruction of nature by the unrestricted use of pesticides, and the dangers of overuse (Carson 2003). This was a direct imputation of the chemical industry, because the pesticide products contained many chemicals.

Chemists are human, and the realization uncontrolled that chemicals can have detrimental effects lead at least some chemists to reflect on their own work. This has
1140 given rise to the concept of *green chemistry*. Although the term has no rigorous definition or quantitative measure (Linhorst 2010), a set of 12 principles or guidelines are proposed:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

- 1170 12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

1175 While these guidelines are clearly written with synthetic chemistry in mind, it does not mean that they do not apply to analytical chemistry. For example, Principle 7 suggests that, when possible, one should use hydrogen rather than helium as mobile phase in capillary gas chromatography: hydrogen is renewable, whereas helium is a finite resource and from time-to-time there are reports of shortages (Kornblut 2019).

1180 One large area of the greening of chemistry is changing the use of solvents. Principle 5 recommends that solvents use be avoided, if possible — most solvents used in chemistry are ultimately derived from petroleum and are toxic to some degree. But solvents play a large role in many kinds of chemistry, and eliminating their use in the near future seems unlikely. Searching for and characterizing bio-derived, non-toxic, non-persistent solvents is an active field of research (Clarke et al. 2018).

1185 But there are a few solvents in already current use that are inherently “green”, such as water or ethanol.

1185 One such naturally green solvent is carbon dioxide.

2.1.2 Carbon dioxide as a green chemical

Carbon dioxide as a chemical is used in industry in a few key areas.

- Carbon dioxide is often used in firefighting, in the form of portable fire extinguishers or room flooding systems. In this last use it is displacing the ozone-depleting halomethane (Halon).
- When liquid water is supersaturated with carbon dioxide, the gas desolvates slowly in the form of streams of tiny bubbles. This phenomenon makes beverages prepared from water supersaturated with carbon dioxide (or *carbonated water*) interesting to drink, and a large, international beverage industry is based on carbonated water.
- Carbon dioxide has a freezing point of -77 °C, and the solid can be conveniently obtained by evaporating liquid carbon dioxide at atmospheric pressure. The evaporating liquid rapidly cools the stream of carbon dioxide, lowering the temperature of the stream to below the freezing point, and the gas crystallizes into the solid. The resulting ‘snow’ can be compressed into blocks, which only slowly sublimates into gaseous carbon dioxide, keeping the temperature at the freezing point. Packing frozen food products together with this ‘dry ice’ allows for it to be transported cold.
- Pellets of dry ice can be entrained in a jet of air, and used to abrade surfaces for cleaning (Spur, Uhlmann, and Elbing 1999). This use of carbon dioxide can displace toxic solvents or abate the noxious dust produced by blasting operations.
- Carbon dioxide is a ‘natural refrigerant’ (Pearson 2005), and can be used to displace hydrofluorocarbon refrigerants, which are potent, long-lived greenhouse gases.

- Carbon dioxide can be used as a preservative and anti-oxidant in packaged food. If air in a packaged food is removed by purging the headspace with carbon dioxide, the growth of microbes can be discouraged, extending the shelf life of the product (Jacobsen and Bertelsen 2002).
- 1215 • Carbon dioxide can be used to extract compounds from natural products.

Of these uses, extractions are economically the most important.

2.2 Extractions using carbon dioxide

2.2.1 Commercial extractions

There are several commercial processes that use carbon dioxide to extract valuable

1220 products from plant material.

Plant oils

Vegetable oils are obtained from various crops, and can be extracted from the plant material by pressing, heating or extraction. High-pressure carbon dioxide has been used to extract vegetable oils from various plants, although it seems that this process 1225 has only found niche applications so far (Eisenmenger et al. 2006; Grażyna and Anna 2018).

Hops

Hops is an essential component in the brewing of beer. It imparts a desired bitter flavour, stabilizes the beer during storage, and assists with foam formation (Schönberger and Kostelecky 2011). Hops is a seasonal crop with a limited growing range, but the demand for beer is not limited to certain areas or seasons. The creation of hops extract makes it possible for brewers to benefit from hops without owning a hops plantation or storing and transporting dried hops over long distances. All hops extracts produced today are extracted by carbon dioxide (Hunt et al. 2010).

Coffee

Coffee is an international industry, with coffee drunk in many cultures and in many forms. One of the attractions of coffee is the effects of the psychoactive substance found in the coffee bean, *caffeine*. Caffeine is a mild stimulant and promotes wakefulness. A small proportion of coffee drinkers enjoy drinking coffee, but prefer to 1240 avoid the stimulant effect, which might induce insomnia or irritability. For these coffee drinkers the market supplies *decaffeinated coffee*.

Given the large amount of coffee traded (an estimated 167.47 million bags of coffee in the 2018-2019 coffee year (*Coffee Market Report December 2018 2018*))¹, if only a small percentage of coffee needs to be decaffeinated, it will be a large amount of coffee to process, and industrial processes will be necessary to supply the demand.

Decaffeination of coffee is achieved by selectively extracting the caffeine from green (*i.e.* unroasted) coffee beans using carbon dioxide. This is the largest use of carbon dioxide for extraction (Ramalakshmi and Raghavan 1999). The extracted caffeine is sold for use in medication and 'energy' drinks.

¹The factoid that "coffee is the second-most traded commodity after oil" has been proven to be untrue (Greenberg 2017).

1250 **2.2.2 Analytical Extractions**

Extraction is not only an industrial process, but is part and parcel of analytical chemistry. The first extractions using carbon dioxide was not aimed at developing an industrial operation, but to develop methods for analytical chemistry. This method is usually called SFE, for supercritical fluid extraction.

1255 **2.2.3 Why carbon dioxide?**

But what makes carbon dioxide a suitable solvent for extraction?

There are two aspect to this question. The first is about the *greenness* of carbon dioxide. It is non-toxic, non-persistent, non-flammable, non-corrosive, inexpensive, commercially available, and a waste product. (It goes without saying that this carbon dioxide is sourced from a carbon-neutral source, perhaps the brewing industry.)

1260 The second aspect of the desirability of carbon dioxide lies in its physical properties and the conditions under which we use it.

1265 Chemists will intuitively understand that gaseous carbon dioxide has no solvating properties, and that liquid carbon dioxide should not behave much differently than any other solvent. Both these statements are true under 'normal' circumstances.

But consider the case of an isobaric cooling of a volume of gas. The gas-liquid transition takes place because energy is removed from the system. At some point the kinetic energy of some of the molecules becomes less than the energy of the intermolecular forces, and the molecules prefer to clump together, *i.e.* it condenses.

1270 The remaining gas molecules receive the excess energy, and therefore stay in the gas state, until more energy is removed, leading to more of the gas condensing. During this process the temperature remains constant, and this temperature is known as the boiling point.

Now consider a solute (solid or liquid) in the same volume of gas being cooled. In this case, as the gas cools, the gas-solute intermolecular forces can become stronger than than the gas-gas intermolecular forces at a temperature which is higher than the boiling point. In such a case the gas molecules will clump around solute molecules, while the kinetic energy of the gas molecules are still too high to allow condensation. Now the gas has obtained solvating properties and the solute will become truly dissolved in the gas.

1275 The same effect can be imagined to happen during the isothermal compression of a gas.

If there are more than one solute in the volume of gas, some might dissolve in the gas, while others one might not. This means that the solvating gas can be *selective*. It can also be seen that the solvating power of the gas will depend on the temperature and the pressure of the gas. This means that the solvent becomes *tunable*.

While the dense gas has solvating properties, it still has the physical properties of a gas:

Diffusivity The solvating gas maintains its low diffusion coefficients, which means that it can easily diffuse into porous material, and that solutes will rapidly diffuse through it.

Surface tension The solvating gas has a low surface tension, which means that it will readily 'wet' surfaces and penetrate porous material.

Viscosity The solvating gas has a low viscosity, which means that it takes little energy to pump it.

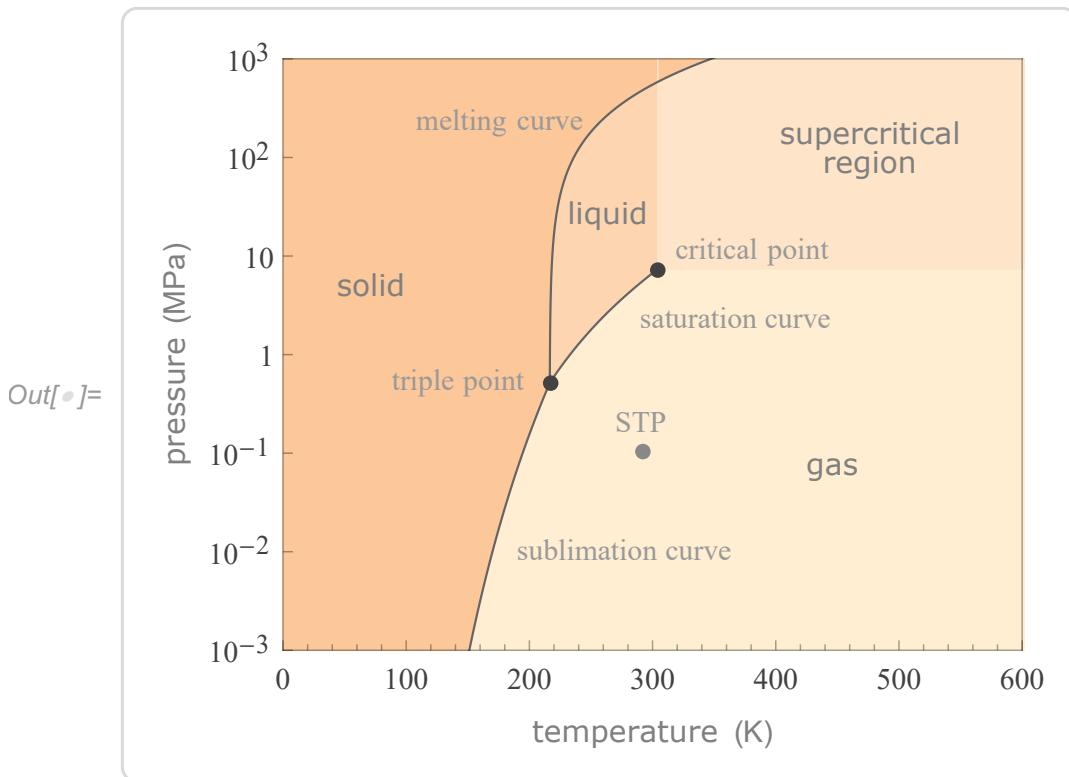


FIGURE 2.2: The phase diagram of carbon dioxide

For historical reasons such solvating gases are known as a 'supercritical fluids', because they were first obtained by heating a liquid at high pressure (Berche, Henkel, and Kenna 2009), so that the temperature and pressure of the substance is higher than its *critical point*. The critical pressure of a substance is the pressure above which it is impossible to create a gas-liquid phase transition by isobaric cooling, and the critical temperature is the temperature above which it is impossible to create a gas-liquid phase transition by isothermal compression. When the gas is at its critical temperature and critical pressure, it is at its critical point. The critical point is very different from the *triple point*: there is no equilibrium involved (See figure 2.2). The terms 'supercritical fluid' and 'dense gas' are synonyms (Randall 1982) — the adjective 'dense' in 'dense gas' of course implies that the gas behaviour is far from that of an ideal gas.

There are no discontinuities in binary diffusivity when temperature is changed from above to below the critical temperature (Lauer, McManigill, and Board 1983). Hence extractions are often done under conditions which are not technically 'supercritical' but still yields its benefits.

The critical pressure of carbon dioxide is 304.12 K (31.10 °C), and the critical pressure is 7.39 MPa (72.9 atm). This temperature and pressure are easy to achieve in the laboratory with standard chromatographic instrumentation, or in an industrial plant with standard process engineering technologies.

Carbon dioxide is gaseous at ambient conditions. This means that once it has been used in its role as extractant, and it is exposed to the atmosphere, it will rapidly evaporate, without needing added heat, and leaving no residues.

1320 Any pure compound will have a supercritical point. Compounds with technologically feasible supercritical points and useful chemical properties include ammonia, methanol, CFCs/Freon, hydrocarbons (propane, butane), water and sulfur hexafluoride. All of these lack green attributes: hydrocarbons pollute, the CFCs deplete ozone, sulfur hexafluoride is a potent greenhouse gas, and methanol and water are liquid at ambient conditions.

1325 For these reasons the term supercritical fluid extraction is practically synonymous with extraction using high-pressure carbon dioxide.

It is also possible to use supercritical fluids as reactants. This topic falls outside the scope of this discussion.

Modifiers

1330 The carbon dioxide molecule has zero dipole moment and the bulk fluid a low dielectric constant, so supercritical carbon dioxide is expected to be a non-polar solvent. (Although in practice the solvent behaviour is more complex, partly explained by the high quadrupole moment of the carbon dioxide molecule (Raveendran, Ikushima, and Wallen 2005).)

1335 While the solvating power of a supercritical fluid is certainly ‘tunable’ by adjusting its pressure and/or temperature, the range in solubility might be quite limited in practice. Just as with other solvents, it is possible to add a co-solvent or *modifier* to the supercritical carbon dioxide. This makes it possible to increase the solubility of polar compounds in the supercritical fluid. Methanol, ethanol, formic acid, and water are examples of suitable green modifiers for carbon dioxide (Herrero et al. 1340 2010).

1345 When modifiers are used the carbon-dioxide, modifier and solute forms a system with four degrees of freedom (modifier percentage, solute concentration, pressure, and temperature), which can become difficult to model. While this is a challenge for process engineers who need to design efficient industrial systems, analytical chemists can afford to be pragmatic and use heuristics to find suitable conditions (Wells, Zhou, and Parcher 2003).

Practical extractions

1350 Figure 2.3 shows a schematic diagram of a system set up for supercritical fluid extractions.

Carbon dioxide (a) is readily available from suppliers of industrial gases, and high-purity grades are available. Chromatography-grade solvents are usually used as modifiers (d). High-pressure pumps (HPLC type) are used to compress the carbon dioxide (b) and the modifier (c), which are mixed together at the appropriate ratio.

1355 The mixture gets pumped into the (optionally heated (f)) extraction cell (e), which contains the material that needs to be extracted. Having extracted the extract from the material, the supercritical fluid passes through a pressure-control mechanism (g). This allows the pressure of the supercritical fluid to drop to ambient, turning it into a low-density non-solvating gas. The extract becomes desolvated, and precipitates in the collection vessel (h). The operation of the system might be either static or dynamic: in static operation the supercritical fluid is pumped into the system, the flow is stopped, and the matrix/fluid mixture is given time to approach equilibrium. Then the fluid is expelled and the extract collected. In dynamic operation the supercritical fluid is pumped through the extraction cell and the extract collected 1360 continuously.

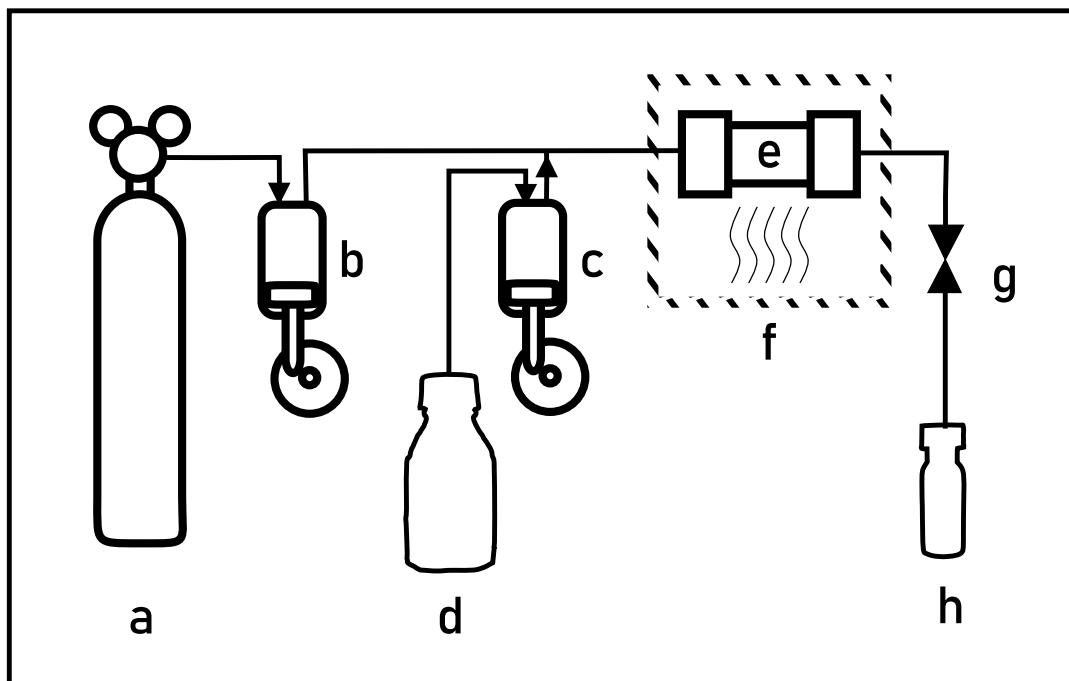


FIGURE 2.3: A diagram of an SFE system. (a) CO₂ supply (b) High-pressure SF pump (c) High-pressure modifier pump (d) Modifier reservoir (e) Extraction cell (f) Pressure control (g) Collection vessel

2.3 Supercritical Fluid Chromatography

An analyte will extract out of a matrix into a given solvent with a certain efficiency and at a certain rate. While this is important while finding an optimum extraction method, otherwise its relevance is limited.

1370 However, *different* analytes will extract out of a matrix with *different* efficiencies and at *different* rates. In a 1906 paper the Russian botanist Tsvet applied this observation to the dynamic extraction of a bed of calcium carbonate that had mixture of plant pigments applied at the inlet end, using petrochemical solvents. The different extraction efficiencies and rates of adsorption and desorption on the calcium carbonate surface lead to the *separation* of the compounds in the mixture. Tsvet called this method of separation *chromatography* (Ettre and Sakodynskii 1993a; Ettre and Sakodynskii 1993b). With time this method became generalized, and today chromatography is a major, established scientific field with many ramifications and a myriad of applications.

1380 Because of the different technologies used in its applications, chromatography is conventionally classed by the state of its mobile phase as either *gas chromatography* (GC) or *liquid chromatography* (LC). However, as we have seen, solvating gases can also extract analytes from solid stationary phases, and hence the term *supercritical fluid chromatography* (SFC) was created for these kinds of separations.

1385 Supercritical fluid chromatography as practised today bears a great resemblance to *high performance liquid chromatography* (HPLC). The main reason for this is that there is a large overlap between the technology used for HPLC and the technology needed for SFC. In particular, both use high-pressure pumps and columns packed

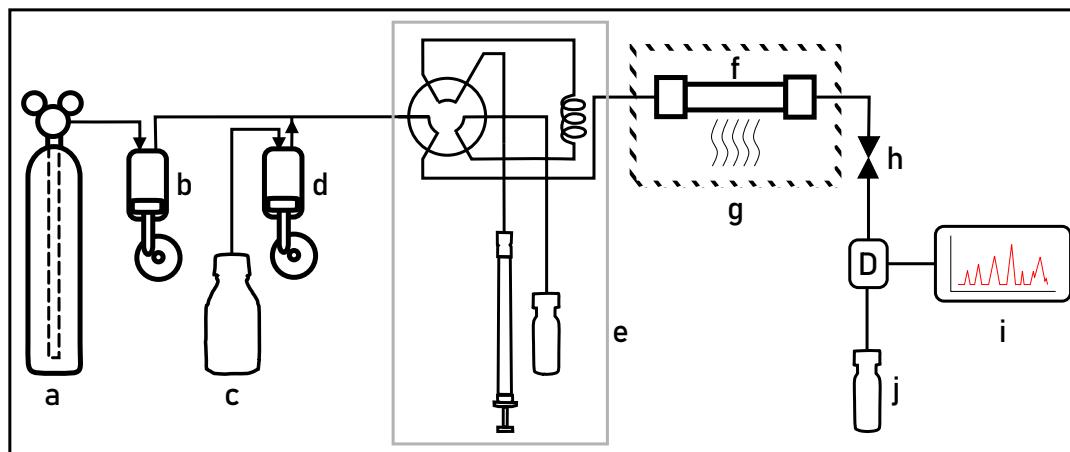


FIGURE 2.4: A diagram of an SFC system. (a) CO_2 supply (b) High-pressure SF pump (c) Modifier reservoir (d) High-pressure modifier pump (e) Injection system (f) Column (g) Optional heating (h) Back-pressure control (D) Detector (i) Data system (j) Optional fraction collection.

with particles of very small diameter, and use optical detectors. The same instrument manufacturers who supply HPLC instrumentation also supply SFC instrumentation.

2.3.1 SFC and FID

But SFC was not always a technique based on HPLC technology. In the 1980s SFC was practised using open tubular columns and flame detectors, so the instrument designs looked more like GC instruments than HPLC instruments, and SFC was sold as a replacement for GC (Poole 2003).

During this era the detectors used for SFC was the flame-based detectors used for CG, in particular the flame ionization detector (FID).

The *flame ionization detector* was invented near-simultaneously in South Africa and New Zealand (Ettre 2008). The core of the system is a flame of hydrogen gas burning in pure air. The measured signal is the conductivity of the flame plasma, which is measured by applying a -100 V potential difference between electrodes at the tip and the base of the flame. There are very few free ions in the hydrogen flame, so the conductivity is normally low. But organic compounds introduced into the flame creates a number of free ions, which increases the conductivity of the flame gases. The change in conductivity is measured by measuring the current between the two electrodes, using an electrometer.

As a first approximation the signal produced by the FID is proportional to the number of carbon atoms in the analyte. This is rather surprising, until the mechanism of its working is elucidated. At high temperature in the hydrogen-rich core of the flame, all hydrocarbon atoms are reduced to methane (Holm and Madsen 1996). Once it gets into contact with the hot oxygen in the outer layers of the flame there is a chemi-ionization reaction. The electric field acting on the ions creates a flow of ions, which can be measured as an electric current.

The FID's shining strength as a detector is its tremendous linear dynamic range of 10^7 . Combining the linear dynamic range with its carbon sensitivity makes it an excellent detector for quantifying organic compounds.

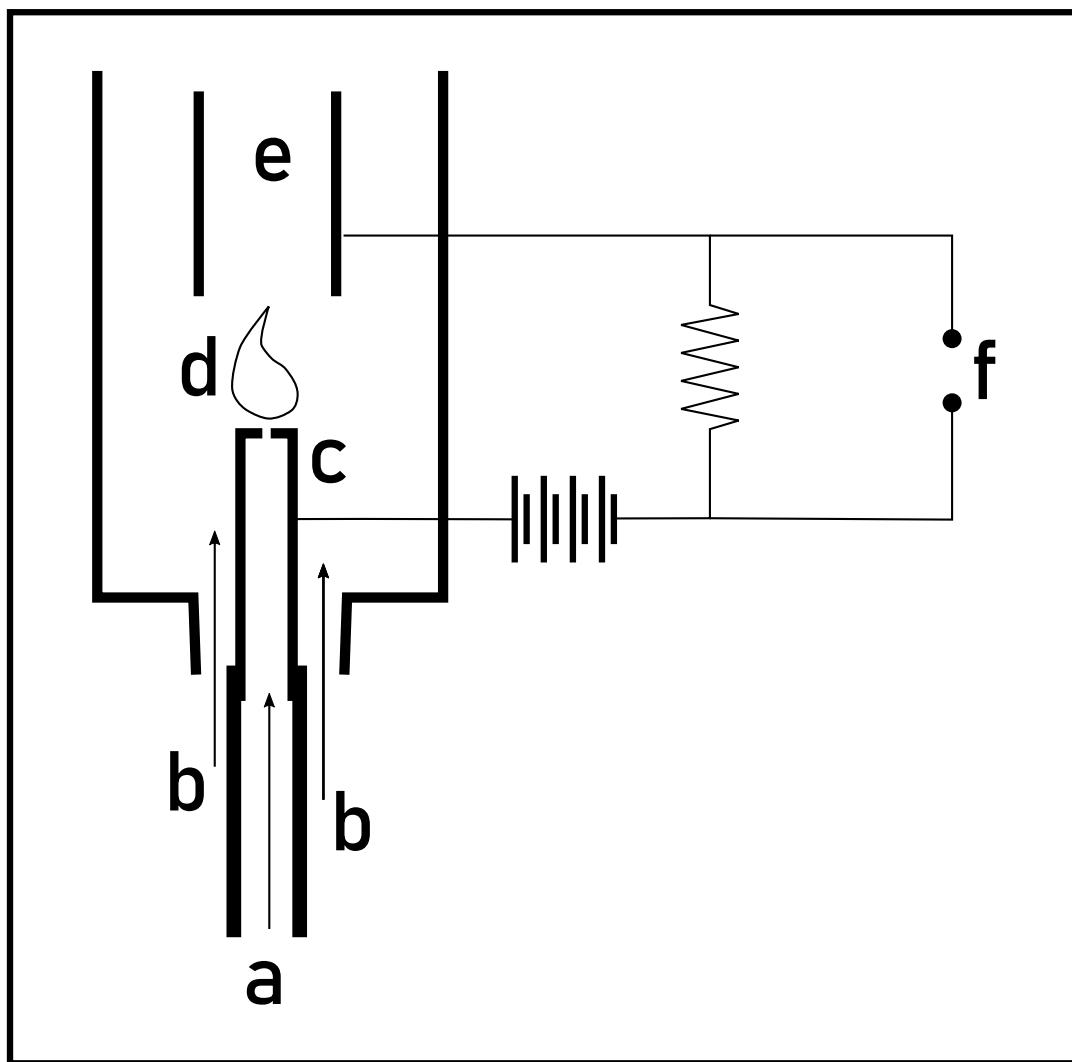


FIGURE 2.5: A schematic diagram of the flame ionization detector. (a) Mixture of column eluate and hydrogen gas (b) Clean air (c) Metallic flame tip electrode (d) Collector electrode (e) Conductivity signal

During period of history that SFC was seen as a variant of GC, the FID was the detector of choice. But when SFC started looking like HPLC, and the selectivity of the chromatography started being manipulated by adding modifiers (see Section 2.2.3), the FID lost its utility. The quantity of modifier added to the carbon dioxide mobile phase swamps the FID detector, making it useless as a detector. In contrast, if the chosen modifiers are transparent at the relevant wavelengths, optical detectors are more useful in SFC using modified carbon dioxide as a mobile phase.

1425 2.3.2 SFC \times GC

In chromatography, the analyte in the eluate can be detected to yield information about the sample, or fractions of eluate can be collected for further purification or characterization, or both. If fractions are collected, there is nothing that prevents the chromatographer from subjecting a collected fraction to another chromatographic separation.

For example, a synthetic chemist might use column chromatography to separate their target compound from side-reaction compounds, collecting fractions of the eluent. If the compounds are colourless, the chemist might use *thin-layer chromatography* (TLC) to examine the fractions for presence and purity of the relevant compounds.

If the product and the side-product were co-eluting it would not help to use the same chromatographic system (*i.e.* combination of stationary phase and mobile phase) for the TLC examination, because the co-elution would not become apparent. If, however, the chemist changed the mobile phase, or switched to a different stationary phase for the TLC examination, then it is quite likely that the two compounds would be separated.

For example, if a synthesis involving sugars were being attempted, two sugar enantiomers would likely co-elute on a silica clean-up column. Investigating the sugar fraction using a TLC plate with a chiral stationary phase would reveal the presence of stereoisomers.

1445 The second, chiral separation (on TLC) is said to be *orthogonal* to the first (packed column) separation.

Such a separation is an example of a two-dimensional (2D) separation. In analytical chromatography, 2D separations are powerful tools.

The simplest 2D chromatography is called *heart-cutting*. In such a case a fraction of interest is collected from the first dimension (¹D) separation, and subjected to a second dimension (²D) separation. For example, a fraction collected from an HPLC separation could be injected into a gas chromatograph. The separation on the GC dimension would obviously be very different from the separation on the HPLC dimension, and therefore we can say that the orthogonality is high.

1455 Heart-cutting is a useful way to get detailed information from a sample, but it is technically demanding and labour-intensive. It is usually employed for challenging separations in well-understood samples, because peaks of interest in the first dimension must be captured for injection on the second dimension.

If, however, one collects the eluate in equal fractions and do identical separations on each of the fractions, then one enters the domain of *comprehensive multidimensional chromatography*. The comprehensive coupling of orthogonal chromatographies does not demand a previous understanding of the sample, and doing exactly the same separation for each fraction allows the process to be automated.

A 2D separation can be called comprehensive if the following three criteria are met (Giddings 1987):

1. Every part of the sample is separated by two distinct chromatographic processes.
2. Equal percentages of all sample fractions are separated by the second process.
3. Compounds resolved by the first dimension separation remains resolved.

¹⁴⁷⁰ To effectively distinguish between heart-cut and comprehensive 2D couplings, a terse nomenclature was developed. Simple coupling between systems is designated by a hyphen ("‐"), for example HPLC-GC. This corresponds to the usual notation of a coupled detector coupled to a chromatograph, for example GC-FID or GC-MS. Comprehensive coupling is denoted by a multiplex sign ("×"), for example GC×GC. If ¹⁴⁷⁵ it is not clear from the context, the detector can be specified using a hyphen, as in GC×GC-MS.

Of the comprehensive coupled chromatography techniques, GC×GC is the most mature, with a selection of powerful instruments on the market.

¹⁴⁸⁰ This thesis further explores the implementation of SFC×GC, as first developed by Venter and Rohwer (A. Venter and Rohwer 2004; A. Venter, Makgware, and Rohwer 2006).

In this implementation of SFC×GC, fractions of the eluate of the SFC is transferred to the GC. The mobile phase is changed from carbon dioxide to hydrogen in the modulating interface, and the GC dimension is a conventional open-tubular ¹⁴⁸⁵ capillary separation with FID detection.

Any volatile modifiers or additives added to the SFC mobile phase will be separated from the analytes by the GC dimension. This makes it possible to use the FID as a detector in an SFC×GC chromatograph where the SFC is based on HPCL technology.

¹⁴⁹⁰ The ²D separations are *fast* chromatographic separations, *i.e.* separations optimized for speed, sacrificing resolution. This is achieved using fast temperature programming of the GC separation.

The high orthogonality of the SFC and the GC separations enables novel comprehensive 2D chromatography, which we applied to the chemical analysis of biodiesel.

In a book that I took from a shelf

...

Ancient proverb

1495

3

Literature survey

3.1 SANS 1935

3.1.1 Subsection 1

3.1.2 Subsection 2

1500

3.2 SFC

3.3 Fast Gas Chromatography

To do (1)

$pV \neq nRT$

The universal gas law does not apply to supercritical fluids

4

Instrumentation: Supercritical Fluid Chromatography

1505

This thesis discusses the development of a comprehensively coupled (supercritical fluid \times gas) chromatograph and its application to the analysis of biodiesel. The discussion on the experimental work divides naturally into two parts: this chapter discusses the supercritical fluid chromatography (SFC) and the next chapter discusses the gas chromatography (GC).

4.1 SFC

As discussed in Chapter 2, an SFC chromatograph consists of a supply of mobile phase, a pump, a pressure control system, a modifier control system, a column, a pressure relief system and a detector

4.2 Mobile phase

As mobile phase we used carbon dioxide. The benefits of carbon dioxide as an solvent and mobile phase is discussed in Chapter 2.

We used 99.995 % pure carbon dioxide supplied by Air Products. Our colleagues in industry also use food grade or technical grade carbon dioxide and they have not reported any significant impurities.

As modifier we used LiChrosolv®methanol from Merck. This is an 'HPLC-grade' solvent, of which the purification is optimized for the removal of UV-absorbing impurities. Using this grade of solvents is important when using optical absorbance or fluorescence detectors, because lowering levels of impurities improve limits of detection. It is quite likely that a less expensive grade of modifier would also be suitable for our SFC, because we do not use an optical detector.

1510

1515

1520

1525

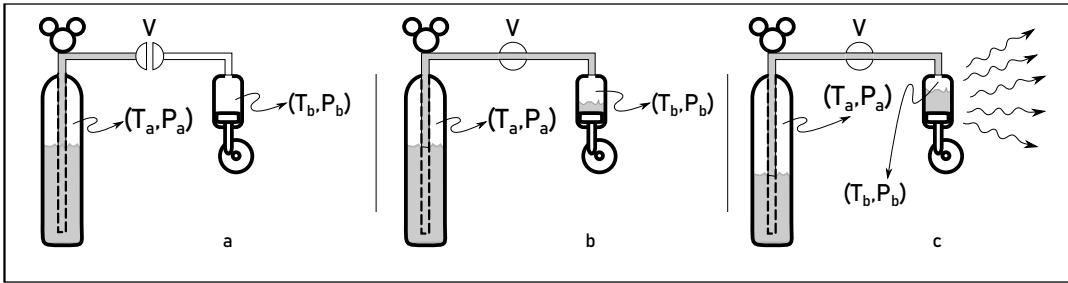


FIGURE 4.1: Diagram to help explain the filling of the carbon dioxide pump. (a) The pressure in the reservoir P_a is much higher than the pressure in the receptacle P_b . The valve is closed, so there is no flow. (b) The valve is open and some carbon dioxide has flowed from the reservoir to the receptacle. But $P_b = P_a$, so there is no flow. (c) When the temperature in the receptacle $T_b < T_a$, then $P_b < P_a$, following Gay-Lussac's law. Flow will continue until all the vapour in the receptacle has condensed.

4.3 Pump

As pump we used the robust, reliable Varian 8500 HPLC pump because it was available. This pump had its control electronics removed, and it was controlled from a personal computer by software written for the purpose.

The Varian 8500 pump is driven by a stepper motor. This kind of motor turns in discrete steps, instead of at a constant rate. It is driven by pulses of electric current, rather than a continuous current, and therefore the speed of the motor can be controlled by varying the rate of the pulses. This makes it relatively simple to control the speed of the motor from a computer.

The Varian 8500 pump has a built-in pressure transducer that provided an electronic signal proportional to the pressure at the pump outlet.

The Varian 8500 pump is a single-piston pump with a 250 ml capacity that needs to be refilled between strokes. Refilling means that one has to stop chromatography, which makes it important to fill the pump to full capacity, so that chromatographic runs are not interrupted. This means that the pump needs to be filled with carbon dioxide in the liquid phase rather than the vapour phase. Compressing either would create the appropriate phase for doing chromatography, but compressing a vapour would leave one with a much smaller volume of high-pressure carbon dioxide than compressing a liquid.

Filling a pump with liquid carbon dioxide is more difficult than one might imagine.

Imagine a reservoir of liquid carbon dioxide, equipped with a dip tube, connected to an empty receptacle via a valve (V). (See Figure 4.1) One can assume that the receptacle is empty and contains only carbon dioxide vapour at atmospheric pressure, say 1 atm. The vapour pressure of the vapour above the liquid in the reservoir is about 55.3 atm (5.6 MPa). When the valve (V) is opened the high-pressure vapour in the reservoir will expel the liquid carbon dioxide through the dip tube and through the valve, into the receptacle. In the low-pressure environment of the receptacle the carbon dioxide will boil. Soon there will be some liquid carbon dioxide in the receptacle, with the rest of the receptacle volume filled with gaseous carbon dioxide. When the system comes to equilibrium the pressure in the receptacle (P_b)

will equal the pressure in the reservoir (P_a), and there will be no flow of liquid carbon dioxide. One can attempt to now increase the flow by increasing the volume of the receptacle (for example by withdrawing a pump piston), and hence decreasing the vapour pressure there. But any flow from the reservoir will lead to expansion of the headspace of the reservoir. This will lead to cooling of the vapour, and therefore lower pressure and therefore lower flow. The final result of this process is that the receptacle is never filled to capacity with liquid.

The only way to restore the flow from the reservoir to the receptacle is to create a pressure difference $P_a - P_b$. While it is possible to create an overpressure in the reservoir by adding a headspace gas, it is technically challenging and expensive. It is simpler to use the Gay-Lussac gas law. According to this law the ratio of the pressure to the temperature of a gas is constant so that $\frac{P_b}{T_b} = k$. This means that a decrease in temperature will lead to a decrease in pressure. The way to fill the reservoir to capacity is to ensure that the temperature of headspace vapour T_a is higher than the temperature of the headspace vapour T_b . Because safety regulations prohibit the heating of a cylinder of pressurized gas, the way to ensure $T_a < T_b$ is to cool the receptacle. This cools the headspace vapour, and following the Gay-Lussac law the pressure P_b decreases, the difference $P_a - P_b$ increases and the liquid flows until the receptacle is filled to capacity.

In the case of the Varian 8500 pump the cooling of the pump was achieved by wrapping a coil of copper tubing around the cylinder, and pumping a chilled heat-exchange fluid through it. A chiller with a mechanically cooled tank with a 20 l capacity was filled with a solution of 5.0 l of diethyl glycerol in about 10 l of water. This mixture has a freezing point of -15°C , which can be cooled by the chiller without freezing. (If the coolant freezes a layer of ice forms on the cooling plate of the chiller, which isolates the remaining liquid from the cooling plate and limits the minimum temperature of the coolant.) An inexpensive submersible water pump (designed for decorative water fountains) was used to pump the coolant through the circuit. This pump can deliver 800 l of water per hour at a head of 1.2 m.

For some experiments we also used a SFT-10 pump from Supercritical Fluid Technologies (Newark, Delaware). This is a purpose-built two-piston pump with a sapphire valve seats and a Peltier-cooled head. This is a much better technology than the HPLC pumps. It takes up less space and does not need refilling, since it feeds directly from the cylinder. This pump had its own microprocessor controllers on board, and flow and pressure could simply be commanded from the PC through a USB cable.

4.3.1 Pressure control system

The aim of chromatography is to separate chromatograms by a certain distance. But the days of separating coloured compounds in glass packed columns are long past and the direct measurement of distances are now relegated to thin-layer chromatography. Instead, we have to make do with proxies for distance such as *retention volumes* or *retention times*.

Retention times are particularly convenient today, because it can easily be measured by computer systems.

Retention times, however, depend on a known flow rate of the mobile phase through the column. The flow rate need not be constant, although for the sake of simplicity a constant flow rate is preferred. Ideally, the flow rate should also be adjustable.

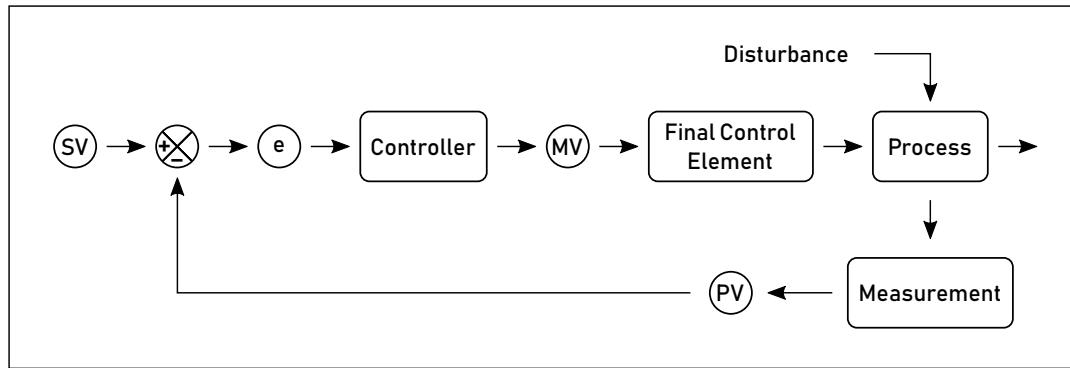


FIGURE 4.2: Schematic diagram of a closed-loop control system. (SV) Set Value, (PV) Process Variable, (e) Error, (MV) Manipulated Variable

The need for an adjustable, constant flow rate can be met by using a control system. Control systems are well understood by engineers, among whom it is a major field of study (Koenig 2009).

Figure 4.2 shows a diagram of a simple process control system. Some aspect of the process under control is measured, which yields the *process variable* (PV). The PV is compared to the *set value* (SV), and the *error* (e) is obtained by finding the difference. The error is provided to the controller, which calculates the *manipulated variable* (MV). The MV is used to drive the final control element, which adjusts the process with the aim of producing a smaller error.

Chromatographic systems conventionally work under pressure control or flow control regimes. Either is suitable: constant pressure systems usually yield constant flow if other parameters are held constant. Because flow measurement is more complex than pressure measurement, pressure control is the older, simpler and less expensive control method. Also, in SFC the solvent strength of the mobile phase is pressure/density dependent. We therefore selected pressure control as our control regime.

In our system the pressure measured by the on-pump sensor was the process variable (PV). This was compared to the set value (SV) set on the computer console. The controller was a software algorithm, implemented as a virtual instrument in the programming environment LabVIEW. The controller computed an output value for the manipulated variable (MV), which was the rate at which pulses were sent to the pump, in hertz. The digital input/output (DIO) interface of a National Instruments PCI-6014 multifunction data acquisition board created those pulses and sent them to the pump's electronic interface.

The software used a PID (Proportional-Integral-Derivative) controller module, with the Integral and Derivative contributions disabled. The simpler proportional control was found totally adequate for our purpose, and it can be improved in future by finding an appropriate tuning method and applying it with the integral and/or derivative activated.

4.3.2 Modifier Control

The modifier needs to be present in the mobile phase at a known and controlled concentration.

There are various SFC-modifier mobile phase supply units on the market. They tend to be expensive and complex, because they require the use of two controlled,

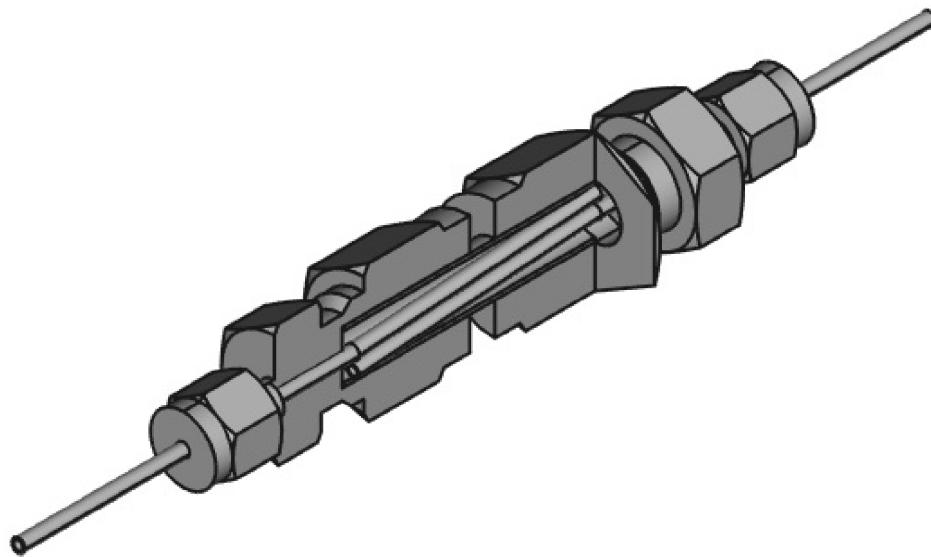


FIGURE 4.3: A cutaway diagram of the mixing chamber design. The chamber is designed for the mixing of the modifier and the supercritical carbon dioxide.

¹⁶⁴⁰ high-pressure pumps. Given that our needs were rather modest, we elected to use a simpler system.

Instead of accurately pumping the supercritical fluid and the modifier, we only pump and control the supercritical carbon dioxide and add measured volumes of modifier.

¹⁶⁴⁵ The modifier control unit consisted of a six-port valve, a fixed-volume measuring loop, and a mixing chamber.

The unit operates by filling the measuring loop with modifier, and then switching the measuring loop into the flowing mobile phase. The modifier is washed into the mixing chamber, where it is intimately mixed with and dissolved in the supercritical ¹⁶⁵⁰ carbon dioxide. The concentration of modifier in the mobile phase is determined by the switching rate of the sampling valve. Given that about 3 volumes of supercritical carbon dioxide is needed to wash the modifier out of the loop, the highest concentration of modifier that can be added in this manner is about 25 %.

Figure 4.3 shows the chosen design of the mixing chamber. The inlet and outlet ¹⁶⁵⁵ pipes of the mixing chamber extend far into the chamber, to break up plug flow and encourage rapid mixing.

The modifier injection valve position was commanded from the controlling PC by electronic voltage pulses.

4.4 Sample injection

¹⁶⁶⁰ The sample inlet was a two-position rotary valve with an internal sampling volume (Figure 4.4). In one position the sampling volume was filled with a syringe, and

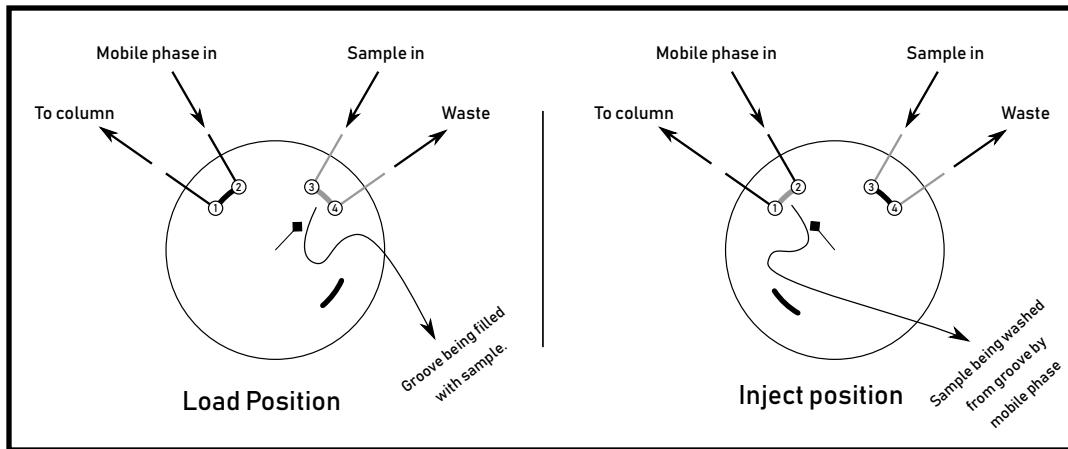


FIGURE 4.4: A schematic diagram of the sampling valve.

when the valve was commanded to inject the sampling volume was switched into the carrier mobile stream.

The reader might be more familiar with the six-port valve as an injection system.
 1665 The benefit of the internal groove injection valve is that it allows a much smaller volume to be injected. Using this small volume makes it possible to inject samples without dilution, which simplifies sample preparation. A drawback of this design is that it is not possible to vary the volume of sample injected.

The sample volume was $5 \mu\text{l}$

1670 The injection valve position was commanded from the controlling PC by electronic voltage pulses.

4.4.1 Column

The separation power of a chromatographic system can be modelled by the equation

$$R_s = \left(\frac{\sqrt{N}}{4} \right) \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{\bar{k}}{1 + \bar{k}} \right) \quad (4.1)$$

were, R_s is the *peak resolution*, N is the *number of plates*, α is the *selectivity*, and \bar{k} is the *retention factor*.
 1675

The number of plates N can be increased simply by making the column longer, at the cost of increasing the time of the run.

The maximum length of the column is determined by the pressure drop available
 1680 that will still yield adequate flow. In capillary gas chromatography the openness of the column and the low viscosity of the gas-phase mobile phase routinely allows columns 100 metres long at inlet pressures of a few atmospheres. In HPLC the high viscosity of the mobile phase and the narrow, tortuous pathways between the small particles of the packing material means that the columns are typically 100 - 200 mm long, requiring hundreds of atmospheres of inlet pressure for adequate flow.

1685 The low viscosity of an SFC mobile phase allows operation of much longer HPLC-type packed columns. This provides a much higher number of plates in the chromatographic system than HPLC.

The SFC column we used in the SFC×GC system was a set of five HPLC columns (150 mm × 4.6 mm, 3 μm particles) (Restek, Pinnacle DB Silica) connected in series.

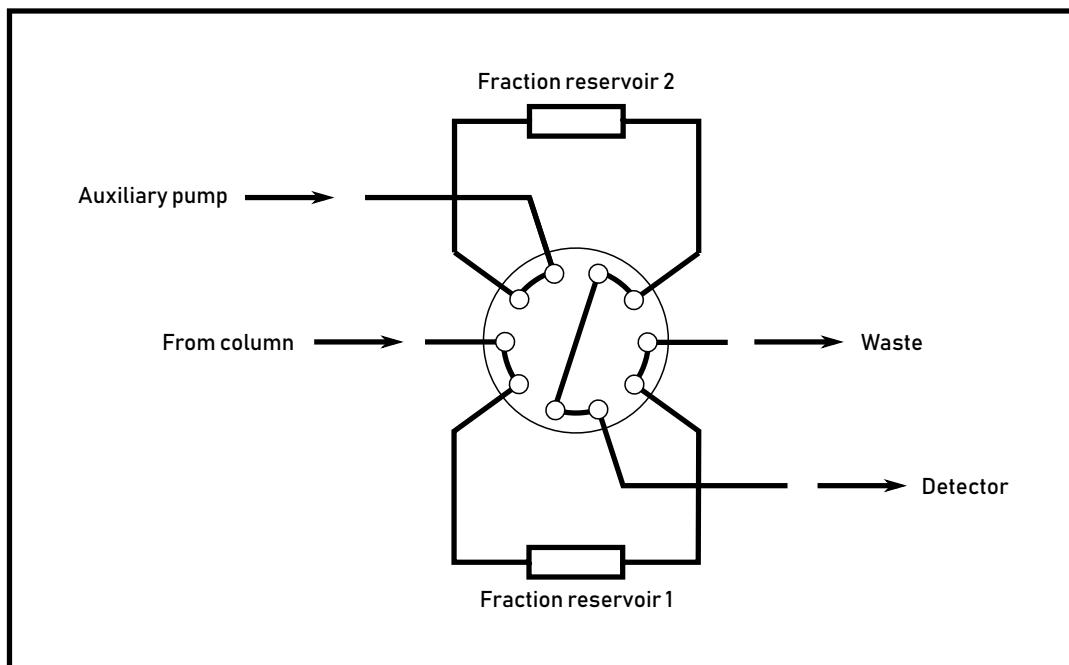


FIGURE 4.5: A schematic diagram of a valve configured to allow continuous-flow fraction collection.

1690 The stationary phase in this column is 'bare silica', which is usually considered 'polar'. That means that the packing of the column consists of porous silica particles with no organic phase covering its surface, and hence one that will interact strongly with polar molecules. In contrast, the ubiquitous 'C18' stationary phase used in reverse-phase HPLC is 'non-polar'. The particles of such a stationary phase
1695 are coated with octadecyl chains bonded to its surface, and hence will tend to interact strongly with non-polar molecules. The base material of the particles is usually silica, but that is only because manufacturing uniform particles of a given size from silica is a mature technology and not because silica is important to the separation mechanism. (In fact, some care has to be taken to deactivate the silica so that it does
1700 not contribute to the retention. Such a mixed retention mechanism can lead to peak tailing.)

4.4.2 Stopped-flow

1705 Among analytical chemists it is the convention that chromatographic runs are done without interruptions. In our SFC \times GC chromatograph we collect fractions of SFC eluate and separate them by GC. It is possible to collect, store and inject fractions of SFC eluate while maintaining continuous flow, for example using a dual storage loop system like the one depicted in Figure 4.5. But such systems require careful selection of volumes, fraction collection reservoirs with matching volumes, and an auxiliary pump.

1710 Instead of such a system, we opted for a more versatile and simpler stopped-flow system. In this system a fraction of the SFC eluate is collected, and then the flow through the column is stopped. While the flow is stopped the collected fraction is subjected to separation by GC.

1715 In packed columns, "eddy diffusion is always the main cause for peak broadening at any temperature and at high velocities" (Gritti and Guiochon 2006). During

the period that the flow is stopped only longitudinal diffusion contributes to peak broadening, which is small compared to eddy diffusion in dense mobile phases. Using the simple stopped-flow technique of sample collection will therefore not have a major effect on the resolution of the ^1D chromatography.

1720 The flow in the SFC was stopped by a six-port rotary valve using three of the ports, directing flow either to a blocked-off port or to the depressurizer, in effect making it an on-off controller.

4.5 Pressure Relief

1725 No matter the kind of SFC system one uses, at some point the eluate needs to be depressurized. This can be before or after the detector. If depressurization happens after the detector, then the details of the mechanism doesn't matter much, because the information has been obtained and the eluate can be discarded. If, as in our case, the depressurized eluate needs to still pass the detector, it is important to not lose the resolution achieved by the column. This means that the design of the depressurizer requires some care.

1730 The main concern in depressurizer design is premature desolvation of analytes. This causes *discrimination*, which is the differential treatment of substances where identical treatments are required. In particular, compounds of higher molecular weight tend to desolve first from the supercritical fluid, and might precipitate in the wrong place if the depressurizer is not designed to prevent it.

1735 Depressurization can be done either statically or dynamically. In a dynamic system there is an active element that controls the flow of the eluate in such a way as to maintain the pressure upstream of the active element of the controller. Such a device is often called a *back pressure regulator*, and is usually an electro-mechanical device with digital control. They tend to be complex and expensive.

In static depressurization there is no active pressure control. A simple *restrictor* is used to limit the flow between the high pressure of the SFC and the low-pressure outlet.

1745 Textbooks often discuss different restrictor designs. (The book by Luque de Castro, Valcárcel, and Tena 1994, provides an example.). Our preferred depressurizer was the 'integral' or Guthrie design (Guthrie and Schwartz 1986). Figure 4.6 shows the steps in manufacturing the Guthrie restrictor.

1750 We found this restrictor robust and fairly simple to manufacture. It was possible to adjust the flow to a given flow rate. This design of restrictor should eliminate discrimination, because the decompression takes place in a very short space.

However, the Guthrie design proved prone to blockage. These blockages could not be eliminated by incorporating a $0.5 \mu\text{m}$ filter before the restrictor, which prompted an investigation into the cause of blockages.

1755 To rule out the possibility that it was particles that caused the Guthrie restrictor to become blocked, we first had to determine the diameter of the orifice. This proved to be harder than expected: optical microscopy was not able to give a simple, unambiguous measure of the orifice diameter.

1760 Scanning electron microscopy (SEM) showed that the orifice diameter of a Guthrie restrictor is about $10 \mu\text{m}$, as shown in Figure 4.7. This makes it very unlikely that particles with an origin in the SFC system blocked the restrictor: even the $3 \mu\text{m}$ particles from the column packing material should not block this restrictor.

Experience had taught us that the restrictor did not block if the flow was continuous. It was only when the pressure in the restrictor cycled that blockages occurred.

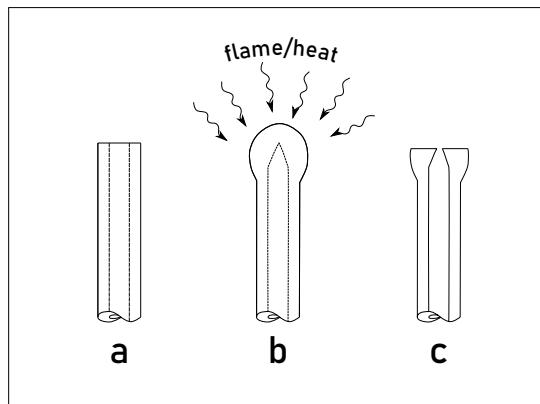


FIGURE 4.6: The steps of making a Guthrie restrictor. (a) Cut length of quartz capillary (b) Heat with flame to soften glass and create internal cone (c) Grind down end to expose orifice of the appropriate size.

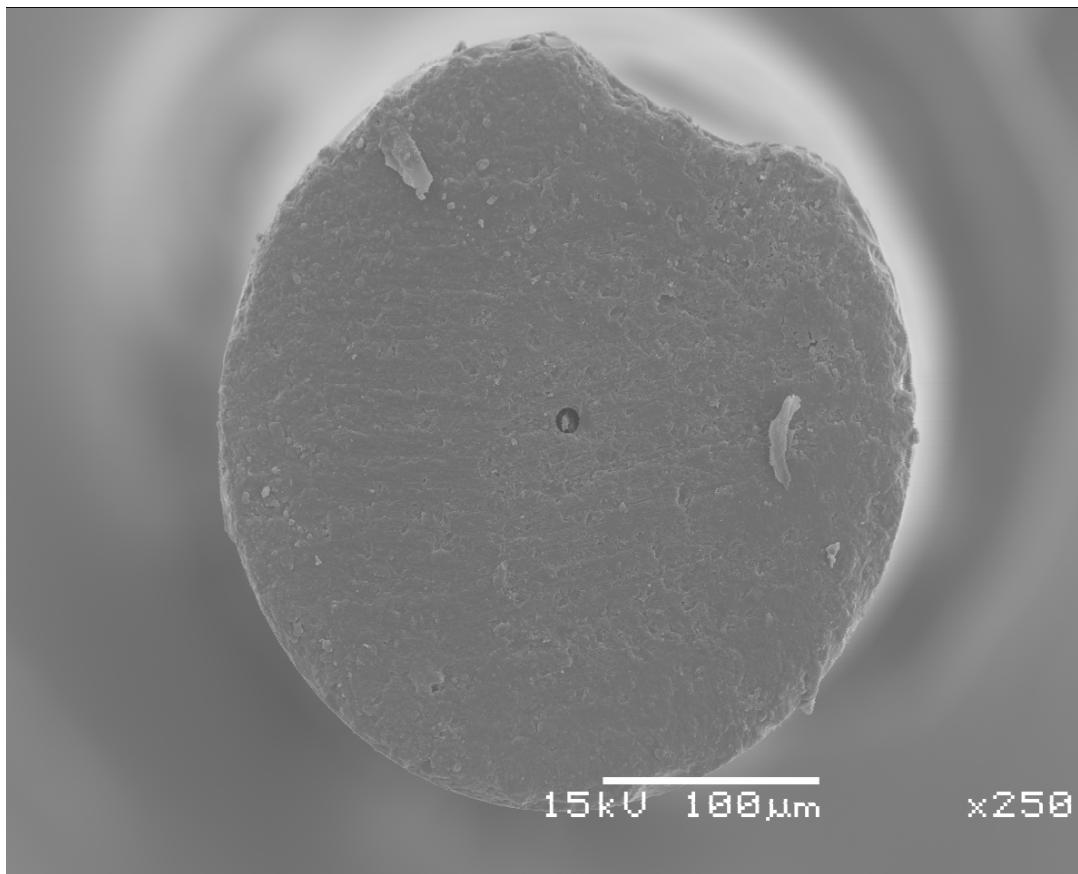


FIGURE 4.7: An electron microscope photograph of a restrictor tip, showing the size of the orifice.

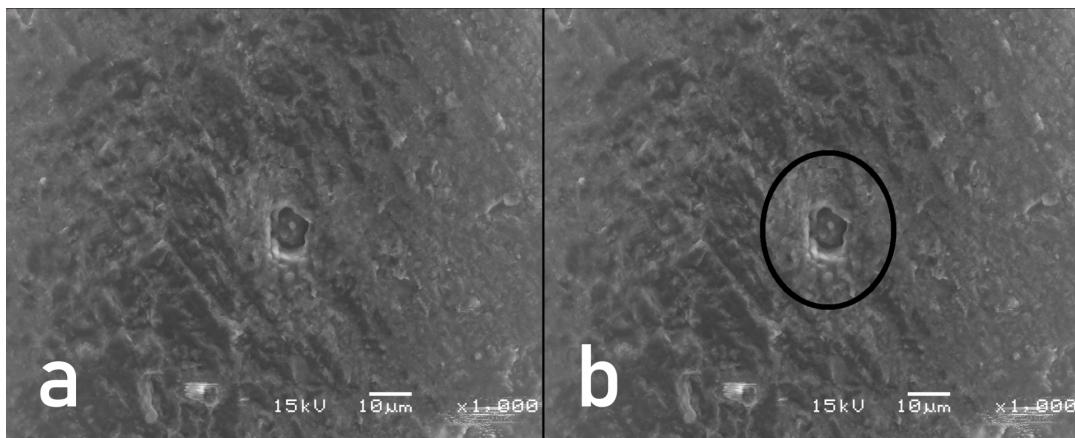


FIGURE 4.8: An electron microscope photograph of a blocked restrictor orifice. (a) Original image (b) Image with black circle showing estimated original orifice location

To eliminate the possibility that it was material from the stop valve (see Section 4.4.2)
1765 that caused the blockages, we cycled the pressure by switching the pump on and off, allowing the pressure to bleed off through the restrictor. This way of cycling the pressure did not prevent blockages.

1770 Examination of blocked restrictors with electron microscopy revealed that the restrictors became blocked by a soft material. Backscatter SEM mode allows the energy of X-rays to be measured by energy-dispersive spectrometry, which yields information about elemental composition. While much care must be taken before this information can be used for quantitation, it revealed that the deposited material contains significant quantities of carbon and oxygen, and possibly some chlorine. This points to the probability that the material blocking the column is organic in nature, and possibly polymeric. See Figure 4.8.
1775

We could not determine the origin of the material, but it seems likely to be the column, because cycling the pressure without a column did not cause a blockage. We eliminated the possibility of blockage by sample material by using a brand new column. We suspect that the blocking material might be remnants of surfactants used in the synthesis of the silica gel stationary phase. These surfactants are leached out of the column packing by the highly diffusive supercritical fluid mobile phase, and they then precipitate in the restrictor when the pressure drops and the compounds desolvate. Repetitive pressure cycles causes a build-up of material which gradually blocks the orifice.
1780

The smallness of the orifice contributes to the plugging problem. With a diameter of 50 μm, a solid sphere that fits in this capillary will have a volume of .065 nl, or 65 pl. This means that nanogram quantities of material can easily block the restrictor.
1785

Being satisfied that an unfortunate combination of restrictor design and column packing was the likely cause of the blockages, we decided to choose a different restrictor design. The choice was a simple linear restrictor and we trusted that heating the end of the restrictor would prevent discrimination.
1790

The linear restrictor was 800 mm long and had an internal diameter of 0.050 mm.

4.6 Detector

When SFC was first developed, a capillary column was the usual column, and an FID was the usual detector. In current use, however, packed columns used with mobile phase modifiers predominate and flame detectors have lost their place: the high concentration of modifiers in the mobile phase would swamp the signal from analytes or saturate the detector. Therefore modern SFC uses predominantly UV/Vis optical detectors.

In the supercritical fluid chromatograph described in this chapter there was no dedicated detector: the role of the detector was taken by a gas chromatograph. This gas chromatograph collected fractions from the SFC, and separated them in fast chromatographic runs with an FID detector, yielding comprehensive 2D chromatograms. This chromatograph-as-a-detector is described in Chapter 5.

There are no significant technical limitations to column temperature programming in the order of a few hundred degrees per minute and equally rapid cool-down rates.

Wolfgang Bertsch, pessimist, 1997

5

1805

Instrumentation: Fast temperature programmed gas chromatography

This thesis discusses the development of a comprehensively coupled (supercritical fluid \times gas) chromatograph and its application to the analysis of biodiesel. The discussion on the experimental work divides naturally into two parts: the previous chapter discusses the supercritical fluid chromatography (SFC) and this chapter discusses the gas chromatography (GC).

5.1 Speed of analysis

In principle, comprehensively coupled chromatography (as discussed in Section 2.3.2) could be performed by manually or mechanically collecting equal-sized fractions from a ^1D chromatograph, and then injecting a portion of each fraction into a different (^2D) chromatograph. This would meet all the criteria for comprehensively coupled chromatography. In practice, such an approach would be slow, labour-intensive, expensive, and error-prone.

But reliable devices were invented that can repeatedly collect and re-inject fractions of eluate *while the ^1D chromatograph is still running*. These devices became known as *modulators* and made comprehensively coupled chromatography practical. Today GC \times GC is an established technique: the annual GC \times GC Symposium is in its 15th year, and major reviews are published regularly (J. V. Seeley and S. K. Seeley 2013; Prebihalo et al. 2018).

In GC \times GC the entire 2D chromatogram is finished within the duration of the ^1D run. This is made possible by using short, narrow-bore columns with thin-film stationary phases in the ^2D separation, which allows *fast chromatography*.

In LC \times GC and SFC \times GC with packed ^1D columns using stopped-flow modulation (as described in Section 4.4.2) the total run time can be longer, but not indefinitely longer. Firstly, in dense mobile phases diffusion is not zero, so the stopped-flow time should be minimized to prevent unnecessary peak broadening. Secondly, total run times must be practical: while it's not inconceivable to have experiments that run for days, complex instrumentation can reliably run for such long periods is expensive.

1835

The time it takes for a stopped-flow SFC \times GC run can be calculated from

$$t_T = t_{SFC} + \frac{t_{SFC}}{t_m} \times t_{GC}$$

where t_T is the total time, t_{SFC} is the time the unmodulated SFC run would take, t_m is the interval between sampling events (better known as the *modulation period*), and t_{GC} is the time for each GC run.

1840 Examining the expression shows that we can decrease t_T by increasing t_m , but there is limit to this: if the modulation time becomes too long, the separation obtained in the 1D separation might be lost, which would mean it could no longer be considered comprehensively coupled chromatography. So the only way to decrease the total run times is to reduce t_{GC} , the GC run time.

1845 For example, if a typical SFC run takes 20 minutes, and fractions are collected for every 5 seconds of SFC run, it means there will be $20 \times 60/5 = 240$ fractions collected. Each of these fractions must be injected into a GC chromatograph. If each GC run took 1 minute, the SFC \times GC run would last $240\text{minutes} = 4\text{hours}$. Run times this long is not unheard of in analytical chromatography, but deciding on such 1850 long run times depends heavily on context. Finding the proverbial biomarker for Alzheimer's disease would justify such a long run time: routine quality control of a commodity biofuel would not.

This discussion should make it clear that for successful SFC \times GC the GC must be *fast*.

1855 5.2 Fast gas chromatography theory

The theory of fast gas chromatography has been well developed^{To do (2)}, and every chromatographer who has looked into faster chromatography has met the chromatographer's trilemma (See Figure 5.1): Any chromatographic method that involves trade-offs between speed, resolution, and capacity can maximize only one 1860 at a time¹. The fastest chromatogram will have low capacity and low resolution, the highest resolution chromatogram will be slow and have low capacity, and the chromatogram of a sample with a high concentration of analyte will be slow and have low resolution (Klee and L. M. Blumberg 2002).

We avoided the trilemma by not bothering with optimizing column capacity. 1865 Sample capacity in capillary GC is a function of film thickness and column diameter. We decided to use the workhorse of GC, the 0.25 mm internal diameter column with a 0.25 μm film thickness. The stationary phase was a proprietary cross-linked polysiloxane polymer (Restek Rx i ®-5Sil MS), designed to mimic the behaviour of a 5% diphenyl/95% dimethyl polysiloxane stationary phase. With the phase ratio/column capacity fixed, the remaining trade-off is between speed and resolution.

The experienced chromatographer will know that there is only one optimum flow rate, the minimum of the Van Deemter curve $\hat{h} = \frac{B}{u} + Cu$, or under conditions of high pressure drop, the equivalent equation by Blumberg (Leonid M. Blumberg 1997) $\hat{h} = \frac{B}{\bar{u}^2} + C_1 \bar{u}^2 + C_2 \bar{u}$.

1875 For a given column diameter and stationary phase, it is not possible to run a faster chromatogram with higher resolution. Any attempt to increase the speed will lead to lower resolution. If the mobile phase flow rate is at an optimum, a shorter column will yield a lower void time, but the number of plates will be lower so the

¹This trilemma applies only to capillary chromatography. When using packed columns the capacity can be readily increased by using a column with a larger diameter and a larger amount of packing.

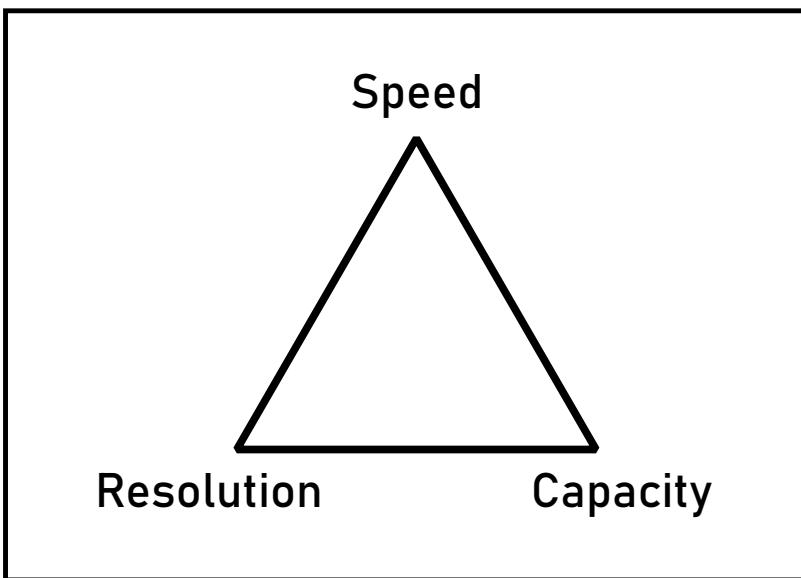


FIGURE 5.1: The chromatographer's trilemma.

separation will not have the time to complete, resulting in decreased resolution. If
1880 the column length is kept constant but the flow is increased, the plate height will be greater, so the same length of column will have fewer plates, and hence decreased resolution.

For this reason, the official methods of separating the fatty acid methyl esters (FAMEs) found in biodiesel require columns 100 m long (AOCS 2017), and run times
1885 of hours. These systems have just enough theoretical plates to separate the chemically very similar FAMEs

For any given column, the only way to make GC separations faster is to generate excess resolution. Fewer theoretical plates will then be necessary to obtain an optimal resolution. Excess resolution can be obtained by increasing the selectivity
1890 α , or by selective detection (e.g. an electron capture detector). In practical terms this means using a column with a different stationary phase or a different detector. A non-chromatographic way to generate excess resolution is often termed 'sample cleanup'. While usually considered part of sample preparation, it is an additional, pre-chromatographic separation step that removes non-analyte compounds, so that
1895 only relevant compounds need to be separated from each other.

In SFC \times GC excess resolution is generated in the ^1D SFC separation. By separating compounds by their group types first (A. Venter, Makgwane, and Rohwer 2006), the ^2D GC separation, in which separation is dominated by volatility, needs only resolve chemically similar peaks. The excess resolution generated by can be traded for faster chromatography using either, shorter columns, higher flow rates,
1900 temperature programming, or a combination of the above. Fortunately the literature shows that in deciding which approach to follow does not invoke a dilemma, and the recommendations are quite clear. It has been shown that superior resolution is obtained when shorter columns are used rather than higher flow rates (Klee and L. M. Blumberg 2002). In her thesis Gail Reed (Reed 1999) compared shorter columns against faster flow, and showed that shorter columns produce superior results over faster flow. Then she concluded:

"Fast temperature programming should be used for fast GC rather

Table 1. Typical 7890B GC Oven Ramp Rates

Temperature range (°C)	120 V Oven* rates (°C/min)	Fast ramp rates** (°C/min) Dual-Channel	Fast ramp rates** (°C/min) Single-Channel***
50 to 70	75	120	120
70 to 115	45	95	120
115 to 175	40	65	110
175 to 300	30	45	80
300 to 450	20	35	65

* Results obtained with line voltage maintained at 120V

** Fast ramp rates require power > 200 volts at > 15 Amps.

***Requires G2646-60500 oven insert accessory.

FIGURE 5.2: The temperature-rate table from the Agilent 7890B chromatograph data sheet (Agilent Technologies 2019).

than a smaller internal diameter. Fast temperature programming has been largely underutilized; however, new instrumentation will make it possible to more fully exploit fast temperature programming rates. Fast temperature programming rates allow for the use of short columns with normal i.d.s and film thicknesses which makes sample capacity less of a problem for this mode of fast GC compared to other means of fast GC.”

In line with this recommendation, the fast GC therefore used a short GC column (1 m long) that used a correspondingly fast temperature program.

5.3 Temperature programming

Temperature programming is, of course, not necessary only for fast chromatography, but has long been implemented to avoid the *general elution problem* (Skoog, Holler, and Crouch 2007). This problem can be summarized as follows: in separations of complex mixtures, it becomes unlikely that one set acceptable operating conditions (temperature, flow and stationary phase) will give satisfactory (fast enough with acceptable resolution) separations for all the compounds of interest. As discussed above, there is only one optimum flow, and it is impractical to change the stationary phase during a run, so the only parameter to change is the temperature.

The technology for temperature programming in GC is well developed, and every column manufacturer specifies temperature limits for isothermal and ramped temperature programs for every stationary phase.

5.4 Temperature ramp rates

When early experimenters realized the importance of temperature control in GC, they used oil baths^{To do (3)}, but quickly realized that leaks could allow oil into the column. Oil that entered the column would then contaminate the stationary phase, rendering it useless. Therefore, in the modern, conventional gas chromatograph the column is heated in an air bath with very precise temperature control. Blumberg and Klee (L. M. Blumberg and Klee 2000) recommend that a good initial temperature ramp rate is $10\text{ }^{\circ}\text{C}$ per void time (t_m). For long columns the void times are long, and the ramp rates can be low. As illustration, Figure 5.2 shows the temperature ramp rates of a state-of-the-art chromatograph. By contrast, for short, narrow-bore columns, the ramp rate needs to be thousands of Celsius degrees per minute.

1940 The low ramp rate of conventional air baths are cause by three factors:

- The low heat capacity of air
- The poor thermal conductivity of air
- The mass of the oven that needs to be heated.

1945 There is very little that can be done about these matters. In theory it would be possible to switch oven gas to hydrogen for higher thermal conductivity, and construct a low-mass oven using, say, advanced resins for construction, but this would probably involve significant safety and cost issues. What is required is a complete redesign of the heating principle.

5.4.1 Resistive heating

1950 Fortunately the heating rate problem has a technologically simple solution, *resistive heating*. When a constant electric field is applied to a metal, the free electrons in the metal will be accelerated by the electric field. But the electrons are within the crystal lattice of the metal, and the mean free path is very short. The electrons will therefore collide with atoms in the crystal lattice, scattering inelastically. The energy lost in the inelastic collisions will increase the vibrational frequency of atoms, and this energy will appear as heat. The number of electrons and their average (drift) speed will determine the current (I), and the electric field is best described by the applied voltage (V). The current I is proportional to the applied voltage, and the ratio $\frac{V}{I}$ defines the proportionality constant R , called the resistance, which is a function of 1955 conductor material and dimensions. The total power dissipated to heat (P) is given by $P = IV$ or, equivalently, $P = I^2R$ or $P = \frac{R}{V^2}$.

(Alternative methods of heating by electromagnetic fields are *inductive heating* and *dielectric heating*.)

1965 The rate at which the piece of metal heats up depends on the power dissipated, the mass of the metal, and its heat capacity. Applying a voltage V to a metal element in close proximity to the column will heat the metal, and therefore the column in contact with it. If the volume of the metal is small enough, and the current high enough, the temperature of the metal element will increase, and with it the temperature of the column. By suitable manipulation of V , then, the temperature of the 1970 column can then be changed at any desirable rate.

This technology has been reviewed (Wang, Tolley, and Lee 2012; M. R. Jacobs, Hilder, and Shellie 2013), and a few technologies for resistive heating of capillary columns have emerged:

- Direct heating of a metal column or a columns coated with metal layers
- Collinear heating
- Coaxial heating

1980 The first SFC \times GC work done (A. Venter and Rohwer 2004) used a directly heated metal column. While this approach proved the concept, experience showed two shortcomings. Firstly, metallic columns are usually designed with specific high-temperature applications in mind. This means that metal columns are not available with all the stationary phases available in fused-silica columns. Secondly, it was harder than expected to control the temperature accurately. The temperature was

determined by a thermocouple glued to the column, which was sensitive to local variations.

Agilent™ supplies a ‘low thermal mass’ column, which includes collinear heating wire and a collinear sensing element bundled with a short silica column. This approach requires that the collinear heating element be wrapped in close contact with the column.

For the work presented in this thesis, we used a coaxial heater. This heater is in the form of a thin-walled stainless steel tube that carries the electric current. The column is threaded inside the stainless steel tube, so that it is in close contact with the heater, giving reliable heat transfer. The metal tube is simultaneously used as a sensing element that reports the average temperature of the tube, and thereby the temperature of the column.

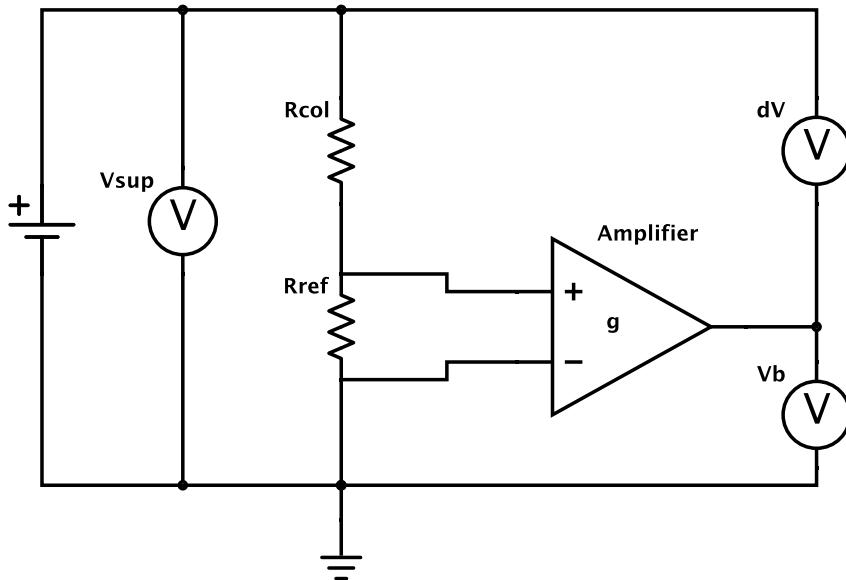


FIGURE 5.3: Electric circuit diagram of the coaxial heater.

The electrical resistance of a conductor is determined by its shape, the material it is made of, and the temperature of that material. In a conductor of given shape and dimensions, therefore, a knowledge of the resistance implies a knowledge of the temperature. By following changes in the resistance, one can determine changes in the temperature, and by comparing resistance at certain temperatures with known temperatures, one can get a calibrated temperature from a given resistance.

High-powered resistive heating implies low resistance. Measuring the *absolute value* of low resistance is technologically challenging [To do \(4\)](#). But a fairly simple electronic circuit can be used to *compare* the resistance of the coaxial heater with that of a reference resistor.

The circuit is supplied by a voltage V_{sup} , in general an unknown value. V_{col} and V_{ref} represents the voltage drop over the respective resistors.

Because the current I through the circuit is the same for both R_{col} and R_{ref} , it is true that $\frac{R_{col}}{V_{col}} = \frac{R_{ref}}{V_{ref}}$, and therefore

$$R_{col} = R_{ref} \frac{V_{col}}{V_{ref}} \quad (5.1)$$

The voltage drop across R_{ref} is too small to be directly digitized., and therefore it is amplified by the amplifier with gain g , so that $V_b = gV_{ref}$. V_b is measured, as is dV , the potential difference between the supply and the amplifier output.

$$V_{sup} = V_{col} + V_{ref}$$

$$V_{sup} = dV + V_b$$

$$V_{col} + V_{ref} = dV + V_b$$

$$V_{col} + V_{ref} = dV + gV_{ref}$$

$$V_{col} = dV + gV_{ref} - V_{ref}$$

$$V_{col} = dV + V_{ref}(g - 1)$$

$$\frac{V_{col}}{gV_{ref}} = dV/gV_{ref} + V_{ref}(g - 1)/gV_{ref}$$

$$\frac{V_{col}}{V_{ref}} = gdV/gV_{ref} + gV_{ref}(g - 1)/gV_{ref}$$

$$\frac{V_{col}}{V_{ref}} = gdV/V_b + (g - 1)$$

This proves that $\frac{V_{col}}{V_{ref}}$ is a linear function of dV/V_b . A quick check for correctness of the expression: for a unity-gain amplifier $g = 1$, and $\frac{V_{col}}{V_{ref}} = dV/V_b$.

5.5 Calibration

The assumption is that the temperature is a function of the resistance of the column, or $T = f(R_{col})$. Because $R_{col} = m(dV/V_b) + c$, we can say that $T = f^{-1}(dV/V_b)$. Through a calibration procedure f^{-1} can be approximated by a polynomial or lookup table.

5.5.1 Heating control and temperature programming

5.5.2 Temperature uniformity

It is highly desirable that the coaxial heater should give uniform heating. There is no guarantee that this will be the case. We did not analyse the problem theoretically, but the following factors need to be considered:

Resistivity's dependence on temperature

The resistance of a metal increases with temperature. This means that if one section of the coaxial heater should get hotter than the rest, its resistance will increase. If the current were to remain constant, more power would be dissipated in this section ($P = I^2R$). If more power is dissipated, the temperature will increase, leading to a higher resistivity, leading to higher power dissipation, leading to a higher temperature, in a runaway cycle. If the supply voltage was held constant a higher resistance in one section would mean a lower current overall, but still a higher power dissipation in the section with higher temperature.

Thermal conduction

Each section of the coaxial heater is in thermal contact with its neighbours. If it were to get hotter, the heat will flow from the hotter section to the cooler neighbouring sections. This will tend to even out any temperature differences.

Radiation

An object radiates heat, which can be approximated by the Stefan-Boltzman law:

$$P = A\epsilon\sigma T^4$$

where A is the surface area of the object, ϵ is the *emissivity* of the surface, σ is the Stefan-Boltzman constant, and T is the absolute temperature of the object.

If a section of the coaxial heater were to become hotter than the other sections, it would therefore radiate more heat. The increased power dissipation by the higher resistance will therefore be partially offset by a higher radiation. This will tend to moderate moderate temperature differences.

Convection

When a part of the coaxial heater is hot, it will heat the air around it, through radiation and conduction. This air might then move, through buoyancy or any other force, and end up next to another part of the coaxial heater. This second part could then be heated up by the transported air. For example, a vertically mounted coaxial heater can be expected to develop a temperature gradient from bottom to top, as natural convection lets hot air transfer heat from the lower end of the heater to the upper end. In this way temperature gradients could be established and maintained.

Examining thermal uniformity by imaging

The effect of the combination of resistivity's temperature dependence, thermal conduction, radiation, and convection on the temperature uniformity of the coaxial heater could be mathematically or numerically modelled, but such an endeavour would fall outside the scope of this project. Experience had not lead us to expect any significant temperature non-uniformity, but we welcomed the opportunity to get empirical confirmation.

Thermal imaging is the process by which infrared radiation from objects can be captured in a photographic process. At near-ambient temperatures objects emit copious amounts of infrared radiation, and higher the temperature, the more is emitted. Using specialized optics and sensors allows the capture of that radiation in a camera, which can produce an image of a scene that shows objects based on their surface temperature. The technological capability of thermal imaging has improved markedly over the past years

Using a FLIR™ T660 thermal imaging camera we obtained a video of the coaxial heater executing a temperature ramp. This camera uses a 640×480 focal plane uncooled bolometer array as a detector, which is sensitive to radiation in the range $7.5 \mu\text{m}$ to $14 \mu\text{m}$. Figure 5.4 shows the setup used to record the thermal video.

Figure 5.5 is a frame from the video, analysed to give estimates of the temperatures on spots on the coaxial heater. The maximum temperature difference between any two points is 17.5°C , and there are no marked gradients.

This examination of the uniformity of the coaxial heater put to rest any fears that unexpected temperature gradients would interfere with the fast gas chromatography.



FIGURE 5.4: This photograph shows the setup used to record the thermal video.

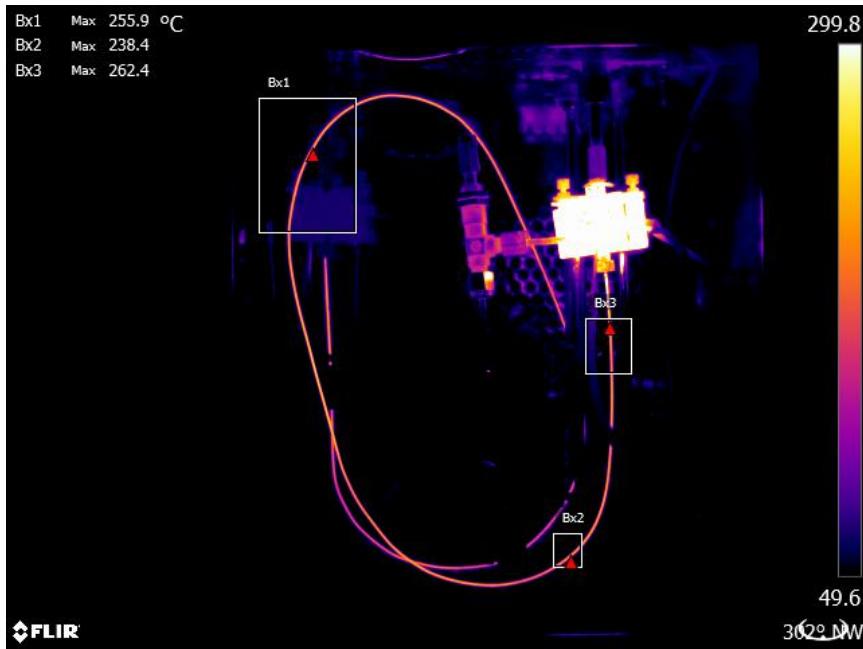


FIGURE 5.5: A thermograph of the coaxial heater at high temperature. It shows that there are no runaway hot spots.

5.5.3 Temperature calibration

When doing temperature-programmed gas chromatography it is desirable to have an absolute measurement of the column temperatures. This makes it possible to translate and compare methods between instruments. It was therefore necessary to calibrate the temperature of the coaxial heater. Calibration is the comparison of measurement values from a device under test with those of a calibration standard of known accuracy. In the case of the temperature calibration of the coaxial heater, it means comparing the results of the temperature as measured by the coaxial heater with a standard temperature.

The problems of measuring a temperature inside a tube with a bore of 0.8 mm are not trivial.

The following technologies exists to measure temperatures:

- Liquid-in-glass thermometers
- Sealed liquid or gas sensing instruments and bimetallic sensors.
- Electrical resistance temperature measurement using metallic sensors
- Thermistors and semiconductors
- Thermoelectric temperature measurement
- Disappearing filament optical pyrometer
- Photoelectrical optical pyrometers
- Total radiation pyrometers.

Liquid-in-glass thermometry would not be applicable because of the size of the devices, and because they don't give a desirable electrical signal.

In recent years the technology for measuring temperature by radiant energy methods have improved markedly and has become affordable, in the form of thermal cameras. However, at lower temperatures the accuracy of the recorded temperature depends heavily on the emissivity of the measured material. Thermal imaging will also only measure the outside wall surface temperature of the heater, and not the temperature of the inside of the coaxial heater. So, while thermal imaging settled questions about heater uniformity (Section 5.5.2), it was not considered ready to serve as a calibration standard.

This leaves us with resistance temperature measurement with metallic sensors, thermistors and semiconductors, and thermoelectric temperature measurement.

Electrical resistance measurement using metallic sensors might have been feasible, if sensing elements of the appropriate dimensions were commercially available. A further difficulty with this method of temperature measurement is that long, thin conductors would be needed to connect the sensing element to the electronics. These conductors would add to the resistance measured by the sensing element, requiring complex correction or multi-wire measuring methods.

Thermistor and semiconductor devices could, in principle, be made small enough for the job, but commercially available devices come in 'packages' that are too large. Besides, the temperature range used in GC (-50°C to 400°C) does not fall inside the operating temperature range specified by manufacturers of semiconductor devices (-55°C to 125°C for military devices).

Thermoelectric temperature measurement then remains, and was used to calibrate the coaxial heater. In particular, the *Seebeck effect* was exploited, which is the

observation that a temperature gradient imposed on a metallic conductor will generate an electrical potential along the gradient. Therefore, a circuit of two dissimilar metallic conductors will generate a voltage when there is a temperature gradient along the conductors. The voltage generated is a function of the temperature difference between the junctions of the two metals. Such a pair of dissimilar conductors used to generate a voltage is known as a *thermocouple*. Thermocouples are widely used in industry for measuring temperatures, and the technology is well established.
2135 Thermocouples don't have to be calibrated. They are usually constructed from well-characterized alloys that generate predictable voltages for given junction temperatures. Thermocouple alloys that have been standardized are known as 'types'. We selected the general-purpose Type K thermocouple. Thermocouple wire can be purchased in varying gauges, down to 25 µm in diameter, and the signal processing for thermocouple signals have been standardized.
2140

McGee (McGee 1988) states that thermocouple junctions can be made by welding, crimping, soft soldering, hard soldering, bolting, or simply twisting the wires together.
2145

Because of the temperature range expected to be measured (-50 °C to 400 °C) the option of soft soldering does not apply, because soft solders have a melting points around 200 °C. The possibility of corrosion and mechanical vibration suggest that
2150 twisting the wires together will not form a reliable joint, and of course there are no sub-millimetre bolts on the market.

This leaves welding, crimping and hard soldering as methods for making thermocouple junctions. The option of crimping was not explored, chiefly because we have no knowledge of technology or devices that can crimp hair-fine wire. Our
2155 knowledge of crimping suggest that shows another problem: the final crimped connection has a diameter many times the diameter of the wire. This precludes the application of crimping in this context.

Hard soldering is usually done with high-temperature flames, and on contact the flames will rapidly burn the fine wires. The temperatures required for hard
2160 soldering is still lower than the melting point of the wires, so that hard soldering is not excluded, but we did not have the knowledge or the technology to solve the associated problems.

Welding was found to be an accessible technology for forming small, reliable joints in fine fine thermocouple wire.

2165 5.5.4 Thermocouple Welding

Welding is the process of joining two metal parts by melting a portion of each part, allowing the molten metal first to mix, and then solidify. This creates a permanent joint between the two metals. Welding is widely practised as an industrial process.

Various sources of heating can be used, and we decided to use electricity. A 24 V
2170 direct current, adjustable bench power supply was used. The two wires of the thermocouple was twisted together, and the twisted pair was connected to one pole of the power supply. A carbon electrode was connected to the other pole. The carbon electrode was carefully brought closer to the thermocouple pair until a spark jumped across the air gap. When the spark turned into an arc, the heat of the arc melted the
2175 thermocouple. The molten metal would then contract into a spherical globule, which grew as the arc added more heat. As more of the metal of the wire melted, the globule would move away from the carbon electrode, until the gap became too large to sustain the arc. The current would then stop, and leaving a spherical welded bead at the end of the wires. The process could be repeated as often as necessary to obtain

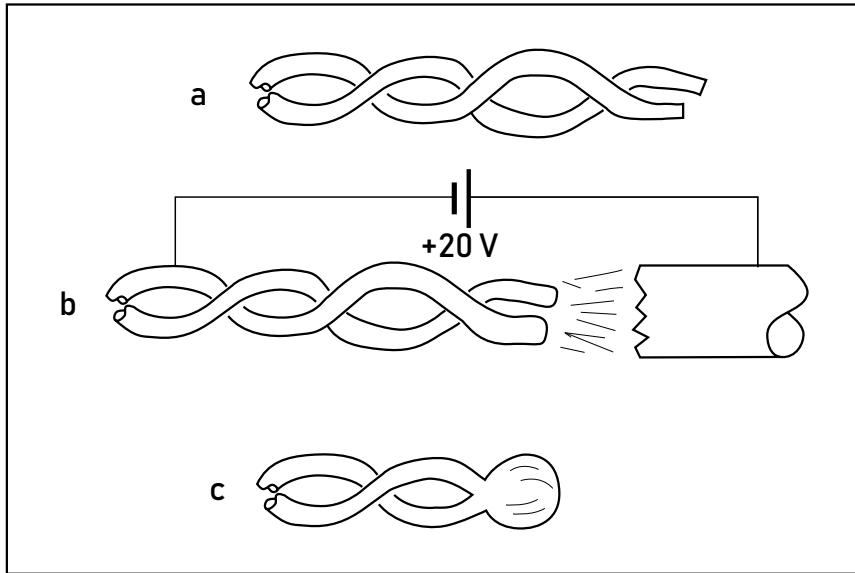


FIGURE 5.6: The process of welding fine wires to make thermocouples
 (a) Wires twisted together (b) Electric arc heating up the wires (c)
 Wires welded with a well-formed bead.

- 2180 a bead of the desired size. The steps of the process is shown in Figure 5.6. It is worth noting that it is absolutely necessary to form an arc: if the carbon electrode happened to touch the wire so that a current flowed directly from the wire to the carbon electrode the wire would rapidly heat up over its length, and melt. It is also interesting to note that it seemed necessary to have a roughly broken carbon electrode surface:
 2185 a polished surface would not generate an arc, or even make electrical contact with the wires. This might be because the graphite used for the electrode was formulated for use in pencils.

5.5.5 Termocouple probe construction

- 2190 To measure the temperature inside the coaxial heater required the thermocouple used for the measurement had to be inserted into the coaxial heater. For this we used fused silica capillaries with an inside diameter of 0.25 mm and an outside diameter of 0.4 mm. These were easily obtained in the form of worn-out chromatographic columns. A thinner capillary was used to draw the wires into the probe capillary, in a process described in Figure 5.9.

2195 5.5.6 Thermocouple interfacing

- The Type K thermocouple has a sensitivity of approximately $41 \mu\text{V}^{\circ}\text{C}^{-1}$. This means the voltage generated at the temperature range of interest is too small to be conveniently digitized and needs to be amplified. Because the Type K thermocouple is so commonly used in industry, amplifiers have been developed specifically for thermocouple signal conditioning. We chose the AD595 integrated circuit amplifier. The component's data sheet explains it best: "The AD595 is a complete instrumentation amplifier and thermocouple cold junction compensator on a monolithic chip. It combines an ice point reference with a precalibrated amplifier to produce a high level (10

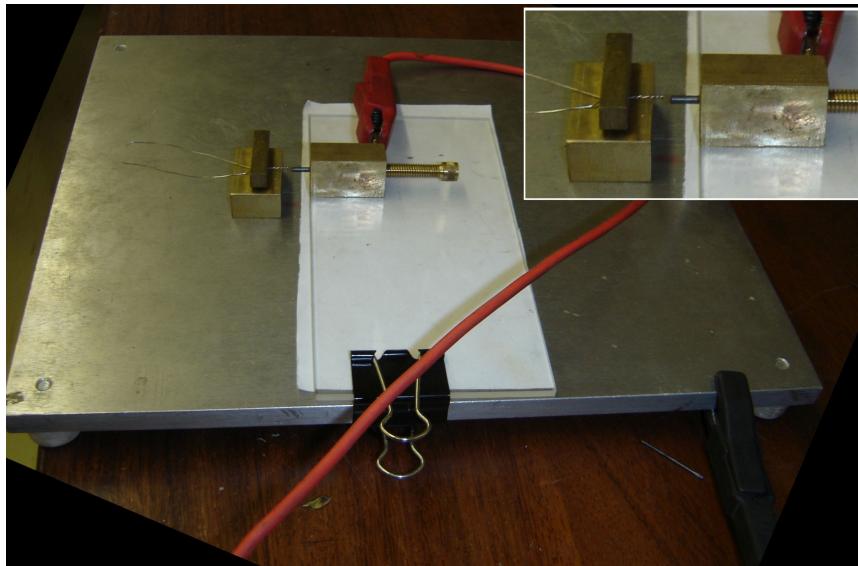


FIGURE 5.7: A view of the fine-wire thermocouple welder. The wire shown in the photograph is much thicker than that actually used. It is shown clamped between the clamping bar and the clamping weight. A thin sheet of acrylic serves to isolate the positive electrode from the negative base. The carbon electrode can be advanced towards the thermocouple twist using the screw. The black clamp at the bottom right-hand corner attached to the base plate and the red clamp attached to the screw housing provide a potential difference of approximately 20 V between the carbon electrode and the thermocouple.

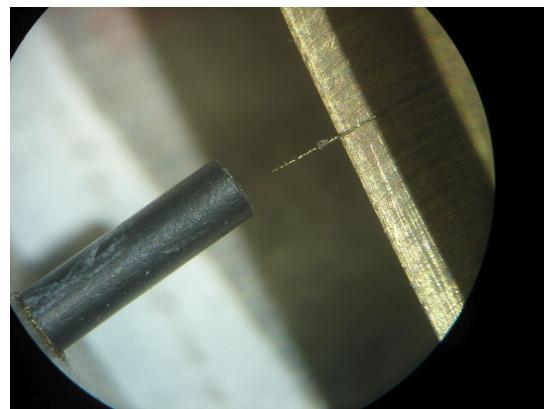


FIGURE 5.8: A microphoto of a twisted wire ready to be welded. The black carbon electrode is 2 mm in diameter.

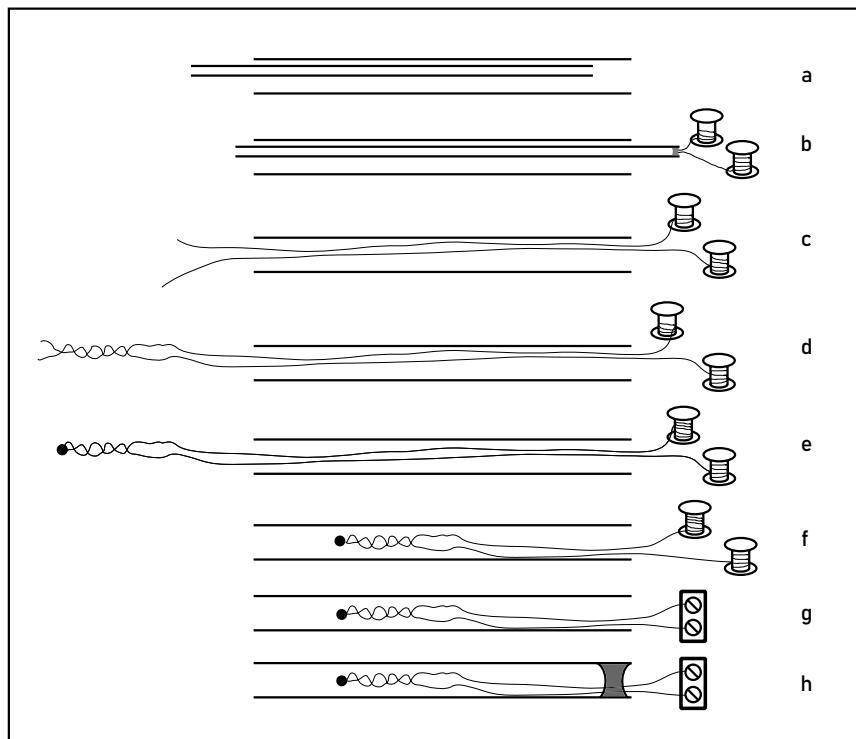


FIGURE 5.9: (a) A narrow capillary is threaded inside a wider one (b) The ends of a pair of thermocouple wires are fitted inside the end of the narrow capillary and anchored with cyanoacrylate adhesive. (c) The wires are pulled through the wider capillary using the narrow capillary. (d) The ends of the wires are twisted together, creating a mutual mechanical anchor. (e) The ends of the wires are welded together. (f) The wires are pulled back into the thick capillary, locating the junction at the desired position in the capillary. (g) The wires are trimmed and connected to a terminal block. (h) A drop of cyanoacrylate adhesive is used to anchor the wires permanently in the capillary.

2205 mV/°C) output directly from a thermocouple signal." (*Monolithic Thermocouple Amplifiers with Cold Junction Compensation 1999*) The output of the AD595 can be directly digitized and fed to the computer.

5.5.7 Calibration procedure

2210 The International Vocabulary of Metrology (*International vocabulary of metrology – Basic and general concepts and associated terms (VIM) 2019*) define **calibration** as "[an] operation that, under specified conditions, in a first step, establishes a relation between the **quantity values** with **measurement uncertainties** provided by **measurement standards** and corresponding **indications** with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a **measurement result** from an indication."

2215 In the first step of calibration, the **quantity values** used in the calibration was the temperature value of the thermocouple probe as provided by the thermocouple voltage, the AD595 amplifier, the digitization and the subsequent calculations according to the AD595 data sheet. The **measurement standards** were the known responses of the thermocouple (Ripple 1995), the amplifier and the digitization system. The
2220 **indication** was the voltage ratio $\frac{dV}{V_b}$. As this was a first attempt a calibration, **measurement uncertainties** were omitted.

2225 To calibrate the coaxial heater, the heater and its assembly was installed in the oven of the Varian 3300 GC as it would be when in use. The detector was removed, and the thermocouple probe was threaded into the coaxial heater through the detector stem, through the heated T-piece block, and into the coaxial heater. The probe was inserted so far that the thermocouple junction was about half-way between the inlet end and the detector end of the coaxial heater.

2230 When the system was set up as it would be in use, the coaxial heater was cooled down, and a power ramp applied. The temperature of the thermocouple was recorded, together with the voltages dV and V_b . A curve could then be plotted of thermocouple temperature T_{TC} against the voltage ratio $\frac{dV}{V_b}$ (Figure 5.10). This revealed the shape of the function $T(\frac{dV}{V_b})$, and completed the first step of the calibration.

2235 The second step of a calibration is to establish a **measurement result** from an **indication**. It would be traditional to fit a mathematical function such as a polynomial to the curve, but a numerical method was chosen instead. We fitted a B-spline to the curve, and extracted coordinates on the curve from this. An interpolation function was then used to obtain the measurement result T from the indication dV / V_b .

2240 The calibration could be checked by setting the current through the coaxial heater to a minimum, at which not enough heat is generated to affect its temperature. Then the oven of the Varian 3300 GC could be set to a range of different temperatures. Once equilibrium was reached the reported temperature of the coaxial heater and the air bath temperature could be compared, and adjustments made to the calibration

5.5.8 Cold spots

2245 For the fastest temperature programming the heating element should be as light as possible, and carry the largest necessary current. In resistive heating, the current doing the heating must be carried to the coaxial heater using a conductor. To prevent the feed conductor from heating up it must have a low resistance, and this low resistance is achieved by making the conductor as 'thick' or as 'heavy' as necessary, meaning that it should be constructed of a material with a high mass per unit length.

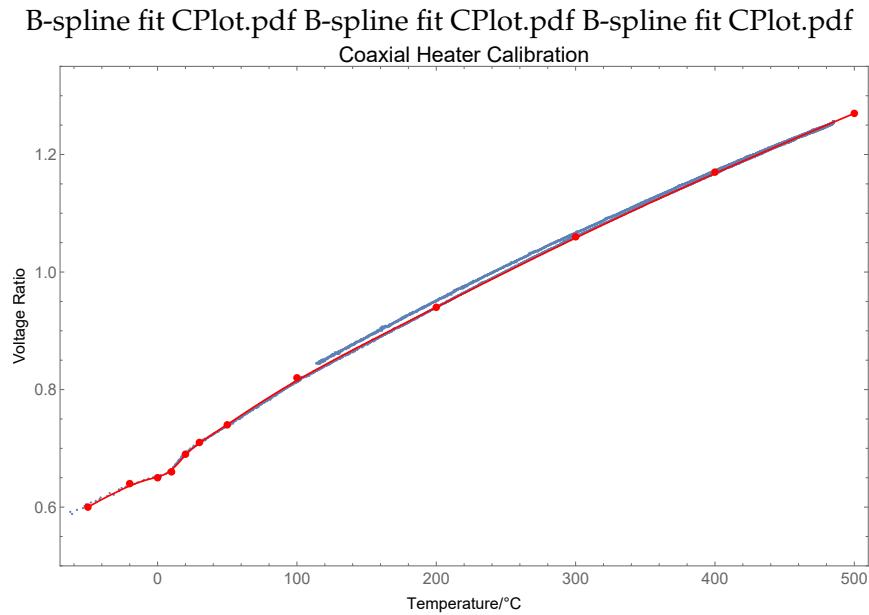


FIGURE 5.10: Calibration curve for the coaxial heater.

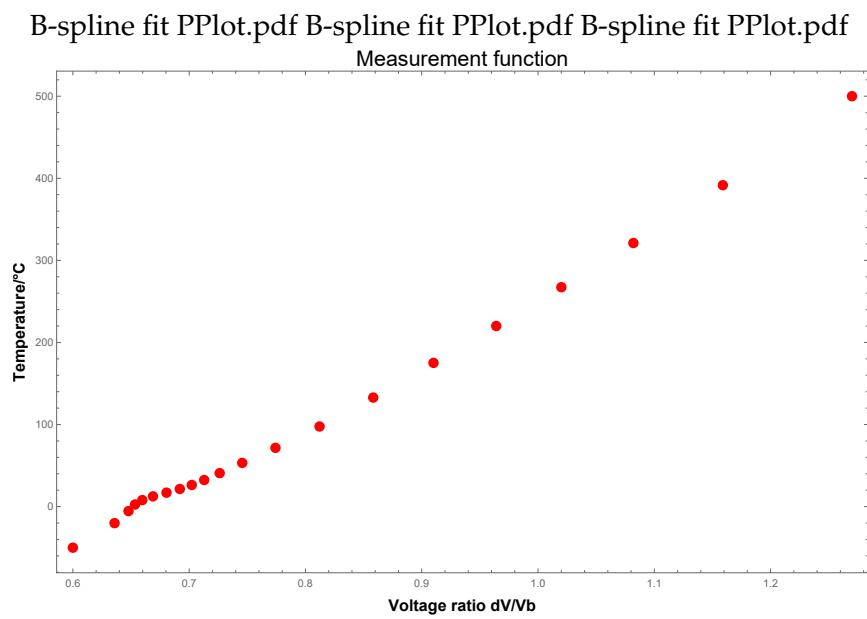


FIGURE 5.11: Measurement curve for the coaxial heater.

2250 Good electrical metallic conductors are invariably also good thermal conductors, and therefore the area around the junction of the feed conductor to the coaxial heater will always have a lower temperature than the nominal temperature of the heater. In capillary GC this is undesirable: a cold spot in a column can wreak havoc with retention times and peak shapes.

2255 Conversely, if an attempt is made to reduce the contact area between the feed conductor and the thin material of the coaxial heater, a hot spot might develop, which could burn a hole in the coaxial heater tube or damage the column.

2260 The electrical connection between the feed conductor and the coaxial heater was therefore designed in the form of an externally heated block. This block was kept at a higher temperature than the highest expected temperature of the chromatographic temperature program. This prevented the formation of cold spots in the coaxial heater, which might lead to cold spots in the column, while also offering a large contact area so that hot spots do not develop. Each end of the coaxial heater therefore ended in one of the heated blocks, where it was brazed in place. Each 2265 block had a brass tail, to which an electric feed-wire was soft-soldered. Each block was heated by four 100 W Hotset™ electrical cartridge heaters, with dimensions of 6.5 mm × 40 mm. The cartridge heaters were switched on and off by solid state relays controlled from the computer. The temperature of the block was monitored through a thermocouple mounted in blind holeand the amount of power to the 2270 heaters was controlled by pulse width modulation (PWM) implemented in software.

5.5.9 Cold column

In a cold GC stationary phase the retention factor k' is very high. This means that the analytes migrate slowly relative to the mobile phase. The lower the temperature, the higher k' becomes, so that for very low temperatures the migration of the 2275 analyte becomes negligible. In effect, the analytes are 'trapped'. This trapping, also called *cryotrapping* or *cryofocusing* is useful in various aspects of gas chromatography, such as two-stage thermal desorption or thermal modulation in GC \times GC. In one such application a programmable temperature vaporizing inlet (PTV) was used to trap complex hydrocarbon fractions from an SFC for injecting into a GC \times GC system (Potgieter et al. 2013).

2280 In the SFC \times GC instrument described here, cryotrapping was used as the second stage of a two-stage modulator. (The stop valve described in Section 4.4.2 represents the first stage.) The column was cooled down to very low temperatures, which trapped any analytes eluting from the first dimension in a narrow band on the GC column. Once the required amount of fraction had been collected, the flow from the 2285 first dimension would be stopped by closing the stop valve. Then the temperature ramp of the fast GC could start. As the coaxial heater warmed up the column the the values of k' would decrease, and the analytes would start migrating.

The first SFC \times GC chromatograph cooled the column by using the cryo-cooling 2290 function of the Varian 3300 GC (A. Venter and Rohwer 2004; A. Venter 2003). The purpose of this function is to cool the GC column down to sub-ambient temperatures, and is needed when analysing very volatile compounds. In such cases the k' values at or near room temperature are too low to provide adequate retention, and the cryo-cooling function permits temperature programs to start at sub-ambient 2295 temperatures. .

The Varian 3300 cryo-cooling function works by injecting liquid carbon dioxide into the column oven. The evaporating liquid carbon dioxide absorbs energy from

the air, which lowers the temperature of the air in the oven. A control system controls the amount of carbon dioxide admitted and the amount of heat added through the oven heaters, thereby keeping the oven at the required temperature.

While the cryo-cooling function can cool down an oven to cryo-trap analytes, there are two reasons why it is not a suitable method for practical trapping in SFC \times GC. The first reason is the quantity of coolant required: doing SFC \times GC runs revealed that about 15 kg of carbon dioxide was consumed per run. A standard cylinder of carbon dioxide contains 33 kg, which implies that a new cylinder would be required every two runs. Such a rate of use is much too high for the intended application of the instrument. The second reason using the GC oven's cryo-cooling function was not suitable for SFC \times GC is that it is much too slow. The time spent on cooling the oven and the column is time that can not be spent doing separations, and cooling a conventional GC oven takes a lot of time: the Varian 3300's cryo-cooling function took 30 s to cool the column down to a low starting temperature. A commercial forced-convection system ("GC Chaser" supplied by Zip Scientific) improves cool down time of an Agilent 6890 GC oven, taking 7 minutes instead of 16, cooling down the oven from 350 °C to 30 °C. Cooling the column in an air bath has the same drawbacks of low conductivity and low heat capacity as air-bath heating has (see Section 5.4).

A system was therefore developed by which liquid carbon dioxide is injected from one end into the space between the column and its coaxial heater. The other end is open to the atmosphere. When the pressure of the carbon dioxide drops from 55 atm to 1 atm, the liquid starts boiling, absorbing large quantities of heat from the surrounding column and coaxial heater, so that their temperatures decrease rapidly. This system solves the speed and coolant quantity problems: because the coolant is in direct contact with the parts that need to be cooled, the cooling is rapid, and because the coolant is applied where it is needed, only a small quantity is required.

The carbon dioxide for cooling the coaxial heater was introduced through the same heated block that provided the electrical connection. (See Section 5.5.8.) A T-piece design allowed the liquid carbon dioxide to be admitted to the end of the coaxial heater, which was brazed to the block. The column exited the block through a micro-union brazed to the block, and the liquid carbon dioxide entered along the side of the T (Figure 5.12 and Figure 5.13). A metering valve allowed the flow rate of the coolant to be adjusted, and a solenoid valve could switch the flow on or off under computer control.

Cryogen supply

The carbon dioxide for cooling was supplied as by Afrox, in high-pressure cylinders each containing 33 kg of technical grade carbon dioxide. Each cylinder was internally equipped with a *dip tube*, a tube that extends from the valve at the top of the cylinder to the bottom of the cylinder. This ensures that when the valve is opened, liquid carbon dioxide is delivered.

Experience taught that for repeatable cooling, the source of liquid carbon dioxide had to be near the solenoid valve. If this was not the case, when the valve was opened initially only carbon dioxide gas would be admitted, followed by a mixture of gas and liquid, and only finally liquid. This is similar to the common experience of opening a water tap after a municipal water supply interruption: a lot of gurgling and spitting before a reliable stream of water flows from the tap. Such unreliable coolant flow leads to unreliable cooling. To solve this problem we installed a reservoir for liquid carbon dioxide on top of the GC. The problem of filling a receptacle

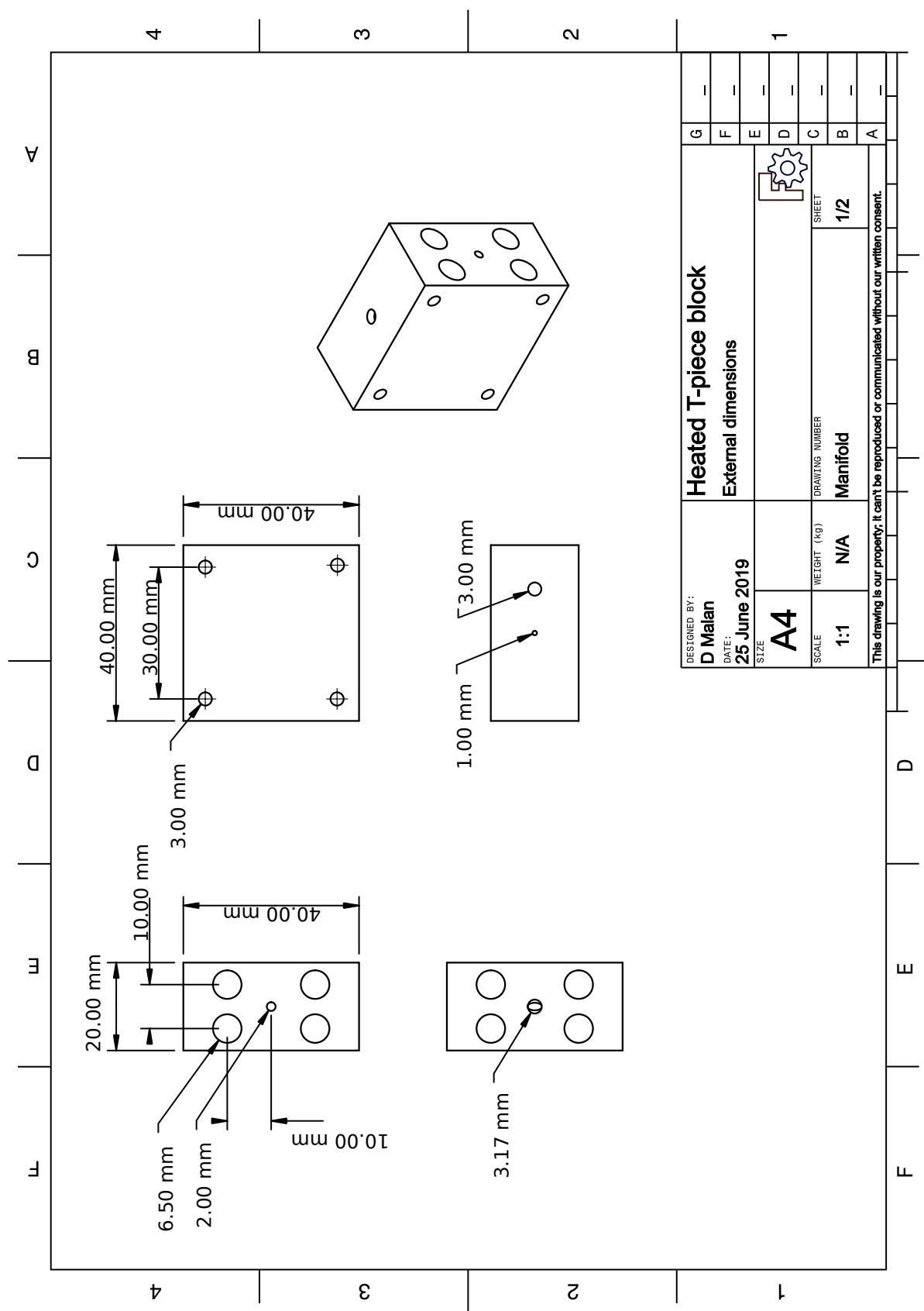


FIGURE 5.12: Dimensions of the heated T-piece blocks

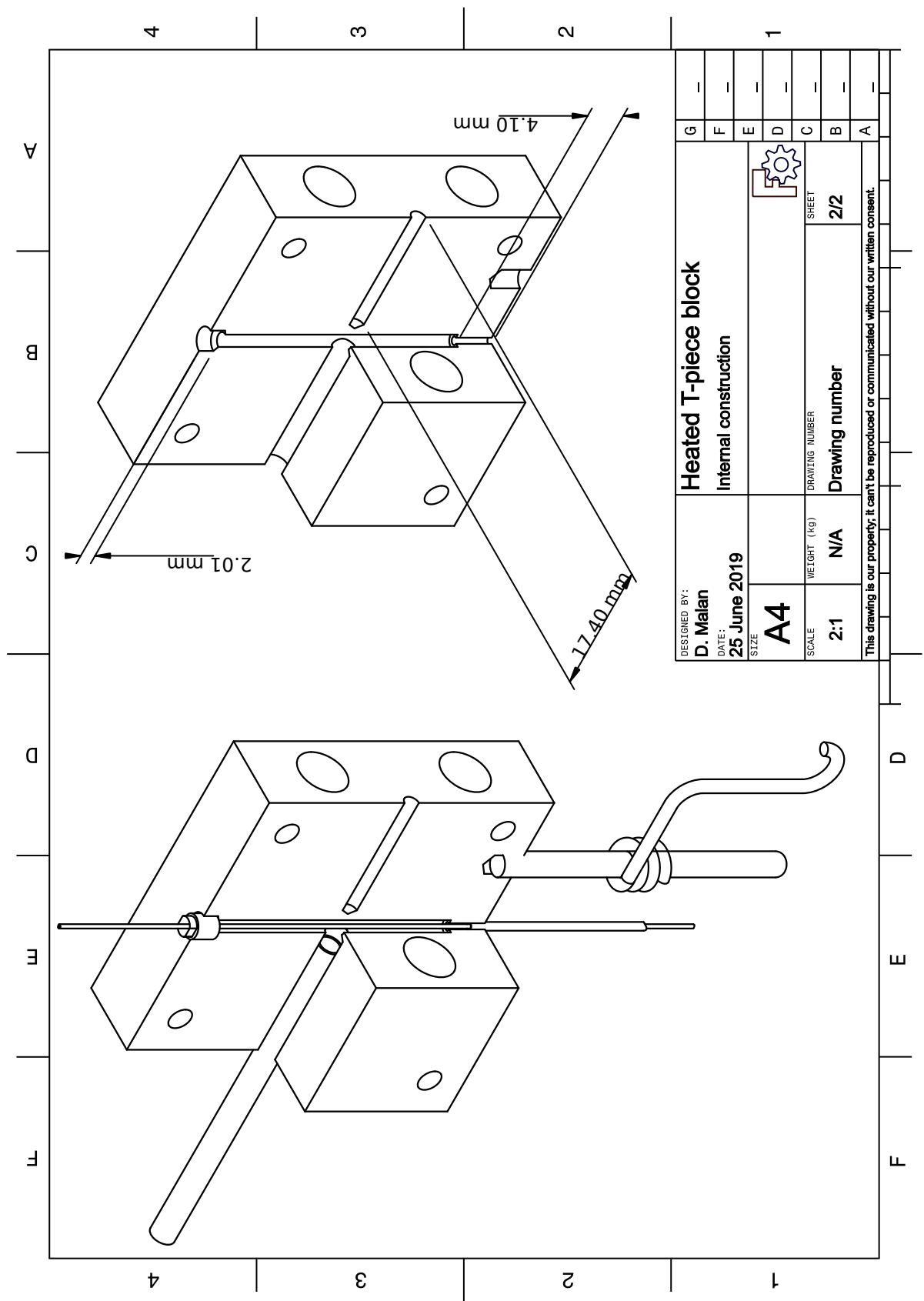


FIGURE 5.13: Internal construction and assembly of the heated T-piece blocks

with liquid carbon dioxide was described in Section 4.3. The final design of the reservoir took the form of a coil of copper tube immersed in a circulating coolant (Figure 5.14). Mounting the reservoir above the cut-off valve allows the liquid to collect at the bottom and allow gas to collect at the top, so that when the valve opens the flow into the coaxial heater contains only liquid.

5.5.10 Column mounting

The T-piece blocks described above (see Section 5.5.8, Section 5.5.9 and Figure 5.13) acted as a mounting point for the coaxial heater. The block is quite heavy, and has to transmit the forces of the coolant tube and the electrical connections. The column runs from the heated inlet/detector to the heated T-piece block, and in between it should not be exposed to any low-temperature cold spots, therefore the gap between the T-piece block and the inlet/detector should be quite small. But the gap cannot be zero, because electrical isolation needs to be maintained. A mechanically stiff and accurate mounting was needed for the T-piece blocks, to allow the precise but adjustable alignment of the T-piece blocks and the inlet/detector.

Through a few iterations a parallel-rail design was developed. These rails were held in place in the Varian 3300 oven by friction, so that they could be adjusted and removed as necessary, yet was stiff enough to transfer the necessary forces without deflecting. The pointed ends of the rails pressed against a solid aluminium plate used as the floor of the oven, and the top, adjustable points pressed against pressure plates which pressed against the roof of the oven. Figure 5.15 shows a technical drawing of the rails as designed.

The T-piece blocks were the electrical connections for the resistive coaxial heater, which meant they needed to be electrically isolated, but they were also heated, which meant that the insulation had to be heat resistant. A commercial available material that met these requirements was found in the form of *silicon mica*, a composite material of mica and a silicone resin. This material has a continuous operating temperature of at least 500 °C, making it ideally suited to GC applications. The silicon mica is also easy to machine, so that it could be shaped to the necessary specifications.

The T-piece blocks were mounted on a pair of cars riding on the round-bar rails. The cars comprised a sandwich design of layers of stainless steel and silicon mica around a pair of brass bushes. Once assembled, the cars offered a set of studs on to which the user could fit and bolt down the T-piece blocks. The position of the cars were determined by a locking collar on one of the rails. Figure 5.16 shows technical drawings of the cars that explains the design.

To do (5)

5.5.11 Heating control

The amount of power supplied to the heater was controlled by a bank of six NPN transistors, connected in parallel to distribute the heat dissipation. The final control signal was a voltage set either by a potentiometer from the front panel, or by the computer. An operational amplifier adjusts the current through the coaxial heater circuit so that a portion of the voltage applied to the coaxial heater is equal to the set-point voltage. By varying the set-point voltage the current through the coaxial heater can be controlled to provide any desired amount of heat ($P = I^2R$).

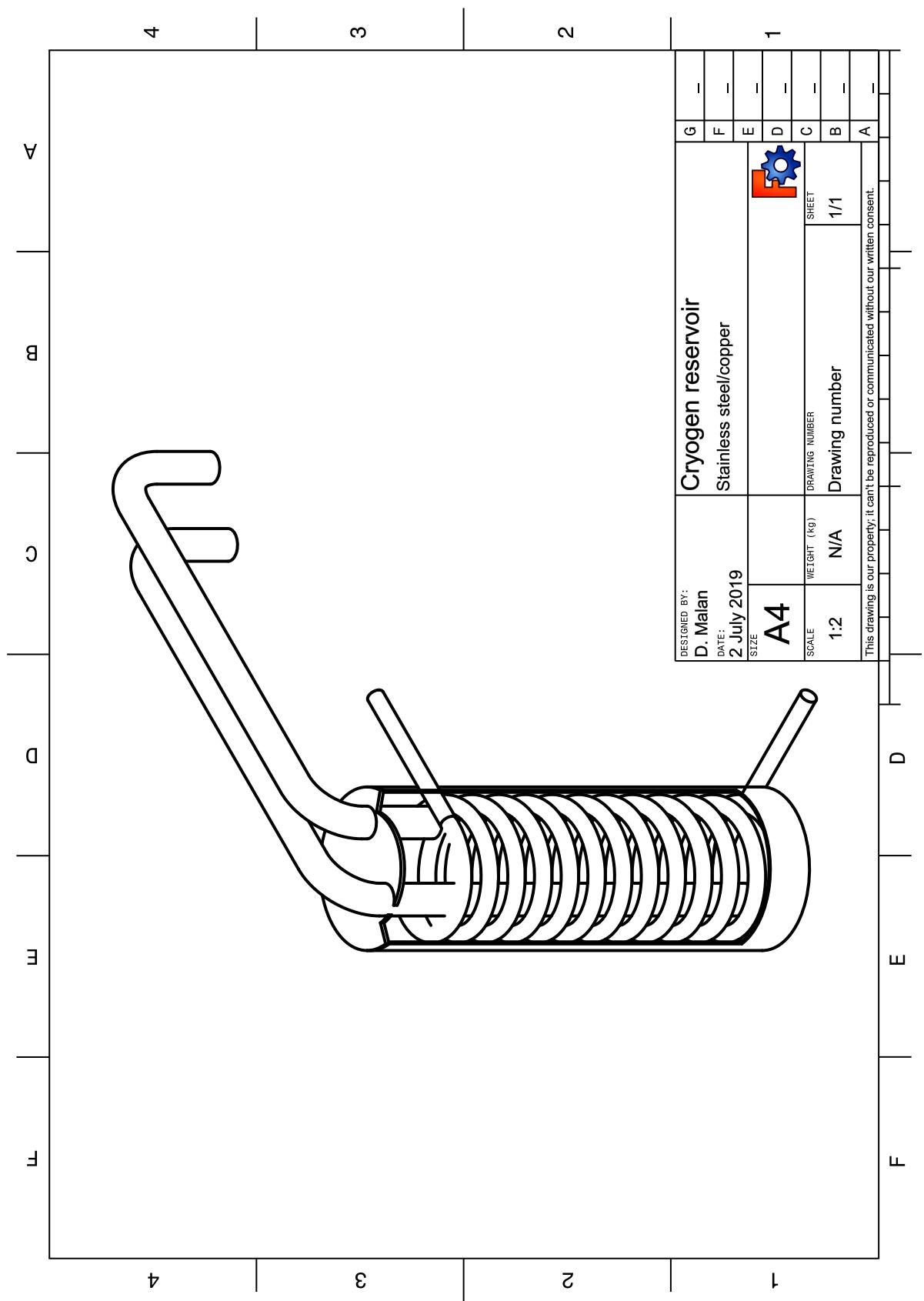


FIGURE 5.14: Cut-away drawing of coolant reservoir.

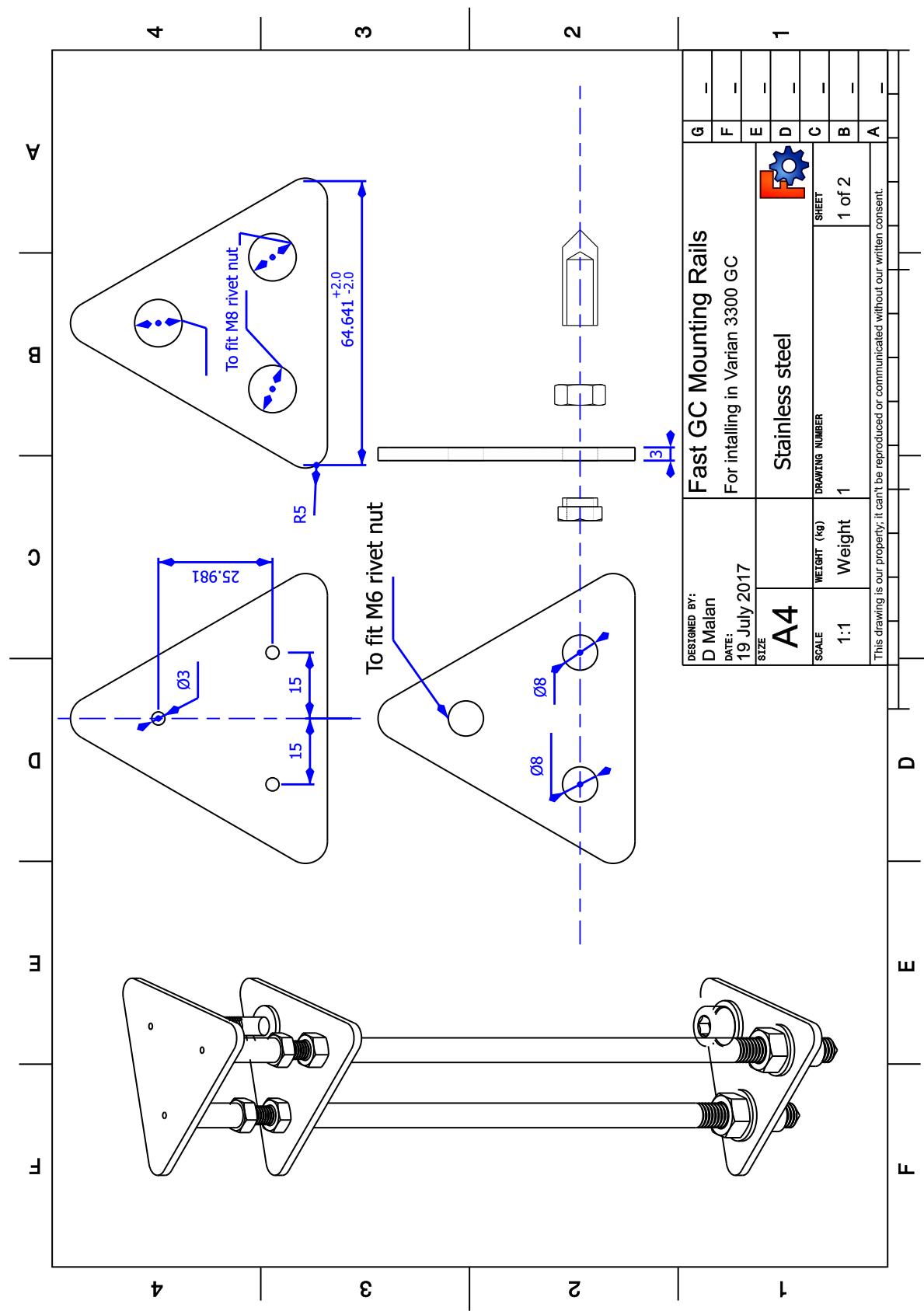


FIGURE 5.15: A technical drawing of the rails carrying the T-piece mounting block.

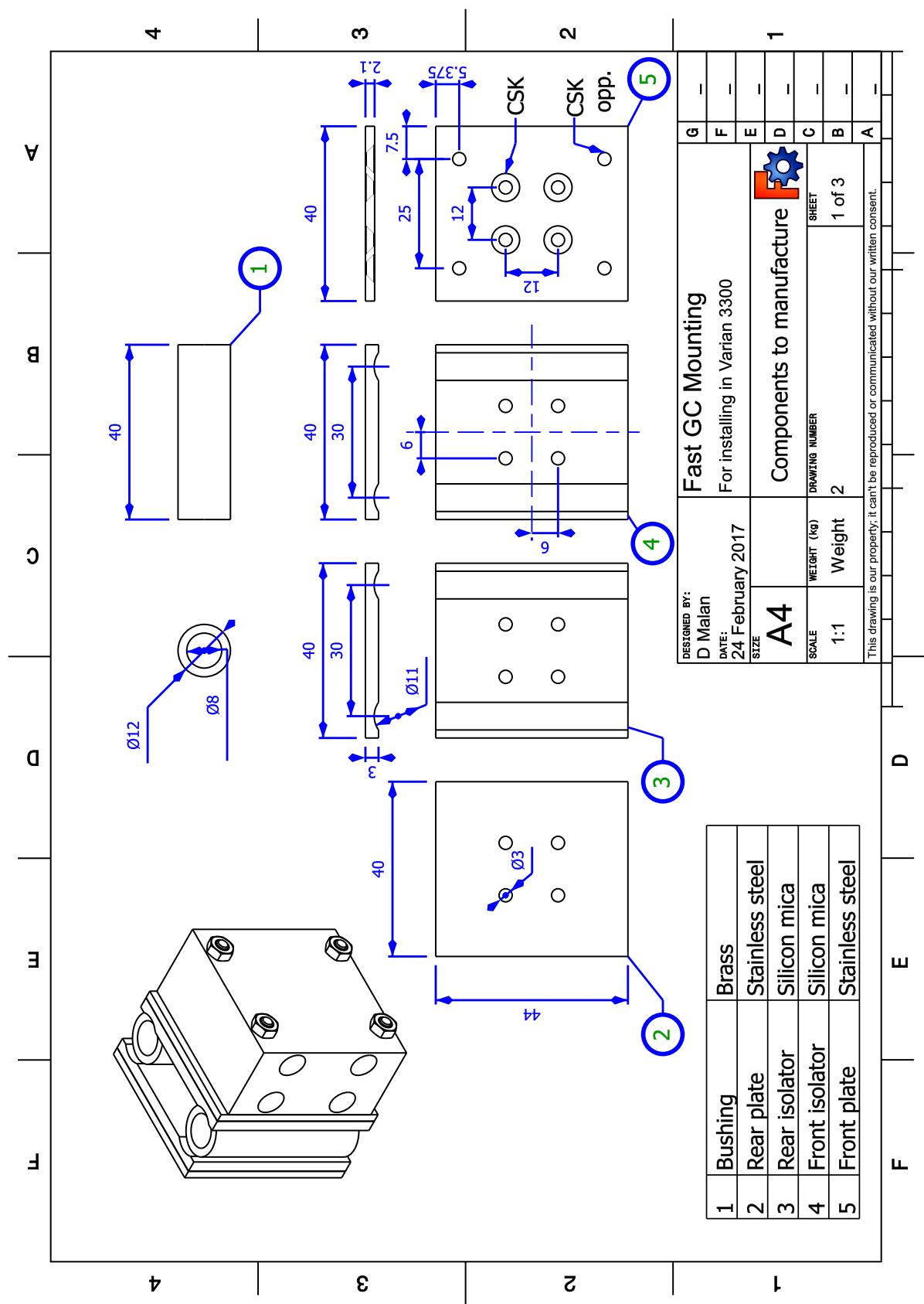


FIGURE 5.16: A technical drawing of the T-piece block mounting.

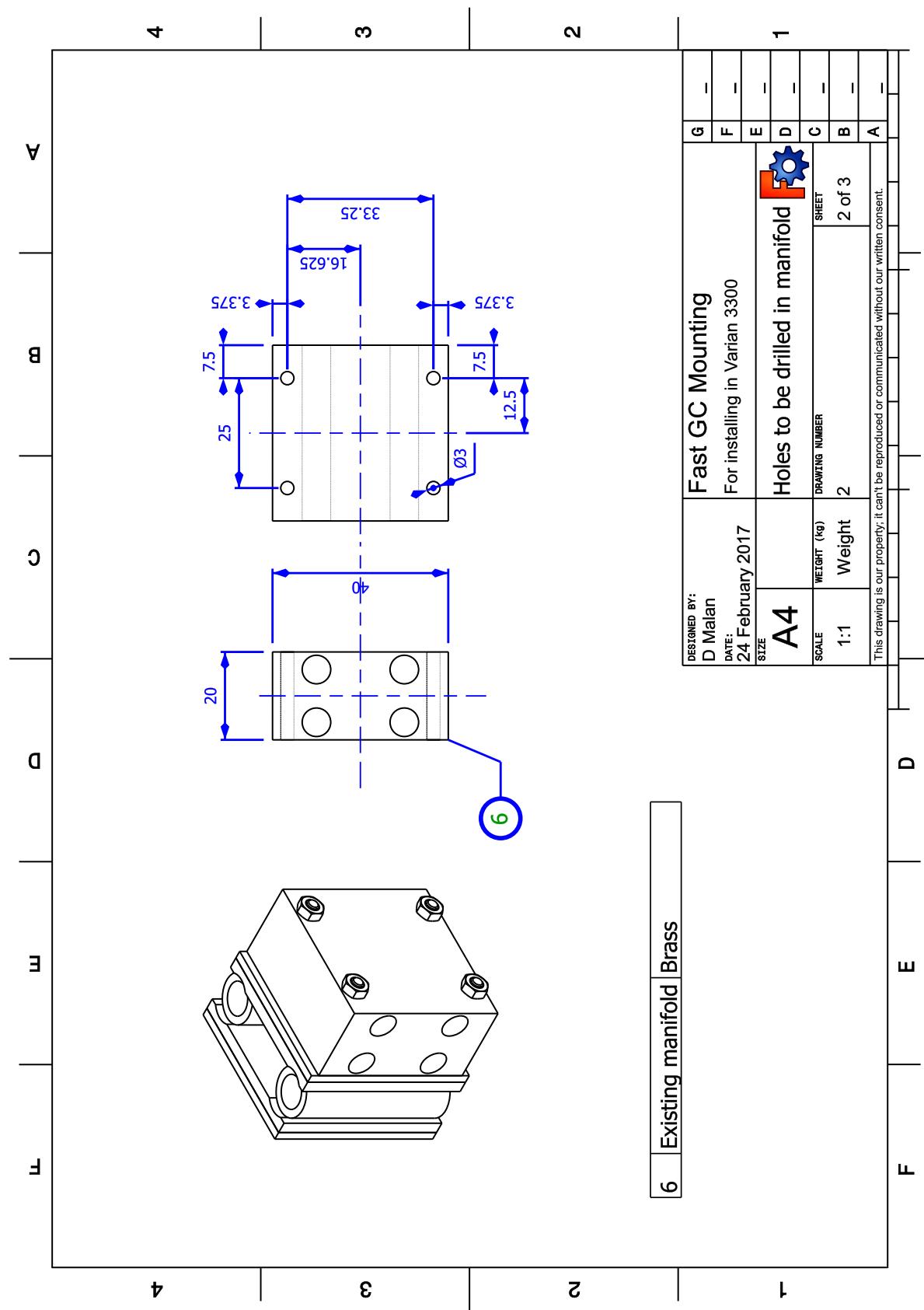


FIGURE 5.17: A technical drawing of the T-piece block mounting.

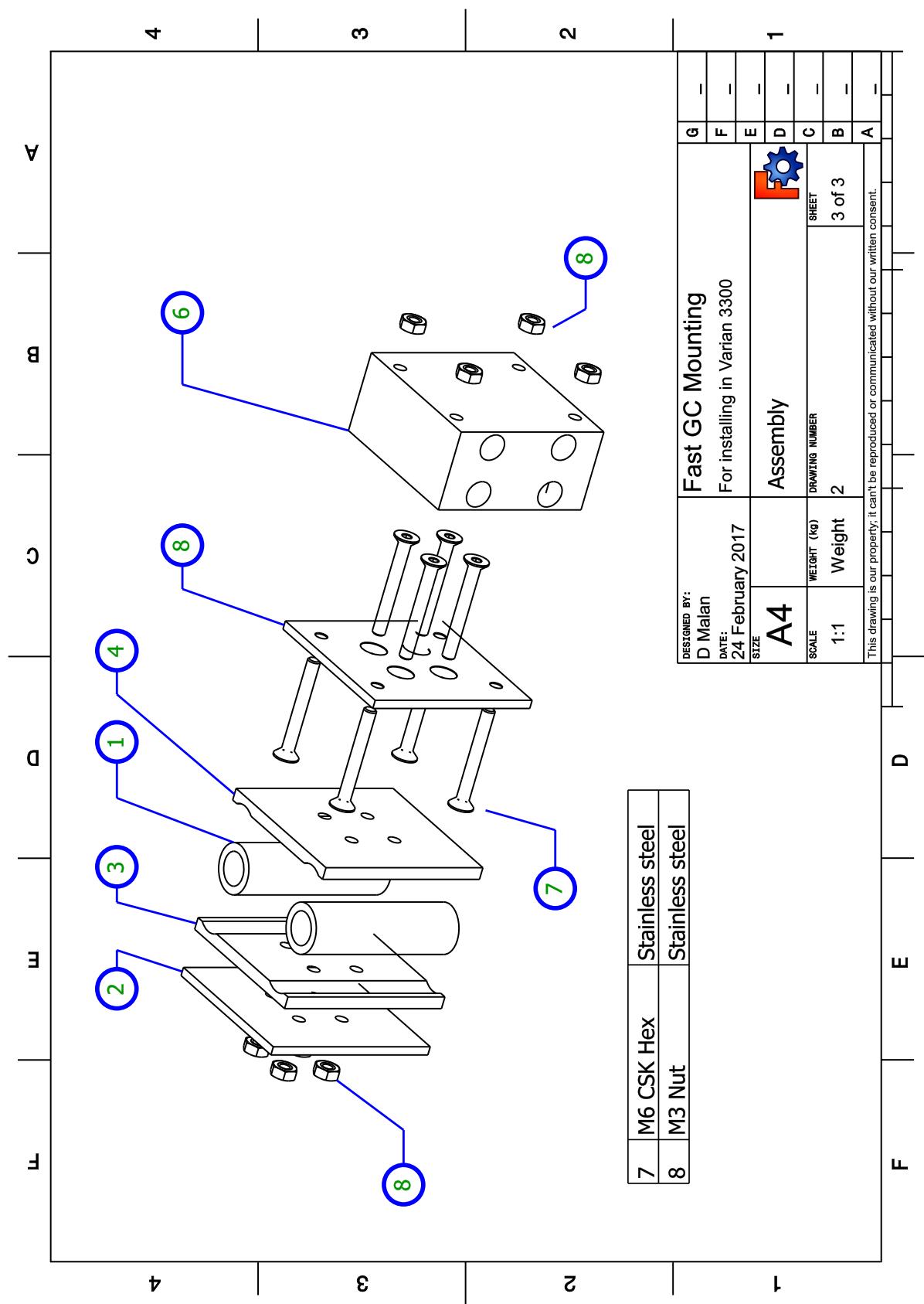


FIGURE 5.18: A technical drawing of the T-piece block mounting.

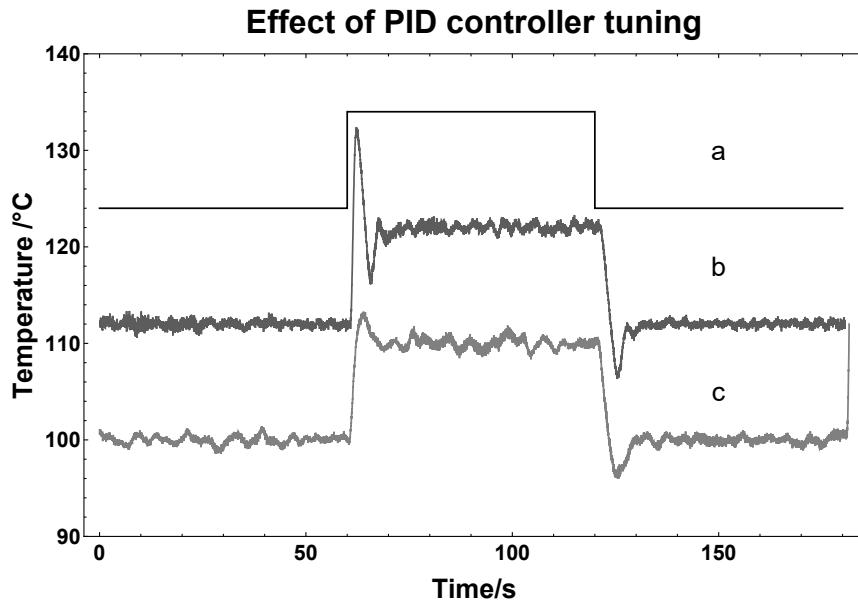


FIGURE 5.19: An illustration of effective PID controller tuning. The trace (a) represents the set point change over time and includes a step change. (b) Before tuning the temperature overshoots and then undershoots the step change in the set point. (c) After the controller has been tuned the overshoot in response to a step change in the set point is minimized.

Temperature monitoring

Independent of the amount of power dissipated in the coaxial heater, the current through the reference resistor was compared to the current through the column. This

2395 ratio corresponds to the resistance of the coaxial heater. This resistance is a function of the temperature of the heater. Through the calibration procedure described earlier, the temperature of the coaxial heater can be calculated. The computer can do this fast enough so that a temperature measurement is available to continuously feed to a control system.

2400 **PID tuning**

A proportional-integral-derivative (PID) controller was used to calculate the amount of power necessary to keep the temperature of the coaxial heater as close to the temperature set point as possible. The temperature set-point, in turn, was given by the desired chromatographic temperature ramp.

2405 The process of determining the best calculation by the PID is called *tuning*, and usually consists of determining the values of a few parameters. The tuning of PID controllers is a complex sub-discipline of process engineering, and outside the scope of this project, but for practical purposes we used a privately-published step-by-step tuning method (Peacock 2008) which is a version of the Cohen-Coon tuning method.

2410 Figure 5.19 shows the effect of an improved loop tuning.

A properly tuned heater helps to improve the repeatability of the chromatography through reliable temperature programs and prevents damage to the column due overheating during set point overshoots.

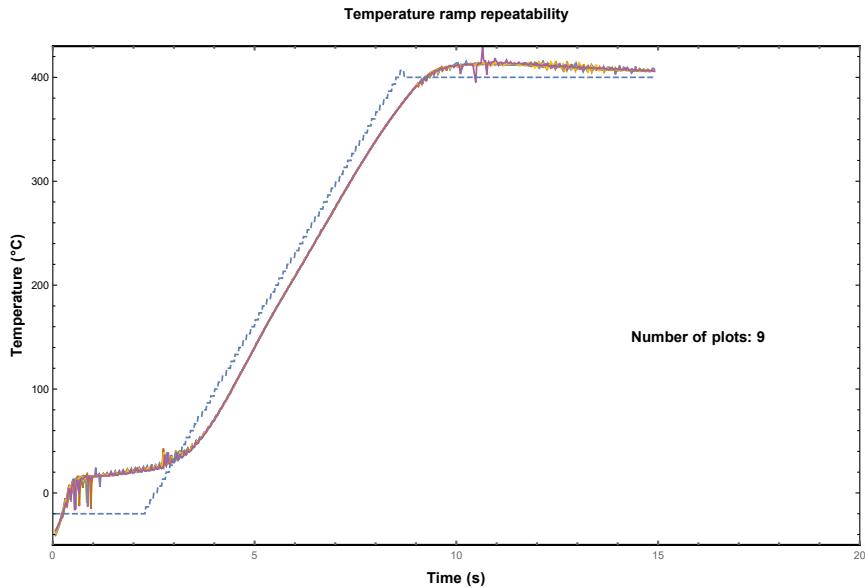


FIGURE 5.20: A graph of 9 identical, consecutive temperature ramps overlaid. The heating rate is $4000\text{ C}^{\circ}/\text{min}$. The temperature follows the set point faithfully up to $350\text{ }^{\circ}\text{C}$.

Heating rates

- 2415 As discussed in Section 5.4, for fast temperature-programmed gas chromatography the ramp rate needs to be in the order of thousands of degrees Celsius per minute. Figure 5.20 illustrates heating ramps executed by the coaxial heater. The heating rate was $4000\text{ C}^{\circ}/\text{min}$, and there are no significant differences between the 9 consecutive ramps.

2420 **Cooling rates**

The project did not demand a precise knowledge of, or control over, the cooling rate of the coaxial heater. The only requirement was that cooling should be as fast as possible. The cooling rate could be adjusted through the metering valve, and an optimum cooling rate of $5100\text{ C}^{\circ}/\text{min}$ was achieved with a carbon dioxide flow rate of around $30\text{ g}/\text{min}$. This allowed the column to be cooled down from $350\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ in about 2 seconds. At this rate the portion of the cycle that is not used for separation is dominated by fraction collection, and further cooling rate increases will not significantly reduce run times.

5.6 Detector

- 2430 The detector used in this fast GC was an unmodified VarianTM 3300 flame ionization detector (FID). The detector bias voltage was supplied by the original electronics, but a stand-alone high-speed electrometer (V.G. Micromass Ltd, Model M406-H) captured the signal, which was then conditioned by a bench-top amplifier (V.G. Micromass Ltd, Model M406) before it was sent to the computer. This electrometer and amplifier were fast enough to detect and amplify the signals generated by the fast GC.

5.7 Data acquisition and control software

The whole SFC \times GC instrument was controlled from a single PC, running a single program. The program was written in LabVIEW 7.1TM (National Instruments). This software was designed to interact very easily with the National Instruments PCI-6014 multifunction data acquisition board. ²⁴⁴⁰ [To do \(6\)](#)

LabVIEW is called a 'visual programming language', because programs are written by dragging icons around a screen, instead of typing text. This visual aspect of it makes it very easy to develop user interfaces and get quick results. However, it is still a programming language, so programming it effectively requires a firm foundation in computer science. ²⁴⁴⁵

5.8 Data capture

In GC \times GC, 2D data is recorded as a continuous FID output stream, as if it is a 1D GC chromatogram, and later converted into a 2D chromatogram, using knowledge ²⁴⁵⁰ of the modulation period. For two reasons we could not use this approach. Firstly, in our instrument the first (SFC) dimension runs in a stop-flow mode making continuous data recording inappropriate. Secondly, the duration of the cooling cycle varies, which would introduce unacceptable variation in ²D retention times.

We therefore constructed 2D chromatograms by recording a GC run for each SFC fraction injected. The ²D retention times were measured from the time the GC fast temperature program started. The ¹D retention times were recorded as the start times of each individual GC run. ²⁴⁵⁵

5.9 Data visualization

For data visualization we used the technical computing system Mathematica 11.3TM (²⁴⁶⁰ Wolfram). First the collected data was converted to a list of three-element lists, with ¹D retention time, ²D retention time, and detector signal as the elements of the inner lists. The Mathematica functions `List3DPlot[]` and `ContourPlot[]` could then be used to plot 3D chromatograms or contour plots respectively.

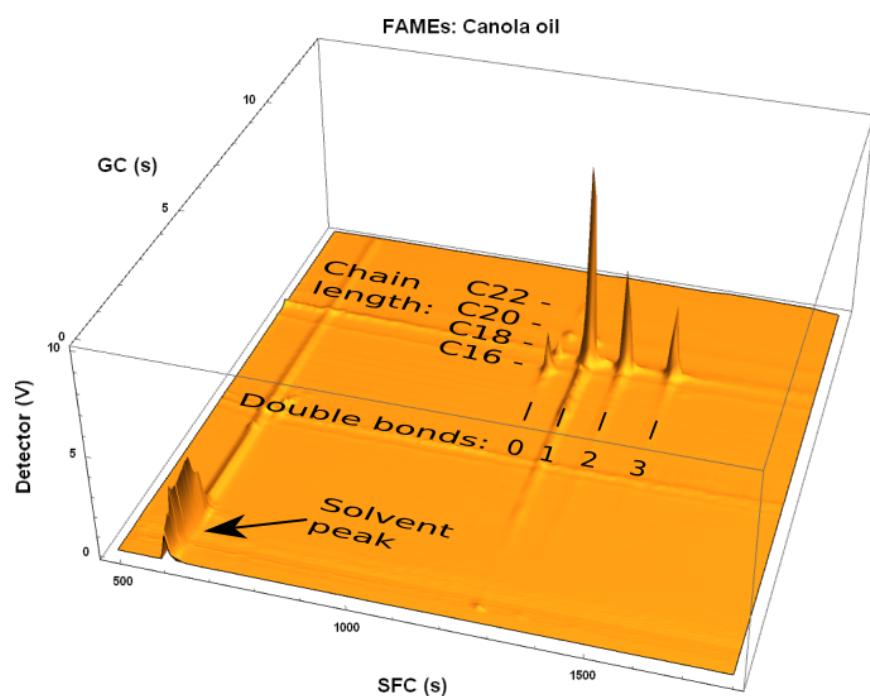


FIGURE 5.21: A 2D SFC \times GC chromatogram

To do...

- ²⁴⁶⁵ 1 (p. 37): autocite Blumberg 1997
- 2 (p. 52): autocite Blumberg1997-Blumberg1999
- 3 (p. 54): autocite oil baths
- 4 (p. 56): autocite low resistance temperature measurement
- 5 (p. 71): Use Figure environment instead of includepdf.
²⁴⁷⁰ Use caption package to suppress labelling of continued figures
. <https://tex.stackexchange.com/questions/64231/how-can-i-create-a-continued-figure-caption>
- 6 (p. 79): Include screenshot of VI

Coconut oil for your skin ...

Polynesian proverb

6

Investigating biodiesel feedstock by SFC×GC

2475

6.1 Main Section 1

6.1.1 Subsection 1

6.1.2 Subsection 2

2480

6.2 Main Section 2

In a book that I took from a shelf

...

Ancient proverb

7

Application: Analysis of biodiesel

7.1 Main Section 1

7.1.1 Subsection 1

2485 7.1.2 Subsection 2

7.2 Main Section 2

In a book that I took from a shelf

...

Ancient proverb

8

Conclusion

8.1 General

- ²⁴⁹⁰ It has been shown that an SFC \times GC instrument can be built using mainly 20th century technology.

8.2 Suggested design improvements

8.2.1 Four-wire resistance measurement

8.2.2 Legs heating and cooling integrated in detector and inlet

- ²⁴⁹⁵ 8.2.3

8.2.4 Subsection 1

8.2.5 Subsection 2

8.3 Main Section 2

Bibliography

- 2500 Abebe, Mimi (Oct. 2008). "History of Ethanol". In: *Journalism & Mass Communications: Student Media*.
- Agence France-Presse (Sept. 17, 2018). "Germany launches world's first hydrogen-powered train". In: *The Guardian*. URL: <https://www.theguardian.com/environment/2018/sep/17/germany-launches-worlds-first-hydrogen-powered-train>.
- 2505 Agilent Technologies (2019). *Agilent 7890B gas chromatography data sheet*. URL: <https://www.agilent.com/cs/library/datasheets/public/5991-1436EN.pdf>.
- Allen, Myles et al. (Nov. 2014). *IPCC fifth assessment synthesis report - Climate Change 2014 synthesis report*. Intergovernmental Panel on Climate Change (IPCC), pp. --116. URL: http://www.ipcc.ch/pdf/assessment-report/ar5/syr/SYR_AR5_LONGERREPORT.pdf.
- 2510 Angelis, Vanda De et al. (June 2007). "Multiperiod integrated routing and scheduling of World Food Programme cargo planes in Angola". In: *Computers & Operations Research* 34.6, pp. 1601–1615. DOI: [10.1016/j.cor.2005.07.012](https://doi.org/10.1016/j.cor.2005.07.012).
- AOCS Official Method Ce 2-66 (2017).
- 2515 Arrhenius, S. (1897). "On the Influence of Carbonic Acid in the Air upon the Temperature of the Earth". In: *Publications of the Astronomical Society of the Pacific* 9.54, p. 14. URL: <http://stacks.iop.org/1538-3873/9/i=54/a=14>.
- Ball, William T. et al. (Feb. 2018). "Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery". In: *Atmospheric Chemistry and Physics* 18.2, pp. 1379–1394. DOI: [10.5194/acp-18-1379-2018](https://doi.org/10.5194/acp-18-1379-2018).
- 2520 Barnett, James A. (2000). "A history of research on yeasts 2: Louis Pasteur and his contemporaries, 1850-1880". In: *Yeast* 16.8, pp. 755–771. DOI: [10.1002/1097-0061\(20000615\)16:8<755::aid-yea587>3.0.co;2-4](https://doi.org/10.1002/1097-0061(20000615)16:8<755::aid-yea587>3.0.co;2-4).
- Berche, Bertrand, Malte Henkel, and Ralph Kenna (June 2009). "Fenômenos críticos: 2525 150 anos desde Cagniard de la Tour". In: *Revista Brasileira de Ensino de Física* 31.2, pp. 26021–26024. DOI: [10.1590/s1806-11172009000200015](https://doi.org/10.1590/s1806-11172009000200015).
- Blumberg, L. M. and M. S. Klee (2000). "Optimal Heating Rate in Gas Chromatography". In: *Journal of Microcolumn Separations* 12.9, pp. 508–514.
- 2530 Blumberg, Leonid M. (Nov. 1997). "Theory of fast capillary gas chromatography. Part 1: Column efficiency". In: *Journal of High Resolution Chromatography* 20.11, pp. 597–604. DOI: [10.1002/jhrc.1240201106](https://doi.org/10.1002/jhrc.1240201106).
- Braun, Peter et al. (May 2018). "Potential Technical Approaches for Improving Low-Temperature NOx Conversion of Exhaust Aftertreatment Systems". In: *Chemie Ingenieur Technik* 90.6, pp. 762–773. DOI: [10.1002/cite.201700122](https://doi.org/10.1002/cite.201700122).
- 2535 Investigation of scaling laws for combustion engine performance. (Oct. 5, 2015). Fall Technical Meeting of the Western States Section of the Combustion Institute (WSS/CI 2015 Fall Meeting) (Provo, Utah, USA). URL: http://sites01.lsu.edu/faculty/smenon/wp-content/uploads/sites/133/2017/02/WSCI_Provo_v5.pdf (visited on 01/18/2019).
- Burke-Kennedy, Eoin (Feb. 16, 2018). "Ireland 2040: €22bn to turn State into low-carbon economy". In: *The Irish Times*.

- Cardona, C.A. and O.J. Sánchez (2007). "Fuel ethanol production: Process design trends and integration opportunities". English. In: *Bioresource technology* 98.12. Cited By :644, pp. 2415–2457. URL: www.scopus.com.
- 2545 Carson, Rachel (Oct. 23, 2003). *Silent Spring*. Houghton Mifflin. 400 pp. ISBN: 9780618249060. URL: https://www.ebook.de/de/product/1865596/rachel_carson_silent_spring.html.
- Chiaramonti, David et al. (Dec. 2014). "Sustainable bio kerosene: Process routes and industrial demonstration activities in aviation biofuels". In: *Applied Energy* 136, pp. 767–774. DOI: [10.1016/j.apenergy.2014.08.065](https://doi.org/10.1016/j.apenergy.2014.08.065).
- 2550 Clarke, Coby J. et al. (Jan. 2018). "Green and Sustainable Solvents in Chemical Processes". In: *Chemical Reviews* 118.2, pp. 747–800. DOI: [10.1021/acs.chemrev.7b00571](https://doi.org/10.1021/acs.chemrev.7b00571).
- Coffee Market Report December 2018 (2018). Tech. rep. International Coffee Organization.
- 2555 Cummins Jr., C. Lyle (1989). *Internal Fire*. Society of Automotive Engineers. ISBN: 978-0898837650. URL: <https://www.amazon.com/Internal-Fire-Lyle-Jr-Cummins/dp/0898837650?SubscriptionId=AKIAIOBINVZYXQZ2U3A&tag=chimborio5-20&linkCode=xm2&camp=2025&creative=165953&creativeASIN=0898837650>.
- 2560 Damerow, Peter (2012). "Sumerian Beer: The Origins of Brewing Technology in Ancient Mesopotamia". In: *Cuneiform Digital Library Journal* 2012:002. ISSN: 1540-8760. URL: http://www.cdl.ucla.edu/pubs/cdlj/2012/cdlj2012_002.html.
- Davidson, Arthur (1998). "Photochemical oxidant air pollution: A historical perspective". In: *Air pollution in the 21st century - Priority issues and policy*. Elsevier, pp. 393–405. DOI: [10.1016/s0166-1116\(98\)80024-1](https://doi.org/10.1016/s0166-1116(98)80024-1).
- 2565 Diamond, Jared M. (2006). *Collapse : how societies choose to fail or succeed*. English. New York: Penguin.
- Doucette, Reed T. and Malcolm D. McCulloch (Feb. 2011). "Modeling the CO₂ emissions from battery electric vehicles given the power generation mixes of different countries". In: *Energy Policy* 39.2, pp. 803–811. DOI: [10.1016/j.enpol.2010.10.054](https://doi.org/10.1016/j.enpol.2010.10.054).
- Duncan, Bryan N. et al. (Jan. 2016). "A space-based, high-resolution view of notable changes in urban NO_x pollution around the world (2005–2014)". In: *Journal of Geophysical Research: Atmospheres* 121.2, pp. 976–996. DOI: [10.1002/2015jd024121](https://doi.org/10.1002/2015jd024121).
- 2570 Eisenmenger, Michael et al. (Oct. 2006). "Pilot-scale supercritical carbon dioxide extraction and fractionation of wheat germ oil". In: *Journal of the American Oil Chemists' Society* 83.10, pp. 863–868. ISSN: 1558-9331. DOI: [10.1007/s11746-006-5038-6](https://doi.org/10.1007/s11746-006-5038-6). URL: <https://doi.org/10.1007/s11746-006-5038-6>.
- Ettre, L. S. (June 2008). "The Invention, Development, and Triumph of the Flame-Ionization Detector". In: *Chapters in the Evolution of Chromatography*. PUBLISHED BY IMPERIAL COLLEGE PRESS AND DISTRIBUTED BY WORLD SCIENTIFIC PUBLISHING CO., pp. 303–320. DOI: [10.1142/9781860949449_0023](https://doi.org/10.1142/9781860949449_0023).
- 2580 Ettre, L. S. and K. I. Sakodynzkii (Feb. 1993a). "M. S. Tswett and the discovery of chromatography I: Early work (1899–1903)". In: *Chromatographia* 35.3–4, pp. 223–231. DOI: [10.1007/bf02269707](https://doi.org/10.1007/bf02269707).
- (Mar. 1993b). "M. S. Tswett and the discovery of chromatography II: Completion of the development of chromatography (1903–1910)". In: *Chromatographia* 35.5–6, pp. 329–338. DOI: [10.1007/bf02277520](https://doi.org/10.1007/bf02277520).
- Flick, Carlos (1980). "The Movement for Smoke Abatement in 19th-Century Britain". In: *Technology and Culture* 21.1, pp. 29–50. ISSN: 0040-165X. DOI: [10.2307/3103986](https://doi.org/10.2307/3103986). URL: <http://www.jstor.org/stable/3103986> (visited on 01/15/2019).
- 2590

- Frauhammer, Jörg, Alexander Schenck zu Schweinsberg, and Klaus Winkler (July 2014). "Catalytic emission control". In: *Gasoline Engine Management*. Springer Fachmedien Wiesbaden, pp. 268–283. DOI: [10.1007/978-3-658-03964-6_18](https://doi.org/10.1007/978-3-658-03964-6_18).
- 2595 Gabbatiss, Josh (Oct. 19, 2018). "Ban new petrol and diesel cars by 2032 instead of current 'unambitious' target, MPs say". In: *The Independent*.
- Gertler, Alan W. et al. (Nov. 1999). "The Impact of California Phase 2 Reformulated Gasoline on Real-World Vehicle Emissions". In: *Journal of the Air & Waste Management Association* 49.11, pp. 1339–1346. DOI: [10.1080/10473289.1999.10463965](https://doi.org/10.1080/10473289.1999.10463965).
- 2600 Gibson, Jennifer et al. (Jan. 2016). "Levels and trends of contaminants in humans of the Arctic". In: *International Journal of Circumpolar Health* 75.1, p. 33804. DOI: [10.3402/ijch.v75.33804](https://doi.org/10.3402/ijch.v75.33804).
- Giddings, J. C. (May 1987). "Concepts and comparisons in multidimensional separation". In: *Journal of High Resolution Chromatography* 10.5, pp. 319–323. DOI: [10.1002/jhrc.1240100517](https://doi.org/10.1002/jhrc.1240100517).
- Grażyna, Wejnerowska and Ciaciuch Anna (Feb. 2018). "Optimisation of oil extraction from quinoa seeds with supercritical carbon dioxide with co-solvents". In: *Czech Journal of Food Sciences* 36.No. 1, pp. 81–87. DOI: [10.17221/122/2017-cjfs](https://doi.org/10.17221/122/2017-cjfs).
- Greenberg, Jon (May 17, 2017). *No, coffee is not the second-most traded commodity after oil*. URL: <https://www.politifact.com/global-news/statements/2017/may/08/starbucks/no-coffee-not-second-most-traded-commodity-after-o/> (visited on 01/31/2019).
- Griffin, John Joseph (Jan. 1, 1838). *Chemical Recreations: A Compendium of Experimental Chemistry, Part 1*. R. Griffin and Company.
- 2615 Gritti, Fabrice and Georges Guiochon (Aug. 2006). "General HETP Equation for the Study of Mass-Transfer Mechanisms in RPLC". In: *Analytical Chemistry* 78.15, pp. 5329–5347. DOI: [10.1021/ac060203r](https://doi.org/10.1021/ac060203r).
- Gumm, Brian (Oct. 22, 2015). *Blowing Smoke: Chemical Companies Say 'Trust Us,' But Environmental and Workplace Safety Violations Belie Their Rhetoric*. Tech. rep. Center for Effective Government.
- 2620 Guthrie, E. J. and H. E. Schwartz (1986). "Integral Pressure Restrictor for Capillary SFC". In: *Journal of Chromatographic Science* 24.6, pp. 236–241. ISSN: 0021-9665. URL: <https://www.worldcat.org/oclc/5127807429>.
- Halliday, Stephen (2001). "Death and miasma in Victorian London: an obstinate belief". In: *BMJ: British Medical Journal* 323.7327, pp. 1469–1471. ISSN: 0959-8138. DOI: [10.1136/bmj.323.7327.1469](https://doi.org/10.1136/bmj.323.7327.1469). eprint: <https://www.bmjjournals.org/content/323/7327/1469.full.pdf>. URL: <https://www.bmjjournals.org/content/323/7327/1469>.
- 2625 Hanmer, Clare and Simone Abram (Dec. 2017). "Actors, networks, and translation hubs: Gas central heating as a rapid socio-technical transition in the United Kingdom". In: *Energy Research & Social Science* 34, pp. 176–183. DOI: [10.1016/j.erss.2017.03.017](https://doi.org/10.1016/j.erss.2017.03.017).
- Harris, Daniel C. (Oct. 2010). "Charles David Keeling and the Story of Atmospheric CO₂ Measurements". In: *Analytical Chemistry* 82.19, pp. 7865–7870. ISSN: 0003-2700. DOI: [10.1021/ac1001492](https://doi.org/10.1021/ac1001492). URL: <https://doi.org/10.1021/ac1001492>.
- 2635 Hayes, John G. et al. (Sept. 2011). "Simplified electric vehicle power train models and range estimation". In: *2011 IEEE Vehicle Power and Propulsion Conference*. IEEE. DOI: [10.1109/vppc.2011.6043163](https://doi.org/10.1109/vppc.2011.6043163).
- Herrero, Miguel et al. (Apr. 2010). "Supercritical fluid extraction: Recent advances and applications". In: *Journal of Chromatography A* 1217.16, pp. 2495–2511. DOI: [10.1016/j.chroma.2009.12.019](https://doi.org/10.1016/j.chroma.2009.12.019).

- Hoffmann, Karl Heinz (Feb. 2008). "An introduction to endoreversible thermodynamics". In: *Atti della Accademia Peloritana dei Pericolanti - Classe di Scienze Fisiche, Matematiche e Naturali* 1, pp. 1–18. ISSN: 1825-1242. DOI: [10.1478/C1S0801011](https://doi.org/10.1478/C1S0801011).
- Holm, Torkil and Jørgen Øgaard Madsen (Jan. 1996). "Methane Formation by Flame-Generated Hydrogen Atoms in the Flame Ionization Detector". In: *Analytical Chemistry* 68.20, pp. 3607–3611. DOI: [10.1021/ac960556y](https://doi.org/10.1021/ac960556y).
- Hunt, Andrew J. et al. (Jan. 2010). "Generation, Capture, and Utilization of Industrial Carbon Dioxide". In: *ChemSusChem* 3.3, pp. 306–322. DOI: [10.1002/cssc.200900169](https://doi.org/10.1002/cssc.200900169).
- International vocabulary of metrology – Basic and general concepts and associated terms (VIM) (2019). 3rd ed. Joint Committee for Guides in Metrology, International Bureau of Weights and Measures. URL: https://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2012.pdf (visited on 07/06/2019).
- IPCC (2014). "2014: Summary for policymakers". In: *Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Ed. by C. B. Field et al. IPCC. URL: https://www.ipcc.ch/site/assets/uploads/2018/02/ar5_wgII_spm_en.pdf.
- Jacobs, Matthew R., Emily F. Hilder, and Robert A. Shellie (Nov. 2013). "Applications of resistive heating in gas chromatography: A review". In: *Analytica Chimica Acta* 803, pp. 2–14. DOI: [10.1016/j.aca.2013.04.063](https://doi.org/10.1016/j.aca.2013.04.063).
- Jacobsen, M. and G. Bertelsen (June 2002). "THE USE OF CO₂IN PACKAGING OF FRESH RED MEATS AND ITS EFFECT ON CHEMICAL QUALITY CHANGES IN THE MEAT: A REVIEW". In: *Journal of Muscle Foods* 13.2, pp. 143–168. DOI: [10.1111/j.1745-4573.2002.tb00326.x](https://doi.org/10.1111/j.1745-4573.2002.tb00326.x).
- Keulemans, A. I. M., A. Kwantes, and P. Zaal (1955). "The selectivity of the stationary liquid in vapour phase chromatography". In: *Analytica Chimica Acta* 13, pp. 357–372. DOI: [10.1016/s0003-2670\(00\)87957-x](https://doi.org/10.1016/s0003-2670(00)87957-x).
- Kimpe, K., P. A. Jacobs, and M. Waelkens (Dec. 2001). "Analysis of oil used in late Roman oil lamps with different mass spectrometric techniques revealed the presence of predominantly olive oil together with traces of animal fat". In: *Journal of Chromatography A* 937.1-2, pp. 87–95. DOI: [10.1016/s0021-9673\(01\)01304-8](https://doi.org/10.1016/s0021-9673(01)01304-8).
- Klee, M. S. and L. M. Blumberg (May 2002). "Theoretical and Practical Aspects of Fast Gas Chromatography and Method Translation". In: *Journal of Chromatographic Science* 40.5, pp. 234–247. DOI: [10.1093/chromsci/40.5.234](https://doi.org/10.1093/chromsci/40.5.234).
- Knothe, Gerhard (2010). "History of Vegetable Oil-Based Diesel Fuels". In: *The Biodiesel Handbook*. Elsevier, pp. 5–19. DOI: [10.1016/b978-1-893997-62-2.50007-3](https://doi.org/10.1016/b978-1-893997-62-2.50007-3).
- Koenig, David M. (Jan. 11, 2009). *Practical Control Engineering: A Guide for Engineers, Managers, and Practitioners*. McGRAW HILL BOOK CO. 474 pp. ISBN: 0071606130. URL: https://www.ebook.de/de/product/7882280/david_m_koenig_practical_control_engineering_a_guide_for_engineers_managers_and_practitioners.html.
- Kornblut, Phil (Mar. 1, 2019). "Helium Shortage 3.0". In: *Gasworld*.
- Kumar, Santosh, Neetu Singh, and Ram Prasad (Sept. 2010). "Anhydrous ethanol: A renewable source of energy". In: *Renewable and Sustainable Energy Reviews* 14.7, pp. 1830–1844. DOI: [10.1016/j.rser.2010.03.015](https://doi.org/10.1016/j.rser.2010.03.015).
- Kyoto Protocol to the United Nations Framework Convention on Climate Change*. (Dec. 11, 1997). URL: <https://unfccc.int/resource/docs/convkp/kpeng.pdf> (visited on 01/25/2019).
- Lauer, Henk H., Douglass. McManigill, and Robert D. Board (July 1983). "Mobile-phase transport properties of liquefied gases in near critical and supercritical

- fluid chromatography". In: *Analytical Chemistry* 55.8, pp. 1370–1375. DOI: [10.1021/ac00259a041](https://doi.org/10.1021/ac00259a041).
- Li, Harry and Radu Curiac (Jan. 2012). "Energy Conservation: Motor Efficiency, Efficiency Tolerances, and the Factors That Influence Them". In: *IEEE Industry Applications Magazine* 18.1, pp. 62–68. DOI: [10.1109/mias.2011.943105](https://doi.org/10.1109/mias.2011.943105).
- Linthorst, J. A. (Apr. 2010). "An overview: origins and development of green chemistry". In: *Foundations of Chemistry* 12.1, pp. 55–68. ISSN: 1572-8463. DOI: [10.1007/s10698-009-9079-4](https://doi.org/10.1007/s10698-009-9079-4). URL: <https://doi.org/10.1007/s10698-009-9079-4>.
- Luque de Castro, Maria D., Miguel Valcárcel, and María T. Tena (1994). *Analytical Supercritical Fluid Extraction*. Springer. ISBN: 3-540-57495-6. URL: <https://www.amazon.com/Analytical-Supercritical-Fluid-Extraction-Lecture/dp/3540574956?SubscriptionId=AKIAIOBINVZYXZQZ2U3A&tag=chimborio5-20&linkCode=xm2&camp=2025&creative=165953&creativeASIN=3540574956>.
- Mansouri, Nazanin (2016). "A Case Study of Volkswagen Unethical Practice in Diesel Emission Test". In: *International Journal of Science and Engineering Applications* 5.4, pp. 211–216. URL: <https://UnivofPretoria.on.worldcat.org/oclc/6158205082>.
- McGee, Thomas D. (1988). *Principles and methods of temperature measurement*. Wiley-Interscience.
- Mekonnen, Mesfin M. et al. (2018). "Water, Energy, and Carbon Footprints of Bioethanol from the U.S. and Brazil". In: *Environmental Science & Technology* 52.24, pp. 14508–14518. DOI: [10.1021/acs.est.8b03359](https://doi.org/10.1021/acs.est.8b03359).
- Ministere de la santé (2018). *Strategic response plan for the ebola virus disease outbreak*. Democratic Republic of Congo. World Health Organization.
- Modanlou, H. D. (2008). "A tribute to Zakariya Razi (865 - 925 AD), an Iranian pioneer scholar." In: *Archives of Iranian medicine* 11.6, pp. 673–7. ISSN: 1029-2977. URL: <https://UnivofPretoria.on.worldcat.org/oclc/269410950>.
- Model Bakery and Brewery from the Tomb of Meketre (1920). Metropolitan Museum of Art The Met Fifth Avenue 1000 Fifth Avenue New York, NY 10028: The Metropolitan Museum of Art. URL: <https://www.metmuseum.org/art/collection/search/544258> (visited on 01/14/2019).
- Mohankumar, S. and P. Senthilkumar (2017). "Particulate matter formation and its control methodologies for diesel engine: A comprehensive review". In: *Renewable and Sustainable Energy Reviews* 80, pp. 1227–1238. DOI: [10.1016/j.rser.2017.05.133](https://doi.org/10.1016/j.rser.2017.05.133).
- Monolithic Thermocouple Amplifiers with Cold Junction Compensation (1999). AD594/AD595. Rev. C. Analog Devices.
- Morris, Hugh (Aug. 16, 2017). "How many planes are there in the world right now?" In: *The Telegraph*. URL: <https://www.telegraph.co.uk/travel/travel-truths/how-many-planes-are-there-in-the-world/#> (visited on 12/18/2018).
- Needleman, Herbert L. (Sept. 2000). "The Removal of Lead from Gasoline: Historical and Personal Reflections". In: *Environmental Research* 84.1, pp. 20–35. DOI: [10.1006/enrs.2000.4069](https://doi.org/10.1006/enrs.2000.4069).
- Paris Agreement (Dec. 12, 2015). UNTC XXVII 7.d. URL: <https://treaties.un.org/doc/Publication/MTDSG/Volume%20II/Chapter%20XXVII/XXVII-7-d.en.pdf> (visited on 01/25/2019).
- Peacock, Finn (2008). *PID Tuning Blueprint*. URL: <http://www.pidtuning.net>.
- Pearson, Andy (Dec. 2005). "Carbon dioxide—new uses for an old refrigerant". In: *International Journal of Refrigeration* 28.8, pp. 1140–1148. DOI: [10.1016/j.ijrefrig.2005.09.005](https://doi.org/10.1016/j.ijrefrig.2005.09.005).

- Petit, J. R. et al. (June 1999). "Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica". English. In: *Nature* 399.6735. Copyright - Copyright Macmillan Journals Ltd. Jun 3, 1999; Last updated - 2017-10-31; CODEN - NATUAS; SubjectsTermNotLitGenreText - Antarctica, pp. 429–436. URL: <https://search-proquest-com.uplib.idm.oclc.org/docview/204481126?accountid=14717>.
- Poole, Colin F. (2003). "Supercritical Fluid Chromatography". In: *The Essence of Chromatography*. Elsevier, pp. 569–617. DOI: [10.1016/b978-044450198-1/50020-3](https://doi.org/10.1016/b978-044450198-1/50020-3).
- Potgieter, H. et al. (June 2013). "Hyphenation of supercritical fluid chromatography and two-dimensional gas chromatography-mass spectrometry for group type separations". In: *Journal of Chromatography A* 1294, pp. 137–144. DOI: [10.1016/j.chroma.2013.04.020](https://doi.org/10.1016/j.chroma.2013.04.020).
- Prebihalo, Sarah E. et al. (Jan. 2018). "Multidimensional Gas Chromatography: Advances in Instrumentation, Chemometrics, and Applications". In: *Analytical Chemistry* 90.1, pp. 505–532. ISSN: 0003-2700. DOI: [10.1021/acs.analchem.7b04226](https://doi.org/10.1021/acs.analchem.7b04226). URL: <https://doi.org/10.1021/acs.analchem.7b04226>.
- Ramalakshmi, K. and B. Raghavan (July 1999). "Caffeine in Coffee: Its Removal. Why and How?" In: *Critical Reviews in Food Science and Nutrition* 39.5, pp. 441–456. DOI: [10.1080/1040869991279231](https://doi.org/10.1080/1040869991279231).
- Randall, L. G. (1982). "The Present Status of Dense (Supercritical) Gas Extraction and Dense Gas Chromatography: Impetus for DGC/MS Development". In: *Separation Science and Technology* 17.1, pp. 1–118. ISSN: 0149-6395. URL: <https://www.worldcat.org/oclc/4661041191>.
- Raveendran, Poovathinthodiyil, Yutaka Ikushima, and Scott L. Wallen (June 2005). "Polar Attributes of Supercritical Carbon Dioxide". In: *Accounts of Chemical Research* 38.6, pp. 478–485. DOI: [10.1021/ar040082m](https://doi.org/10.1021/ar040082m).
- Reed, Gail L. (Sept. 15, 1999). "FAST GC: APPLICATIONS AND THEORETICAL STUDIES". PhD thesis. Virginia Polytechnic.
- Reif, Konrad, ed. (2015). *Gasoline Engine Management*. Springer Fachmedien Wiesbaden. DOI: [10.1007/978-3-658-03964-6](https://doi.org/10.1007/978-3-658-03964-6).
- Reumuth, Georg et al. (Aug. 2018). "Carbon monoxide intoxication: What we know". In: *Burns*. DOI: [10.1016/j.burns.2018.07.006](https://doi.org/10.1016/j.burns.2018.07.006).
- Reuters (Nov. 13, 2018). "Spain to propose ban on sale of petrol and diesel cars from 2040". In: *Sunday Times*.
- Ripple, D. C. (1995). *ITS-90 Thermocouple Database, NIST Standard Reference Database 60*. eng. DOI: [10.18434/t4s888](https://doi.org/10.18434/t4s888).
- Rosen, William (Mar. 11, 2012). *The Most Powerful Idea in the World: A Story of Steam, Industry, and Invention*. UNIV OF CHICAGO PR. 370 pp. ISBN: 0226726347. URL: https://www.ebook.de/de/product/16779670/william_rosen_the_most_powerful_idea_in_the_world_a_story_of_steam_industry_and_invention.html.
- Schönberger, C. and T. Kostecky (2011). "125th Anniversary Review: The Role of Hops in Brewing". In: *Journal of the Institute of Brewing* 117.3, pp. 259–267. DOI: [10.1002/j.2050-0416.2011.tb00471.x](https://doi.org/10.1002/j.2050-0416.2011.tb00471.x).
- Seeley, John V. and Stacy K. Seeley (Jan. 2013). "Multidimensional Gas Chromatography: Fundamental Advances and New Applications". In: *Anal. Chem.* 85.2, pp. 557–578. ISSN: 0003-2700. DOI: [10.1021/ac303195u](https://doi.org/10.1021/ac303195u). URL: <https://doi.org/10.1021/ac303195u>.
- Shabecoff, Philip (June 24, 1988). "Global Warming Has Begun, Expert Tells Senate". In: *New York Times*, p. 1. URL: <https://nyti.ms/2GvL7QI>.

- Shamsul, N. S. et al. (May 2014). "An overview on the production of bio-methanol as potential renewable energy". In: *Renewable and Sustainable Energy Reviews* 33, pp. 578–588. DOI: [10.1016/j.rser.2014.02.024](https://doi.org/10.1016/j.rser.2014.02.024).
- 2795 Skoog, Douglas A., F. James Holler, and Stanley R. Crouch (2007). *Principles of instrumental analysis*. Sixth edition. Belmont, CA: Thomson Brooks/Cole. URL: <https://www.worldcat.org/oclc/77224390>.
- Smeets, Edward et al. (Aug. 1, 2006). *Sustainability of Brazilian bio-ethanol*. Research rep. Universiteit Utrecht, Copernicus Institute, Department of Science, Technology and Society.
- 2800 *South Africa's Intended Nationally Determined Contribution (INDC)* (Nov. 1, 2016). English. UNFCCC. URL: <https://www4.unfccc.int/sites/ndcstaging/PublishedDocuments/South%20Africa%20First/South%20Africa.pdf> (visited on 12/08/2018).
- Spur, G., E. Uhlmann, and F. Elbing (Dec. 1999). "Dry-ice blasting for cleaning: process, optimization and application". In: *Wear* 233-235, pp. 402–411. DOI: [10.1016/s0043-1648\(99\)00204-5](https://doi.org/10.1016/s0043-1648(99)00204-5).
- Szreter, Simon (Mar. 2003). "The population health approach in historical perspective". In: *American journal of public health* 93.12604486, pp. 421–431. ISSN: 1541-0048. URL: <https://www.ncbi.nlm.nih.gov/pmc/PMC1449802/>.
- 2810 Van Niekerk, P. S. (1980). *Doenlikheidstudie ; die gebruik van sonneblomolie as plaasvervanger vir diesel in die R S A*. Die oueur. URL: <https://books.google.co.za/books?id=CcbuoQEACAAJ>.
- Varma, Roli and Daya R. Varma (Feb. 2005). "The Bhopal Disaster of 1984". In: *Bulletin of Science, Technology & Society* 25.1, pp. 37–45. DOI: [10.1177/0270467604273822](https://doi.org/10.1177/0270467604273822).
- 2815 Venter, Andre (2003). "Comprehensive two-dimensional supercritical fluid and gas chromatography (SFC×GC)". PhD thesis. University of Pretoria.
- Venter, Andre, Peter R. Makgwane, and Egmont R. Rohwer (Mar. 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." In: *Analytical chemistry* 78.6, pp. 2051–4. ISSN: 0003-2700. DOI: [10.1021/ac051693a](https://doi.org/10.1021/ac051693a). URL: [http://www.ncbi.nlm.nih.gov/pubmed/16536445](https://www.ncbi.nlm.nih.gov/pubmed/16536445).
- 2820 Venter, Andre and Egmont R. Rohwer (July 2004). "Comprehensive two-dimensional supercritical fluid and gas chromatography with independent fast programmed heating of the gas chromatographic column." In: *Analytical chemistry* 76.13, pp. 3699–706. ISSN: 0003-2700. DOI: [10.1021/ac035538c](https://doi.org/10.1021/ac035538c). URL: [http://www.ncbi.nlm.nih.gov/pubmed/15228344](https://www.ncbi.nlm.nih.gov/pubmed/15228344).
- 2825 Venter, Irma (Oct. 29, 2014). "Renewable energy project set to power BMW's Rosslyn plant". In: *Engineering News*.
- Vincenti, Walter G. (1990). *What engineers know and how they know it : analytical studies from aeronautical history*. English. Baltimore: Johns Hopkins University Press. URL: <http://catdir.loc.gov/catdir/description/jhu051/89049003.html>.
- Wang, Anzi, H. Dennis Tolley, and Milton L. Lee (2012). "Gas chromatography using resistive heating technology". In: *Journal of Chromatography A* 1261, pp. 46–57.
- 2830 Watts, Steven (2005). *The People's Tycoon: Henry Ford and the American Century*. Knopf. ISBN: 978-0-375-40735-2. URL: <https://www.worldcat.org/title/peoples-tycoon-henry-ford-and-the-american-century/oclc/829332863>.
- Wells, P. S., S. Zhou, and J. F. Parcher (Jan. 2003). "Unified Chromatography with CO₂-Based Binary Mobile Phases". In: *Analytical Chemistry* 75.1, 18 A–24 A. DOI: [10.1021/ac031212s](https://doi.org/10.1021/ac031212s).
- 2835 Wentz, Dennis A. et al. (2014). *Mercury in the nation's streams - Levels, trends, and implications*. U.S. Geological Survey Circular 1395. Tech. rep. DOI: [10.3133/cir1395](https://doi.org/10.3133/cir1395). URL: <http://dx.doi.org/10.3133/cir1395>.

- Williams, William Henry. (1965). *The Commons, Open Spaces & Footpaths Preservation Society, 1865-1965 : a short history of the society and its work*. English. [London]: [The Society]. ISBN: 978-0-375-40735-2.
- 2845 Wolfram | Alpha (2019a). URL: <https://www.wolframalpha.com/input/?i=otto+cycle> (visited on 07/09/2019).
- (2019b). URL: <https://www.wolframalpha.com/input/?i=diesel+cycle> (visited on 07/09/2019).
- 2850 — (2019c). URL: <https://www.wolframalpha.com/input/?i=brayton+cycle> (visited on 07/09/2019).
- Woodall, L. C. et al. (Dec. 2014). "The deep sea is a major sink for microplastic debris". In: *Royal Society Open Science* 1.4, pp. 140317–140317. DOI: [10.1098/rsos.140317](https://doi.org/10.1098/rsos.140317).
- 2855 World Resource Institute (2004). *The Greenhouse Gas Protocol: A Corporate Accounting and Reporting Standard*. World Resources Inst. ISBN: 1-56973-568-9. URL: <https://www.amazon.com/Greenhouse-Gas-Protocol-Corporate-Accounting/dp/1569735689?SubscriptionId=AKIAIOBINVZYXZQZ2U3A&tag=chimbori05-20&linkCode=xm2&camp=2025&creative=165953&creativeASIN=1569735689>.
- 2860 Wright, J. (Sept. 2002). "Chronic and occult carbon monoxide poisoning: we don't know what we're missing". In: *Emergency Medicine Journal* 19.5, pp. 386–390. DOI: [10.1136/emj.19.5.386](https://doi.org/10.1136/emj.19.5.386).