THE EVALUATION OF LITHIUM CHLORIDE-COATED POROUS SILICA FOR THE GAS CHROMATOGRAPHIC SEPARATION OF PETROLEUM FRACTIONS

H. SAWATZKY, A. E. GEORGE AND G. T. SMILEY

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H. Sawatzky*, A. E. George*, and G. T. Smiley**

ABSTRACT

In this work gas solid chromatographic separation of petroleum hydrocarbons and sulphur compounds on column packings consisting of lithium chloride-coated diatomaceous silica and porous silica beads have been studied. The temperatures required for separating most of these compounds were not above those needed for equivalent gas liquid chromatographic separations, and the efficiencies were comparable. The dialkyl and alkylaryl sulphides had retention values much greater than polynuclear aromatic hydrocarbons of similar boiling points. The retention values are discussed in terms of specific and non-specific interactions in order to show how compounds of similar boiling points were separated according to type. A number of fractions with 20°C boiling ranges that had been collected during gas chromatographic simulated distillations of petroleum were rechromatographed on these inorganic column packings. Interpretations of the separation of oil constituents are made on the basis of the retention data of the pure compounds. These column packings are thermally stable, so they can be used for type separations of high-boiling materials with none of the contamination that could not be avoided in columns packed with relatively unstable highly polar stationary liquid-phase. Thus, these packings are ideal if the separated materials require further characterization such as mass spectroscopy or desulphurization because there will be no contamination by column bleed.

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EVALUATION DE LA SILICE POREUSE RECOUVERTE DE
CHLORURE DE LITHIUM POUR LA SEPARATION CHROMATOGRAPHIQUE
EN PHASE GAZEUSE DES FRACTIONS PETROLIFERES.

par

H. Sawatzky,[*] A. E. George[**] et G. T. Smiley.[***]

        Dans la présente étude les auteurs ont étudié la séparation des
hydrocarbures et des composés sulfureux du pétrole en utilisant une
garniture de colonne qui se compose de silice à diatomées et de silice
poreuse recouverte de chlorure de lithium. Les températures nécessaires
pour séparer la plupart de ces composés ne sont pas supérieures à celles
requises pour effectuer des séparations semblables en chromatographie en
phase gazeuse, de plus l'efficacité est comparable. Les valeurs de
rétention du sulphure de bialkyl et d'alkylaryl sont plus grandes que celles
des hydrocarbures poly-aromatiques à points d'ébullition semblables.
Les valeurs de rétention sont indiquées aux termes des interactions
spécifiques et des interactions non-spécifiques, pour montrer que les
composés à points d'ébullition similaires sont séparés suivant leur type
de structure. Un nombre de fractions ayant des intervalles d'ébullition
de 20°C recueillies au cours des distillations simulées du pétrole par
chromatographie en phase gazeuse, sont rechromatographiées sur ces garnitures
inorganiques de colonne. L'interprétation du résultat de la séparation des
composés pétrolifères est basée sur les valeurs de rétention obtenues pour
des composés purs. Etant donné que les garnitures de colonne sont
thermiquement stables, elles peuvent être utilisées pour séparer des composés
à points d'ébullition élevés sans risquer de contaminer. La contamination
se produit sur des colonnes à phase stationnaire liquide relativement instable
et d'une grande polarité. Donc, les garnitures inorganiques de colonne sont
idéales si les composés séparés exigent plus de traitement comme par exemple
la désulphurisation ou l'analyse par spectrométrie de masse. Dans ce cas,
il n'y aura pas de contamination causée par l'entrainement de la phase
stationnaire de la colonne.

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INTRODUCTION

The gas chromatographic analysis of high boiling petroleum fractions poses a problem in selecting stationary phases that have sufficient thermal stability. Gas-liquid chromatographic separations according to boiling points can be made on materials boiling as high as 600°C on a number of non-polar, thermally stable, stationary, liquid phases. However, for separations according to types of compounds, highly-polar stationary liquid phases are required and they are not as thermally stable as the non-polar phases. These highly polar liquid phases begin to decompose at temperatures above 225°C or even below this temperature, and the decomposition products contaminate the separated materials. This seriously interferes with further characterization especially if mass spectroscopy is to be used.

Much use has been of solid adsorbents such as carbons, aluminas, and silicas, as well as modifications of these materials for gas chromatography (1, 2). However, they have been used only for the separation of low-molecular-weight compounds because the compounds are strongly retained and require high temperatures for elution. The temperatures required are between 50 and 75°C above those required for comparable gas-liquid chromatography. From this it is evident that the temperatures required for the chromatography of high--molecular-weight substances on solids increase the probability of pyrolysis of these substances occurring before elution. Scott (3) claims to have reduced the required temperature considerably by extensive heat treatment of alumina, to decrease the surface area, followed by treatment with sodium hydroxide. Even in this case, the temperature necessary for gas chromatography was considerably higher than for conventional gas-liquid chromatography. A number of papers dealing with salt-containing column packings for gas chromatography have appeared in the literature (3 - 14) of which several

involve temperatures similar to that of conventional gas-liquid chromatography. However, these salt-containing column packings have never become popular. Versino (7) claimed that the lack of general acceptance of these columns was due to a "pump effect" in that substantial amounts of sample had to be injected before satisfactory levels of reproducibility could be obtained and that, if no samples were injected for some time, the reproducibility became poor again. He ascribed this to active sites on the metal surface inside the detector tract.

In a previous report, we described the evaluation of diatomaceous silica (Chromosorb W) and Chromosorb W coated with 15% lithium chloride as column packings for gas chromatography (15). It was shown that high-boiling hydrocarbons and sulphur compounds could be separated according to type on the lithium chloride-coated diatomaceous silica at temperatures not higher than those required for comparable gas-liquid chromatography. The main disadvantage was the difficulty obtaining reproducible results. The "pump effect" was quite noticeable in this work.

EXPERIMENTAL

The lithium chloride was deposited on the diatomaceous silicas, "Chromosorbs" A and W, as well as on the porous silica beads "Porasils" D and F, all sizes between 60 and 80 mesh, by covering them with aqueous solutions of salts and then evaporating the mixtures to dryness. The amounts of the salt used were 50%, 15%, 100%, and 25% of the weights of "Chromosorbs" A and W, and of "Porasils" D and F respectively. The dry mixtures were then fired at between 700 and 750°C for 30 minutes in a muffle furnace.

The columns were made of U-shaped glass tubing 6 feet long and 0.25 inch in external diameter. The chromatograph used was a Varian 2100 fitted with either flame ionization or Melpar sulphur detectors. For the work involving pure compounds, the flow rate of the nitrogen carrier gas was 60 ml/min. For the petroleum fractions, the flow rate was 85 ml/min of helium.

Samples of pure compounds were injected as solutions in benzene in concentrations of either 1 or 0.1% using a 1-μl "Precision Sampling" syringe. The more volatile compounds were injected as vapour taken from the bottles containing them. To get results comparable with those compounds injected as

benzene solutions, the volumes were varied until the detector responses for these vapours were similar to the responses for the compounds injected as solutions.

The distillates of the crude oils were obtained by gas chromatographic simulated distillations using a temperature program of 4°C per minute and a column consisting of 10% SE-30 silicone rubber supported on acid-washed Chromosorb W. Normal alkanes were employed as reference compounds. About 75% of the column effluent was diverted to the collection system where the fractions were trapped in tubes containing acid-washed Chromosorb W. The collection tubes with the desired fractions were kept under nitrogen.

The Chromosorb W from each collection tube that contained a fraction was packed into a glass capillary tube under nitrogen. The capillary tubes and their contents were then injected with a Hewlett-Packard solid injector onto the salt-containing column at room temperature. The column oven was heated to 50°C and then programmed at 4°C/min. The column was calibrated with amounts of normal alkane mixture that gave detector responses comparable to the responses obtained during the chromatography of the petroleum fractions.

<div align="center">DISCUSSION</div>

Column Packings

The authors initial work was on 15% lithium-coated diatomaceous earth (Chromosorb W). For comparison, the uncoated diatomaceous earth was also evaluated. The retention times were slightly higher for normal alkanes on the uncoated than on the lithium chloride-coated diatomaceous earth. However, the efficiency of separation was greatly increased by the salt coating especially if the diatomaceous earth had been washed with acid. This was thought to be due to the removal of aluminum and iron oxides. The aromatic and sulphur compounds were retained longer on the coated than on the uncoated diatomaceous earths. The "pump effect" as described by Versino (7) was serious. Substantial amounts of sample material had to be injected on to these columns before reproducible results could be obtained. The retention increased with time if the columns containing these packings were swept with carrier gas for a considerable period between analyses. If the retention was longer than 10 minutes, the peaks became more ill-defined with increasing time. It appeared as though there were active sites, exposed by the prolonged action of the carrier gas, that had to be covered before reproducible results could be obtained. The addition of more lithium chloride to the Chromosorb W

did not appear to improve the resolution.

In more recent work, this so called "pump effect" was not observed on either "Porasil D" coated with an equal weight of lithium chloride or on "Porasil F" which has much less surface area after being coated with 25% by weight of lithium chloride. However, the column packing that so far has given the most efficient separations is the diatomaceous earth "Chromosorb A" coated with 50% by weight of lithium chloride. This column packing did show a little "pump effect". There was a marked reduction in tailing and a slight reduction in retention time if a few preliminary injections of the compounds being analyzed were made. The beneficial effect of preliminary sample injections would last for several hours unless the column was heated at temperatures much higher than that required to elute these samples. The results obtained during chromatography on these lithium chloride-containing columns were sufficiently reproducible to yield retention values useful for analyses. It should be mentioned that samples such as crude oils that contain some non-volatile components would cause these columns to deteriorate. Also the use of low-grade septa if heated above 250°C was found to spoil the column packings.

Deposition of the lithium chloride from an aqueous solution onto the diatomaceous earths by evaporation to dryness has produced quite acceptable column packings. However, firing at 700°C improves the quality of these packings especially for the Chromosorb A. In the case of the "Porasils" firing was found to be essential to reduce the peak tailing and the column temperature required for separation. In the case of porous "Vycor" glass, even firing did not sufficiently lower the temperature required for chromatography.

All the column packings were fired at 700°C in a muffle furnace in air. Exposure of lithium chloride to air at a temperature greater than its melting point causes the displacement of some of the chlorine with oxygen (16). In our experience, it appeared that some slight oxidation is necessary to obtain high-quality packings. If we fired the packings in a nitrogen atmosphere the results were not as good. On the other hand, sweeping the packing with air during firing caused excessive peak tailing. This oxide formation during firing of lithium chloride does not seem to be mentioned by other workers who used lithium chloride for gas-solid chromatography.

The efficiency of separation of normal alkanes on the lithium chloride-coated Chromosorb A columns was above 1100 plates. With aromatics or

sulphur compounds, higher efficiencies were achieved. The chromatograms obtained during separation of normal alkanes, sulphur compounds, and aromatic compounds are shown in Figures 1, 2, and 3, respectively.

Effect of Sample Size

A point that should be mentioned is that the retention time of compounds injected on these salt column packings was dependent on the sample size. This effect is illustrated in Figure 4. Whatever dilution we used there was no involvement of the linear portion of the Langmuir adsorption isotherm (i.e. sample sizes were not small enough to fall in the range where variation in size has no effect on the retention time). As can be seen from Figure 4, a 50% variation in sample size causes smaller variations in retention as the sample sizes decrease. It was quite obvious that in order to obtain meaningful retention data on the salt-containing column packings, the sample sizes of the materials investigated must be similar in size to the reference compounds. The reference compounds used in this work were normal alkanes and the Kovat's index system was adopted for comparing retentions. Another interesting observation was that the dicyclohexyl behaved differently from most other compounds listed in Table 1 with regard to the effect of sample size. For this compound, the retention time increased with increasing sample size. It can be seen that the amount of solvent has little effect on the retention time. Therefore, the 0.1 μl of 1% solution of a sample in benzene has a retention time of essentially the same value as one μl of a 0.1% solution. Any differences in the observed values are probably due to errors in the syringe delivery.

Specific and Non-Specific Interactions

Of the salts examined, only lithium chloride gave satisfactory results. According to Kiselev, in his work concerning the sorption of pentane and diethyl ether on zeolites with various cations (17), the larger the cation, the greater is the non-specific interaction. Non-specific interaction is defined as the forces involved during the retention of molecules possessing spherical symmetrical electron shells as in inert gases, or having only σ bonds as in the saturated alkanes. Specific interaction on the other hand is due to local concentrations of charges as lone pairs of electrons, π bonds, and acidic hydrogen atoms. All compounds that are retained due to specific interaction are also retained to some extent due to non-specific interaction. In order to separate high-boiling compounds by gas chromatography at the lowest

possible temperature, the non-specific interaction should be as low as possible because it does not cause separation according to the types of compounds. By contrast, considerable amounts of specific interaction is required. The larger the cation the greater the attractive forces due to polarizability or dispersion and this causes increased retention due to non-specific interaction. The smaller the cation the smaller is the non-specific interaction. Therefore, the lithium cation which has a small radius would be expected to give rise to salts with more desirable properties than other alkali metal cations.

Initially the approach for the determination of specific interactions for the various compounds was similar to that of Brookman and Sawyer (18). However, we preferred to express the specific interaction values in terms of differences in Kovat's indices of the compound and of a normal alkane with the same boiling point. It became obvious that this approach was not satisfactory because of the substantially negative values that were obtained for some polynuclear hydrocarbons on columns that had become degraded.

The boiling point of many compounds is affected to a considerable degree by association in the liquid. In normal gas chromatography, this association is reduced considerably, so the non-specific interaction is not directly related to the boiling point. In fact, during gas chromatographic simulated distillation on non-polar columns, many compounds such as polynuclear aromatics were found to have substantially lower boiling points, when normal alkanes are used as reference compounds, than obtained by conventional vapour pressure methods. In our later work, non-specific interaction was obtained by comparison of retention times with normal alkanes on non-polar silicone rubber columns.

Retention Data of Pure Compounds

Some of the retention data in terms of Kovat's indices obtained on the lithium chloride-coated Porasil D under isothermal conditions are shown in Table I. Tables II and III show the retention data of hydrocarbons and sulphur compounds that were obtained by chromatography when the temperature was linearly programmed at 4°C per minute. The interactions on Chromosorb A are somewhat higher as compared with Porasil D. On Chromosorb A most of the data were obtained during temperature programming while on the Porasil they were obtained under isothermal conditions.

When n-butylbenzene was chromatographed isothermally on the Chromosorb A a lower interaction was obtained than under conditions of temperature programming.

This might explain the differences of values between Tables I and Tables II and III. Because the chromatographs of oil fractions were obtained on the Chromosorb A during temperature programming, the values in Tables II and III are more suitable for comparison.

It can be seen that substantial negative values were obtained for both the dicyclohexyl and decalin. In our earlier work on the lithium chloride-coated Chromosorb W, a negative value was obtained for ethylcyclohexane and low values for cyclohexene sulfide and cyclohexyl mercaptan. Quite low values for cyclohexanes have been reported in the literature (8, 18). Sawyer et al (18) ascribed these low values to the fact that not all carbon atoms could contact the adsorbing surface because cyclohexane is not planar. Therefore, these salt columns will separate saturated cyclic structures from other compounds. This might be valuable in the analysis of jet fuels.

On the basis of the two branched alkanes, 2, 3, 4-trimethylpentane and 2, 2, 5-trimethylhexane for which slightly negative specific interactions were obtained, it would seem that the branched alkanes have interactions similar to the normal alkanes. However, if non-planarity is the reason for negative specific interaction it would be expected to apply to branched alkanes.

The specific interaction for all the aromatics is quite substantial, so it should be easy to separate aromatic from saturated hydrocarbons of similar boiling point unless non-planar cyclic structures are attached. For the unsubstituted aromatic hydrocarbons, the specific interaction increases as the cluster size increases up to phenanthrene and anthracene but does not increase further for pyrene. It can be seen that the specific retention obtained for the aromatic structures increases markedly with the number of electron-donating groups that are attached to them. Thus hexamethylbenzene involved a specific interaction of over 500 whereas benzene was less than 200. It was observed that cyclohexylbenzene had a specific interaction similar to benzene. In this case, the electron-donating effect of the cyclohexyl group appeared to be offset by its non-planarity.

Large specific interactions were obtained for the dialkyl and alkyl aryl sulfides. Dibutyl sulfide possessed a specific interaction of 950 and all the other dialkyl and alkyl aryl sulfides had specific interactions of well over 500. On the basis of this work it would appear that these sulfides should be readily separable from hydrocarbons of similar boiling point. By contrast the aromatic sulphur compounds involved specific interactions similar to or

lower than comparable aromatic hydrocarbons. Thus the specific interaction
for benzothiophene was the same as for naphthalene and that of dibenzothiophene
was lower than for phenanthrene or anthracene. Diphenyl sulfide involved
lower specific interaction than diphenylmethane. From the above, it is clear
that electron-donating groups attached to the sulphur atom increase the
specific interaction. From the value obtained for diphenyldisulfide, it
appears that the specific interaction is not much greater for aromatic
disulphides than for the aromatic monosulfides. Oxygen analogs of some of
the sulphur compounds involved substantially greater specific interaction.
In previous work we found that alkyl mercaptans involved specific interactions
as large as 400 for n-alkyl mercaptans but aryl mercaptans had lower values.

Chromatography of Petroleum Fractions

In order to show how these salt-coated siliceous column packings
can be used to separate petroleum fractions, several chromatograms of fractions
from two crude oils are shown in Figures 5 to 12. The oils came from the
Lathom and Lloydminster fields of Alberta, Canada. All initial fractions were
collected during gas chromatographic simulated distillation on a thoroughly
conditioned column of SE-30 silicone rubber supported on acid-washed
Chromosorb W.

The distillation cuts had boiling point ranges of 250 - 270°C;
270 - 290°C; 290 - 310°C; 310 - 330°C; and 330 - 350°C respectively. In terms
of Kovat's Indices these ranges would be 1383 - 1495; 1495 - 1620; 1620 -
1760; 1760 - 1905; and 1905 - 2060. These indices were considered to be the
non-specific interactions and are marked on the abscissa of the chromatograms.

The re-chromatography of the 20°C fractions on the salt columns show
both the flame ionization and the Melpar sulphur traces. Although the Melpar
sulphur detection is not quantitative and is influenced by types of sulphur
compounds as well as by the presence of non-sulphur material, it clearly shows
the separations obtained. This Melpar detector might be more valuable than
the microcoulometric system in fingerprinting oils for identification purposes.
All of the flame ionization traces of the Lathom fractions (Figures 5 - 8) show
two envelopes of peaks. The first envelope of peaks generally end fairly
abruptly near the limit of the non-specific interactions. Then there is a
valley between the two envelopes. If the boiling ranges were narrower, the
valleys would probably be nearer to the base line.

In all the chromatograms of the Lathom fractions, there is

considerable material with negative specific interaction which indicates the probable existence of substantial amounts of non-planar saturated cyclic hydrocarbons. It seems that, as the boiling points of the fractions increase, the initial materials that elute involve greater negative specific interaction. Possibly substitution on the cyclic structures explains this observation.

In Figure 7 normal hexadecane and heptadecane appear quite prominent. In Figure 8, normal octadecane and, to a much lesser extent, nonadecane are very evident. The second envelopes of peaks in the chromatograms of these Lathom fractions are due to aromatic hydrocarbons and sulphur compounds. Probably the sulphur compounds are mostly substituted benzothiophenes. The tail on the sulphur chromatograms might be due to dialkyl and alkyl aryl sulfides.

As can be seen the Lloydminster fractions (Figures 9 - 12) differ considerably from the Lathom fractions. The first envelopes of peaks decline much sooner in the Lloydminster fractions. In fact, octadecane appears to be in the second envelopes in the 290 - 310°C fraction (Figure 10). In general, the Lloydminster chromatograms are more spread out than the Lathom for both the flame ionization and the melpar sulphur traces. As the boiling point of the fractions increase, there appears to be considerable sulphur-containing material with specific interaction lower than for the Lathom fractions. Also the amount of material involving negative specific interaction increases.

This procedure of trapping narrow-boiling fractions from the gas chromatographic simulated distillation and the rechromatographing on the salt-containing columns can at the present time be done automatically to some extent. In the future, this type of automation will certainly be improved.

Gas chromatography has many advantages over other methods of separation. The temperatures needed for the separations on the salt columns are no higher and sometimes lower than those required for comparable separations on liquid phases. Materials with very high specific interaction are exceptions. These columns are also ideal for coupling with mass spectroscopy because the separated materials do not become contaminated with any column bleed. The only limitation is the thermal stability of the materials to be separated.

LITERATURE CITED

(1) Phillips, G.S.G., and Scott, C.G., "Modified Solids for Gas-Solid Chromatography", Advances in Analytical Chemistry and Instrumentation 6 121 (1968).

(2) Scott, C.G., Nature 187, 143 (1960).

(3) Sawyer, Donald T., et al, Anal. Chem. 43, 941 (1971); 42, 190 (1970); 41, 1381 (1969); 40, 106, 409, 1368, 1847, 2013 (1968); J. Chromat. Sci. 8, 123 (1970).

(4) Hawton, J.J., and Campbell, Philip J., Chromat. Sci. 8, 675 (1970).

(5) Solomon, Paul W., Anal. Chem. 36, 476 (1964)

(6) Gump, Barry H., J. Chromat. Sci. 7, 755 (1969).

(7) Geiss, F., Versino, B. and Schlitt, H., Chromatographia 1, 9 (1968).

(8) Versino, B., and Geiss, F., ibid 2, 354 (1969).

(9) Grob, Robert L., Gondek, Robert J., and Seales, Thomas A., J. Chromatog. 53, 477 (1970).

(10) Onuska, F., Janak, J., Tesanik, K., and Kiselev, A.V., J. Chromatog. 34, 81 (1968).

(11) Vernon, F., J. Chromatog. 60, 406 (1971).

(12) Sawatzky, H., Smiley, G.T., George, A.E., and Clugston, D.M., A.C.S. Div., Fuel Chem. Preprints 15, 83 (1971).

(13) Sauerland, H.D., Biennstoff-Chemic 45, 55 (1964).

(14) Sauerland, H.D., and Zander, M., Erdol Kohle-Erdgas-Petrochemie 19, 502 (1966).

(15) George, A.E., Smiley, G.T., and Sawatzky, H., Dept. of Energy, Mines and Resources, Mines Branch Research Report R249 (1972).

(16) Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II, p. 553, Longmans, Green, and Co., New York, 1922.

(17) Kiselev, A.V. "Gas Chromatography 1964", A. Goldup Ed., Institute of Petroleum, London, 1965, p. 239.

(18) Brookman, David J., and Sawyer, Donald T., Anal. Chem. 40, 106 (1968).

ACKNOWLEDGEMENT

TABLE I

Retention Data on Lithium Chloride-Porasil D Column
(expressed in Kovat's Indices)

Compound	Column Temp. °C	Total Interaction	Non-Specific	Specific
Benzene	25	827	650	177
Dicyclohexyl	75	1104	1307	-203
Tetralin	100	1402	1158	244
Naphthalene	100	1429	1183	246
Phenylcyclohexane	100	1485	1300	185
Biphenyl	150	1684	1360	324
Phenanthrene	150	2103	1773	330
Anthracene	150	2100	1782	318
	200	2138	1782	356
Pyrene	200	2400	2080	320
Benzothiophene	100	1407	1160	247
Ethylphenylsulfide	150	1670	1145	525
Dibutylsulfide	150	2014	1070	944
Diphenylsulfide	150	1814	1560	254
Methylbenzylsulfide	150	1925	1130	795
Dibenzylsulfide	200	2415	1782	633
Dioctylsulfide	200	2669	1920	749
Benzylphenylsulfide	200	2138	1655	483
Dibenzothiophene	200	2014	1740	274
Thioxanthene	200	2078	1808	270
Thianthrene	200	2131	1960	171

TABLE II

Retention Data of Hydrocarbons on Lithium Chloride-Chromosorb A Column
(expressed in Kovat's Indices)

Compound	Total Interaction	Non-Specific	Specific
2, 3, 4 - Trimethylpentane*	724	755	-31
2, 2, 5 - Trimethylhexane*	789	793	-4
Mesitylene	1370	970	400
n-Butylbenzene	1335	1055	280
n-Butylbenzene*	1320	1055	265
Pentamethylbenzene	1757	1263	394
Hexamethylbenzene	1960	1450	510
Tetralin	1445	1158	287
Cis Decalin*	705	1108	-403
1-Methylnaphthalene	1614	1300	314
2-Methylnaphthalene	1614	1287	327
1, 2-Dimethylnaphthalene	1773	-	-
1, 4-Dimethylnaphthalene	1766	-	-
Phenylcyclohexane	1528	1300	228
Biphenyl	1790	1360	430
Diphenylmethane	1800	1426	374
Phenanthrene	2167	1773	394
2-Methylphenanthrene	2330	1897	433
9-Methylanthracene	2350	1949	401

*Determined isothermally.

TABLE III

Retention of Sulphur and Some Oxygen Compounds
on Lithium Chloride-Chromosorb A Column
(Expressed in Kovat's Indices)

Compound	Total Interaction	Non-Specific	Specific
Ethylphenylsulfide	1675	1145	530
Diphenylsulfide	1857	1560	297
Diphenyldisulfide	1987	1665	312
Dibenzothiophene	2050	1740	310
Thioxanthene	2167	1808	359
Diphenylether	1766	1397	369
Dibenzofuran	1895	1479	416
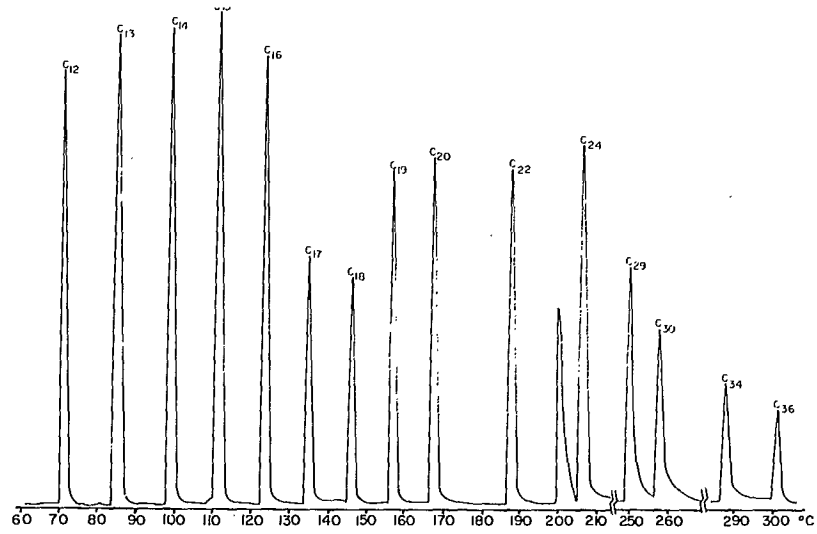
Figure 1.   Chromatography of Normal Alkanes on LiCl-Chromosorb A
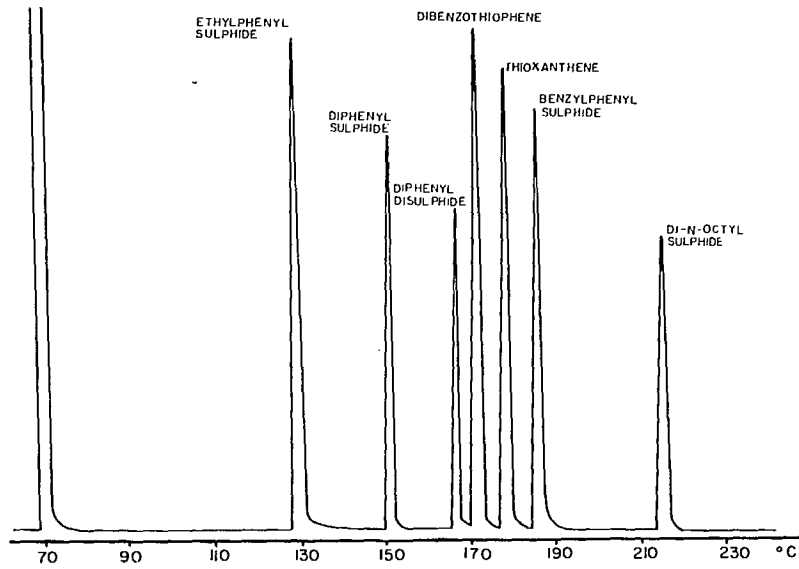
Figure 2.   Chromatography of Sulphides on LiCl-Chromosorb A
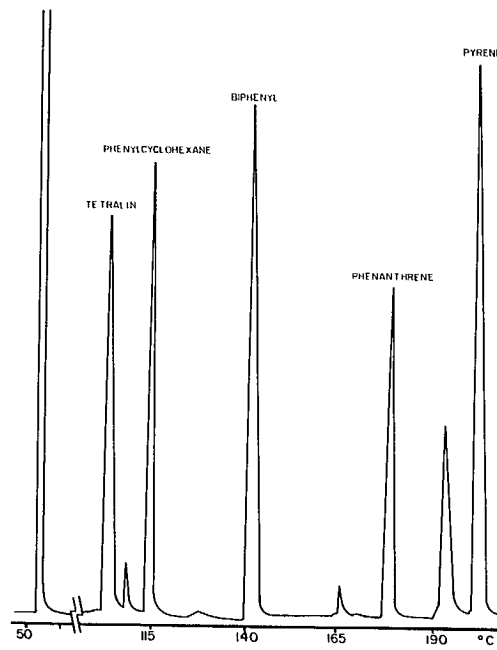
Figure 3. Chromatography of Aromatics on LiCl-Chromosorb A
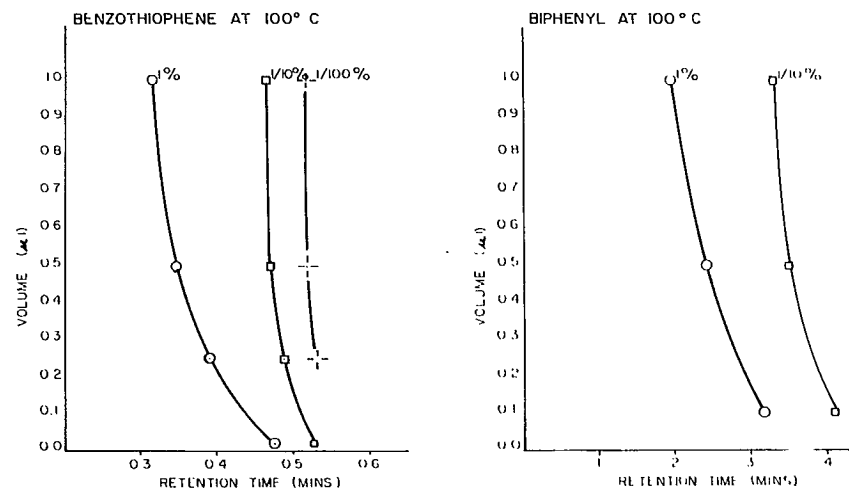
Figure 4. Effect of Sample Size on Retention Time
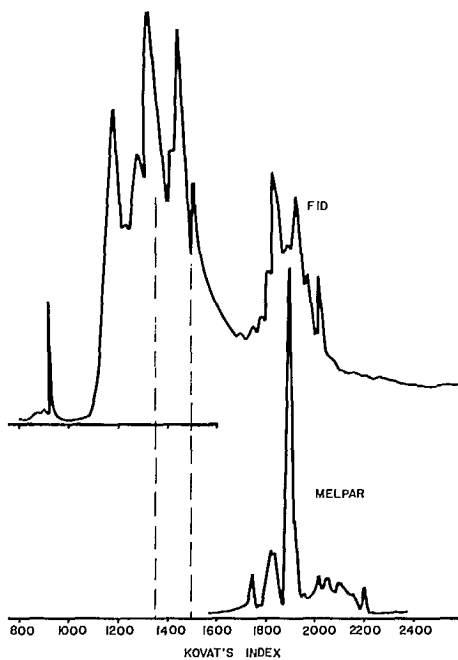
Figure 5. Lathom, b.p. 250-270°C, LiCl-Chromosorb A
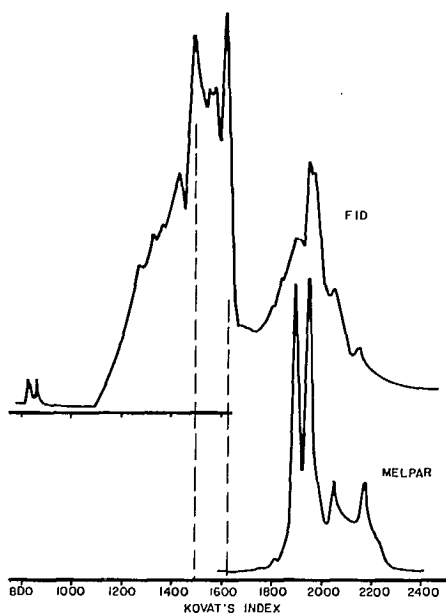
Figure 6. Lathom, b.p. 270-290°C, LiCl-Chromosorb A
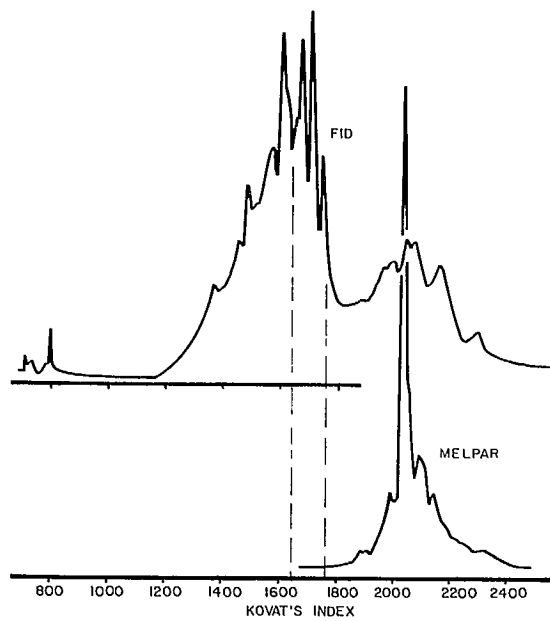
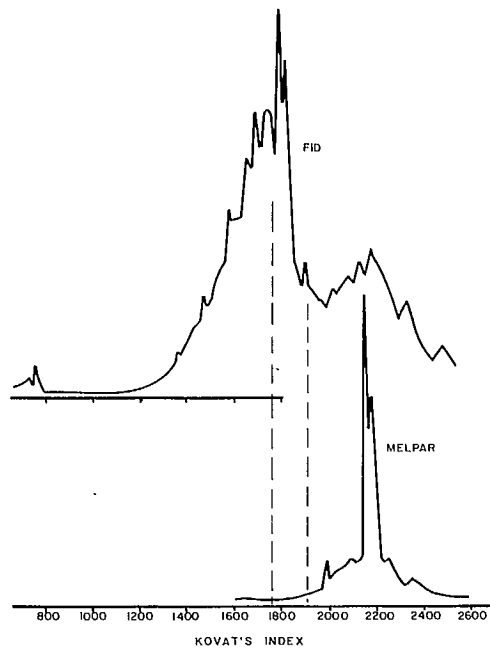Figure 7. Lathom, b.p. 290-310°C, LiCl-Chromosorb A
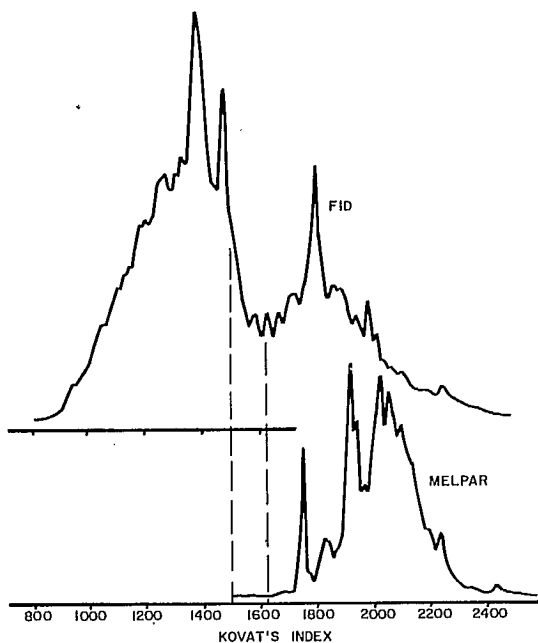

Figure 8. Lathom, b.p. 310-330°C, LiCl-Chromosorb A

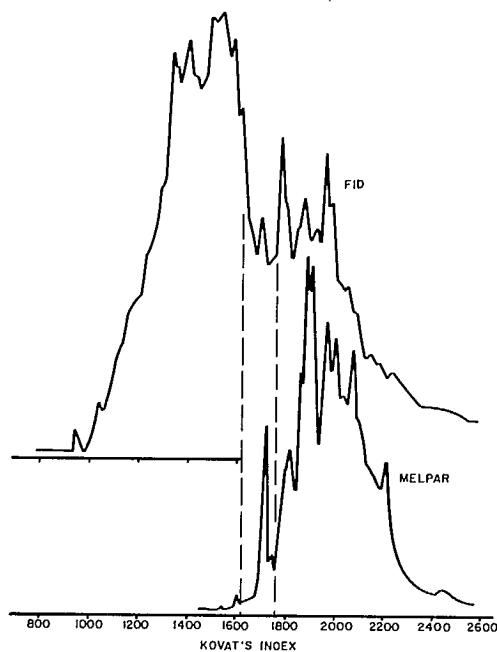Figure 9.   Lloydminster, b.p. 270-290°C, LiCl-Chromosorb A

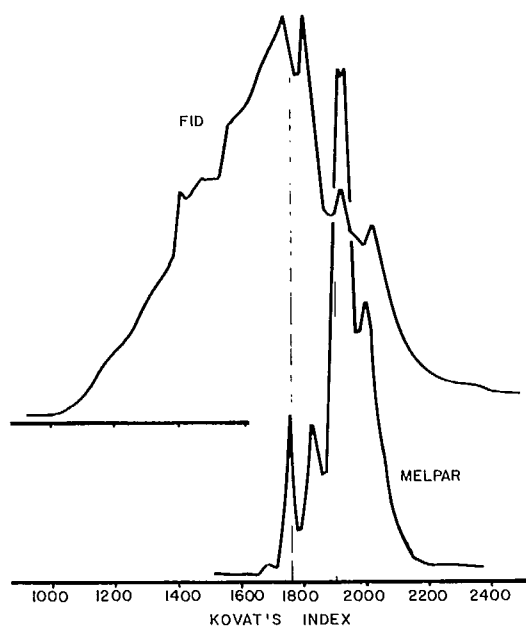Figure 10.   Lloydminster, b.p. 290-310°C, LiCl-Chromosorb A

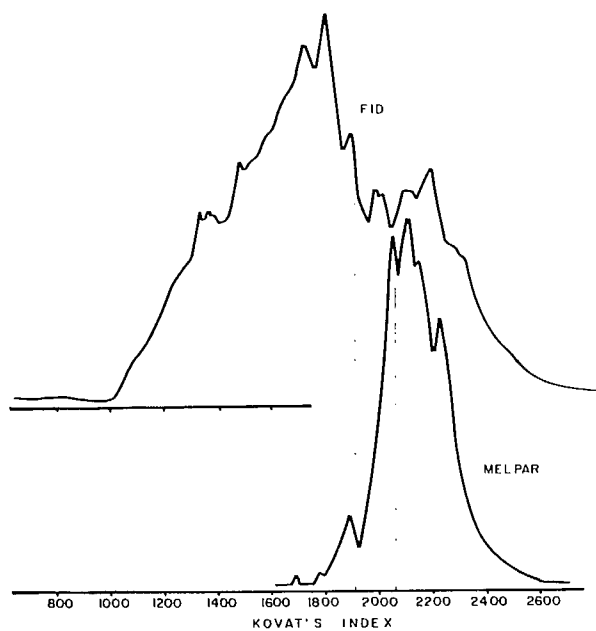Figure 11. Lloydminster, b.p. 310-330°C, LiCl-Chromosorb A

Figure 12. Lloydminister, b.p. 330-350°C, LiCl-Chromosorb A