

## GAS CHROMATOGRAPHIC SEPARATION OF SULFUR COMPOUNDS FROM ATHABASCA BITUMEN

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### INTRODUCTION

In this work we have attempted to develop a simple separation method for investigating the sulfur compounds in the distillable portion of the Athabasca bitumen. This involves gas chromatographic techniques using a specific sulfur detector.

The Athabasca bitumen contains very little material boiling in the gasoline and kerosene ranges. Therefore, at this time, the sulfur compounds in these fractions are not of main interest.

The sulfur compounds in the gasoline and kerosene fractions in some crude oils have been intensively investigated by the workers involved in API projects and others (1, 2, 3). The methods for separating the sulfur compounds that were developed by these workers entail numerous steps, some of which have to be repeated several times. Also, these methods become more difficult to apply as the boiling temperature of the material under investigation increases. Most of these methods of separation were developed prior to the availability of specific sulfur detectors for chromatography.

It was clear that the separation of the sulfur compounds in the Athabasca bitumen would be difficult if the classical methods were used; therefore, simpler methods were sought. We decided to attempt to develop a separation procedure that consisted of subjecting narrow distillation fractions to gas chromatographic separation techniques. The fraction that was used had a distilling temperature corresponding to 333°C at atmospheric pressure and most of the work discussed in this paper deals with this fraction.

### EXPERIMENTAL

The fraction of Athabasca bitumen used for this study was obtained by iso-propanol extraction (4). This extract was distilled in a rotary film molecular still (Arthur F. Smith Inc. model 50-2) in which the liquid contacted only glass and "Teflon" at 200°C and 20  $\mu$  pressure. The distillate from the molecular still was fractionated using a spinning annular still (Nester Faust model NFA-100) at a 10:1 reflux ratio and at a reflux rate of 15 drops/min. The estimated efficiency of this still is in the range of 125-200 plates at atmospheric pressure. The fraction that was used for developing our technique distilled at a temperature of 79.5°C under 10  $\mu$  pressure which corresponds to 333°C at atmospheric pressure.

## Gas Chromatographic Separations

### (a) Preparative

A "Varian Aerograph" model 2100 gas chromatograph was employed for the preparative separations. Two glass columns 3/8 in. ID and 20 ft long were used. One was packed with 10% Carbowax 20M on acid washed Chromosorb W, 60-80 mesh. The temperature was programmed at 1°/min from 150 to 245°C and then held isothermally at this level. The carrier gas was nitrogen and flow rate was 200 ml/min. The effluent was split and 1/9 of it was diverted into the "Melpar" detector.

The other column was packed with 15% Hyprose [octakis (2-hydroxypropyl) sucrose] on acid washed Chromosorb W, 60-80 mesh. The temperature was programmed at 0.5°/min from 125 to 190°C at which temperature it was held isothermally. The nitrogen carrier gas flow rate was 620 ml/min. Also 1/13 of the effluent was diverted into the detector.

The effluent not passing into the detector was led into traps; each containing 0.25g of packing consisting of 10% Carbowax 20M on acid washed Chromosorb W, 60-80 mesh. The sample size for both columns were 10  $\mu$ l per run. Repetitive runs were made until the packing in the traps contained sufficient material for rechromatography. Samples of the packing in the various traps that contained the various effluent cuts were then subjected to rechromatography on the analytical gas-solid chromatographic column.

### (b) Analytical

In this case the gas chromatograph was a "Tracor" model MT 220 instrument. Two columns were employed. An inorganic column consisted of a glass column 4 mm ID and 22 ft long packed with 15% lithium chloride on acid washed Chromosorb W, 60-70 mesh. The packing was prepared by adding a solution of the salt to the Chromosorb and evaporating the water by heating with stirring. The dry solid mixture was then fired at 700°C for 30 min in a muffle furnace. This mixture was packed into the column, with suction, in a dry atmosphere. During the rechromatography the temperature of this inorganic column was programmed at a rate of 1°/min from 50°C to 200°C. The flow rate of the helium carrier gas was 65 ml/min. Each injected sample consisted of 18 mg of packing containing trapped material from the preparative chromatographic step. These samples were packed into thin-walled glass capillary tubes and injected with a solid injector purchased from Hewlett Packard. The glass tubes were crushed in the injection chamber during injection. The effluent stream was split diverting 80% to a mass spectrometer and the rest to the detector.

The other analytical column used for chromatography of other distillate fractions consisted of a 2 mm ID and 20 ft long glass column packed with 5% Carbowax 20M on acid washed Chromosorb W, 60-80 mesh. The column temperature was programmed at 0.8°/min from 100°C to 220°C and then

held isothermally at this temperature. Helium was the carrier gas and its flow rate was 30 mls/min. The distillate fractions analyzed on this column were injected as 0.5 $\mu$ l samples.

(c) Detector

A "Melpar" model FPD 100 AT consisting of both flame photometric and flame ionization units was used. The photometric unit was fitted with the filter required for sulfur detection. In the chromatograms shown the term "Melpar" refers to photometric sulfur detection.

Mass Spectrometry

Low resolution mass spectrometry was performed with a CEC 21-104 instrument connected to a "Tracor" MT 220 gas chromatograph through a Biemann-Watson stainless steel enriching device.

High resolution mass spectra were obtained on a CEC 21-110 mass spectrometer using the direct inlet and the photoplate detector.

RESULTS AND DISCUSSION

A preliminary survey of organic stationary phases was made in order to find suitable phases for separating sulfur containing components. As expected, non-polar phases gave little separation but the polar phases showed considerable promise. Many polar phases were tested and Carbowax 20M appeared to be the most suitable taking into account the separation achieved over the entire chromatogram. From Fig 1 it can be seen that the major portion of the sulfur-free material is eluted first, and then the sulfur trace follows showing two humps of peaks and shoulders. Although there were some differences, all the polar phases that were tested seemed to separate on a similar basis.

The Hyprose [octakis (2- hydroxypropyl) sucrose] containing column gave the best resolution of the second hump. The sulfur chromatogram obtained with Hyprose is shown in Fig 2. Unfortunately, very poor flame ionization responses were obtained using this stationary phase. This poor response is believed to be due to deposition of material bled from the column into the detector. The temperature of the detector was limited to 170°C. When a short Carbowax 20M after column was attached, the bleeding into the detector was reduced but the response was still poor.

The chromatograms shown in Fig 1 and 2 were obtained from the preparative columns. Narrower columns of the same length did not improve resolution. Fractions were collected using both columns. However, only the results from the Hyprose column are discussed because they were superior.

As all the polar organic stationary phases that were tested appeared to separate on similar basis, it seemed unlikely that the separations would be substantially improved by rechromatography on another organic phase. References dealing with gas chromatographic separations of hydrocarbons on column packings containing

inorganic salts have appeared in the literature (5, 6, 7). It was found that these salt containing packings can be used for our bitumen fractions and they seem to separate on a basis different from the polar organic phases.

Of all the combinations of different salts and supports tested, the one containing lithium chloride on acid washed Chromosorb W appeared to be the best. Neither the salt nor the Chromosorb W alone brought about any separation. The lithium chloride, when deposited on the Chromosorb by evaporation of an aqueous solution was fairly effective, but firing the dry packing at 700°C improved the separations substantially. The salt contents were varied from 0.1% to 25% and the optimum content was found to be about 15% by weight.

The material trapped out during the preparative chromatography was rechromatographed on the column containing the lithium chloride and the Chromosorb W. Poor results were obtained from fractions trapped out during the first hump period from both preparative columns. However, much better results were obtained from fractions collected during the second hump period with the one from the Hyprose being better than from the Carbowax 20M.

The fractions 7, 8, 9, 10 and 11, shown in Fig 2 were rechromatographed on the inorganic column. When Fraction 8 which is responsible for the large peak was chromatographed, it was further resolved as shown in Fig 3. It can be seen that more sulfur-free material was separated and that there is some, though not complete, agreement between the sulfur and Flame ionization chromatograms indicating that there is some sulfur-free material present together with that containing sulfur. It should be mentioned that the "Melpar" sulfur response is not linear and is partially masked by the presence of other materials.

The sulfur rechromatograms obtained from Fractions 9, 10 and 11, are shown in Fig 4. It can be seen that some of the peaks in the chromatogram from Fraction 8 are also evident in that from Fraction 9, but there are differences as will be discussed later with the mass spectral data. It should be mentioned that the detector response obtained during the chromatography of Fraction 8, as shown in Fig 3, was actually much greater than when the chromatograms in Fig 4 were obtained indicating that there was more material in Fraction 8.

The effluent from the salt-containing column was split and 80% of it was fed into a mass spectrometer. Scans were made of all materials causing significant sulfur peaks. Inorganic gas chromatographic columns are ideal for direct coupling to mass spectrometers since the spectra do not become complicated by column bleed.

Characterization, so far, has been made only on the basis of mass spectrographic data. From the data obtained from the low resolution mass spectrometer coupled with the gas chromatograph it was not possible to ascertain which of the ions contained sulfur. Therefore a sample of Fraction 8 as shown in Fig 2 was analyzed by high resolution mass spectrometry. The two most abundant parent ions had m/e ratios of 218.11380 and 212.15593 which correspond to empirical formulae of  $C_{14}H_{18}S$  and  $C_{16}H_{20}$  with errors of +0.00088 and -0.00056 respectively. There also were two minor parent ions with m/e ratios of 232.12764 and 226.17113 and these correspond

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to the formulae  $C_{15}H_{20}S$  and  $C_{17}H_{22}$  with errors of  $-0.00093$  and  $+0.00101$  respectively.

On the basis of these formulae it would appear that the most likely sulfur compounds in Fraction 8 consist mainly of isomeric benzothiophenes with six, and to a lesser extent, seven carbons in side chains. All the significant fragment ions that would be expected from these benzothiophenes were observed. The ions that appeared to be sulfur-bearing had  $m/e$  ratios of 217, 203, 189, 175, 161 and 147.

The sulfur-free parent ions would appear to be naphthalenes with 6 or 7 carbons in side chains. The sulfur-free fragment ions had  $m/e$  ratios of 197, 183, 169, 155 and 141. These are the ones expected for such naphthalenes.

The salt containing column seemed to cause some separation of isomers of both the benzothiophenes and the naphthalenes. Considerable hydrocarbon material was separated from the benzothiophenes but some still remained. When Fraction 8 was rechromatographed the most abundant sulfur-bearing ions had  $m/e$  ratios of 189 and 175 in the majority of scans. This might be interpreted as due to the presence of benzothiophenes with propyl and butyl side chains. In a few scans the ion with  $m/e$  ratio of 203 was quite abundant and in only one scan was the 217 ion prominent. The 161 ion was less prominent and the 147 considerably less, and sometimes not distinguishable from the background.

During rechromatography of Fraction 8 there appeared to be a minor series of ions that had not been noted in the high resolution mass spectra. The parent ions of this series had  $m/e$  ratios of 228 and 214 with the latter being the most abundant. The fragment ions had  $m/e$  ratios of 213, 199, 185, 171, 157, 143 and 129. Possibly these ions might have been derived from indenenes with 7 and 8 carbon atoms in side chains.

The benzothiophenes, naphthalenes and to some extent the indenenes appeared to persist during the rechromatography of Fractions 9, 10 and 11. It was noted that with the exception of the scans taken at E and F during rechromatography of Fraction 9 the main sulfur-bearing ion had a  $m/e$  ratio of 161. This indicates that the material in Fraction 9 was different from that in Fraction 8 although there was some overlapping. This 161 ion was not very prominent in Fractions 10 and 11.

During the later stages of rechromatography of Fraction 9 and then during rechromatography of 10 and 11 another ion series became evident. The parent ion had a  $m/e$  ratio of 210 and fragment ions were found at  $m/e$  ratios of 195 and 181. Possibly these ions might be derived from naphthalenes substituted with a third non-aromatic ring.

Unfortunately at this time there is insufficient mass spectral data on benzothiophenes for more comprehensive structure assignment. The fact that the naphthalenes and indenenes appeared to accompany the benzothiophenes is not considered a major problem. These hydrocarbons did not interfere with mass spectroscopy of the sulfur

compounds. Also, they would not be expected to interfere with characterization involving desulfurization because the products from sulfur compounds would be of lower molecular weight than the hydrocarbons. Also, these accompanying hydrocarbons must be similar to the sulfur compounds and can be considered as an aid in characterization.

The fact that a single chromatographic separation on Hyprose separated the benzothiophenes from the other sulfur compounds is considered to be a major achievement. Other workers (8), after a lengthy series of treatments, arrived at an inseparable mixture of benzothiophenes and naphthalenes. But these were of lower molecular weight and had fewer isomers than the benzothiophenes discussed in this presentation. Thus we have had some success in finding a method for separating sulfur compounds that is much simpler than those developed prior to the availability of specific sulfur detectors for gas chromatography.

Similar gas chromatographic separations can be applied to higher boiling fractions as shown in Fig 5.

#### CONCLUSIONS

A single gas chromatographic separation of a 333°C boiling distillate fraction of Athabasca bitumen on a Hyprose-Chromosorb W column could isolate the major portion of what appeared to be benzothiophenes with 6 and 7 carbon atom side chains from the other sulfur compounds.

Several peaks were obtained; all of them appearing to be due to benzothiophenes. Rechromatography of the fractions causing the sulfur peaks on a salt-containing column further resolved the apparent benzothiophenes. At the present time the bases for these separations are not clear.

#### ACKNOWLEDGMENT

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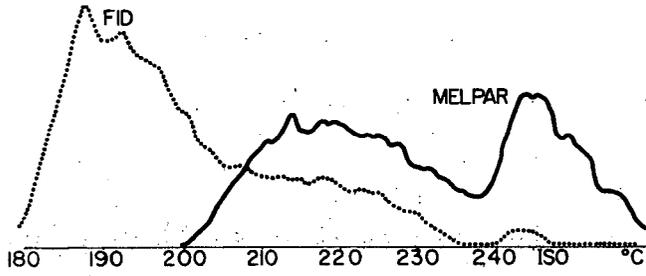


Figure 1. Chromatography Separation on Preparative Carbowax 20M Column

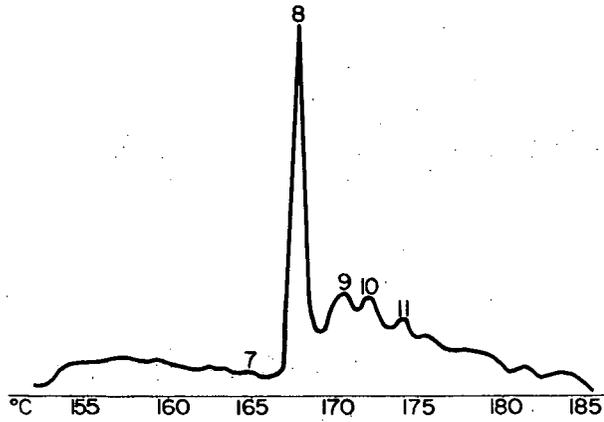


Figure 2. Separation on Preparative Hyprose Column

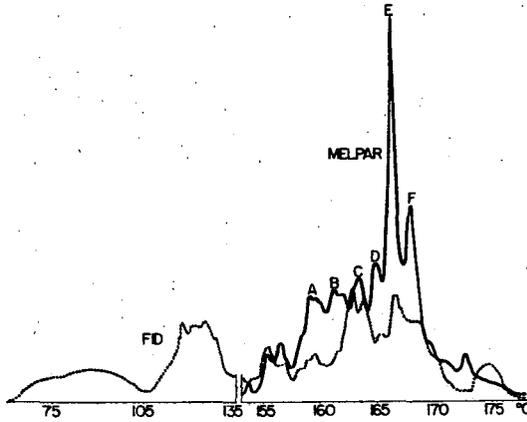


Figure 3. Rechromatography of Fraction 8 (Figure 2) on LiCl-Chromosorb W Column

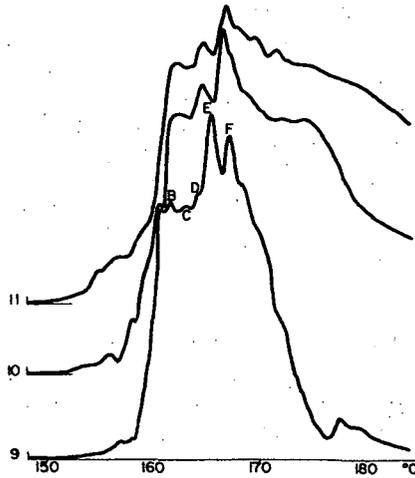


Figure 4. Rechromatography of Fraction 9, 10 & 11 (Figure 2) on the LiCl-Chromosorb W Column

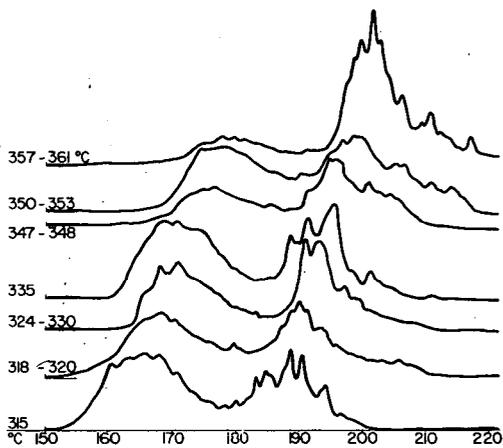


Figure 5. Sulfur Chromatograms of Various Distillate Fractions  
(Analytical Carbowax 20 M Column)