# Organic Geochemical and Petrographic Analysis of Pure Macerals from the Ohio Shale

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PROCEEDINGS

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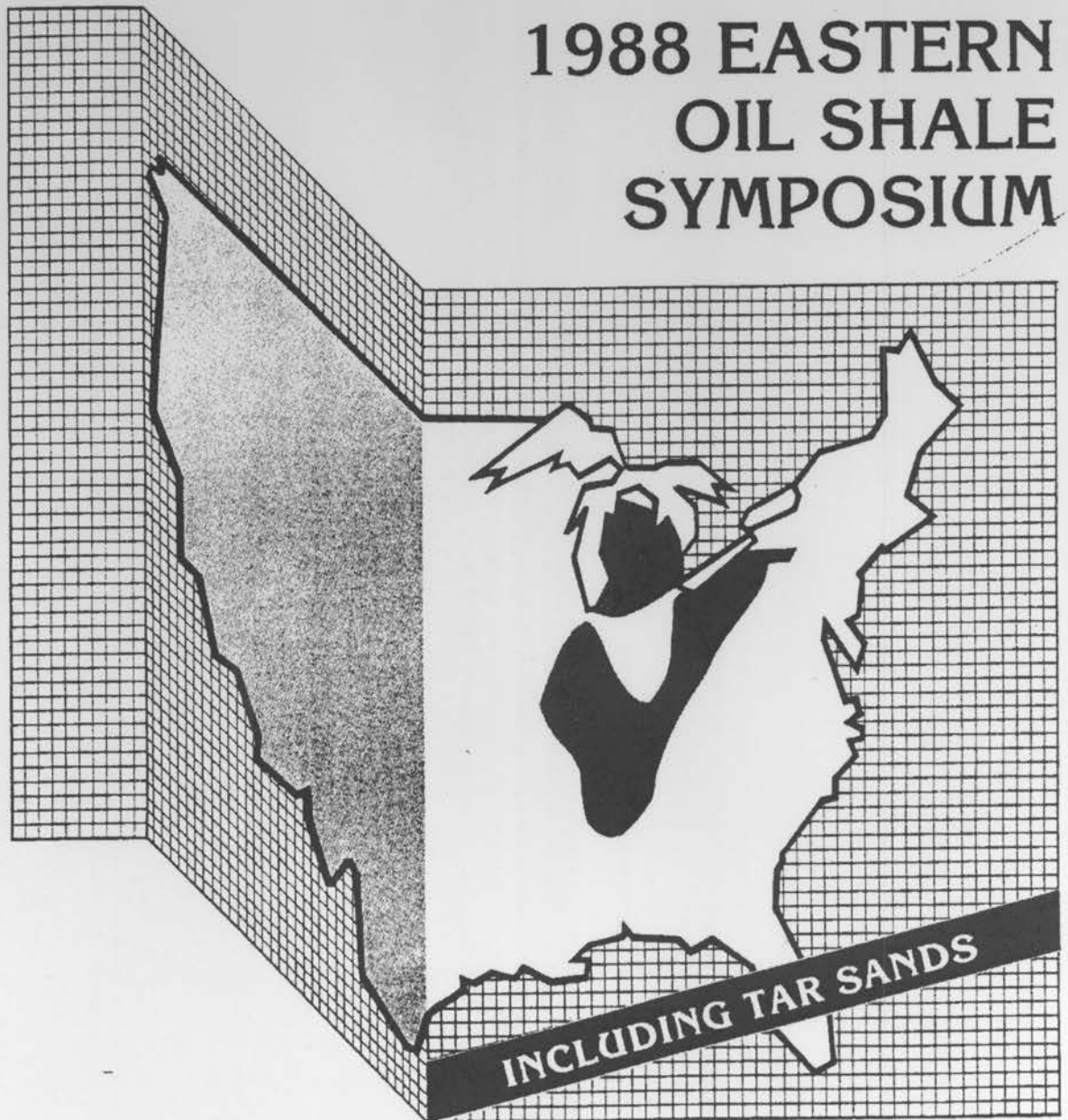
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# ORGANIC GEOCHEMICAL AND PETROGRAPHIC ANALYSIS OF MACERALS FROM THE OHIO SHALE

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## Abstract

Recent advances now permit the separation of coal into constituent macerals of high purity using density gradient centrifugation (DGC). With the availability of pure macerals, the chemical structure of each can be investigated separately, without the interactive interference of the other macerals or mineral matter.  The present study is a preliminary effort applying these methods to the study of oil shale kerogen.

We have used a sample from the Huron Member of the Upper Devonian Ohio Shale from Logan County, Ohio.  Whole rock petrographic examination revealed intact *Tasmanites*, telalginite of unknown derivation and a weakly fluorescing matrix.  Pyrite is abundant, including framboidal and euhedral pyrite imbedded within macerals.  The kerogen concentrate was subjected to DGC.  The resulting profile shows a single, broad main peak, consisting of mixed telaginite, amorphinite and rare vitrinite. Variable amounts of entrapped minerals apparently account for the broad range of density within the peak, with the organic assemblage being fairly consistent.  In future work, it is recommended that the kerogen be micronized prior to DGC to permit a cleaner separation.

In order to investigate the chemistry of macerals, pyrolysis is preferred over simple extraction, since soluble native bitumen is mobile and may migrate from the maceral of origin into a neighboring one, acting as a natural contaminant.  Pyrolysis techniques assure that the data reflects the nature of indigenous material only.  The Ohio Shale kerogen and 4 DGC fractions were subjected to micro-scale, anhydrous, *in vitro* pyrolysis, followed by GCMS of the saturate and aromatic LC fractions of the pyrolyzate.  The 4 DGC fractions are nearly identical in both their saturate and aromatic molecular distributions, consistent with the petrographic observations.  To further demonstrate the efficacy of the method, a pure sporinite isolated from a coal in the Pennsylvanian Brazil Formation of Indiana was also analyzed.  The sporinite pyrolyzate can readily be distiguished from that of the Ohio Shale alginite by the distributions of *n*-alkanes, isoprenoids, phyllocladane derivatives, extended tricyclic terpanes, hopanes, moretanes, steranes, alkylbenzenes and thiophene derivatives.  Py-LC-GCMS is an effective and versatile characterization tool, as it provides a great number of molecular parameters.

## Introduction

Because of their complex, heterogeneous nature, kerogen and coal pose enormous difficulties for the analytical chemist. However, recent advances permit coal to be separated into its constituent macerals, using the technique of density gradient centrifugation (DGC).[1] With the availability of pure macerals, the chemical structure of each can be investigated separately, without the interactive interference of other macerals or the catalytic effect of minerals, simplifying the task of the analyst.

Pyrolysis is especially well suited for maceral work. Previous work on maceral concentrates used rapid, high temperature pyrolysis coupled with a gas chromatograph and/or a mass spectrometer (py-GC, py-MS, py-GCMS).[2-6] High purity macerals separated by DGC in our laboratory have also been analyzed by py-GC and py-MS.[7,8] Slow, lower temperature, confined pyrolysis, both hydrous and anhydrous, has been successful in work on whole kerogens.[9-11] Hydrous and anhydrous methods give similar results at low temperatures, providing that the sample is free of minerals.[12]

The present project is an outgrowth of our work on pure coal macerals and is a preliminary effort aimed at separation and analysis of kerogen constituents. The density fractions were examined chemically, for the biological marker compounds produced by anhydrous *in vitro* pyrolysis, as well as petrographically.

## Methods

The sample used is from the Huron Member of the Upper Devonian Ohio Shale from the Bellefountaine Outlier in Logan County, Ohio. McLaughlin *et al.* describe the outcrop in detail.[13] For comparitive purposes, we also used a coal sample from the "Upper Block" coal seam of the mid-Pennsylvanian Brazil Formation, Park County, Indiana.

Figure 1 summarizes the analytical scheme. Powdered rock was soxhlet extracted in $CH_2Cl_2$. The extracted rock was demineralized by HCl and HF treatments, followed by centrifugation in a liquid of 1.6 g $cm^{-3}$. The material filtered from the supernatant was soxhlet extracted a second time in $CH_2Cl_2$, to remove bitumen which had adhered to clay minerals. Aliquots of the kerogen were subjected to density gradient centrifugation, the details of which have been published previously.[1]

As indicated in figure 1, the kerogen in various stages of preparation and the DGC fractions were made into pellets for petrographic analysis. They were examined in reflected light, both white and UV.

Whole kerogen and DGC fractions were also pyrolyzed *in vitro*. 250-300 mg of dry sample were placed in a 2 ml glass ampule, which was flushed with a stream of argon, sealed and placed in a Eurotherm 4303-3 tube furnace for 72 hr. The kerogen was held at 320° C and the DGC fractions were heated at 340°. Pyrolyzates were extracted by sonicating the cracked ampule in methylene chloride.

The whole rock extract (Extract 1), the demineralization residue extract (Extract 2) and the pyrolyzates were dried and separated by liquid chromatography (LC) into "saturate", "aromatic", "polar 1" and "polar 2" fractions (silica gel, with $C_6H_{14}$, 9:1 $C_6H_{14}$: $CH_2Cl_2$, $CH_2Cl_2$ and 1:1 $CH_2Cl_2$:$CH_3OH$ as the respective eluants). The saturate and aromatic fractions were analyzed by gas chromatographic mass spectrometry (GCMS) with a 25 m OV-1 column, temperature programmed from 100 to 300° C at 3° $min^{-1}$, using a Hewlett Packard 5890A GC coupled with an HP 5970B Mass Selective Detector.

## Results and Discussion

### Extractable Organic Matter

The extract of the demineralization residue (Extract 2) contains 50% more polar compounds than does the whole rock extract (Extract 1) probably because of the release of polars bound to charged clay particles. The saturate fraction of Extract 2 contains proportionately more cyclic compounds than Extract 1. The truncation of lower molecular weight alkanes is more severe in Extract 2, because of the requisite drying after acidification. It is interesting to note that the sterane and other biomarker distributions are the same in both extracts. Due to the retention of the polar fraction by the clays, it is necessary to perform the second extraction to ensure a bitumen-free kerogen after demineralization.

Using data from m/z 217 mass chromatograms, standard $C_{29}$ sterane maturity ratios were computed for Extract 1. Values of 0.51 for $\alpha\alpha\alpha$ 20S/(20S+20R) and of 0.48 for $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ indicate that the sample is incipiently mature for oil generation.

### Whole Kerogen

Petrographic analysis reveals intact *Tasmanites*, *Tasmanites*-like telaginite fragments and scattered, rare vitrinite particles. There is ample pyrite, including framboids and euhedra encapsulated within alginite. In petrographic preparations that had been acid-digested, the vitrinite surface appears granular, possibly an extraction artifact. Such vitrinite cannot be used for reflectance measurements.

The extract and whole kerogen pyrolyzate of the Ohio Shale sample show significant differences. The pyrolyzate contains 57% more asphaltenes than Extract 1 and only one third of the saturates. Aromatic yield percentages are approximately the same for both. The saturate fractions also show important distinctions. There are proportionately less isoprenoids, steranes, hopanes and tricyclic terpanes in the pyrolyzate. There are relatively more higher molecular weight *n*-alkanes and *n*-alkylcyclohexanes.

The primary purpose of this study is not to imitate the natural process of petroleum generation, but to chemically characterize the kerogen. As long as pyrolysis is performed in a consistent manner, meaningful comparisons of kerogens and macerals can be obtained.

### Separation of Kerogen

Density gradient centrifugation of the Ohio Shale kerogen gives essentially a single broad peak ranging from 1.13 to 1.50 g $cm^{-3}$ (fig. 2). Petrographic examination of fractions within this peak reveals a weakly-fluorescing brown amorphinite, bits of telalginite, some of which are *Tasmanites*-like, and pyrite encapsulated by alginite. Within the peak, pyrite content increases with increasing density. Thus, the variable amount of entrapped pyrite accounts for the broad density range of the peak. In future experiments, kerogen must be micronized to permit complete pyrite removal prior to DGC. There is also a minor decrease in the telalginite/amorphinite ratio with increasing density. The small peak at 1.03-1.04 g $cm^{-3}$ (fig. 2) is composed of intact and fragmented *Tasmanites*, without pyrite.

For analysis of individual macerals, pyrolysis is preferred over simple extraction since the native bitumen is mobile and may migrate from its maceral of origin into a neighboring one, acting as a natural contaminant.[14] Four fractions in the 1.13-1.50 g $cm^{-3}$ density range were chosen for pyrolysis, composited in each case to give adequate quantities (fig. 2).
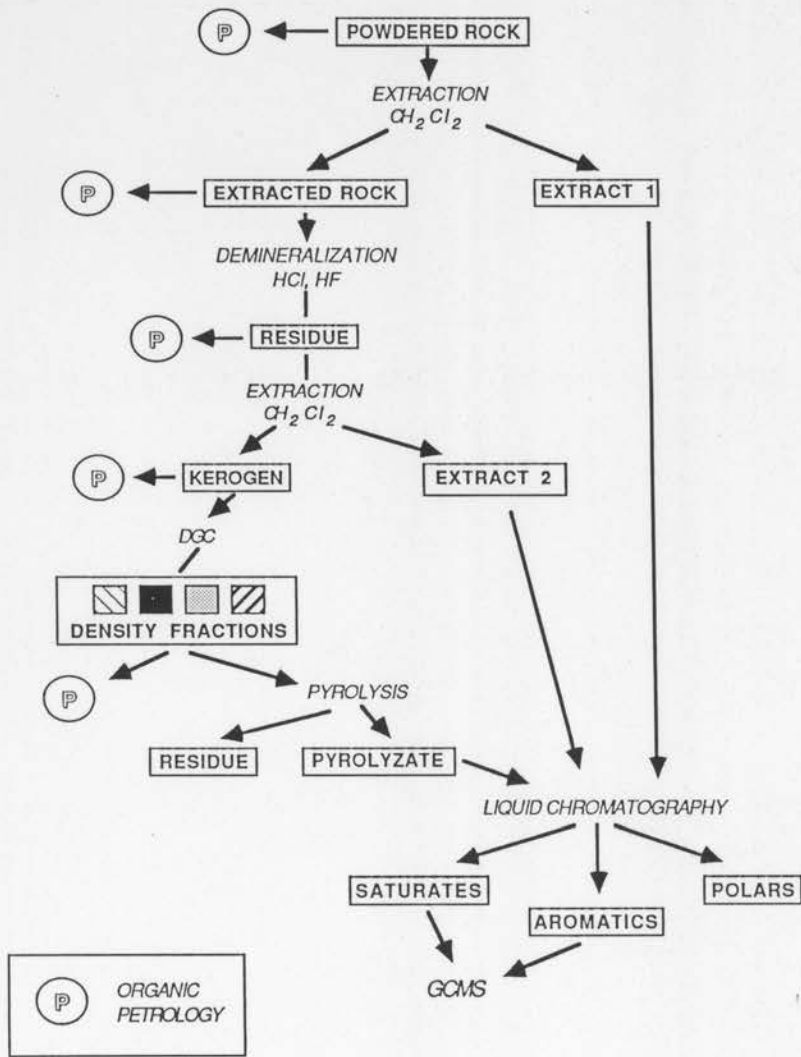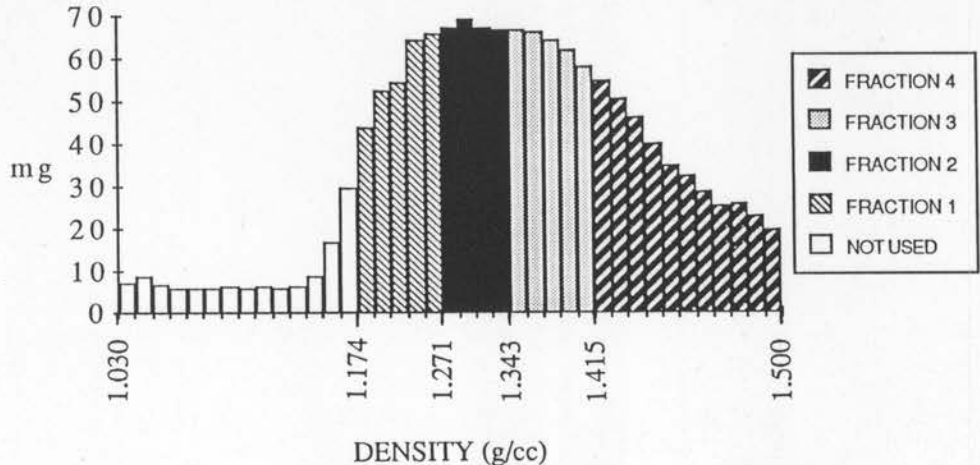
Figure 1.    Summary of analytical procedures.



DENSITY (g/cc)

Figure 2.    Density gradient centrifugation profile of Ohio Shale kerogen. Fractions used in pyrolysis are shown.

FRACTION 1

FRACTION 2

B

C

FRACTION 3

J

L

K

FRACTION 4

M/Z 99
N-ALKANES, ISOPRENOIDS

M/Z 217
STERANES
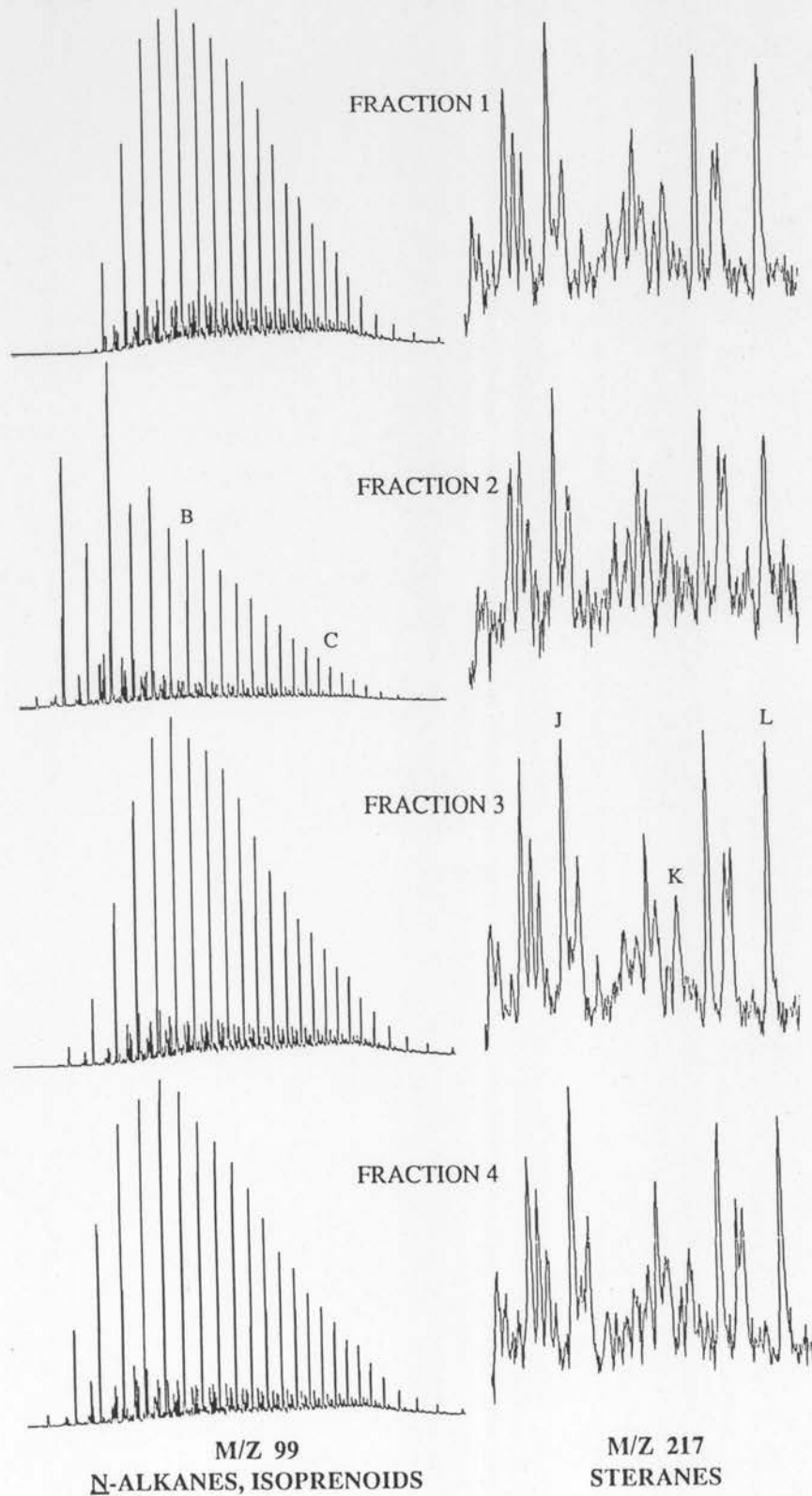
Figure 3.    Ohio Shale DGC fraction pyrolyzates — GCMS of saturates.

Unfortunately, there was insufficient sample of density <1.13 g cm$^{-3}$. The pyrolysis temperatures were increased slightly (to 340° C, 20° above that used for the whole kerogen) in an attempt to reduce the yield of polar compounds, which dropped to 62% of the total, as compared to 72% for the whole kerogen at lower temperature.

The pyrolyzates of all four fractions are extremely similar. The distribution of $n$-alkanes show maxima in the $C_{18}$ to $C_{20}$ range (fig. 3). Fraction 2 shows an even-odd predominance in the $C_{16}$ to $C_{20}$ range. This may or may not have been present in other fractions, but cannot be determined due to a greater loss of the lower molecular weight compounds of Fractions 1, 3 and 4 during sample preparation. The sterane distributions are complex, but virtually identical (fig. 3). As examples of aromatic compounds, figure 4 shows the distributions of methylphenanthrene, methylanthracene, methyldibenzo-thiophene and methylnaphthothiophene isomers. Again, these are virtually the same for the four fractions, as are the scale factors of the m/z 198 chromatograms relative to the m/z 192. One slight, but significant difference between the fractions is the increase of the hopane/sterane ratio from 2.8 to 4.1 with increasing fraction density. This suggests that organic matter found in the higher density fraction has been subjected to a more extensive bacterial degradation, since hopanes are derived from the lipids of procaryotes. This subtle chemical distinction within the DGC fraction parallels the minor decrease in the alginite/amorphinite ratio discussed previously. The otherwise great degree of similarlity in the pyrolyzates indicates that the four density fractions contain essentially the same organic matter, consistent with petrographic observations.

*Comparison of Alginite and Sporinite*

To demonstrate the ability of pyrolysis-LC-GCMS to characterize macerals, we compared a representative Ohio Shale fraction (Fraction 3) with a pure sporinite, separated by DGC from micronized, demineralized coal from the Brazil Formation of Indiana. Vitrinite reflectance shows that maturity differences between the Ohio Shale sample (≈0.50 % $R_O$) and the coal (0.58% $R_O$) are not great. Thus the pyrolyzate biomarker assemblages from the two samples should reflect primarily organic matter type rather than maturation differences.

The saturate fractions of the two maceral pyrolyzates are clearly dissimilar, with an $n$-alkane maximum at $C_{19}$ for the alginite and at $C_{28}$ for the sporinite (fig. 5). The tetracyclic terpanes, on the m/z 123 partial chromatogram (principally kaurane and phyllocladane derivatives) are prominent in the sporinite, as is typical of terrestrial material. Such compounds are not very important in the marine, more ancient Ohio Shale. On the m/z 191 chromatograms, the most striking differences are with the extended tricyclic terpanes, which are prominant in the alginite and nearly absent in the sporinite, and the moretanes, which are relatively much stronger in the sporinite. The sterane distributions are also distinctive. Regarding $C_{29}$ $5\alpha(H),14\alpha(H),17\alpha(H)$ 20R steranes, $C_{29} \approx C_{27} >> C_{28}$ in the case of the alginite, whereas for the sporinite, $C_{29} >> C_{28} > C_{27}$.

The aromatic fractions of the pyrolyzates also show important differences. For example, the m/z 91 chromatogram of the sporinite is fairly simple, showing an homologous series of alkylbenzenes (fig. 5). The corresponding chromatogram for the alginite is more complex. In addition to the alkylbenzene series, there is evidence for a greater diversity of aromatic compounds which also produce a fragment ion at m/z 91. The m/z 192 trace shows that the sporinite produces more of the methylanthracenes (peaks Q and T) than does the alginite. The m/z 198 traces for the two samples are also very dissimilar, indicating different organosulfur distributions in each. The data from the saturate and aromatic fractions point to the applicability of the pyrolysis-LC-GCMS method to the characterization of macerals. The large number of molecular parameters that can be evoked for this purpose gives this technique its advantage.

### Conclusions

1) With the availability of pure macerals, the chemical structure of each can be investigated separately, without the interactive interference of the other macerals or mineral matter.

2) In order to investigate the chemistry of macerals, pyrolysis is preferred over simple extraction, since soluble native bitumen is mobile and may migrate from the maceral of origin into a neighboring one, acting as a natural contaminant. Pyrolysis techniques assure that the data reflect the nature of indigenous material only.

3) Kerogen pyrolyzates differ from solvent extracts with their overall lesser amounts of isoprenoids, steranes and hopanes. The pyrolyzates of the four density fractions of the Ohio Shale sample are nearly identical in both their saturate and aromatic molecular distributions, consistent with the petrographic observations.

4) The pyrolyzate of other macerals, such as sporinite, can readily be distiguished from the Ohio Shale alginite by the distributions of $n$-alkanes, isoprenoids, phyllocladane derivatives, extended tricyclic terpanes, hopanes, moretanes, steranes, alkylbenzenes and thiophene derivatives. Py-LC-GCMS is an effective and versatile characterization tool, as a great number of molecular parameters are available.

5) Variable amounts of pyrite, encapsulated within alginite particles, prevent the proper separation of kerogen by density gradient centrifugation. In future work, it is recommended that the kerogen be micronized to permit thorough pyrite removal prior to DGC.

| PEAK | IDENTIFICATION | M/Z |
|---|---|---|
| A | Phytane | 99 |
| B | $n$-$C_{20}$ | 99 |
| C | $n$-$C_{30}$ | 99 |
| D | $C_{23}$ Tricyclic Terpane | 191 |
| E | $C_{29}$ Tetracyclic Terpane | 191 |
| F | $C_{29}$ Hopane | 191 |
| G | $C_{29}$ Moretane | 191 |
| H | $C_{30}$ Hopane | 191 |
| I | $C_{30}$ Moretane | 191 |
| J | $C_{27}$ $\alpha\alpha\alpha$ 20R Sterane | 217 |
| K | $C_{28}$ $\alpha\alpha\alpha$ 20R Sterane | 217 |
| L | $C_{29}$ $\alpha\alpha\alpha$ 20R Sterane | 217 |
| M, N | $n$-Alkylbenzenes | 91 |
| O, P, R, S | Methylphenanthrenes | 192 |
| Q, T | Methylanthracenes* | 192 |
| U, V, W | Methyldibenzothiophenes | 198 |
| X, Y, Z | Methylnaphthothiophenes* | 198 |

*(\* tentative assignment)*

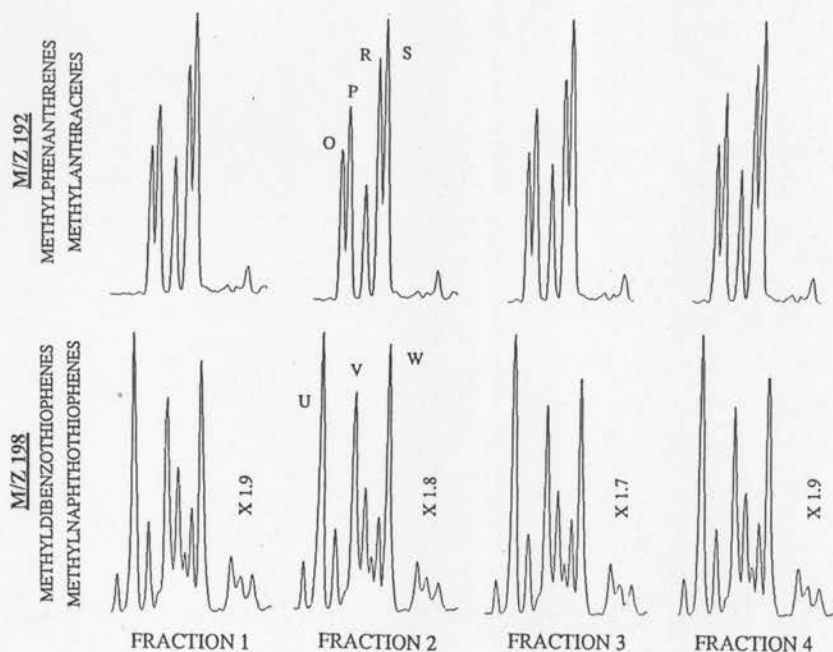Table 1.        GCMS peak identifications.

Figure 4.      Ohio Shale DGC fraction pyrolyzates — GCMS of aromatics.

## References

1.  Dyrkacz, G.R. and Horwitz, E.P., 1982, "Separation of coal macerals", *Fuel*, Vol. 61, pp. 3-12.

2.  Larter, S.R. and Douglas, A.G., 1980, "A pyrolysis-gas chromatographic method for kerogen typing", *Adv. Org. Geochem. 1979*, pp. 579-583.

3.  van Graas, G., de Leeuw, J.W. and P.A. Schenck, 1980, "Analysis of coals of different rank by Curie-point pyrolysis-mass spectrometry and Curie-Point pyrolysis-gas chromatography-mass spectrometry", *Adv. Org. Geochem 1979*, pp. 485-494.

4.  Meuzelaar, H.L.C., Harper, A.M., Pugmire, R.J. and Karas, J., 1984, "Characterization of coal maceral concentrates by Curie point pyrolysis mass spectrometry", *Intl. Jour. Coal Sci.*, vol. 4, pp.143-171.

5.  Senftle, J.T., Larter, S.R., Bromley, B.W. and Brown, J.H., 1986, "Quantitative chemical characterization of vitrinite concentrates using pyrolysis-gas chromatography. Rank variation of pyrolysis products", *Org. Geochem.*, vol. 9, pp. 345-350.

6.  Nip, M, de Leeuw, J.W., Schenck, P.A., 1988, "The characterization of eight maceral concentrates by means of Curie point pyrolysis-gas chromatography and Curie point pyrolysis-gas chromatography-mass spectrometry", *Geochim. Cosmochim. Acta*, vol. 52, pp. 637-648.

7.  Senftle, J.T., Yordy, K.L., Barron, L.S. and Crelling, J.C., 1988, "Analysis of mixed kerogens from Upper Devonian New Albany Shale I. Evaluation of kerogen components derived from density separation", *Proceedings, 1987 Eastern Oil Shale Symposium*, Kentucky Energy Cabinet, Lexington KY.

8.  Crelling, J.C., Pugmire, R.J., Meuzelaar, H.L.C., McClennen, W.H. and Karas, J. (in press), "Chemical structure and petrology of resinite from the Hiawatha "B" coal seam", submitted to *Energy and Fuels*.

9.  Monthioux, M., Landais, P. and Monin, J.-C., 1985, "Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia", *Org. Geochem.*, vol. 8, pp. 275-292.

10. Lewan, M.D., Bjorøy, M. and Dolcater, D.L., 1986, "Effects of thermal maturation on steroid hydrocarbons as determined by hydrous pyrolysis of Phosphoria Retort Shale", *Geochim. Cosmochim. Acta*, vol. 50, pp. 1977-1987.

11. Comet, P.A., McEvoy, J., Giger, W. and Douglas, A.G., 1986, "Hydrous and anhydrous pyrolysis of DSDP Leg 75 kerogens— A comparative study using a biological marker approach", *Org. Geochem.*, vol. 9, pp.

12. Huizinga, B.J., Tannenbaum, E. and Kaplan, I.R.,1987, "The role of minerals in the thermal alteration of organic matter—III. Generation of bitumen in laboratory experiments", *Org. Geochem.*, vol. 11, pp. 591-604.

13. McLaughlin, J.D., McLaughlin, R.L. and Kneller, W.A.,1987, "Organic geochemistry of the kerogen and bitumen from the Ohio Shale by pyrolysis-gas chromatography", *Intl. Jour. Coal Geol.*, vol. 7, pp. 21-51.

14. Allan, J. and Larter, S.R., 1983, "Aromatic structures in coal maceral extracts and kerogens", *Adv. Org. Geochem. 1981*, pp. 534-545.

ALGINITE FRACTION 3 — OHIO SHALE

SPORINITE BRAZIL BLOCK SEAM — INDIANA

**M/Z 99**
N-ALKANES, ISOPRENOIDS

**M/Z 123**
TETRACYCLIC DITERPANES

**M/Z 191**
HOPANES, EXTENDED TRICYCLIC
AND TETRACYCLIC TERPANES

ALGINITE FRACTION 3 — OHIO SHALE

SPORINITE BRAZIL BLOCK SEAM — INDIANA

**M/Z 217**
STERANES

**M/Z 91**
ALKYLBENZENES

**M/Z 192**
METHYLPHENANTHRENES
METHYLANTHRACENES

**M/Z 198**
METHYLDIBENZOTHIOPHENES
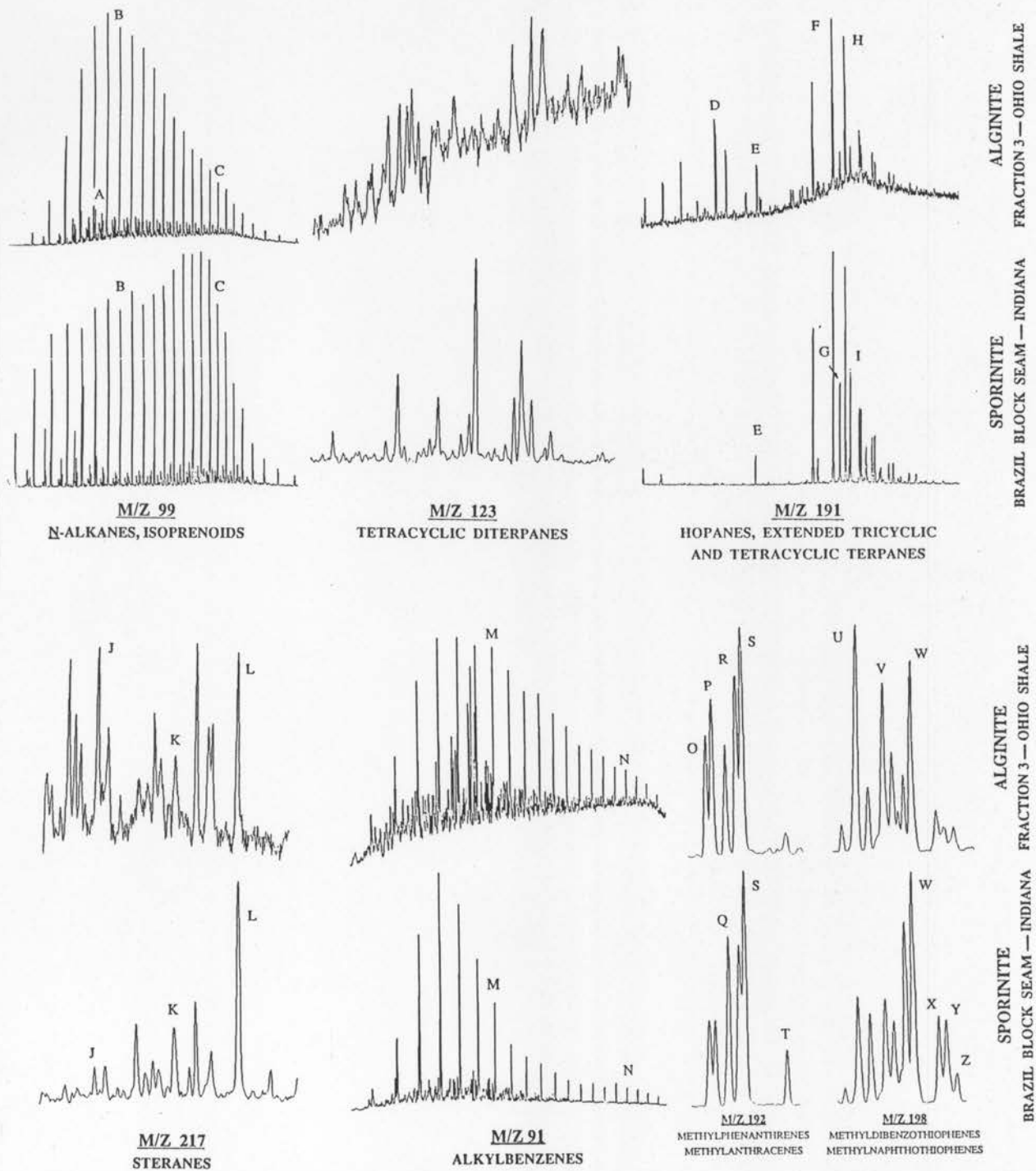METHYLNAPHTHOTHIOPHENES

Figure 5.    GCMS of DGC fraction pyrolyzates, Ohio Shale alginite and Brazil Formation
sporinite (saturates and aromatics).