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GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY
OF A
HIGH BOILING POINT BITUMEN FRACTION
INVOLVING
COLUMN PACKINGS WITH LITHIUM CHLORIDE

by

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INTRODUCTION

In our previous work involving the chromatography of narrow boiling range distillate fractions of bitumen, very impressive chromatograms could be obtained with column packings in which polar organic stationary phases, such as, "Hyprose" (Octakis (hydroxy propyl) sucrose) were used. Unfortunately the samples collected from the column effluents were unsuited for further characterization; such as, by mass spectroscopy and desulphurization techniques, because of contamination by the thermal decomposition products from these polar organic stationary phases. Therefore, it was decided that columns containing inorganic packings should be employed because they are thermally stable and the samples do not become contaminated.

EXPERIMENTAL

Column System

This consisted of 8 vertical lengths of 28 in. x 1/2" packed glass columns joined in series. The connections between these columns were made between the bottom of one column to the top of the next column so that the carrier gas flowed downward through all the columns. In this way, the carrier gas would not move the packing material or form bubbles in it.

The column packing was prepared as follows: a solution of 37.5 g of lithium chloride in 1000 ml of water was placed into a large evaporating dish and 250 g of acid washed Chromosorb W, 45-60 mesh was added. The excess water covering the Chromosorb was evaporated with 2-250 watt heating lamps. The salt residue on the sides of the evaporating dish was washed down into the wet Chromosorb. The mixture was dried very slowly in a drying oven. The final temperature of this oven was 210°C. The dry mixture was transferred to a large porcelain casserole with the minimum amount of handling and fired in a muffle furnace at 700°C for 30 min. When packing the columns with this lithium chloride and Chromosorb mixture much care was taken to avoid breaking of particles.

Chromatography and Collection of Fractions

A Varian 2100 equipped with the flame photometric "Melpar" detector was used. The detector was fitted with the optical filter required for sulphur detection so that both flame ionization and sulphur traces could be obtained. The helium carrier gas flow rate was 650 ml/min. The column effluent was split 1:10, diverting the smaller amount into the detector and the rest to the collection system. The injection port and detector were kept at 200°C and the glass outlet to the collection system at 250°C. The glass outlet terminated into a ball and socket joint so that the collection tubes could be attached. These tubes contained 50 mg of acid washed Chromosorb W (45-60 mesh) each. The sample size of the bitumen fraction injected was 2.0 μ l. The oven temperature was increased at 1°/min from 130°C for the first 8 cuts and then at 10°/min to 250°C and held isothermally for the final cut.

Bitumen Fraction

This fraction was obtained by distillation in the spinning annular still at a reflux ratio of 10:1, at 113-115°C at 0.100 mm pressure. This would correspond to a boiling temperature of 348°C at atmospheric pressure.

DISCUSSION AND RESULTS

The chromatogram showing both the flame ionization and the melpar sulphur traces is shown in the figure. The vertical lines in the figure indicate the periods during which the various samples were taken. The percentages of the sulphur in the bitumen fraction that are accounted for by the various samples are as follows:

1	-	0.02%
2	-	2.38%
3	-	7.15%
4	-	8.90%
5	-	8.14%
6	-	7.75%
7	-	10.83%
8	-	7.66%
9	-	<u>23.24%</u>

Total 67.07 + 10% to the detector = 73.8%

It can be seen that less than 75% of the sulphur in the material injected can be accounted for by the sulphur analyses of the samples. This has been the case with all our chromatographic samples. There are two explanations for this. One is that some of the sulphur compounds are retained by the column. The other explanation is that when these chromatographic samples that were held in chromosorb were swept into the combustion furnace during the analyses, the portion of the sulphur being oxidized to sulphur trioxide was greater than in the case when the diluted bitumen sample and standards were analyzed. When the diluted bitumen samples and standards were analyzed, the organic diluent might compete for oxygen with the sulphur compounds and thus reduce the tendency for sulphur trioxide formation. The sulphur trioxide is not titrated by the coulometer. The sulphur analyses discrepancy has not been investigated. Of course, some losses also occur during collection but these are not considered to be very large.

All the characterization of the sulphur compounds and also the hydrocarbons in the chromatographic fraction so far have been done only by mass spectroscopy. Fractions 3 and 7 were analyzed by both high resolution and low resolution mass spectroscopy. The other fractions were only analyzed by the low resolution spectrometer. During the high resolution spectroscopy only the major ions were considered.

Ions derived from possible dibenzothiophenes and naphthalenes were very abundant. The 212 ions were confirmed by the high resolution mass spectrometer (HRMS) as $C_{14}H_{12}S$ and $C_{16}H_{20}$ with abundance of the former being the very much greater than the latter. The compounds from which these ions were derived might be dibenzothiophenes with two attached alkyl carbon atoms and naphthalenes with six attached alkyl carbon atoms. These apparent naphthalene ions are believed to be fragmentation products because their boiling points are too low to be included in the bitumen fraction that was chromatographed as described in this report. Another ion species has a m/e ratio of 226 and was confirmed by HRMS to be $C_{15}H_{14}S$. This was very abundant in both fractions 3 and 7. These ions might be derived from

dibenzothiophenes with three alkyl carbon atoms. The 212 ions were strongly produced from fraction 3 but diminishingly produced in later fractions. They were not significantly produced by fractions 6-9. The 226 ions could be abundantly obtained from all fractions. There were some other heavier ions that might be due to naphthalenes but they were not significantly abundant.

Of the fragment ions in this series the 211 ions were confirmed by HRMS to be mostly $C_{14}H_{11}S$ with some $C_{16}H_{19}$ in fraction 3. In fraction 7 only the $C_{14}H_{11}S$ was significantly abundant. The 211 ion were very abundant in all fractions but more so in the early fractions. The 197 ions were very abundant in fraction 3 but then decreased and were not significant in fractions 7-9. There were some 225 ions in fractions 4-8. The 169 ions which could not be derived from the dibenzothiophenes, and might be derived from naphthalenes, were significant only in fraction 4. The 183 ions which, also would be expected to be derived from naphthalenes were strong in fraction 2, weaker in 3 and 4, and after that, insignificant. Thus, it would appear that most of the ions in this series were derived from dibenzothiophenes with a much smaller amount being derived from naphthalenes.

The 260 ions become increasingly apparent in fractions 7, 8 and 9. HRMS of fraction 7 confirmed this as $C_{17}H_{24}S$, which might be a benzothiophene with 9 attached alkyl carbon atoms. Other ions that might be parent ions of benzothiophenes with m/e ratios of 274 and 288 were noticeable only in fraction 9.

Of the fragment ions that might have been derived from benzothiophenes, the 161 ion was confirmed by HRMS to be $C_{10}H_9S$ in fraction 3. This abundance started high, decreased and then increased again. The 175 ion abundance was fairly constant in fractions 3-7 and then increased very markedly. The 189 ion became apparent in fraction 5 and then increased markedly. This ion was confirmed in 7 by HRMS to be $C_{15}H_9$ and therefore, at least in fraction 7, was not significantly derived from benzothiophenes. The 203 ion became apparent in fraction 5 and then increased rapidly. In general, it appears that these benzothiophenes with 9 or more attached alkyl carbon atoms were not abundant

in the early fractions but became more prevalent in the later ones.

There is some evidence that might be interpreted as indicating the presence of benzothiophenes with an attached saturated ring. The HRMS shows an ion with m/e of 158 and with a formula of $C_{10}H_6S$. This might be a benzothiophene with a cyclobutadiene ring attached. This ring can readily be formed by fragmentation in the mass spectrometer of saturated rings attached to aromatic structures. There were some parent peaks at 300, 286, and 272 in fraction 8 which might belong in this series but this is doubtful because of the high masses. The 244 ions were present during the spectroscopy of fractions 4 and 5, 215 ions in fractions 7 and 9, and the 201 ions in fractions 4, 5 and 9. The fragment ions might have been derived from the cyclo alkyl benzothiophenes.

Other sulphur containing ions produced an m/e of 171. The HRMS indicated two species of ions, both of medium intensity. One had a formula of $C_{11}H_7S$ and the other $C_{13}H_{15}$. The hydrocarbon fragment could be derived from indenenes and the sulphur containing fragment might be a thia-acenaphthenyl ion. Perhaps this might have been derived from a naphthyl alkyl sulphide, or the thia-acenaphthenes themselves might be found in the bitumen. No possible parent ions could be found in this series. The 171 ions were strong in fraction 3, decreasing to nil in fractions 7-9. The 185 ions were found in fractions 2, 3, 5 and 9; the 199 ions in fractions 3, 4, 5 and 9; the 213 ions in 3 and 5; and the 227 ions in 4 and 5.

The other sulphur bearing ions that became apparent were the ones with m/e ratios of 270 which the HRMS in fraction 7 showed to be $C_{15}H_{26}SO_2$. Some of these ions were found in fractions 4, 7 and 9. If this is a sulphone then it might be an oxidized tricyclic alkyl sulphide.

Undoubtedly there are many sulphur compounds present in the bitumen fractions that could not be detected by mass spectroscopy because they became too fragmented. These compounds require investigation by desulphurization techniques.

There are other hydrocarbons besides the ones discussed with the sulphur compounds. One series could contain anthracenes, phenanthrenes, or both. In this series the unsubstituted compounds would give rise to parent

ions with mass of 178. The HRMS of fraction 3 confirms this to be $C_{14}H_{10}$. When both anthracene and phenanthrene alone were chromatographed in the same manner as the bitumen fraction, the phenanthrene was eluted at a lower temperature than the bitumen, so that it could not be a constituent of the bitumen fraction. Anthracene was eluted at the same time as the early sulphur fractions so that it could be part of the fraction. However, the 178 ion is fairly abundant in fraction 3 and then decreases as expected for anthracene. However, an increase in abundance of the 178 ion in later fractions indicate that there are other compounds producing these ions.

The 192 ions that might be due to methyl phenanthrenes or methyl anthracenes were not produced in significant amounts. The 206 ions that might be derived from the trinuclear aromatics with two alkyl carbon atoms were absent in the earlier fractions, predominant in fractions 5, 6, and 7 but decreased in fractions 8 and 9. The 206 ions were confirmed to be $C_{16}H_{14}$ by HRMS in fraction 7. The 220 ions were only present in fraction 9.

The 205 fragment ions were about 23.30% as abundant as the 206 ions in fractions 5, 6, and 7. In fraction 8 they were not significant but in fraction 9 they were more abundant than the 206 ions. The 191 ions are very substantial in fraction 4 and are increasingly more abundant in every later fraction. It was confirmed to be $C_{15}H_{11}$ by HRMS in fraction 7. However, literature references dealing with the mass spectroscopy of alkyl anthracenes and phenanthrenes show that the 191 fragment ions should be much more abundant than the parent ions and therefore there must be other compounds in the bitumen fraction, besides the phenanthrenes and anthracenes, that produce these ions.

Another structure that might be considered is tetra-hydrofluoranthene. It has a molecular weight of 206 and during mass spectroscopy the parent ion has an abundance of 67% of the fragment ion at 178. The possibility of such a compound might explain the presence of the 178 ions during spectroscopy of the later fractions.

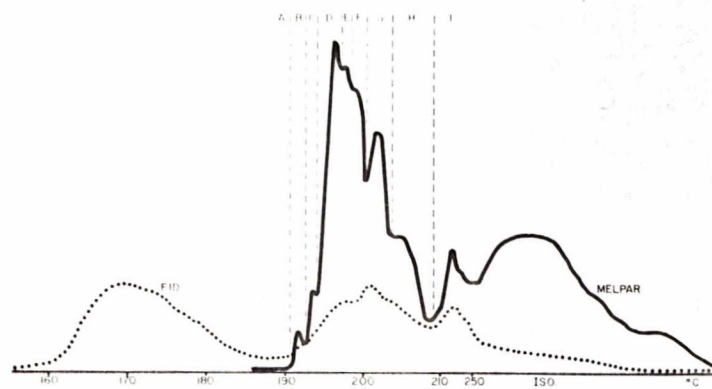
Another series of possible hydrocarbons present might be the fluorenes.

The 236 ions were confirmed by HRMS of fraction 3 to be $C_{18}H_{20}$ which might be a fluorenes with 5 carbon atoms in chains. The ion was found in small amounts in 3, 4 and 5. It was insignificant in all other fractions. The 222 ion was found in fractions 3 and 9, with the latter containing a fair amount. The 208 ion was substantial in fraction 2 but decreased in 3, 4 and 5, then appeared again in substantial amount in fraction 9. In fraction 3 the 193, 179, and 165 ions were confirmed by HRMS to be $C_{15}H_{13}$, $C_{14}H_{11}$ and $C_{13}H_9$ respectively. The 193 ion was quite substantial in 2, then decreased in 3 and 4 but then reappeared in fraction 9 in great abundance. The 179 ions were strong in all fractions, but lower in 6 and 7, and then very strong in 9. The 165 ions were very strong in 2 and 3, strong in 4, 5 and 6 and not apparent in 7, 8 and 9. The 207 ions were present in all fractions but 8 and very abundant in fraction 9. The 221 ions were found in fractions 3, 4, 1 and 9.

There are two series of ions whose parent ions of 252 and 238 have been confirmed by HRMS of fraction 7 to be $C_{19}H_{24}$ and $C_{18}H_{20}O$ for the 252 ion and $C_{18}H_{22}$ and $C_{17}H_{18}O$ for the 238 ion. The 252 ions are substantial in fractions 7, 8 and 9, while the 238 ion are present in fractions 4-9 with large amounts in the last two fractions. There are some 266 ions in fraction 9. Some 224 ions were found in fractions 7-9 in increasing amounts. There were some 210 ions in fraction 5.

The fragment ions in this series were the 195, 209, 223, 237 and 251 ions. The 195 ions were found in increasing amounts in fractions 7-9. The 209 ions were strong in all fractions but very strong in 8 and 9. The 223 ions were found in fractions 7-9 in increasing amounts. The 237 ions could be found in fractions 7-9. The 251 ions appeared to be absent.

The hydrocarbons in the series just mentioned could be naphthalenes with a saturated ring attached or biphenyls or acenaphthenes. The oxygen containing ions might be derived from these hydrocarbons in which carbon atoms to the aromatic cluster might have become oxidized.



CHROMATOGRAPHIC SEPARATION ON PREPARATIVE LICI COLUMN
OF BITUMEN FRACTION BOILING AT 348 °C