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MATURATION STUDIES OF CANADIAN EAST COAST OILS

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APRIL 1977

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
CANMET REPORT 77-42

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MATURATION STUDIES ON CANADIAN EAST COAST OILS

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H. Sawatzky*, A.E. George*, R.C. Banerjee**,
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ABSTRACT

Five Canadian east coast Cretaceous oils, Heron H-73, Adolphus 2K-41, Sable Island E-48, Cohasset D-40 and Primrose N-50 were chemically investigated in an attempt to establish their degree of thermal maturation. Saturated, monoaromatic, diaromatic and polyaromatic hydrocarbons and polar material were separated by silica-alumina chromatography. The separated hydrocarbon and polar material fractions were studied further by gas chromatography.

The chromatographic results, optical activity data of the saturated hydrocarbons and the gasoline content present evidence of the thermal immaturity of the Heron and Adolphus oils. Sable Island, Cohasset and Primrose oils are mature.

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ÉTUDE DE LA MATURATION DE CERTAINS PÉTROLES DE LA COTE EST DU CANADA

par

H. Sawatzky*, A.E. George*, R.C. Banerjee**,
G.T. Smiley*** et D.S. Montgomery****

RÉSUMÉ

Les auteurs soumettent à une analyse chimique cinq échantillons de pétrole de la côte est du Canada dont l'origine remonte au Crétacé et qui ont été prélevés dans les puits Heron H-73, Adolphys 2K-41, Sable Island E-48, Cohasset D-40 et Primrose N-50, afin de déterminer leur degré de maturation thermique. Des hydrocarbures saturés, monoaromatiques, diaromatiques et polyaromatiques, ainsi que des fractions polaires sont séparés par chromatographie silice-alumine. Les hydrocarbures et les fractions polaires ainsi dissociés sont analysés plus à fond par chromatographie en phase gazeuse.

Les résultats des chromatographies, les données sur l'activité optique des hydrocarbures saturés et la teneur en essence indiquent que les pétroles Heron et Adolphys ne sont pas parvenus à la maturité thermique. En revanche, les pétroles Sable Island, Cohasset et Primrose sont mûrs.

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INTRODUCTION

The Heron, Adolphus, Sable Island, Cohasset and Primrose east coast oils were investigated at the request of J.D. McAlary of the Resource Geology Division of the Resource Management and Conservation Branch, Department of Energy, Mines and Resources, Ottawa.

The objective of this investigation was to chemically assess the degree of thermal maturation of a series of petroleum samples taken off the east coast of Canada. This assessment, together with geothermal studies on coal and possibly other minerals in the area, could eventually provide a more coherent understanding of the thermal history of the region which would facilitate future petroleum exploration. This is of major importance in the Energy Program of the Department.

The chemical criteria for evaluating maturity were based to a large extent on a previous CANMET study on simulating the geothermal maturation of Athabasca bitumen by hydrocracking (1,2) and correlating the results to Cretaceous oils of different degrees of maturity in the Alberta basin. Several criteria were considered in this investigation since many factors could be involved in determining the chemical nature of the oil, (e.g., fractionation during migration, deasphalting, biodegradation or the nature of the source material).

EXPERIMENTAL

1. Samples - The following samples were investigated:

Sable Island E-48

The geographical location of this well is above a salt dome on the western tip of Sable Island with the salt occurring at a depth of 10,000 feet. The oil sample was obtained at a depth of 4790-4795 feet in the upper Logan Canyon formation of Late Cretaceous age.

Heron Heavy Oil H-73

The geographical location of this well (44°00'52"N, 52°25'00"W) is approximately 245 statute miles south of St. John's, Newfoundland. It was drilled on the north flank of a salt dome and the oil was recovered from a depth of 7525'-7565' in Upper Cretaceous limestone.

Adolphus 2K-41

The well is located on a salt dome about 200 miles east of St. John's, Newfoundland (47°00'37"N, 48°22'00"W) in the Atlantic Ocean. The sample was obtained at a depth of 8560-8685 in Upper Cretaceous sandstone.

Cohasset D-40

The well is located on the Scotian Shelf about 30 miles west of Sable Island (43°51'6.52"N, 65°37'13.89"W) on the crest of a low relief anticline. The sample was collected from production tests between 6100'-6600' in a Lower Cretaceous sandstone.

Primrose N-50

The well is located about 35 miles east of Sable Island on top of a salt dome. The oil was recovered from Cretaceous dolomites at a depth of 5408'.

2. Separations and Analyses

Removal of Asphaltenes and Volatiles

The asphaltenes of each sample were precipitated by dilution with 20 volumes of normal pentane. The asphaltenes were separated by filtration, extracted with pentane in a soxhlet extractor and dried, first on a water bath, then under reduced pressure at 50°C. The main pentane-solubles and washings were combined and n-pentane completely evaporated from these maltenes, followed by distillation of the volatile materials boiling below 200°C to yield a deasphaltened, relatively non-volatile fraction for further analysis.

Hydrocarbon-Type Separation

The gasoline fractions distilling below 200°C were analyzed for saturate and aromatic contents on a silica gel column using the fluorescent indicator adsorption method (ASTM D1319-70). All the aromatics in these fractions were considered to be mononuclear.

The oils that had been deasphaltened and topped to 200°C were separated into hydrocarbon-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar material and basic nitrogen compounds on a dual-packed (silica gel and alumina gel) liquid-solid chromatographic column developed by the API Project 60, and modified in our laboratory (3). A modification, scaled down from the original procedure by a factor of 10 and in which pressure was applied to increase the speed of separation, was used in this investigation. The polyaromatics were eluted by benzene; the polar material was eluted by a mixture of polar solvents (methyl alcohol, ethyl ether and benzene) and the basic compounds were eluted by pyridine at 100°C.

The numbers of moles of the mononuclear and dinuclear aromatic structures were determined using average molecular weights that were obtained from gas chromatographic simulated distillation data, assuming that the material eluting when half of the sample had distilled represented the average molecular weight.

Gas Chromatography

The gas chromatographic separations were made on glass columns 0.6 cm OD, 0.4 cm ID and 152 cm long packed with 5% OV-1 (dimethyl silicone gum) on acid-washed chromosorb W (diatomaceous earth), 60-80 mesh, using a flame ionization detector.

The saturated hydrocarbons (+ C_{10}) were separated on an OV-1 SCOT capillary column. In all cases the column oven was programmed from 30°C to 250°C at 4°C/min. The Heron viscous sample was diluted with n-pentane and then an appropriately larger sample size was injected.

3. Optical Rotation of the Saturates

The polarimeter used for this work was a "Model A" manufactured by Bellingham and Stanley Ltd., using a sodium D light as the light source.

All optical activity values except those of the Heron heavy oil were obtained from the undiluted samples. The saturated hydrocarbon fraction from the Heron heavy oil H-73 contained waxes which crystallized at room temperature and therefore its optical activity was measured in a 20% benzene solution. A 40-cm-long polarimeter tube was used for the benzene solutions, and a 9.4-cm-long one for the undiluted samples. The blank rotation readings were determined using pure benzene and air as references for the diluted and undiluted samples respectively. The rotation readings were taken by five persons, each making five readings for each determination. The results are expressed using the standard error of the mean.

RESULTS AND DISCUSSION

In establishing the criteria for evaluating the levels of maturity of these oils, much use has been made of the results obtained during the hydrocracking study of Athabasca bitumen (1). The bitumen was converted to materials resembling more thermally mature cretaceous oils.

The criteria used have been established as follows:

1. Saturated hydrocarbons content - increases with maturation due to cleavage of alkyl and cycloalkyl groups from aromatic structures.
2. Molecular weight - average molecular weight decreases, per cent gasoline increases and per cent asphaltenes diminishes.
3. Number of moles of mononuclear aromatic compounds per unit weight - increase dramatically, which appears to be caused by aromatization of highly cyclic saturates.
4. Polar and basic compounds - decrease markedly because of their thermal instability.
5. Optical activity of the saturated hydrocarbons - decreases because of racemization, aromatization and dilution with new materials formed during geothermal maturation.
6. Steranes and terpanes - diminish and eventually disappear.

<u>Heron Oil</u>

This oil is of low maturity by all criteria. The saturated hydrocarbon content is low. The molecular weights of the components are high, as shown by the fact that asphaltenes content is 38.4% (Table 1), the gasoline fraction is non-existent and the gas chromatograms of the various components (Figures 1, 2, 3, 4) show a predominance of high molecular weight components. The number of mononuclear aromatic structures is low, and there is a low ratio of mono-to-dinuclear aromatic compounds (Table 4). The content of polar materials is high, the optical activity of the saturated hydrocarbons (Table 2) and the metal contents are also high. The high background in the region of 2600-3300 KI of the gas chromatogram of the saturated hydrocarbons indicates steranes and triterpanes. The large peak at 3000 KI may be due partially to normal C_{30} and partially to steranes or triterpanes.

Adolphus Oil

This oil has some low molecular weight material and is also low in asphaltenes (Table 1). However, according to the gas chromatograms, there is a large portion of high molecular weight material and the distillation residue is almost 39%.

The ratio of mono-to-dinuclear aromatic structures is of the same order as that of the Heron oil, indicating a low level of maturity (Table 4). The high content of saturated hydrocarbons (Table 3) may be accounted for by a source material that was already high in these compounds (4).

The amount of polar materials is not very high but that may be because the source materials contained small quantities of these compounds or they may have been held back by the rock during migration.

The optical activity is quite substantial (Table 2) which is explained by the appreciable amount of material in the 2500-3000 KI region of the saturated hydrocarbon gas chromatogram.

This is regarded as an oil that has undergone some thermal alteration but is still of low maturity.

Sable Island Oil

The saturated hydrocarbon content is quite high (Table 3) and accordingly this oil is considered mature. It can be seen from the gas chromatogram (Figure 1) that there is only a small amount of normal alkanes in this oil and the peak for pristane is predominant. This may be ascribed to biodegradation but may also be caused by a source material lean in precursors of normal alkanes.

The average molecular weight is low, indicated by the high gasoline content, the absence of asphaltenes, and the small amount of distillation residue in USBM method (Table 1). The gas chromatograms of the saturates, mononuclear aromatics and dinuclear aromatics (Figures 1 to 3) show the presence of mostly low molecular weight materials. The major portion in the dinuclear aromatics chromatogram, is due to low molecular weight peaks, which are believed to be alkyl naphthalenes. This also is observed in the more mature Cretaceous oils in western Canada (2).

The ratio of mono-to-dinuclear aromatic structures is substantial (Table 4) and the amount of polar compounds is relatively low (Table 3). The optical activity is negligible and there is little evidence of steranes and triterpanes.

From the above evidence this oil is considered to be fairly mature.

Cohasset Oil

This oil has a very high saturated hydrocarbon content (Table 3). The molecular weights are low, as evidenced by the high gasoline content, negligible distillation residue, the gas chromatograms, and the absence of asphaltenes. The ratio of mononuclear-to-dinuclear aromatic structures is high (Table 4) and the relative amount of polar materials is very low. The optical activity is quite low (Table 2) and there is no evidence of steranes or triterpanes. All these factors point to a high level of maturity.

In the chromatogram of the mononuclear aromatics (Figure 2), there are a number of well-resolved peaks in the 2800-3500 KI region and these may be due to aromatized steranes.

Primrose Oil

The saturated hydrocarbon content is lower than in the other mature oils (Table 3) which may be due to a different source material. However, the aromatic hydrocarbon content is high.

The gasoline content is not very high, but on examination of the gas chromatograms it becomes obvious that there is very little high molecular weight material present. This oil has no asphaltenes.

The mononuclear aromatic content is high and so is the ratio of the number of its structures to the number of dinuclear aromatic structures (Table 4). This is an indication of high maturity.

The polar materials content is low and so is optical activity. There is little evidence of steranes or triterpanes. This oil is mature.

CONCLUSIONS

Chemical analyses and optical activity determinations of the five Canadian east coast Cretaceous oils for establishing their degrees of thermal maturation categorize the Heron and Adolphus oils as geochemically immature, while Cohasset, Sable Island and Primrose oils are mature oils.

ACKNOWLEDGEMENT

The authors are grateful to the Geological Survey of Canada for financial support of this research program.

REFERENCES

1. George, A.E., Banerjee, R.C., Smiley, G.T. and Sawatzky, H. "Simulated geothermal maturation of Athabasca bitumen." Pending publication in the Bulletin of Canadian Petrol. Geol.

2. Montgomery, D.S., Clugston, D.M., George, A.E., Smiley, G.T. and Sawatzky, H. "Investigation of oils in the western Canada tar belt." Oil Sands-Fuel of the Future, published by Canadian Society of Petroleum Geologists, 3:168-183; 1974.

3. Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S. "Hydrocarbon-type separation of heavy petroleum fractions." Fuel 55:16-20; 1976.

4. Moore, L.R. "Organic geochemistry." Ed. Eglinton, G. and Murphy, M.T.J.; Springer-Verlag, New York, 11:267-68; 1969.

TABLE 1

Characteristics Of The East Coast Oils

Characteristic	Heron H-73	Adolphus 2K-41	Sable Island E-48	Cohasset D-40	Primrose N-50
Formation Age	UC*	UC	UC	LC*	UC
Depth ft	7525-7565	8560-8685	4790-4795	6100-6600	5408
Temperature °F	150	175	130	122	133
Sulphur Content wt %	6.27	2.56	0.05	Nil	0.13
Gasoline Content vol %	trace	14.5	42.7	53.2	27.0
Asphaltene Content wt %	38.4	1.9	-	-	-

* UC = Upper Cretaceous

* LC = Lower Cretaceous

TABLE 2

Optical Activity of the Saturated Hydrocarbon Fractions of the Deasphaltened East Coast Oils

Oil Sample	Optical Rotation per gram of Saturated Hydrocarbons
Heron H-73	$0.2441^{o} \pm 0.008^{o}$
Adolphus 2K-41	$0.0725^{o} \pm 0.003^{o}$
Sable Island E-48	negligible
Cohasset D-40	$0.0304^{o} \pm 0.002^{o}$
Primrose N-50	$0.0215^{o} \pm 0.004^{o}$

TABLE 3

Compound-Type Distribution In The East Coast Oils

Compound-type		Heron	Adolphus	Sable Island	Cohasset	Primrose
Saturates,	wt %	9.9	64.1	69.8	84.8	55.6
Monoaromatics,	wt %	8.5	11.4	17.9	9.1	26.4
Diaromatics,	wt %	8.6	7.0	6.9	3.4	11.9
Polyaromatics,	wt %	11.6	6.4	3.7	1.3	4.2
Polar Compounds,	wt %	18.9	5.5	1.7	1.1	1.5
Basic Compounds,	wt %	4.0	3.7	0.6	0.3	0.4
Saturates/Aromatics	wt %	0.34	2.58	2.45	6.14	1.31
Asphaltenes,	wt %	38.4	1.9	-	-	-

TABLE 4

Moles Of Monoaromatic And Diaromatic Types Per 100 Grams Oil

Aromatic type	Heron	Adolphus	Sable Island	Cohasset	Primrose
Monoaromatics, wt %	0.020	0.036	0.099	0.052	0.162
Diaromatics, wt %	0.029	0.018	0.032	0.015	0.059
Mono-/Diarom. wt %	0.07	2.0	3.1	3.5	2.7

TABLE 5

Aromatic-types As Percentage Of Total Aromatic Content In The East Coast Oils

Aromatic type	Heron	Adolphus	Sable Island	Cohasset	Primrose
Monoaromatics, wt %	29.6	46.0	62.8	65.9	62.1
Diaromatics, wt %	30.0	28.2	24.2	24.6	28.0
Polyaromatics. wt %	40.4	25.8	13.0	9.4	9.9

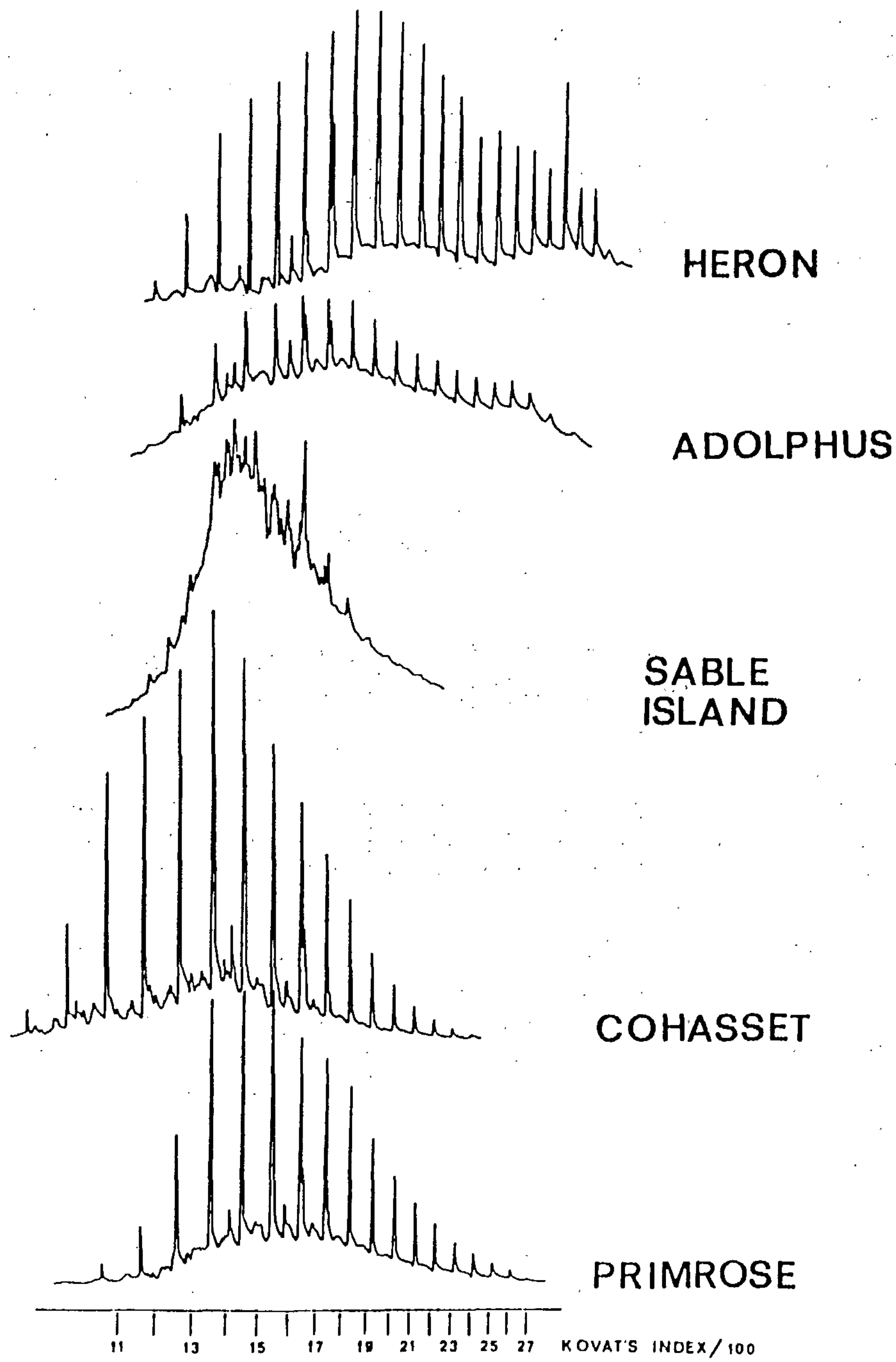

FIGURE 1 - GAS CHROMATOGRAMS OF SATURATES

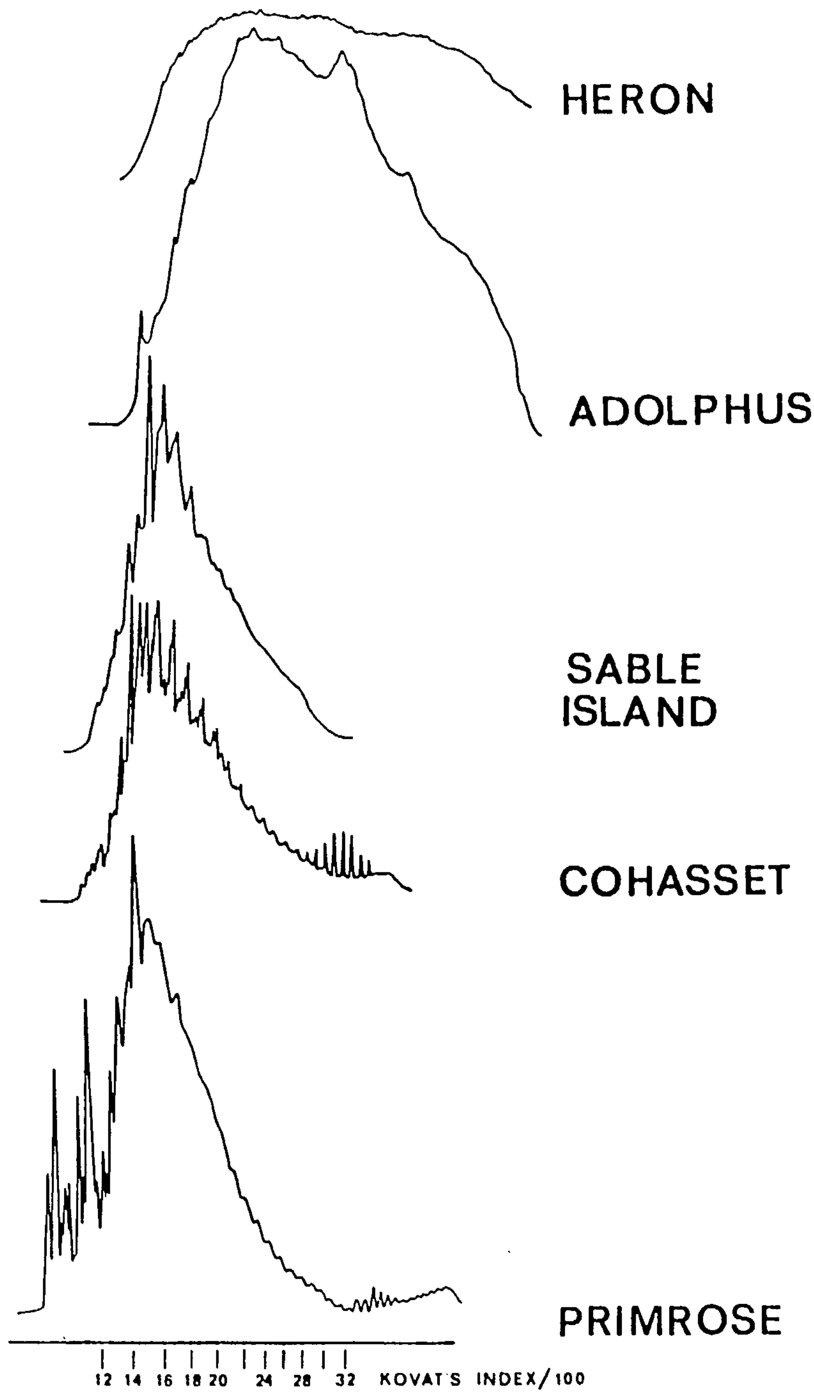

FIGURE 2 - GAS CHROMATOGRAMS OF MONOAROMATICS

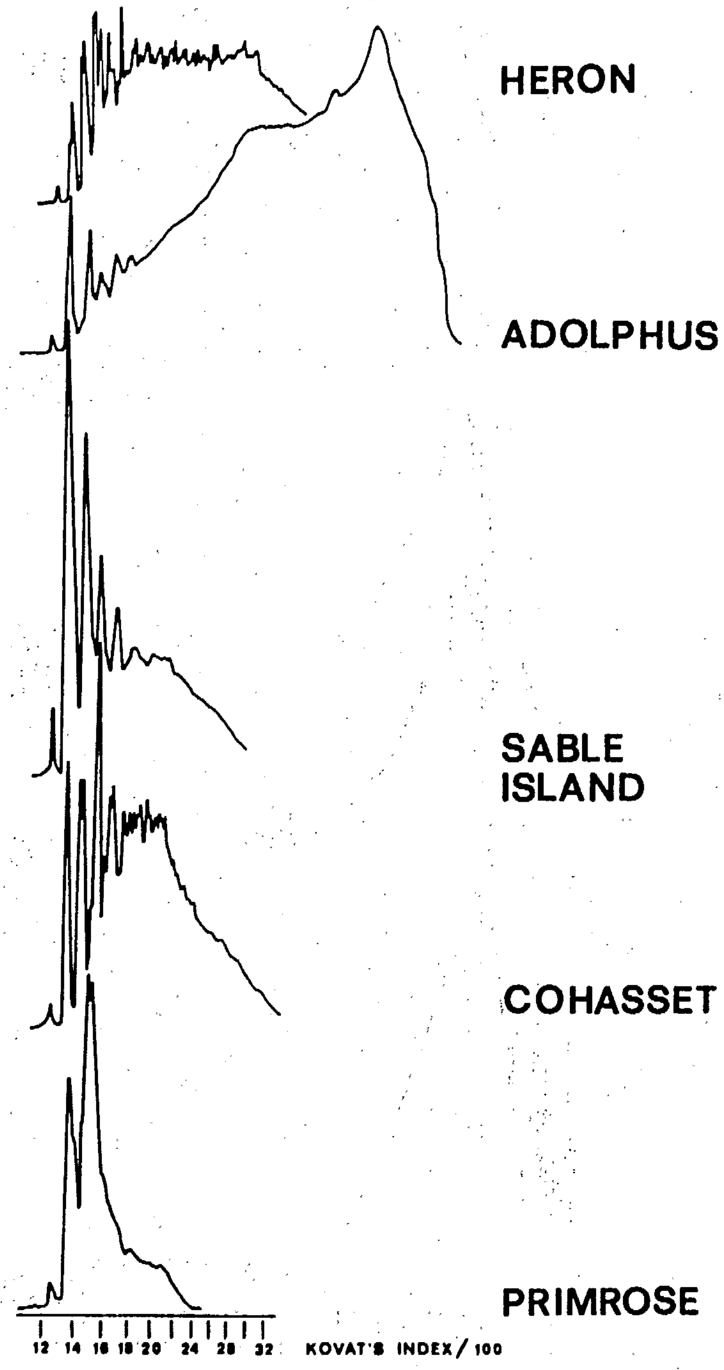

FIGURE 3 - GAS CHROMATOGRAMS OF DIAROMATICS

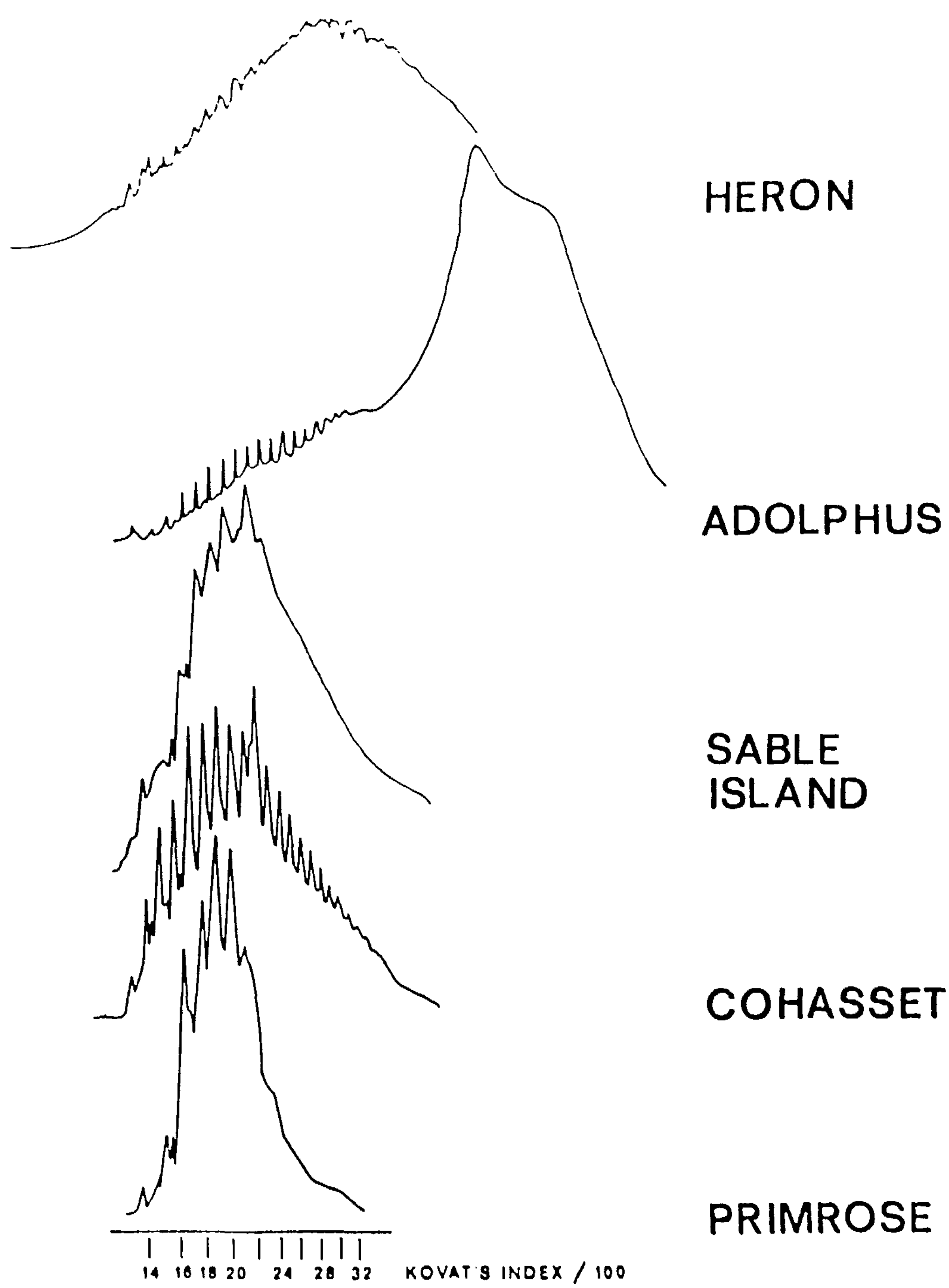

FIGURE 4 - GAS CHROMATOGRAMS OF POLYAROMATICS

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