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## GEOCHEMICAL INVESTIGATION OF OILS IN THE WESTERN CANADA TAR BELT

D. S. MONTGOMERY, D. M. CLUGSTON, A. E. GEORGE, G. T. SMILEY

AND H. SAWATZKY

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### GEOCHEMICAL INVESTIGATION OF OILS IN THE WESTERN CANADA TAR BELT

by

D.S. Montgomery\*, D.M. Clugston\*\*, A.E. George\*\*, G.T. Smiley\*\*\*, H. Sawatzky\*\*

#### ABSTRACT

In this investigation the hydrocarbons and sulphur compounds in the gas oils of the Athabasca, Cold Lake and Lloydminster heavy oils have been studied by a combination of liquid, gas-liquid and gas-solid chromatographic techniques coupled with mass spectrometry. The results were compared with those for the Medicine River oil which is lighter, thermally mature and lies in a reservoir of the same geological age.

The distillates were fractionated into hydrocarbon types (i.e. saturates, mononuclear, binuclear and polynuclear aromatics). This allowed a comparative study of the normal alkanes and isoprenoid hydrocarbons, pristane and phytane, in the  $\mathbf{C}_{16}$  to  $\mathbf{C}_{19}$  range of the saturates. Also the structural changes in the aromatic hydrocarbon types, as indicated by both gas chromatography coupled with mass spectrometry, have been followed up. The results were interpreted geochemically with reference to the thermal and biological aspects of degradation.

It is quite clear that these oils are closely related although there are some distinct differences. The number of isomers of the sulphur compounds appear to be low in comparison with the number of possible isomers, suggesting some selective mechanism of formation.

<sup>\*</sup>Head, \*\*Research Scientist, \*\*\*Technologist, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

#### UNE INVESTIGATION GEOCHIMIQUE DES HUILES BRUTES DANS LA CEINTURE DE GOUDRON A L'OUEST DU CANADA

par

D.S. Montgomery\*, D.M. Clugston\*\*, A.E. George\*\*, G.T. Smiley\*\*\*, H. Sawatzky\*\*

#### RESUME

Dans la présente étude les auteurs ont analysé les hydrocarbures et les composés sulfureux dans le gas oil des huiles brutes lourdes de l'Athabasca, Cold Lake et Lloydminster. L'étude est fondée sur l'utilisation de la chromatographie en phase liquide, chromatographie en phase gazeuse, chromatographie gas solide, et la spéctrometrie de masse. Les résultats obtenus sont comparés avec ceux de l'huile de Medicine River qui est plus légère, thermiquement mûre et qui se trouve dans un réservoir de la même ère geologique.

Les distallats ont été fractionnés en classes d'hydrocarbures (des hydrocarbures saturés, monoaromatiques, diaromatiques, et polyaromatiques). L'application de ce protocole d'analyse a permis la comparaison des n-alcanes avec les isoprénoides, pristane et phytane, dans la région C<sub>16</sub> - C<sub>19</sub> des hydrocarbures saturés. Il fut possible également de suivre les changements structuraux des classes aromatiques par la chromatographie et le spectromètre. Les données sont geochimiquement interpretées en rapport avec l'aspect thermique et l'aspect biologique de la dégradation. Bien que ces huiles soient étroitement alliées il ya quelques différences distinctes. Le nombre d'isomères des composés sulfureux est peu elevé comparé au nombre d'isomères possible, suggérant un mecanisme selectif de formation.

<sup>\*</sup>Chef, \*\*Chercheur Scientifique, \*\*\*Technicien, Centre de recherche sur les combustibles, Direction des mines, ministère de l'Energie, des Mines et des Resources, Ottawa, Canada.

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#### INTRODUCTION

It is generally believed that the heavy oils in the Lower Cretaceous reservoir rocks extending from west central Alberta through the Athabasca tar sands area into western Saskatchewan belong to a single oil system, which implies similar modes of origin (19). A number of hypotheses (4, 7, 9, 11, 12, 15, 16, 17, 19) have been put forward to explain the source and accumulation of Athabasca heavy oil. For example, the oil may be Devonian in origin and has escaped through fissures allowing the light ends to evaporate (11, 16), or it may have originated "in situ" from organic material deposited with the sand (4, 9). The former hypothesis has been disputed and substantial evidence presented that the Athabasca oil is young, immature and not evaporated, altered or polymerized (7, 12, 15, 17). Recently, some workers (1, 2, 5, 20) have expressed the opinion that the heavy oils are conventional oils that have been biodegraded and water-washed resulting in viscous, asphaltic and sulphurous oils.

The present study involved the heavy distillate ranges (gas oils) from Athabasca bitumen, Cold Lake bitumen and Lloydminster oil, with Medicine River oil included as a Cretaceous, thermally mature oil for comparison. Each gas oil was subjected to a preliminary type-separation by liquid chromatography to provide saturate, monoaromatic, biaromatic and polyaromatic fractions. Subsequent gas chromatography mass spectrometric analysis was used to shed light on the nature and relative abundances of the compounds in the various oils.

#### EXPERIMENTAL

#### Samples:

The following samples were investigated:

- 1. The pentane extract from the Athabasca bituminous sand obtained from the quarry of Great Canadian Oil Sands Ltd.
- 2. The Abasand saturates fraction separated some time ago by Montgomery and Boyd (3).
- 3. Cold Lake bitumen obtained by steam injection at 1500 ft. from the Mannville Pool by Imperial Oil Co.
- 4. Lloydminster oil produced by Husky Oil Co. from the Sparky formation location 9A-3-50-1(W4), depth 1893 ft.
- 5. Medicine River oil produced by Hudson Bay Oil and Gas Co. from the Glauconite zone, location 2-17-39-4W5M, depth 7326 ft.

All samples were distilled in a molecular still (Arthur F. Smith Inc., Model 50-2) at  $75\text{-}250\,\mu$  pressure and 225-230°C. The light ends were collected in a dry ice trap between the still and the vacuum pump. The separation scheme is shown in Figure 1.

#### Liquid Chromatography:

The distillates were separated on a dual packed (silica gel and alumina gel) chromatographic column following the procedure developed by the U.S. Bureau of Mines in conjunction with A.P.I. project 60 (6). Fractions were obtained by collecting 200 ml fractions of the eluent and evaporating the solvents by gentle warming under a stream of nitrogen. In this manner fractions containing saturated, monoaromatic, biaromatic hydrocarbons and polyaromatic hydrocarbons and polyaromatic hydrocarbons and polar materials were obtained.

#### Gas Chromatography

Simulated Distillation: The fractions obtained from liquid chromatography were gas chromatographed on non-polar silicone rubber (SE-30) (5 ft. U-shaped glass columns, 1/4 in 0.D.) to achieve separations according to boiling points. Normal alkanes were used as reference compounds. The column effluent was split between a flame ionization detector and a trapping out assembly in a ratio of 1:9. Each collecting tube contained 10 mg of chromosorb W. The column effluent could also be directed to a Dohrmann microcoulometric quantitative detector to determine the sulphur contents of the various peaks. Cuts were trapped out in the boiling range of C<sub>16</sub> and C<sub>18</sub> for the saturates in order to test for the presence of the isoprenoid hydrocarbons pristane and phytane. The aromatic fractions were cut to trap out major peaks in the spectra or regions in the area of the Kovat's indices of normal alkanes.

Rechromatography and Mass Spectrometry: The samples collected from simulated distillation were rechromatographed on lithium chloride-coated silica as described in a previous publication (14). The column effluent was split between a flame ionization detector and a mass spectrometer in a ratio of 1:4. The mass spectrometer used was a C.E.C. 21-104 equipped with a Watson-Biemann type enriching device and operated at an ionization potential of 70 eV and with electric scan.

#### RESULTS AND DISCUSSION

The molecular distillation yields and sulphur contents of the four oils are shown in Table 1. If the proportion of light ends is considered to be an indication of the extent of thermal maturation of an oil, it can be seen from Table 1 that the Athabasca oil would be the least mature and the Medicine River the most thermally mature.

TABLE 1

Distillate Yields and Their Sulphur Contents

	Athabasca	Cold Lake	Lloydminster	<u>Medicine River</u>	
Light ends, wt.%	4.5	5.9	12.5	44.8	
Distillate, wt.%	37.5	31.0	36.0	43.5	
Distillate Sulphur, wt.%	2.90	2.85	2.50	0.80	

The liquid chromatograms obtained from the A.P.I. type separations are shown in Figure 2 and the hydrocarbon type distributions in Table 2. It is

TABLE 2
Hydrocarbon Type Distribution in the Distillate

	<u>Athabasca</u>	Cold Lake	Lloydminster	Medicine River
Saturates, wt.%	37.1	42.6	50.7	69.6
Monoaromatics, wt.%	21.3	22.9	22.7	13.0
Biaromatics, wt.%	15.8	14.1	13.1	7.1
Polyaromatics, wt.%	25.6	20.5	13.6	10.3
Total Aromatics, wt.%	62.9	57.4	49.3	30.4
Saturates/Aromatics	0.60	0.74	1.03	2.29

apparent that a marked increase in saturated hydrocarbon content, with a concomitant decrease in total aromatic content occurs in the order Athabasca, Cold Lake, Lloydminster and Medicine River. Trends in this series are better illustrated if each aromatic type is considered as a percentage of the total aromatic content as shown in Table 3. While the Athabasca, Cold

TABLE 3

Aromatic Types as Percentage of Total Aromatic Content

	<u>Athabasca</u>	Cold Lake	<u>Lloydminster</u>	Medicine River
Monoaromatics	34.0	39.8	46.0	42.8
Biaromatics	25.2	24.5	26.5	23.3
Polyaromatics	40.8	35.6	27.5	33.9

Lake and Lloydminster samples follow increasing monoaromatic content and decreasing polyaromatic content trends, Medicine River oil is slightly anomolous.

#### Saturated Hydrocarbons

The simulated distillation chromatograms of the saturates are shown in Figures 3-6. The predominant peaks in Medicine River saturates are normal alkanes as expected for an undergraded thermally mature oil. The chromatograms from the other oils show no predominant normal alkanes. All oils show maxima in the region of normal  $C_{17}$ . Also it should be noted that both the Athabasca and Lloydminster fractions show substantial amounts of material in the  $C_{27}$  to  $C_{29}$  range in which steranes are expected.

Normal alkanes to isoprenoid ratios are often used as indicators of the extent of biodegradation of oils. Therefore cuts were trapped out from the simulated distillates in the boiling range of  $\rm C_{17}$  -  $\rm C_{18}$  normal alkanes and rechromatographed on lithium chloride-coated silica. During the rechromatographic separations cyclic materials are eluted before the noncyclic saturates. In the Medicine River cuts, Figures 7 and 8, the normal  $\rm C_{17}$  and normal  $\rm C_{18}$  are more prominent than the corresponding isoprenoid hydrocarbons pristane and phytane. This is a thermally undegraded mature oil. According to the work of Tissot et al. (18) in the investigation of the processes of maturation in oils from the L. Toarcian Paris basin, the isoprenoids are dominant during early stages but the normal alkanes become dominant later during maturation.

The rechromatograms of the corresponding simulated distillation cuts from the Lloydminster are shown in Figures 9 and 10. The normal  $^{\rm C}_{17}$  and  $^{\rm C}_{18}$  contents are much lower than those of the pristane and phytane. This can be explained by immaturity as well as biological degradation or by both factors. Possibly the source material also influences the contents of normal alkanes and isoprenoids that are derived from it. In contrast to some of

the results obtained by Winters et al. (20), the normal alkanes content of the Lloydminster oil was not found to increase with molecular weight up to the  $C_{30}$  region.

The rechromatograms of the Cold Lake cuts are shown in Figures 11 and 12. The contents of both the normal alkanes and isoprenoids are low. It can be argued in this case that the degradation has been quite extensive as both normal alkanes and isoprenoids have been reduced.

In the case of the Athabasca cuts the results are conflicting. The only indication of either normal alkanes or isoprenoids is the shoulder in the position where a peak for normal C<sub>18</sub> could be expected as shown in Figure 13 for the sample from the Great Canadian Oil Sands quarry. In contrast, the chromatograms from corresponding cuts from the sample obtained from the Abasand quarry show peaks for the normal alkanes as well as the isoprenoids, Figures 14, 15, 16. Also the normal alkanes are more predominant than the isoprenoids which is contrary to the expected if biodegradation had been involved.

A comparison of the cyclic material in Medicine River, Lloydminster and Athabasca saturated hydrocarbons in the  $\rm C_{19}$  to  $\rm C_{25}$  range is shown in Table 4.

TABLE 4 Approximate Composition of Cyclic Saturates in the  $C_{19}$  to  $C_{25}$  range

	Medicine River	<u>Lloydminster</u>	<u>Athabasca</u>
Monocyclic, %	25	13	trace
Bicyclic, %	33	35	31
Tricyclic, %	33	30	44
Tetracyclic, %	7	22	25
Pentacyclic, %	-	trace	trace

In this table only the cyclic material is discussed which constitutes a small portion of the Medicine River saturates but a major portion of the

heavy oils. The main cyclic material in the Medicine River saturates in this molecular weight range consists of mono, di and tricyclic compounds. The Lloydminster contains only half the amount of monocyclics as the Medicine River and the Athabasca has almost no monocyclic material. The Athabasca saturates are the most highly cyclized saturates, followed by the Lloydminster with the Medicine River saturates containing the least highly cyclized material.

The lower content of monocyclics in the heavy oils might be explained on the basis of biological degradation. On the other hand these heavy oils, in particular the Athabasca, might never have had much of this material or it might have become aromatized. The fact that the saturated fractions of Athabasca and Lloydminster oils contain a greater proportion of tri-and tetracyclic compounds than the Medicine River saturates could be interpreted as an indication that they are less mature with the Athabasca being the least mature on the basis of the results of Phillipi (12) and Tissot et al. (18).

#### Mononuclear Aromatic Fractions

The gas chromatograms from the largest mononuclear aromatic fractions obtained from liquid chromatography show no prominent peaks. Nevertheless there is a slight increase in the size of the peaks superimposed on the background in the Medicine River, Figure 18, as compared with the Athabasca, Figure 17. This could be interpreted as arising from a reduction of the number of isomers in the Medicine River sample through thermal maturation. The corresponding chromatograms from other heavy oils, Figures 19 and 20, are similar to that from the Athabasca. It will be noted on comparing these fractions in the order Athabasca, Lloydminster, Cold Lake and Medicine River that there is a progressive increase in the proportion of higher molecular weight material in the region of C<sub>30</sub>. A possible explanation of this is the increasing aromatization of the high molecular weight saturates during thermal maturation.

These fractions have not been very thoroughly investigated. In the  ${\rm C}_{15}$  to  ${\rm C}_{20}$  range the alkyl substitution in the Medicine River fraction is mostly noncyclic although the amount of cyclic material increases with molecular weight. In contrast cyclic alkyl substituents are predominant in the case of the Athabasca and Lloydminster oils. Tissot et al. (18) found that samples from greater depth showed fewer naptheno rings in aromatic fractions than samples from shallower levels. Thus it would appear that the heavy oils are much less mature than the Medicine River oil.

#### Binuclear Aromatic Fractions

The simulated distillation chromatograms of these fractions are shown in Figures 21-24. It can be seen that the bulk of the material in the Medicine River fraction is represented by a few predominant peaks in the flame ionization trace. The most prominent peak appears to represent naphthalenes substituted with two alkyl carbon atoms. The next higher molecular weight peak, which is a doublet, seems to represent naphthalenes with three alkyl carbon atoms and the last well resolved peak naphthalenes with four alkyl carbon atoms. The material from the first peak was lost during trapping out but presumably represents methylnaphalenes. Thus most of the compounds in the binuclear aromatic fraction obtained from liquid chromatography consists of low molecular weight naphthalenes. The unresolved portion appears to contain other alkyl naphthalenes, cycloalkylnaphthalenes and possibly alkyl biphenyls.

In the corresponding Lloydminster chromatogram the same peaks as in the Medicine River fraction are quite prominent but the bulk of the material consists of the less resolved higher molecular weight compounds. The low molecular weight peaks are small in the case of the Cold Lake oil and smaller in the case of the Athabasca fraction. It is possible that some minor loss of the low molecular weight naphthalenes to the light ends occurred during molecular distillation.

The systematic trend in the order Athabasca, Cold Lake, Lloydminster and Medicine River in the direction of simpler chromatograms and an increasing proportion of low molecular weight alkyl naphthalenes is the direction that would be predicted on the basis that alkyl side chains have been eliminated by thermal degradation. In this process, the loss of side chains also reduces the number of possible isomers. Of course, it might be argued that the low molecular weight biaromatics have been lost from the heavy oils through water washing or biological degradation. If this argument was true, it would seem that over half the diaromatics have been lost, which appears extreme.

The chromatograms that were obtained from these biaromatic fractions during simulated distillation with the use of a microcoulometric quantitative sulphur detector are shown in Figures 25-28. The chromatogram from the Athabasca fraction, Figure 25, shows three well resolved peaks, numbered 1, 2 and 3, which appear to represent benzothiophenes with five, six and seven alkyl carbon atoms. Their sulphur peaks are matched by peaks in the flame ionization trace of the higher molecular weight poorly resolved material. The Cold Lake diaromatics fraction, Figure 26, shows similar sulphur peaks, although not as well resolved as for the Athabasca sample. Both the Cold Lake and Athabasca samples contain a considerable amount of higher molecular weight poorly resolved sulphur-containing material. The Lloydminster diaromatic fraction, Figure 27, and even more the Medicine River sample, Figure 28, show well resolved, intense peaks for the low molecular weight alkylbenzothiophenes and relatively little higher molecular weight sulphur compounds.

The fact that the sulphur peaks are so well resolved indicates that the number of isomers of each alkyl benzothiophene is low. This is significant especially as there are so many possible isomers. Also it is significant that the amount of benzothiophenes decreases markedly as the number of substituting alkyl carbon atoms increases beyond seven. Mass spectral data appears to indicate that most of the alkyl groups on these

benzothiophenes are methyls. This explains the restricted number of isomers and why the amounts of benzothiophenes decrease with molecular weight after the benzothiophenes with six alkyl carbon atoms. The similarity of all four oils in the low molecular weight region of the sulphur containing diaromatics and the well resolved nature of the sulphur peaks implies that the alkylbenzothiophenes are formed as a distinct class of compounds. On the other hand, the unresolved higher molecular weight material in the heavy oil samples consists of a multitude of apparently unrelated sulphur compounds which could more easily be rationalized as random degradation products of still higher molecular weight compounds. In this regard, the sulphur chromatograms are very similar to the flame ionization results.

The fact that most of these alkyl groups appear to be methyl groups in all these oils might be interpreted that thermal maturation processes caused cleavage of the alkyl side chains to leave methyl residues. The fact that the benzothiophenes in the heavy oils are similar to the ones in the thermally mature Medicine River oil supports this interpretation.

#### Polynuclear Aromatic and Polar Fractions

Flame ionization and microcoulometric sulphur traces of the chromatograms of the polyaromatic fractions are shown in Figures 29-35. The Athabasca spectra, Figure 32, obtained from the samples collected in the area marked "C" in the liquid chromatogram show a number of intense sulphur peaks which are marked by corresponding peaks in the flame ionization trace. It would appear that the early part of the flame ionization spectrum has mainly sulphur-containing compounds, while the sulphur content drops off sharply in the latter part of the spectrum. From mass spectral data the two most intense sulphur peaks appear to be dibenzothiophenes substituted with three and four alkyl carbon atoms.

Only one fraction of polyaromatic and polar material was obtained for the Lloydminster oil and its sulphur chromatogram, Figure 34, is similar to that described above for the Athabasca sample in that it has a number of well resolved peaks eluting first, although the spectrum contains somewhat more higher molecular weight material. The fact that the main polyaromatic fraction from the Lloydminster oil is comparable to the small early portion of the Athabasca polyaromatics indicates that Lloydminster oil is considerably less complex than is the Athabasca. The main polyaromatic fraction, that is the material eluting after the "C" cut in Figure 2, from the Athabasca was poorly resolved on gas chromatography and very complex, containing some higher molecular weight dibenzothiophenes and a plethora of other compounds.

The sulphur chromatogram from the first polyaromatic Cold Lake fraction (designated by "C" in Figure 2), Figure 33, is similar to that of the other heavy oils. This oil is more similar to the Athabasca than Lloydminster oils in that the largest fraction of the polynuclear aromatic hydrocarbon and polar material is unresolved by gas chromatography.

The corresponding chromatograms from Medicine River oil have little similarity to those from the heavy oils. The chromatogram of the first, but not largest, fraction is shown in Figure 35. The chromatogram of the largest fraction is similar to that from the first. No characterization of the material involved has been made.

Possibly the methyl groups on the dibenzothiophenes might be residues of larger alkyl groups that were degraded during thermal maturation as in the case of the benzothiophenes. Dibenzothiophene itself is susceptible to biological degradation (10). It does not seem likely that a few methyl groups would prevent degradation, so any biological degradation must have been minimal as far as the Athabasca oil is concerned. Otherwise it should not be possible to find the appreciable concentration of dibenzothiophenes detected in this work.

#### **CONCLUSIONS**

Some of the chemical analysis data suggest that the three heavy oils are immature compared to the lighter Medicine River oil. Thermal maturation increases in the order Athabasca, Cold Lake, Lloydminster then Medicine River. Also the substitution on the binuclear and trinuclear aromatic hydrocarbons and sulphur compounds is predominantly methyl. Thermal degradation would cleave long alkyl chains to residual methyl groups.

Comparative abundance of the normal alkanes and isoprenoid hydrocarbons, pristane and phytane, in the range  $\mathbf{C}_{16}$  to  $\mathbf{C}_{19}$  of the saturate fraction might be explained by biological degradation of the heavy oils. However the normal alkane content of these young oils could be undeveloped yet. More elucidation on this point is required.

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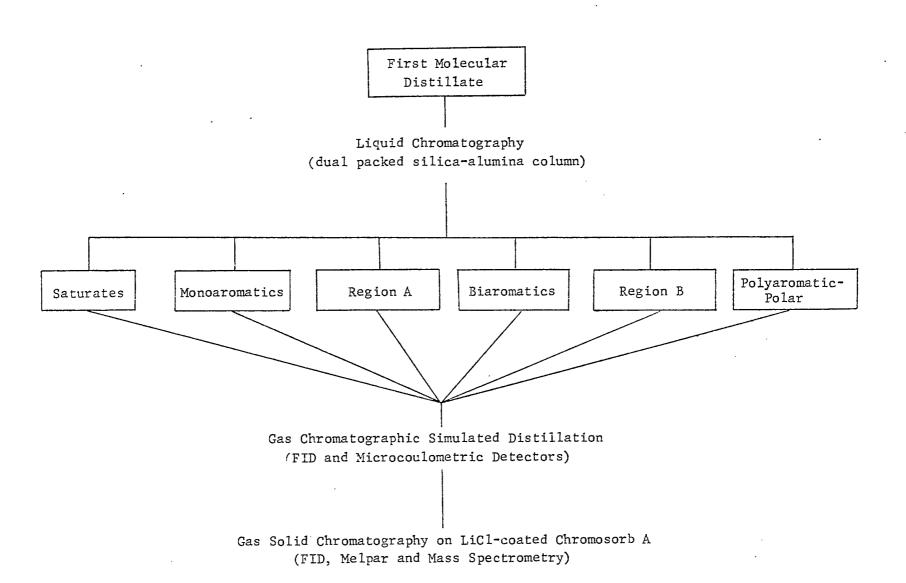
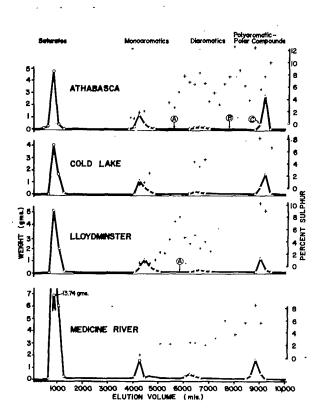


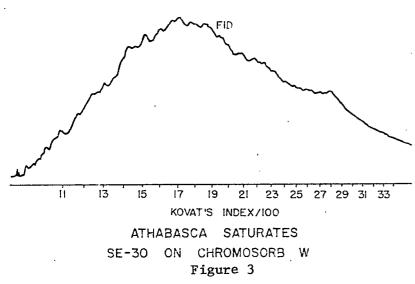
Figure 1

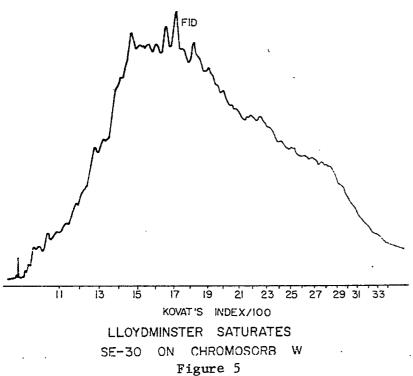


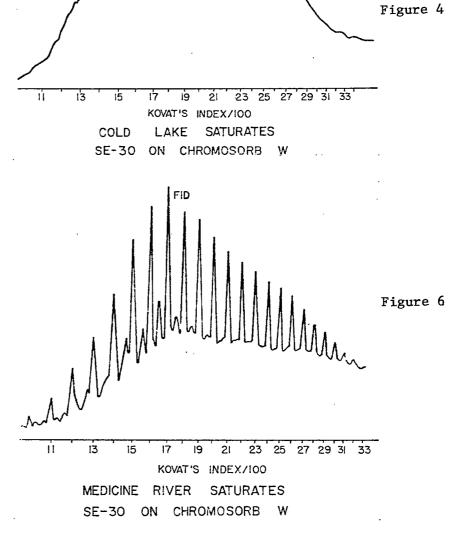
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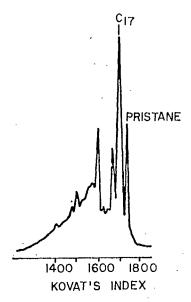
Figure 2





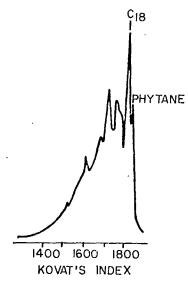






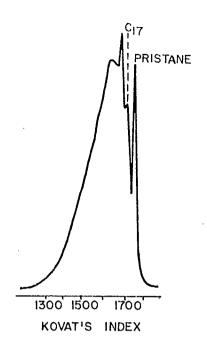
MEDICINE RIVER SATURATES  $C_{17}$  FRACTION  $L_iCI$ -CHROMOSORB A

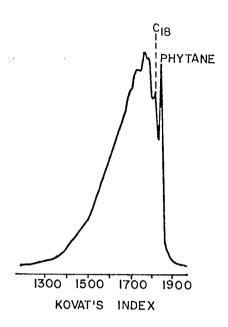
Figure 7



MEDICINE RIVER SATURATES  $C_{18}$  FRACTION  $L_iCl$ -Chromosorb A

Figure 8

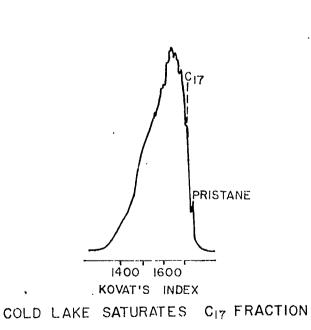


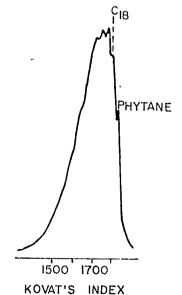


LLOYDMINSTER SATURATES C<sub>17</sub> FRACTION LLOYDMINSTER SATURATES C<sub>18</sub> FRACTION
LiCI-CHROMOSORB A

Figure 9

Figure 10





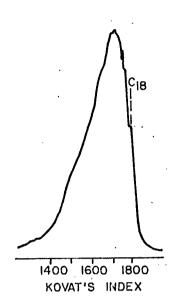
COLD LAKE SATURATES CIB FRACTION

LiCI-CHROMOSORB A

Figure 12

Lici-CHROMOSORB A

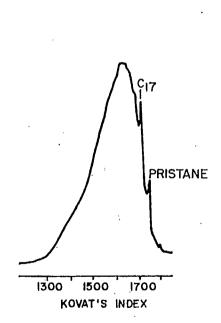
Figure 11



ATHABASCA SATURATES C<sub>18</sub> FRACTION

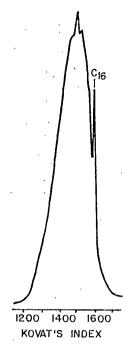
Lici - CHROMOSORB A

Figure 13

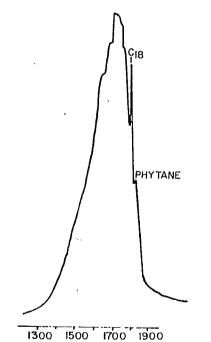


ABASAND SATURATES, C17 FRACTION
LiCI - CHROMOSORB A

Figure 15



ABASAND SATURATES C<sub>16</sub> FRACTION
LiCI - CHROMOSORB A
Figure 14

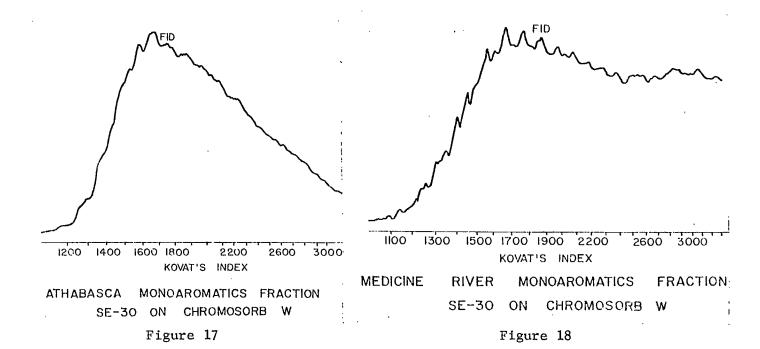


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ABASAND SATURATES C<sub>18</sub> FRACTION

Lici - CHROMOSORB A

Figure 16



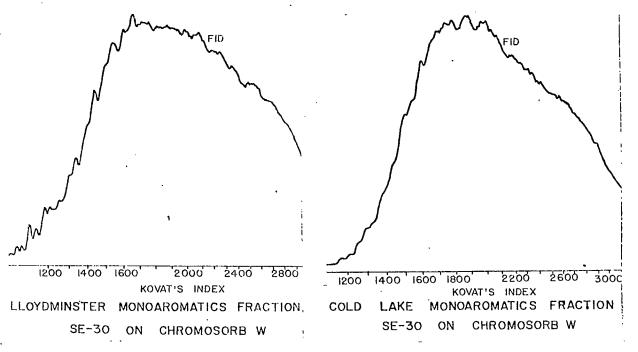


Figure 19

Figure 20

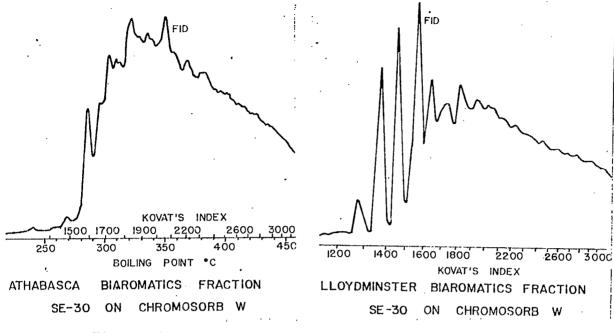
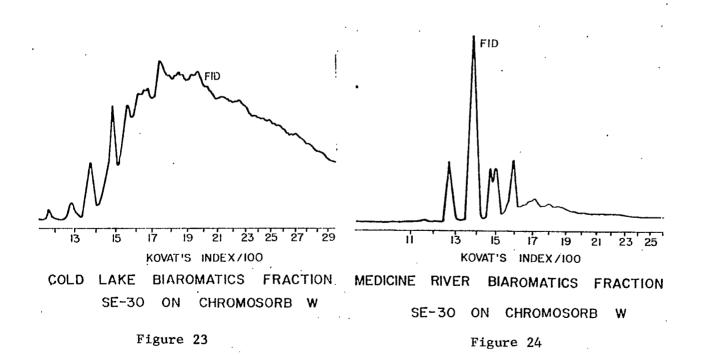
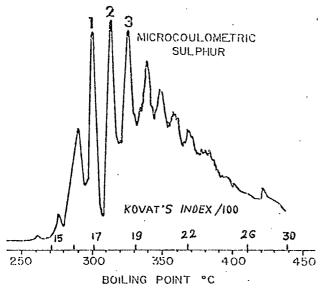


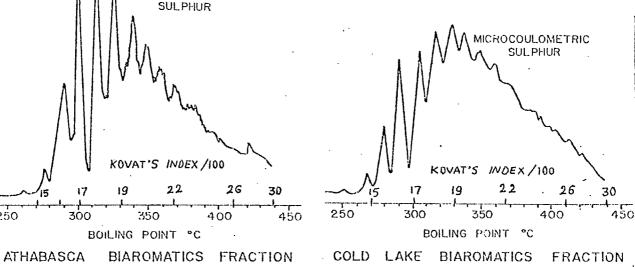
Figure 21

Figure 22

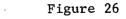




SE-30 ON CHROMOSORB W Figure 25



SE-30 ON CHROMOSORB W



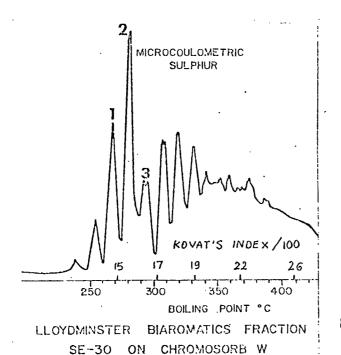
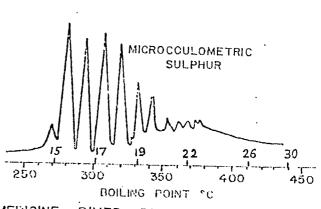


Figure 27



MEDICINE RIVER BIAROMATICS FRACTION SE-30 ON CHROMOSORB W

Figure 28

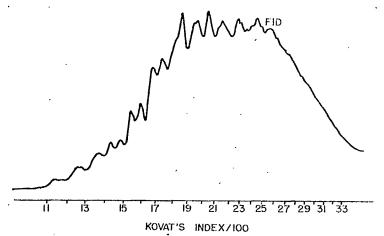


Figure 29

LLOYDMINSTER POLYAROMATICS FRACTION SE-30 ON CHROMOSORB W

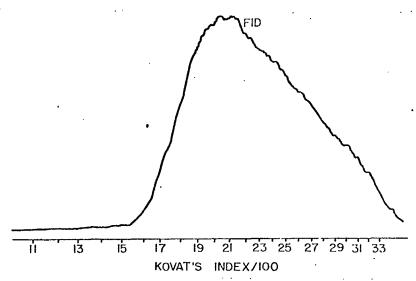
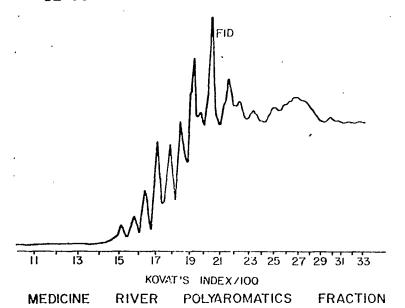


Figure 30

COLD LAKE POLYAROMATICS FRACTION
SE-30 ON CHROMOSORB W



SE-30 ON CHROMOSORB W

Figure 31

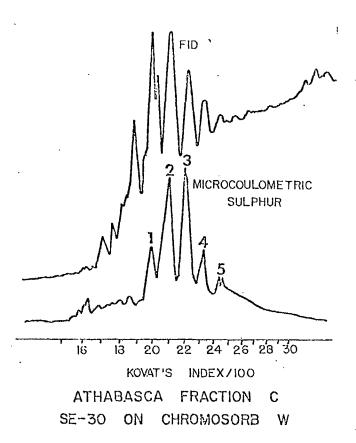


Figure 32

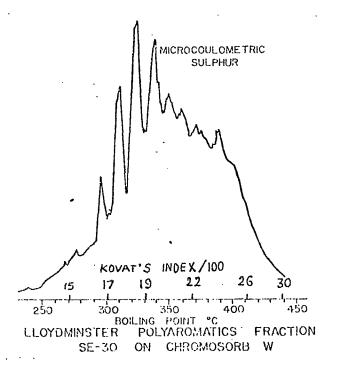


Figure 34

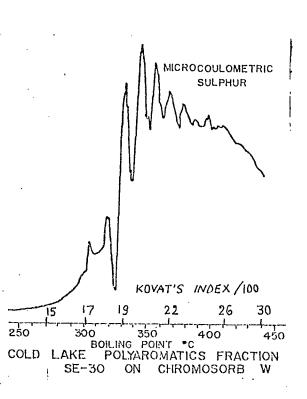
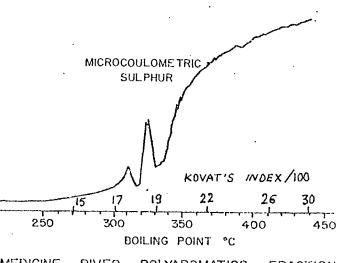


Figure 33



MEDICINE RIVER POLYAROMATICS FRACTION
SE-30 ON CHROMOSORB W

Figure 35

