Oil/oil correlation by aid of chemometrics

K. ØYGARD[1], O. GRAHL-NIELSEN[2] and S. ULVØEN[2]

[1]Exploration and Production Laboratories, P.O. Box 300, 4001 Stavanger, Norway
[2]Department of Chemistry, N-5014 Bergen-University, Norway

Abstract—Twenty crude oils from 10 wells in a North Sea oil field were correlated by way of multivariate analysis of gas chromatographic parameters. The whole oil chromatograms showed distinct differences between oils from different formations due to differences in biodegradation. They were, however, insufficient for a complete classification. That was achieved by the chromatograms of the aromatic fraction. Among the aromatics, the biphenyls were best suited for classification.

Key words: oil/oil correlation, chemothermics

INTRODUCTION

A wide range of parameters has been used in crude oil correlation. This includes both composite properties like carbon isotope ratio, optical rotation, vanadium/nickel ratios, total amounts of various classes of components, as well as absolute or relative amounts of single components, both paraffinic, naphthenic and aromatic, ranging from C_4 to polycyclic alkanes of low volatility (Hunt, 1979).

The most common method of data treatment is visual inspection, either of chromatographic tracings directly or of distribution patterns of homologous series (e.g. Volkman *et al.*, 1983). Others have employed ratios between pairs of hydrocarbons, e.g. pristane/phytane, or ternary diagrams (e.g. Bockmeulen *et al.*, 1983). To handle all the variables at the same time, there are advanced methods of multivariate data analysis presently available (Derde and Massart, 1982; Clerc, 1983).

Very few attempts have been made on the multivariate approach: principal component analysis has been employed on GC–MS analyses of steranes and triterpanes (Hohn *et al.*, 1981) and on HPLC analysis of petroporphyrins (Hohn *et al.*, 1982). Principal component analysis is, however, a display method, and is only considered as a preliminary investigation of a data set to obtain a basis for further multivariate treatment (Derde and Massart, 1982). A method to generate indexes of correlation based on mass chromatograms of oils has been developed, but this method only allows the correlation of two oils at a time (Flory *et al.*, 1983).

In the investigation presented here, 20 North Sea oils sampled at various depths in 10 wells, as shown in Table 1, are correlated.

Table 1. Geological setting of crude oils from the block in the North Sea

Oil No.	Well	Formation	Type of test	Depth (m)
1	1	Brent	DST 2	1839–1844
2	1	Brent	DST 1	1930–1935
3	1	Brent	DST 3	1788–1792
4	3	Brent	DST 3	1895–1900
5	3	Brent	DST 2	1935
6	4	Brent	DST 1A	1880–1885
7	4	Brent	DST 2	1824–1826
8	5	Brent	DST 1	1925–1927
9	8	Brent	DST 1	1869–1873
10	14	Brent	RFT 4	1926.5
11	14	Brent	DST 1	1933.5–1937.5
12	9	Brent	RFT	1840
13	9	Brent	DST 3	1904–1910
14	9	Cook	DST 1	2103–2109
15	9	Cook	DST 2A	2084–2090
16	7	Cook	DST 1	1858–1865
17	11	Statfjord	DST 1	2018–2028
18	11	Trias	FIT	2081
19	13	Trias	DST 1	2107–2114
20	13	Statfjord	DST 2	2003–2009

K. ØYGARD *et al.*

The field is divided by several faults (Fig. 1) and oil is found in four geological structures (Fig. 2). The main emphasis has been to use the information contained in the patterns of a large number of paraffins and aromatics, to describe relationships between oils from various structures in different fault zones.

The multivariate data program, SIMCA, developed by Wold (1981) was used (Albano *et al.*, 1981). Here principal component models for groups of related oils are developed, and similarities between oils and groups of oils are numerically expressed. Relative importance of the various analytical parameters in describing the data set is also expressed.

The analytical data used were obtained by capillary gas chromatography, both of the whole oils and the aromatic fraction, the latter obtained by silica gel fractionation. Further analysis was done by GC–MS.

EXPERIMENTAL

For gas chromatography of whole oil, 0.5 μl was injected into a split injector with split ratio of 1 : 80. A 25 m × 0.22 mm Cp-Sil 5 fused silica column was used with helium as carrier gas at 22 cm s^{-1} at 10°C. The oven was programmed from 70 to 200°C at 4°C min^{-1}, and further from 200 to 310°C at 8°C min^{-1}.

LEGEND :

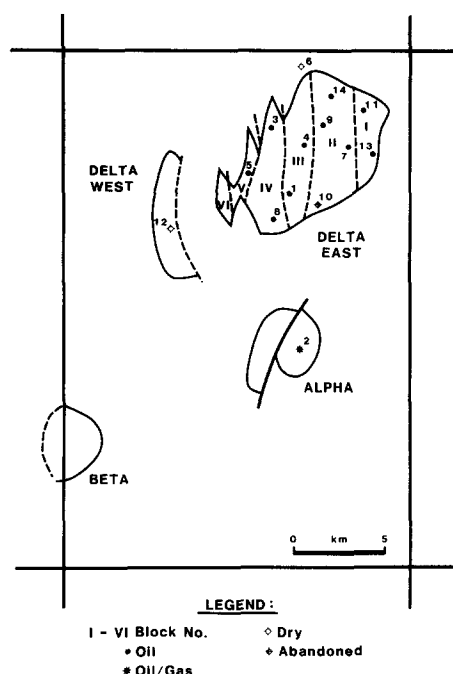| I – VI Block No. | ◇ Dry |
| • Oil | ✦ Abandoned |
| ✳ Oil/Gas | |

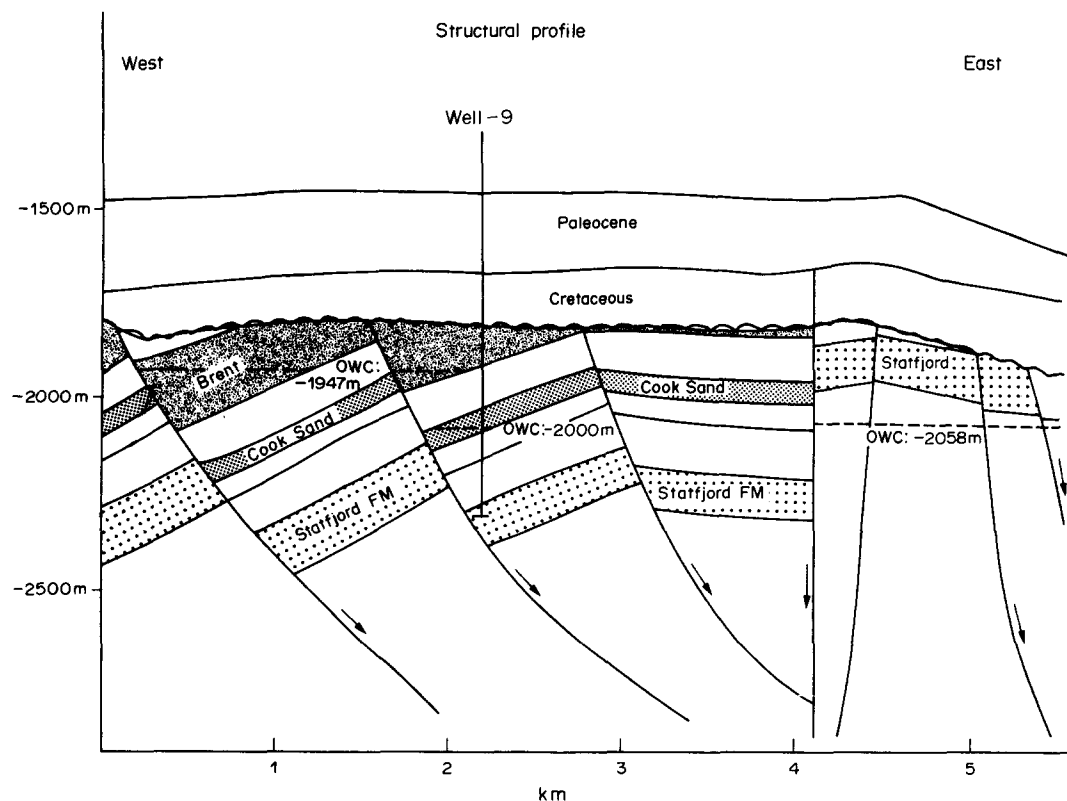Fig. 1. Map over the block where the different wells are drilled.

Fig. 2. Structural profile over the well 9, where three of the four structures are shown.

The area of the peaks in the chromatograms was electronically integrated on an HP 5880 integrator.

For analysis of aromatics, they were first fractionated from whole oil by MPLC on silica gel after the method of Radke *et al.* (1980). The aromatics were here obtained in hexane solution and, after concentrating this by evaporation of most of the hexane, 1 µl was chromatographed by splitless injection and, otherwise, the same conditions as for whole oil.

The aromatics were also analysed by gas chromatography with mass spectrometric detection. The gas chromatography was performed on the same column as above in an HP 5790 gas chromatograph programmed from 100 to 200°C at 4°C min^{-1}. The column was mounted directly into the ion source of an HP 5993 C quadropole mass spectrometer.

The molecular ions of the aromatics naphthalene, biphenyl, phenanthrene and dibenzothiophene and their C_1, C_2 and C_3 alkyl derivatives were monitored. In this manner, chromatographical patterns, as shown in Fig. 3, were obtained. The typical appearance of these patterns, the regular increase in reten-

tion times with increasing alkyl substitution within each class, and the fact that their molecular weights were used for detection, leave no doubt about the identity of the various clusters.

The total area of each cluster of isomers was integrated above the baseline, resulting in a total of 16 areas for each of the 20 samples. This 16 × 20 matrix was used for multivariate analysis. From the whole oil chromatograms, 27 altogether, due to replicate chromatography of some of the 20 oil samples, 68 peaks in the range from n-C_{11} to n-C_{30}, including all n-alkanes, were selected. This resulted in a matrix of 27 × 68 numbers. Another matrix, with 27 × 48 numbers, was obtained by exclusion of the n-alkanes from the former. Finally, the 23 chromatograms, including some replicates, of the aromatic fraction gave rise to a 23 × 58 matrix.

For multivariate analysis the values of the peak areas were normalized to the average peak area for each sample. The data were scaled within each set by dividing them by the standard deviation over the whole set for each peak. The two main principal
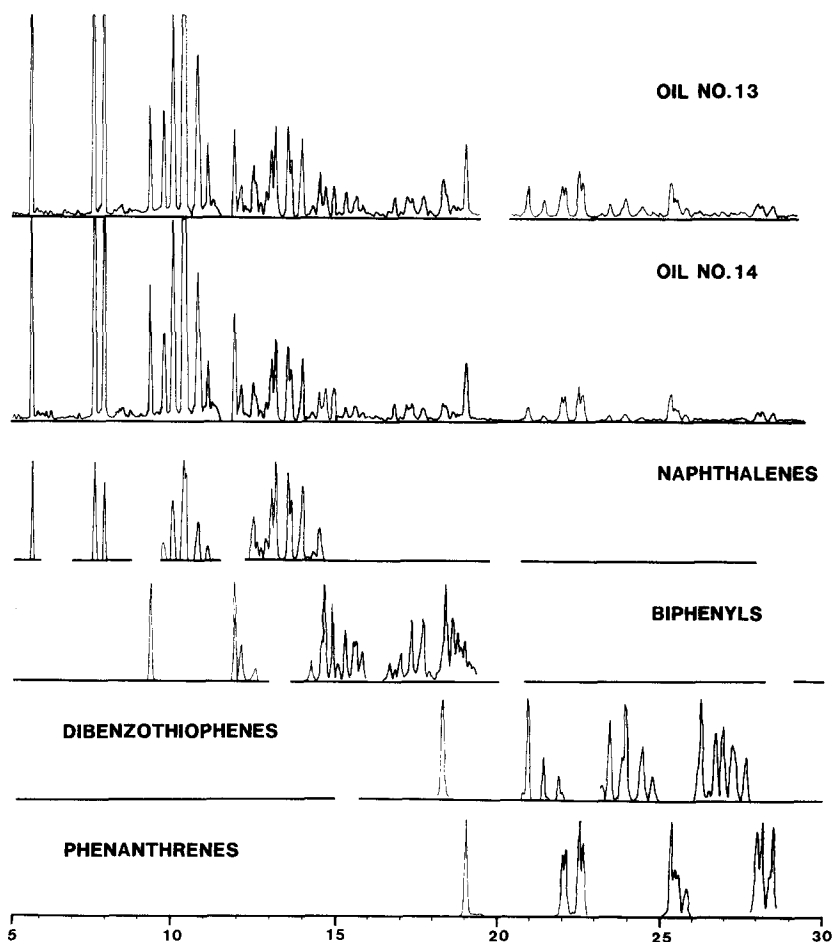

Fig. 3. Typical GC–MS chromatograms of the oils and the naphthalenes, biphenyls, dibenzothiophenes and phenanthrenes.

components were computed for each data set, and
the samples were plotted against them for display
purposes, i.e. Figs 5–7 and 9. Within each set, models
for the different classes were determined. It was also
checked if the oils really belonged to their respective
classes.

RESULTS AND DISCUSSION

Typical gas chromatograms of some of the oils are
shown in Fig. 4. There are prominent differences,
particularly with respect to the n-alkane content,
which is due to biodegradation. The plot of the first
principal component against the second, of the data
based on all 68 peaks in the total chromatograms is
shown in Fig. 5. It is seen that the largest variance is
along the first principal component. The oils from the

Brent structure group together, although there is a
significant difference within that group of oil too. The
Brent oils have the lowest n-alkane content. The oils
from the Cook and Statfjord structures form the
other extreme due to high amounts of n-alkane.
There is a close relationship between the oils from
wells 7 and 13 which come from different structures
on each side of a fault.

The two oils from various depths in well 9 fall
between the Brent and Cook/Statfjord samples. The
two oils from the Trias reservoir are separated from
the other oils along the second principal component,
showing that they have variability in some other
components than those causing the difference be-
tween the Brent, Cook and Statfjord oils.

It should be noted that the gas chromatographic
replicates are close together in the display, indicating
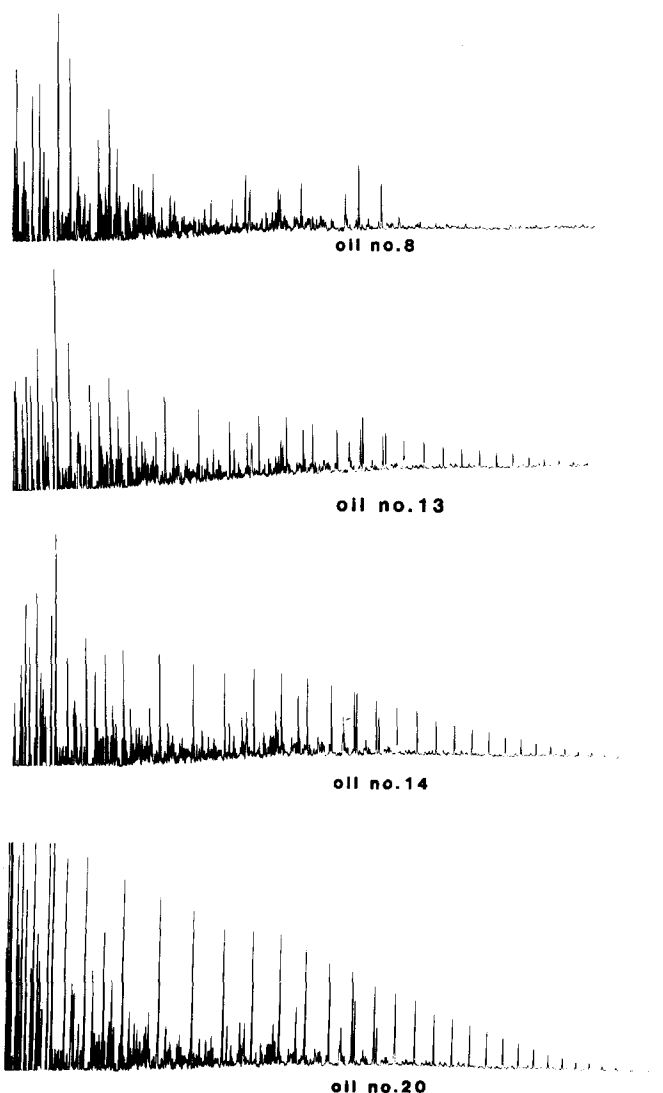that analytical variability is insignificant compared to

Fig. 4. Gas chromatograms of four of the samples from the North Sea.
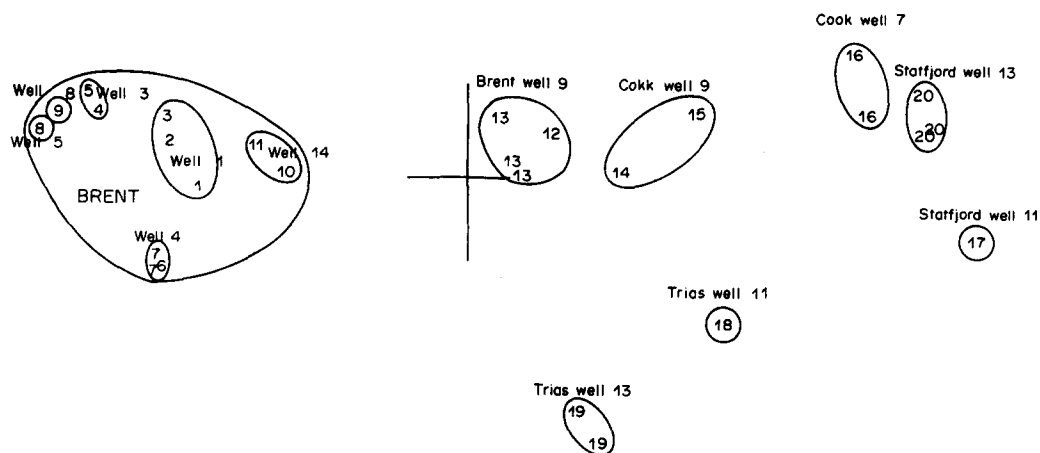
Fig. 5. Plot of the first two principal components of the gas chromatography data of the crude oils.
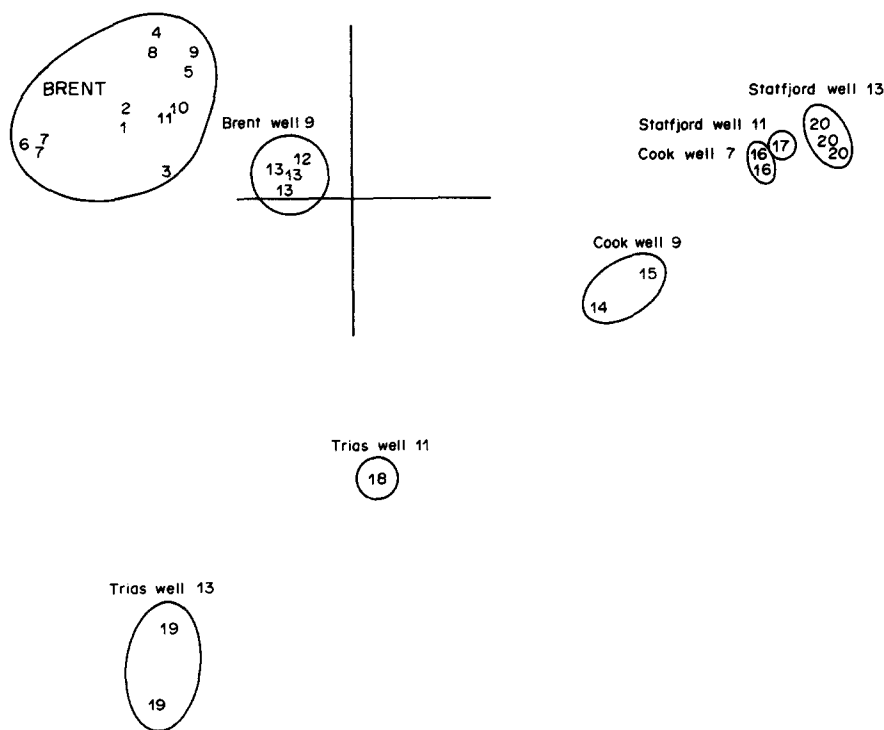

Fig. 6. Plot of the first two principal components of the gas chromatography data of the crude oils without using the n-alkanes.

difference between the samples.

When the n-alkanes were removed from the data set, the remaining 48 components, (predominantly branched alkanes), generate the same separation between the Brent, Cook/Statfjord and Trias classes, as seen from Fig. 6. Even the subclasses are similar. The main differences between the two PC-plots, is that the Statfjord oil from well 11 is more similar to the Cook/Statfjord oils in wells 7 and 13, and that the Brent and Cook oils from well 9 are more separated.

The PC-plot of the data set of the aromatics is given in Fig. 7. Here the Brent oil from well 9 has merged

into the class of the other Brent oils, and sample 15 from well 9 in Cook structure has merged into Cook/Statfjord class. It is seen from Fig. 8 that the oils positively belong to the respective classes. The Brent oils are computed as one class and the Cook/Statfjord as another class. The distances from all the oils to these two class models are calculated as residual standard deviation (RSD) and plotted in Fig. 8.

The most dominating peaks in the discrimination of these two classes are calculated and, by aid of GC–MS, they are found to be biphenyl, naphthalene, phenanthrene and dibenzothiophene and their alkyl
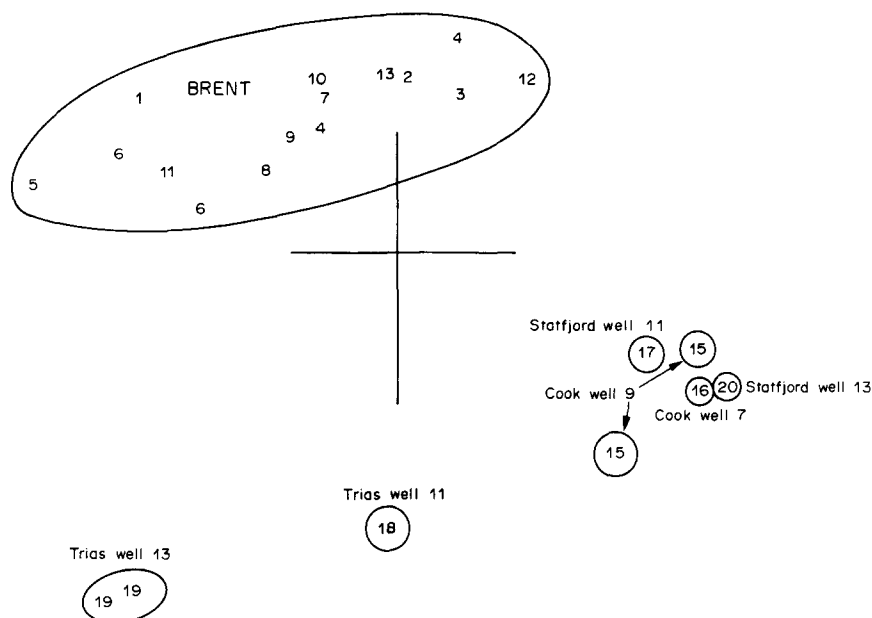
Fig. 7. Plot of the first two principal components of the gas chromatography data of the aromatic fractions.
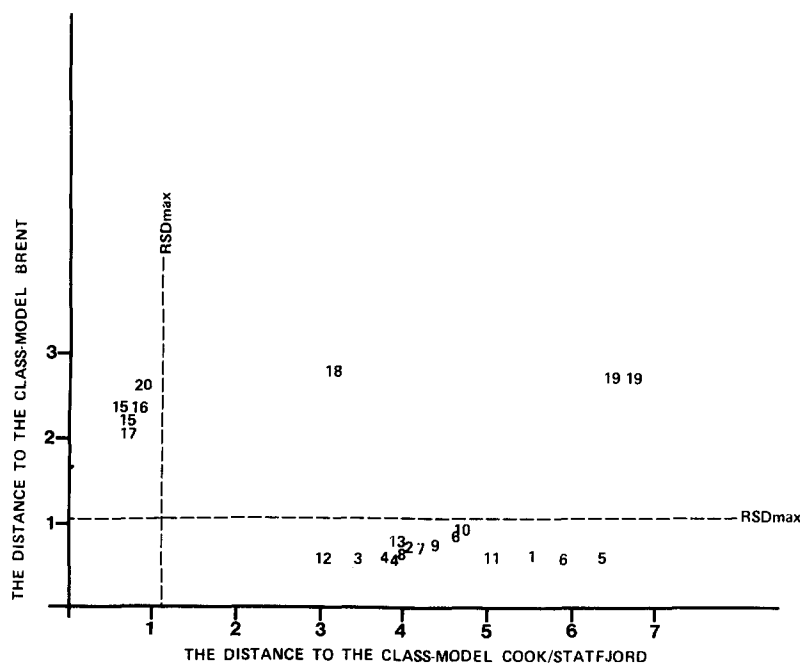

Fig. 8. Class distance plot for the aromatic data. The coordinates are the residual standard deviation for each object fitted to the two class models, Brent and Cook/Statfjord. The dashed line is the limit of the distance for belonging to the classes, due to F-test and $P = 0.01$ (Albano et al., 1981).

derivatives. The C_1, C_2 and C_3 derivatives of the four compounds are the bases for the PC-plot in Fig. 9. The plot generates more or less the same classification as the plot of the total aromatic hydrocarbons (Fig. 7).

CONCLUSION

Chemometric analysis of aliphatic and aromatic hydrocarbons is a good method for classifying oils. The pattern of the aliphatics defines classes of oils
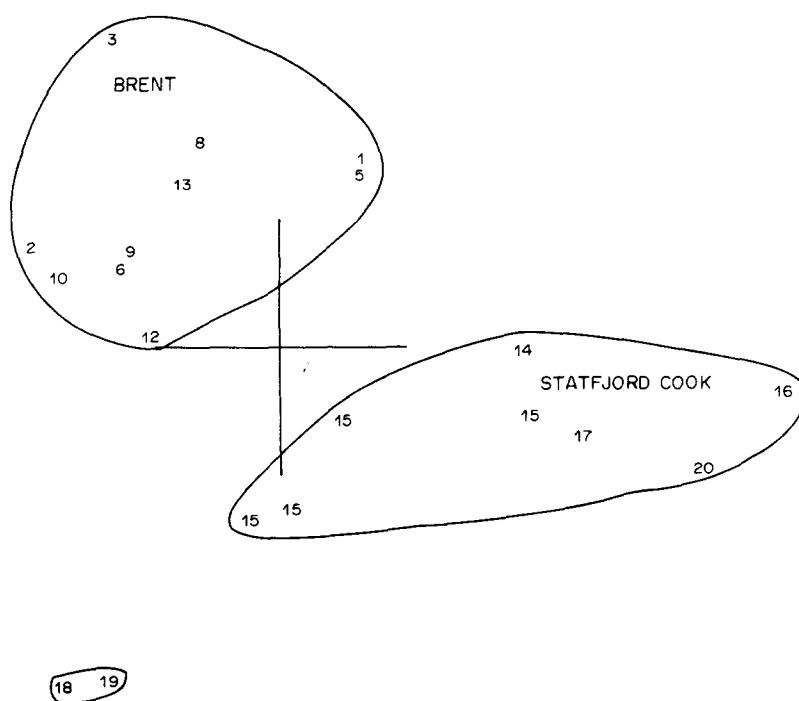
Fig. 9. Plot of the first tw principal components of the GC–MS data of the aromatic fractions.

which predominantly reflect different degrees of biodegradation. The aromatics, however, show that there are three distinct types of oil in the geological area.

The basic differences between the oils are due to differences in the biphenyl, naphthalene, phenanthrene and dibenzothiophene compounds and their alkyl derivatives. Variation in these components could be because of different source rocks, different maturities and geological histories of chromatographic fractionation during migration. For example, Radke and Welte (1983) showed that phenanthrenes vary with maturity. It follows from this study that the relationship of these four compounds to source rock type and maturity should be investigated further.

REFERENCES

Albano C., Blomquist G., Coomans D., Dum W. J. IV, Edlund V., Eliasson B., Hellberg S., Johansson E., Norden B., Sjöström M., Söderström B., Wold H. and Wold S. (1981) In *Proc. Symp. Appl. Stat., Copenhagen* (Edited by Höskuldson A., Conradsen K., Sloth Jensen B. and Esbensen K.), p. 183.

Bailey N. J. L., Jobson A. M. and Rogers M. A. (1973) Bacterial degradation of crude oil: comparison of field and experimental data. *Chem. Geol.* 11, 203–221.

Bockmeulen H., Barker C. and Dickey P. A. (1983) Geology and geochemistry of crude oils, Bolivar Coaskel Fields, Venezuela. *Am. Assoc. Pet. Geol. Bull.* 67, 242.

Clerc J. T. (Ed.) (1983) *Analytical Chimic Acta*, Special issue: Computer Techniques and Optimization (In press).

Derde M. P. and Massart D. L. (1982) Extraction of information from large data sets by pattern recognition. *Fresenius Z. anal. Chem.* 313, 484.

Flory D. A., Lichtenstein H. A., Biemann K., Biller J. E. and Barker C. (1983) Computer process uses entire GC–MS data. *Technol. Oil & Gas J.* Jan 17, 91.

Hohn M. E., Hajibrahim S. K. and Egluiton G. (1982) High-pressure liquid chromatography of petroporphyrins: evaluation as a geochemical fingerprinting method by principal component analysis. *Chem. Geol.* 31, 229.

Hohn M. E., Jones N. W. and Patience R. (1981) Objective comparison of mass fragmentograms by principal component analysis. *Geochim. Cosmochim. Acta* 45, 1131.

Hunt J. M. (1979) *Petroleum Geochemistry and Geology*, Chap. 9. W. H. Freeman, San Francisco.

Kvalheim O. (1983) In preparation.

Radke M. and Welte D. H. (1983) The Methylphenanthrene Index (MPI): A maturity parameter based on aromatic hydrocarbons. In *Advances in Organic Geochemistry 1981* (Edited by Bjorøy M.), pp. 504–512. John Wiley, Chichester.

Radke M., Willsch H. and Welte D. H. (1980) Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Analyt. Chem.* 52, 406.

Volkman J. K., Alexander R., Kagi R. I. and Woodhouse G. W. (1983) Demethylated hopanes in crude oils and their applications in petroleum geochemistry. *Geochim. Cosmochim. Acta* 47, 785.

Wold S. (1981) *Simca 3B Manual*, Umeå.