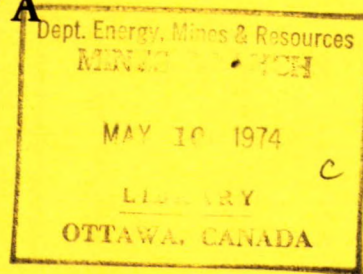


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OTTAWA



*SULPHUR COMPOUNDS IN OILS FROM
THE WESTERN CANADA TAR BELT*

D. M. CLUGSTON, A. E. GEORGE, D. S. MONTGOMERY,

G. T. SMILEY AND H. SAWATZKY

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NOVEMBER 1972

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WESTERN CANADA TAR BELT

by

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

ABSTRACT

The sulphur compounds in the gas oil fractions from some bitumens and heavy oil from Cretaceous reservoirs along the edge of the western Canada sedimentary basin have been investigated. The bitumens were those from the Athabasca oil sands and the Cold Lake deposit, whereas the heavy oil was from Lloydminster field. A Cretaceous oil from a deep reservoir that is believed to be mature has been included for comparison. It appears that the predominant sulphur compounds in these gas oil fractions are alkyl-substituted benzo- and dibenzothiophenes. The dominant isomers for these sulphur compounds seem very few in number.

Composés de soufre provenant des
huiles des gisements d'Athabasca et du Cold Lake de l'ouest canadien
par

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

Résumé

Les composés de soufre provenant des fractions de mazout de certains bitumes et de pétroles lourds des réservoirs Crétacéux longeant la bordure du bassin sédimentaire de l'ouest canadien ont été étudiés. Les bitumes étaient ceux des gisements d'Athabasca et du Cold Lake, tandis que le pétrole lourd venait du champ Lloydminster. Un pétrole Crétacéux, d'un réservoir profond, que l'on croit être mûre fût incluse pour en faire une comparaison. Il semble que les composés de soufre prédominants dans les fractions de mazout sont alkyl-substitués benzo-et dibenzothiophènes. La quantité de composés isomériques apparaît être très minime.

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INTRODUCTION

In this work the sulphur compounds in the gas oil of three Cretaceous heavy oils from the Alberta sedimentary basin were investigated. These crude oils were obtained from the Athabasca, Cold Lake and Lloydminster deposits and are believed by some (1) to belong to the same oil system which implies like modes of origin. The geographic locations of these deposits are shown in Figure 1. This investigation was conducted to develop the analytical capability of following the maturation of the sulphur compounds present in these oils and to permit a comparison with those in the thermally mature Medicine River oil in a reservoir of the same geological age (2).

EXPERIMENTAL

Samples

The Athabasca bituminous sand was obtained from Great Canadian Oil Sands Ltd. and the pentane extract was used in this work. The Lloydminster oil had been taken from the "Sparky" formation at a depth of 1890 ft. and was supplied through the courtesy of Husky Oil Ltd. The Cold Lake bitumen was obtained from Imperial Oil Ltd. and had been produced by steam injection from a depth of about 1500 ft. The Medicine River oil was produced at a depth of 7325 ft. and was donated by the Hudson Bay Oil and Gas Co. Ltd.

Molecular Distillation

The samples were each distilled in an Arthur F. Smith molecular still at pressure ranges of 75-250 μ and temperatures of 225-230°C. The light ends were obtained in the dry ice trap between the still and the vacuum pump.

Chromatographic Separations

The distillates from the oils were separated first by liquid chromatography, then by gas chromatographic simulated distillation according to boiling point and finally by gas chromatography on lithium chloride-coated silica, as shown in the schematic diagram.

Liquid Chromatography

The distillates were separated on a dual-packed (silica gel-alumina gel) chromatographic column according to the procedure developed by the U.S. Bureau of Mines in conjunction with API project 60 (3). The oil fractions were obtained by collecting 200 ml fractions of the eluent and evaporating the solvents by warming and using streams of nitrogen.

Various fractions of saturated, mononuclear aromatic, dinuclear aromatic, polynuclear aromatic hydrocarbons and polar materials were obtained.

Gas Chromatographic Simulated Distillation

The fractions from the liquid chromatography were gas chromatographed according to boiling point using normal alkanes as reference compounds on non-polar silicone rubber (SE-30) columns packed in 5 ft. long U-shaped glass columns of 1/4" O.D. 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 10mg of chromosorb W. The helium carrier gas had a flow rate of 175 ml/min. Sulphur chromatograms were obtained with a Dohrmann microcoulometric quantitative detector which was also used for determining total sulphur contents of the samples. The carrier gas flow rate was 75 mls/min when the coulometric detector was used.

Gas-Solid Chromatography and Mass Spectrometry

The cuts trapped out from the simulated distillations were rechromatographed on lithium chloride-coated silica columns as described in a previous publication (4). The column effluent was split with a portion directed to a flame ionization detector and the other to the mass spectrometer in a ratio of 1:4. This chromatographic step greatly facilitated the interpretation of the mass spectra. In many cases it appeared as though pure compounds were obtained.

The mass spectrometer was a CEC 21-104 equipped with a Watson-Biemann type G.C. interface. The source was maintained at 250°C. An ionization potential of 70 eV was used throughout with a trap current of approximately 80 μ amp. The spectra were scanned electrically.

RESULTS AND DISCUSSIONS

Table 1 shows the molecular distillation yields and distribution of the total sulphur contents in the distillates from the four oils.

TABLE 1

DISTILLATE YIELDS AND THEIR SULPHUR CONTENTS

	<u>Athabasca</u>	<u>Cold Lake</u>	<u>Lloydminster</u>	<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 content, wt.%	2.90	2.85	2.50	0.80

The liquid chromatograms of the four gas oils are shown in Figure 2. The sulphur content of some of the fractions is also shown by plus signs. The proportions of the hydrocarbon types in the distillate fractions of the oils are shown in Table 2.

TABLE 2

DISTILLATE FRACTION HYDROCARBON TYPE DISTRIBUTION

	<u>Athabasca</u>	<u>Cold Lake</u>	<u>Lloydminster</u>	<u>Medicine River</u>
Saturates, wt.%	37.1	42.6	50.7	69.6
Monoaromatics, wt.%	21.3	22.9	22.7	13.0
Diaromatics, wt.%	15.8	14.1	13.1	7.1
Polyaromatics, wt.%	25.6	20.5	13.6	10.3

It can be seen that within the molecular weight range C_{10} to C_{30} there is an increasing trend in the amount of saturates in the sequence Athabasca, Cold Lake, Lloydminster and Medicine River. This trend is reversed for the biaromatic and especially for the polyaromatic-polar fraction.

The saturated hydrocarbon fractions contain traces of sulphur. The use of a Melpar dual detector showed the sulphur compounds were retained much longer than the hydrocarbons when the Lloydminster saturates boiling in the range of the C₂₅ normal alkane were separated by gas-solid chromatography. This is typical of alkyl sulphides.

There was a small amount of sulphur in the mononuclear aromatic hydrocarbon fractions, which did not show any appreciable resolution on the microcoulometric trace obtained during simulated distillation. According to the U.S. Bureau of Mines report (3) describing this type separation, thiophenes and cyclic sulphides could be expected in this fraction.

Sulphur compounds in the largest dinuclear aromatic fractions as well as in the largest polynuclear aromatic hydrocarbon and polar material fractions have been investigated. Also the fractions with high sulphur content in the region between the largest mono- and dinuclear aromatic fractions, and between the largest dinuclear and polynuclear aromatic fractions designated by the letters "A" and "B" respectively on the liquid chromatograms were investigated. The polyaromatic fraction "C" was also analyzed, Figure 2.

In Figures 3 and 4 of the fractions in region "A" the microcoulometric sulphur peaks are well resolved and appear at regular intervals as would be expected for a homologous series of compounds. Most of the sulphur peaks have matching flame ionization peaks. These chromatograms of the fractions from region "A" of both Athabasca and Lloydminster oils are so similar that only one of these fractions has been further studied by mass spectrometry. Since the fraction from region "A" of Lloydminster oil has more material in the lower molecular weight range it was selected for more detailed study.

The material represented by the first four peaks in the flame ionization trace which have matching sulphur peaks #1 to 4 were trapped out and rechromatographed on the lithium chloride-coated silica. The resolved material was studied by mass spectrometry. Only the data thought

to be related to the sulphur compounds will be discussed. The chromatograms of the first three of these trapped out cuts with both the flame ionization and Melpar sulphur traces are shown in Figures 5, 6 and 7. Although the Melpar sulphur trace is not quantitative, whenever matching predominant peaks were obtained on both the flame ionization and the sulphur traces they were considered to represent substantial sulphur-containing material.

The mass spectrum obtained from the material eluting at 153° in Figure 5 contained a molecular ion of m/e 190 and intense fragment ions with m/e 175 and 147, corresponding to a 4-carbon substituted benzothiophene. Spectra taken at higher temperatures in the chromatogram also contained these same ions but in different relative intensities. High relative intensity of the molecular ion and M-15 ion is taken to mean that the side chains on the aromatic nucleus are short - probably methyl - while low relative intensity of M & M-15 relative to the ion corresponding to the aromatic nucleus plus one methylene group is an indication of fewer and longer side chains.

The material eluting at 162° (Figure 6) produced ions at m/e 204, 189 and 147 corresponding to a 5-carbon substituted benzothiophene. As before, the early eluting material appeared to have one long side chain while later in the chromatogram material having more and somewhat shorter side chains appeared. This trend appeared in all chromatograms.

The presence of molecular ions of m/e 202 and 206 in some of these spectra may indicate the presence of cycloalkyl benzothiophenes and thiaindanes respectively.

In subsequent cuts from Lloydminster fraction "A" it appeared that benzothiophenes with six for cut #3 and seven alkyl carbon atoms for cut #4 were present. On the basis of the trend that appears, it is assumed that each successive sulphur peak, obtained during simulated distillation as shown in Figures 3 and 4, represents benzothiophene with an additional alkyl carbon atom. Thus dominant benzothiophene peaks are obtained with as many as eleven substituting carbon atoms in peak #8 and then the amount of sulphur compounds involved in these chromatograms decrease markedly which is not the case for the accompanying hydrocarbons, as shown by the flame ionization

trace. High resolution mass spectral data appears to support the assumption that these compounds are benzothiophenes (5).

The microcoulometric sulphur chromatograms that were obtained during simulated distillation of the largest diaromatic fractions of the four oils are shown in Figures 8 to 11. The dominant peaks are well resolved and appear at regular intervals similar to those from a homologous series of compounds. In the case of the Athabasca fraction which had a high sulphur content the sulphur peaks had matching flame ionization peaks. It seems that the same sulphur compounds appear in all corresponding fractions of the four oils.

The sulphur compounds appear to be alkyl benzothiophenes. The mass spectra of these benzothiophenes show very prominent molecular ions and quite limited fragmentation as though most of the alkyl groups are methyls. This is in contrast to the benzothiophenes with longer alkyl groups found in the small fractions with high sulphur content that were obtained earlier during the liquid chromatography. It would be expected that the benzothiophenes with shorter but more alkyl groups would be retained longer on the electrophilic adsorbents than those with longer but fewer electron donating groups. The fact that most of the alkyl substituents on the benzothiophenes in the largest diaromatic fraction are methyls accounts for the limited number of dominant isomers that appear to be present in these fractions as is shown by the well resolved peaks.

The chromatogram in Figure 8 of the largest diaromatic fraction from the Athabasca oil shows three dominant well resolved peaks numbered 1, 2 and 3 which appear to represent benzothiophenes with five, six and seven methylene groups. With increasing molecular weight the amounts of sulphur compounds decrease and the resolution becomes poorer as would be expected when larger substituting alkyl groups are present causing an increase in the number of possible isomers.

The chromatogram from the corresponding Lloydminster fraction, Figure 9, is similar to that from the Athabasca but appears to contain

considerably more lower molecular weight benzothiophenes, particularly those with four methylene groups represented by peak #2. The Cold Lake fraction, Figure 10, is not very well resolved but also shows peaks that match those from the other oils.

The chromatogram of the corresponding fraction from the Medicine River oil, Figure 11, shows the best resolved peaks which appear to be the same benzothiophenes present in the other oils. This is believed to be a thermally mature oil and it is therefore expected that the alkyl side chains would be reduced to methyl residues. The alkyl naphthalenes that accompanied the benzothiophenes also appeared to possess mostly methyl substitution.

Before leaving the sulphur compounds in the diaromatic fraction it should be mentioned that only the material with well resolved sulphur peaks was examined by mass spectrometry. Possibly in the less resolved higher molecular weight materials other sulphur compounds besides benzothiophenes might be present.

The small fractions with high sulphur content that were obtained in the range "B" of the liquid chromatograms also give sulphur gas chromatograms with fairly well resolved peaks in the sulphur traces of the simulated distillation. Most of the peaks have matching ones in the flame ionization trace, Figure 12. All the high sulphur content fractions in this range "B" of the four oils give similar chromatograms. The material represented at the beginning of the chromatogram is not very well resolved. The first recognizable peak, #1, appears to be due to dibenzothiophenes with mainly two methylene groups. The m/e ratio is 212 and the only fragment ion is at m/e 197 which is the lowest mass fragment found in this series and is assumed to represent the aromatic nucleus, plus one alkyl carbon atom, of the dibenzothiophenes. Then there is a small peak, #2, where dibenzothiophenes with three methylene groups appear to be present. Peak #3 appears to be due to mixtures of dibenzothiophenes with three and four methylene groups. In most cases the fragment ions are more abundant than the parent ions indicating that the situation is similar to that of the benzothiophenes in which the material

with longer chains was eluted in the liquid chromatography before the material that contains more but shorter side chains.

In this fraction mass spectra were not obtained for material of molecular weight higher than the dibenzothiophenes with four methylene groups. It is inferred that the two most prominent peaks, #5 and #6, can be ascribed to dibenzothiophene with six and seven methylene groups. With increasing molecular weight the peaks become less prominent and the amount of sulphur compounds decreases. As can be seen this is quite different from the hydrocarbons that accompany these sulphur compounds.

The first polyaromatic-polar fraction from the Athabasca oil is similar to the largest fraction in this class from the Lloydminster oil. All the simulated distillation chromatograms of the first polyaromatic-polar fractions in the "C" region of the liquid chromatograms are shown in the Figures 13 to 16. As can be seen, sulphur peaks from the three oils are fairly well resolved at least in the lower molecular weight region. It seems that the initial portion of the Athabasca chromatogram, up to Kovats Index of 2400, is due mostly to sulphur compounds. The main sulphur compounds appear to be dibenzothiophenes with three and four methylene groups which are represented by the two predominant peaks #2 and #3. These dibenzothiophenes constitute the major portion of the sulphur compounds in this fraction. Some dibenzothiophenes with two, five and six methylene groups, represented by peaks #1, #2 and #5 respectively, also appear in much smaller quantities.

The predominant sulphur peaks in the Lloydminster and Cold Lake fractions appear to be the same as in the Athabasca but there is more of the unresolved higher molecular weight material than in the Athabasca. In contrast the Medicine River fraction is quite different from the corresponding ones in the heavy oils, Figure 16.

The chromatogram of the largest polyaromatic and polar fraction from the Athabasca gas oil can be seen in Figure 17. This fraction has a sulphur content of more than 7.7% within the distillation range up to a

boiling point of 500°C. Assuming the presence of one sulphur atom per molecule, then about half the fraction would consist of sulphur compounds. Some of the ill-defined sulphur peaks appear, together with matching flame ionization peaks, at intervals in the boiling point suggesting a difference of a methylene group.

According to the mass spectra alkyl substituted dibenzothiophenes or possibly naphthothiophenes seem to be quite prominent in this fraction with the substitution ranging from two to eight methylene groups. It would seem unlikely that most of the alkyl groups would be larger than methyl so the poor resolution of sulphur compounds probably is due to other types of sulphur compounds in addition to dibenzothiophenes. Both dibenzothiophenes and their isomeric naphthothiophenes could also be present.

In the mass spectra there were abundant ions that might be due to naphthobenzothiophenes or phenylbenzothiophenes. The presence of small amounts of alkyl diphenylsulphides is also possible.

ACKNOWLEDGEMENT

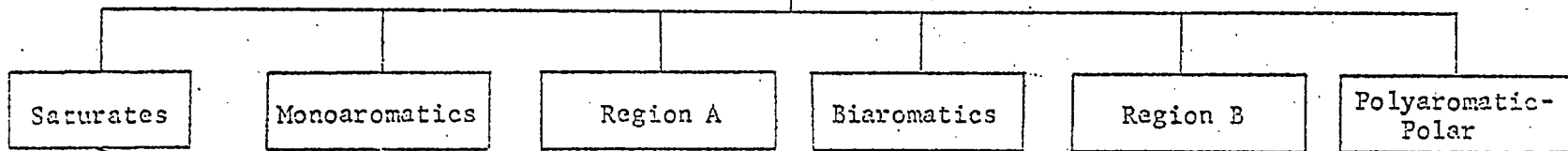
We are grateful to the Husky Oil Co. Ltd. for a sample of Lloydminster oil, to the Hudson Bay Oil and Gas Co. Ltd. for a sample of Medicine River oil, to Imperial Oil Ltd. for a sample of Lloydminster oil and to Great Canadian Oil Sands Ltd. for a sample of Athabasca bitumen. We wish to thank Messrs. T.M. Potter and R.M. Evis for technical assistance.

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First Molecular
Distillate

Liquid Chromatography
(dual packed silica-alumina column)



Gas Chromatographic Simulated Distillation
(FID and Microcoulometric Detectors)

Gas Solid Chromatography on LiCl-coated Chromosorb A
(FID, Melpar and Mass Spectrometry)

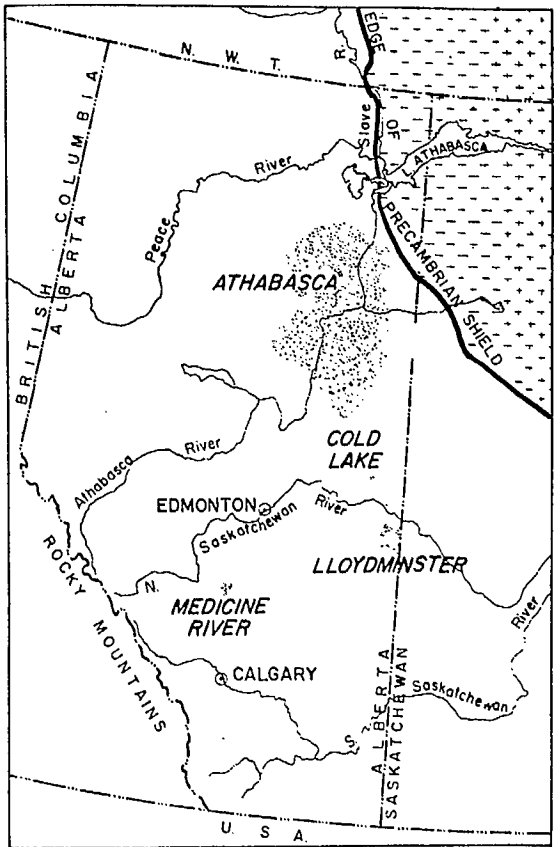
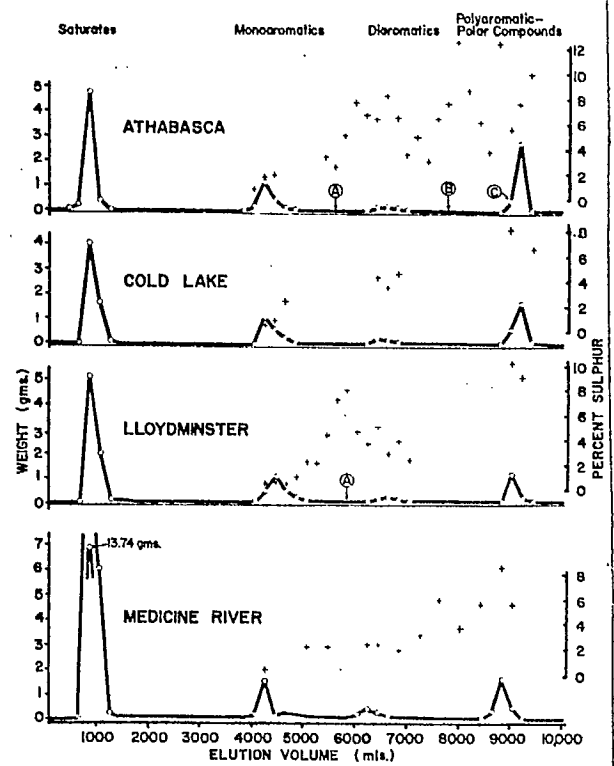
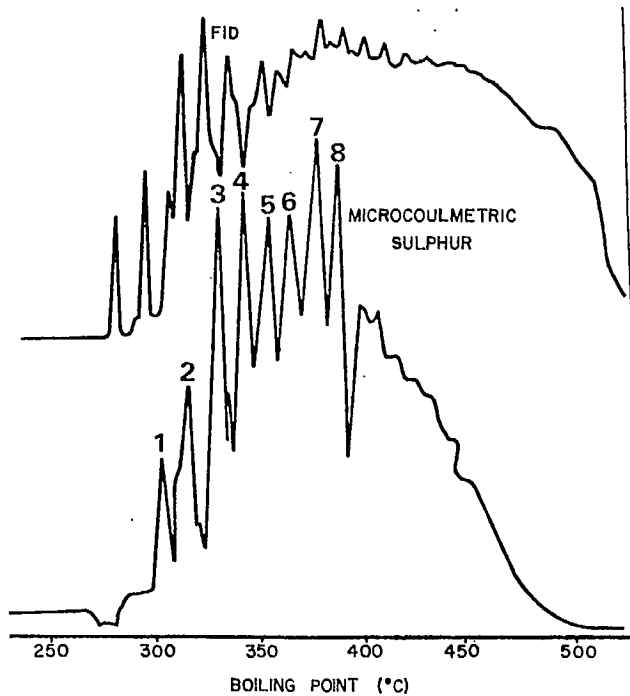


Figure 1



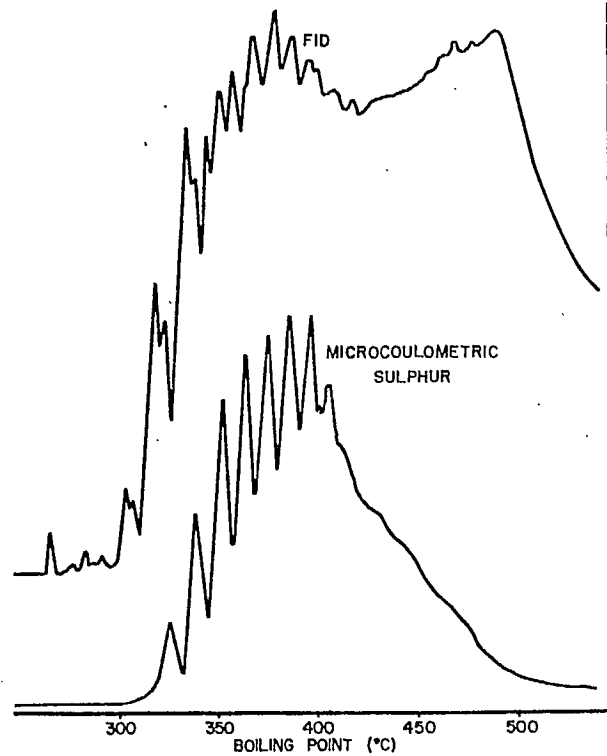
LIQUID-SOLID CHROMATOGRAPHIC SEPARATIONS

Figure 2



LLOYDMINSTER FRACTION A
SE-30 ON CHROMOSORB W

Figure 3



ATHABASCA FRACTION A
SE-30 ON CHROMOSORB W

Figure 4

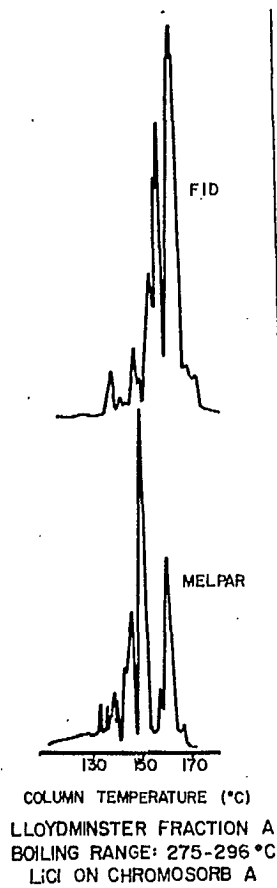


Figure 5

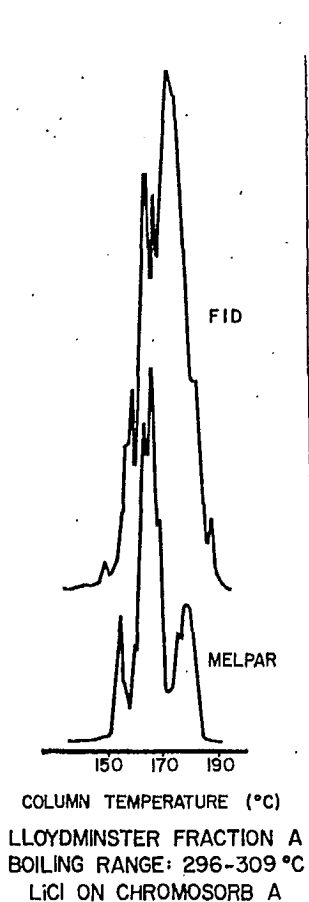


Figure 6

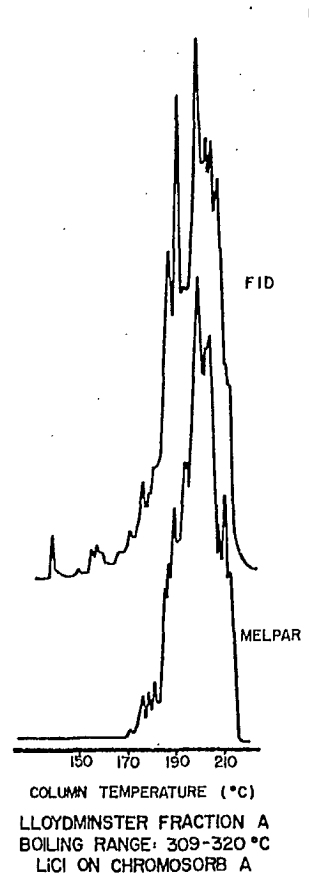
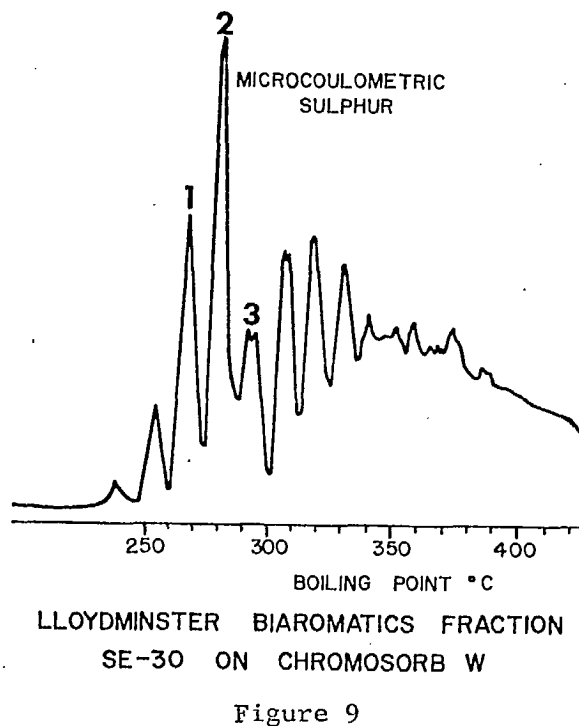
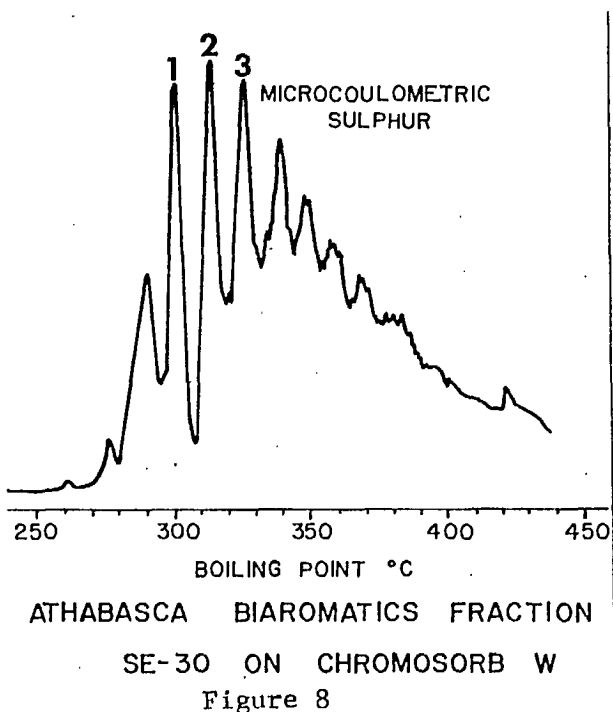


Figure 7



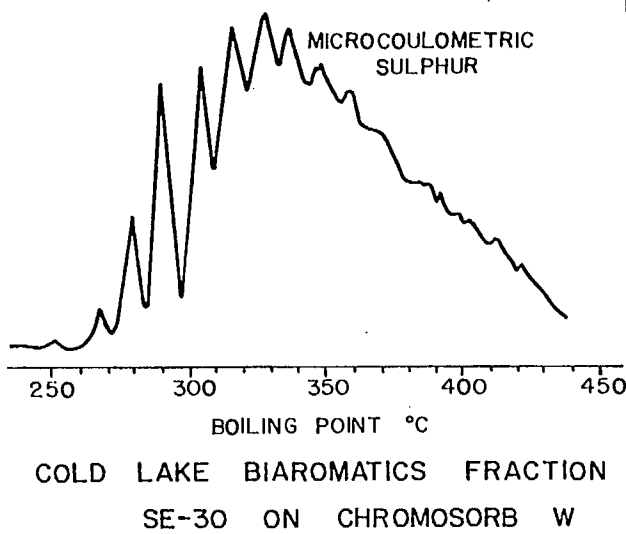


Figure 10

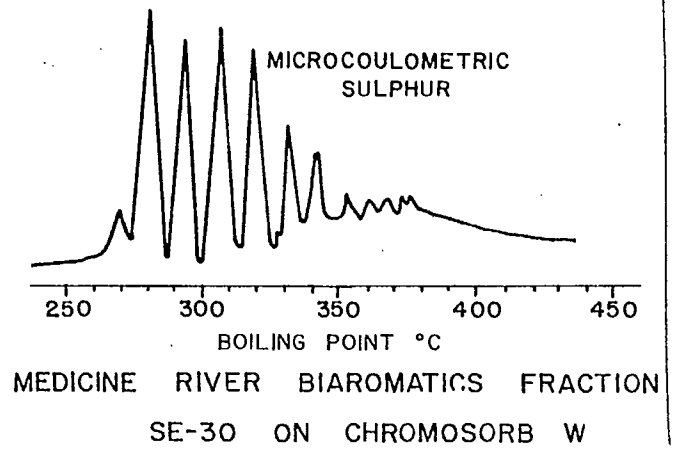


Figure 11

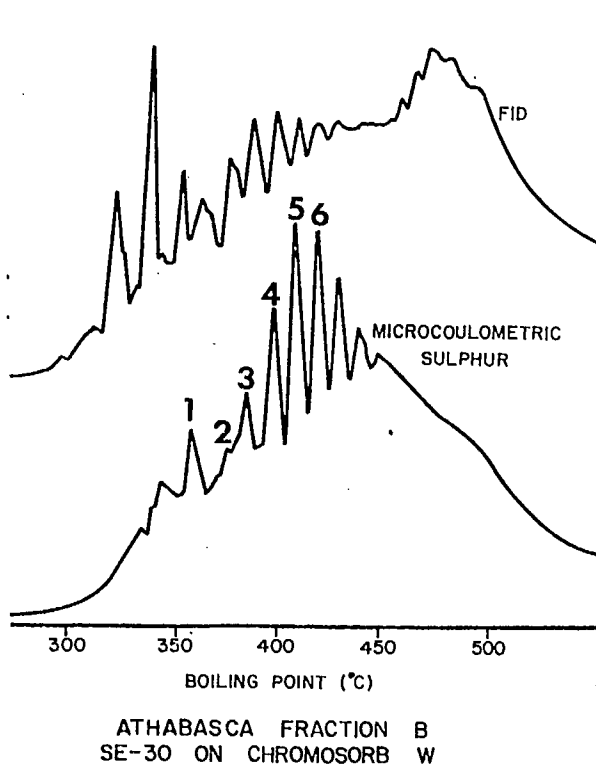


Figure 12

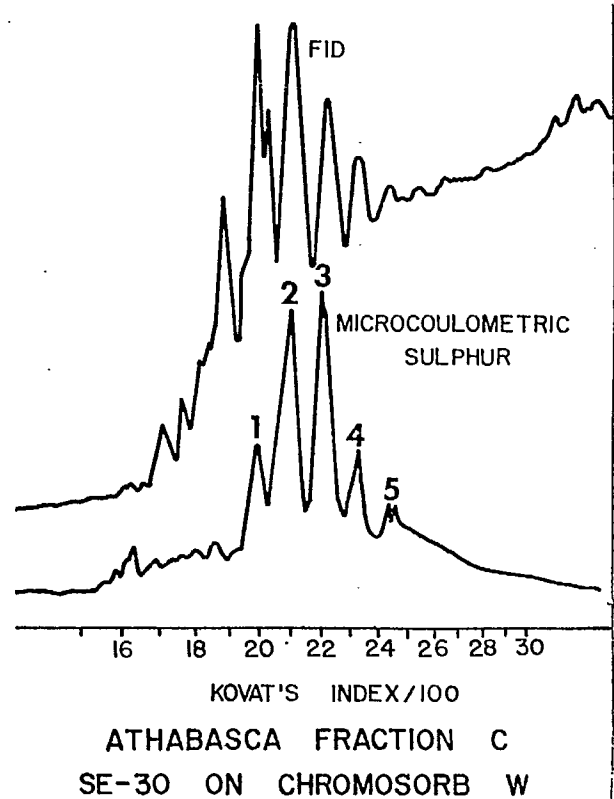


Figure 13

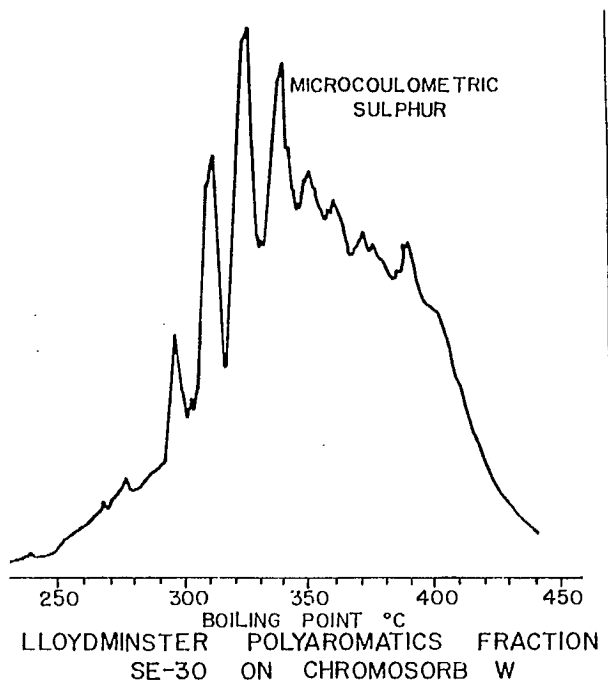


Figure 14

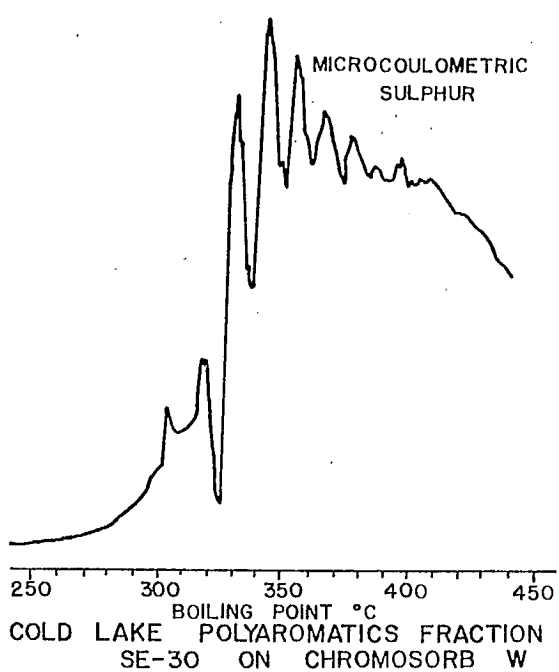


Figure 15

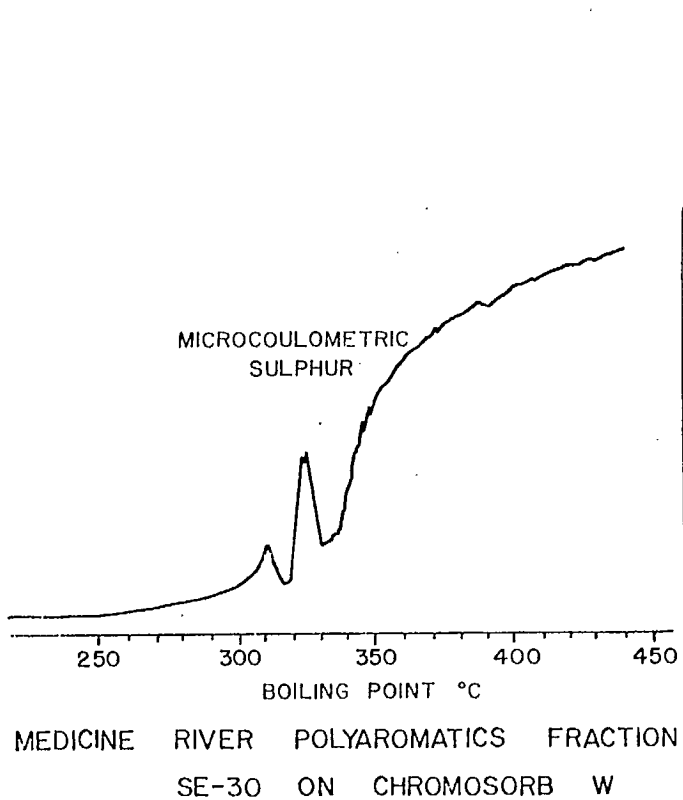


Figure 16

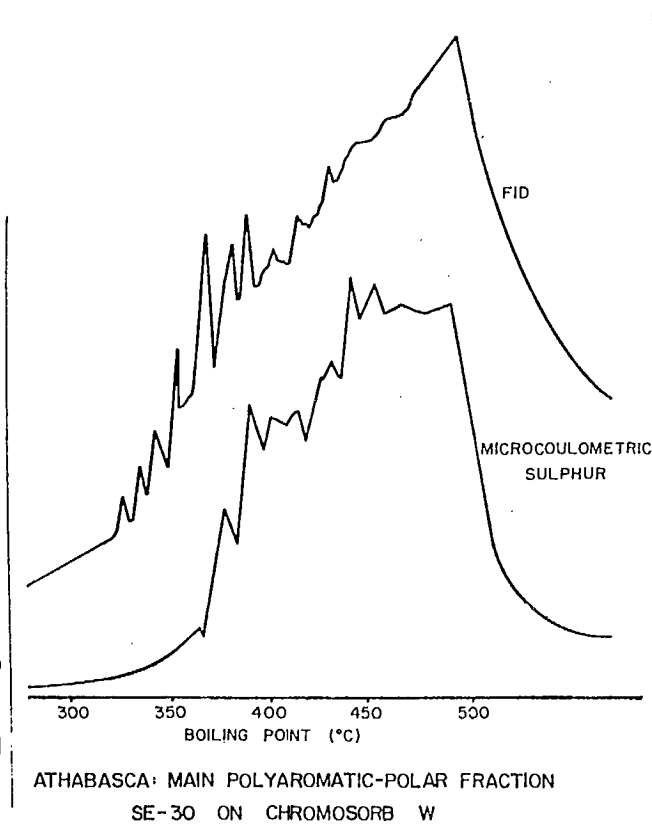


Figure 17

