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EVALUATION OF LITHIUM CHLORIDE-DIATOMACEOUS SILICA SYSTEMS FOR GAS CHROMATOGRAPHY OF PETROLEUM SULPHUR COMPOUNDS

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ABSTRACT

In this study Chromosorb W (diatomaceous silica) as such and also coated with lithium chloride was evaluated as column packing for the gas chromatographic separation of petroleum sulphur compounds. The Chromosorb W by itself was found to be of little value but quite efficient separations could be obtained after coating with lithium chloride, especially if the chromosorb had been acid washed before coating. Unlike other completely inorganic materials that have been used as column packings, the materials evaluated in this work required temperatures no higher than those required for separations on conventional column packings that contain organic liquids. Inorganic column packings are of great value for the investigation of high boiling point materials, like those found in low-grade crude oils, because they are thermally stable.

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EVALUATION DES SYSTEMES A CHLORURE DE LITHIUM
SILICE A DIATOMEES POUR LA CHROMATOGRAPHIE
EN PHASE GAZEUSE DES COMPOSES SULFUREUX DU PETROLE

par

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RESUME

Dans la présente étude les auteurs ont étudié le Chromosorb W (silice à diatomées) seul, puis recouvert de chlorure de lithium, en qualité de remplissage de colonne pour la chromatographie en phase gazeuse des composés sulfureux du pétrole. Le Chromosorb W tel quel était de très peu d'utilité mais on a pu obtenir des séparations très efficaces après l'avoir recouvert de chlorure de lithium, surtout après l'avoir lavé à l'acide avant de le recouvrir. Contrairement aux autres matières entièrement inorganiques qui ont servi de remplissages de colonne, les matières évaluées dans le présent rapport n'ont pas nécessité de températures plus élevées que celles qui sont requises pour les séparations dans le cas des remplissages conventionnelles de colonne qui renferment des liquides organiques. Les remplissages inorganiques de colonne sont d'une grande utilité dans l'étude de matières à point d'ébullition élevé telles que celles trouvés dans les pétroles bruts de basse qualité, parce qu'elles sont thermiquement stables.

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EVALUATION OF LITHIUM CHLORIDE-DIATOMACEOUS
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INTRODUCTION

Sulphur compounds represent a substantial portion of most low-grade petroleums and of the heavy ends of petroleum. They are the major contributors to pollution during combustion of petroleum products, and the removal of sulphur from oils is costly. Though the sulphur compounds in the gasoline and kerosene fractions of some petroleums have been fairly well studied in other laboratories, little is known of the sulphur in heavier fractions. Most low-grade petroleums consist mostly of the heavier fractions.

A better knowledge of these undesirable sulphur compounds might lead to their utilization and to better methods for their removal. Also, this knowledge might aid in understanding the geochemistry of petroleum and thus help in the search for oil deposits. An investigation was initiated to find out whether these sulphur compounds could be used for identifying sources of oil pollution.

Gas chromatography is one of the most convenient and powerful analytical techniques for separating sulphur compounds; therefore, the separation of the sulphur compounds in petroleum appeared to be worth a more detailed examination. The fact that the effluent from the gas chromatograph can be led directly into a mass spectrometer is also a great advantage because of the small weight of sample required for analysis and because of the precise characterizing data that can be obtained very quickly. This technique may be extended by reducing the effluent of the gas chromatograph, thus desulphurizing the petroleum fractions before sending them to the mass spectrometer.

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Unfortunately, elevated temperatures are required for the chromatography of petroleum fractions of higher-molecular-weight than gasolines which are the fractions of principal interest from the points of view of oil spillage finger-printing and geochemistry. At high temperatures, organic materials in the column packings become degraded and the degradation products contaminate the materials that are being separated. Some non-polar silicone rubbers can be used at fairly high temperatures but they separate only according to boiling points and not according to type. So far we have not been able to discover a polar organic material for gas chromatographic columns that is sufficiently stable thermally. Therefore inorganic column packings were considered.

Much use has been made of adsorbents such as carbons, aluminas, and silicas (17, 18, 19) but these adsorbents can be used for only low-molecular-weight compounds. The high temperatures required to elute tightly held high-molecular-weight materials would involve pyrolysis.

A number of articles dealing with salt-containing column packings for gas chromatography have appeared in the literature. Sawyer and co-workers have been the major contributors (1, 2, 3, 4, 5, 6, 7, 8, 11). McCreery and Sawyer (11) studied the gas chromatography of aliphatic, olefinic, and aromatic hydrocarbons as wel as halobenzenes on alumina and florisil (magnesium silicate) coated with sodium sulphate, sodium chloride, sodium molybdate and aluminum sulphate. Sodium chloride appeared to give the best results. Brookman and Sawyer obtained thermodynamic data by gas chromatography on alumina and porasil (porous silica beads) modified with sodium sulphate, bromide, and chloride (6, 7, 8). Hargrove and Sawyer investigated separation efficiencies of alumina modified with sodium sulphate and phosphate (5). Brookman and Sawyer (4) studied specific inter-actions of alumina modified with sodium chloride, sulphate, molybdate, and phosphate. It was claimed that different salts covered up different types of active sites on the alumina. Isbell and Sawyer (3) performed gas chromatography of hydrocarbons on porasil modified with sodium sulphate, sodium chloride, sodium molybdate, sodium phosphate, cobaltous sulphate, aluminum sulphate, and chromic sulphate. Sodium sulphate and phosphate were the best for separating aliphatic

hydrocarbons. Cobaltous sulphate was the best for aromatics. Olefins were not eluted from cobaltous, aluminum, and chromic sulphates. Cadogan and Sawyer (2) investigated the chromatography on silica gel modified with sodium chloride. Also, they studied surface complexes of aromatic molecules with silica gel and "Graphon" coated with lanthanum chloride (1).

Hawton and Campbell identified hydrogenated polyphenyls on column packings consisting of Chromosorb P, coated with chlorides of lithium, caesium, and calcium (10). Gump (12) gas chromatographed polycyclic aromatic hydrocarbons on diatomaceous earths coated with chlorides of alkali and alkaline earth metals. Lithium and caesium chlorides appeared to be the best.

Geiss, Versino and Schlitt (13) studied the gas chromatography of polyphenyls on Chromosorb P coated with various salts. They attributed non-reproducibility to a "pump effect" that was caused by adsorption on the inside surface of the metal tract between the column and the detector. They claim to have eliminated this effect by creating an artificial column bleed with a short after column and this bleed covers the adsorption sites in the metal tract. They also made a survey of salts on supports having different surface areas. If areas were greater than 100 m^2/g, excessive temperatures were required. If the areas were between 0.5 and 5 m^2/g, alkali and alkaline earth halides and hydroxides gave good results. If the areas were less than 0.5 m^2g, as in salts without supports, the alkali and alkaline earth salts were unsatisfactory, but salts of transition metals like cadmium sulphate, cupric sulphate, and silver nitrate could be used. Versino and Geiss (14) compared Chromosorb P and G, caesium chloride, cadmium sulphate, both as pure crystals and crystallized or fired on Chromosorb P, graphitized carbon black, porous polymer, and porous silica beads (porasil) by the adsorption of various C_6 - cyclohydrocarbons. Chromosorb P with fired caesium chloride gave the best separation.

Grob et al (15) studied strontium and barium halides as packing for gas chromatography. Kiselev et al (16) separated polyphenyls on carbon black and Chromosorb P coated with caesium chloride. Scott discussed retention of hydrocarbons on alumina modified with sodium iodide and silver nitrate and

on silica gel coated with lithium bromide. Vernon (21) studied the behaviour of aromatic hydrocarbons during chromatography on alumina modified with sodium hydroxide and impregnated with sodium chloride. He reported Kovat's retention indices and discussed column efficiencies for benzene.

According to Kiselev (22), interactions during gas-solid chromatography may be divided into non-specific and specific types. A non-specific interaction is representative of paraffinic hydrocarbons in which every bond is a sigma bond. Pi-bonded systems can exhibit specific interactions because of the presence of high electron density. The existence of specific interaction presupposes a substrate that couples with the specific centre of the adsorbate. Thus, graphitized carbon shows only non-specific interaction for all compounds but silica or alumina silicates can exhibit non-specific adsorption for aliphatics and a combination of non-specific and specific adsorption for olefins. Kiselev also notes that the usual concept of polar and non-polar adsorbates and adsorbents fails to explain the nature of physical adsorption.

Brookman and Sawyer (6) plotted the logarithms of the retention volumes against the boiling points of various compounds. They obtained a smooth curve for the normal alkanes and it was assumed that the retention of normal alkanes was purely non-specific. Also, it was assumed that the portion of the retention of a compound that was due to non-specific interaction with the column packing was the same as the retention of a normal alkane with the same boiling point. This non-specific portion could be obtained from the curve involving the normal alkanes even though a normal alkane with such a boiling point might not exist. The free energy of specific interaction of each compound was calculated using the value obtained by taking the vertical distance between the logarithm of the retention volume of the compound and the curve for the normal alkanes.

In our work involving bitumen (23, 24) it appeared that the Chromosorb W, coated with lithium chloride, gave the best separation of the inorganic column packings tested. However, an evaluation with pure compounds was required.

EXPERIMENTAL

The column packings consisted of 60 to 80-mesh Chromosorb W, both acid washed and not acid washed, that were used as such, or coated with 15 % lithium chloride. The coating procedure consisted of depositing the lithium chloride on the chromosorbs by evaporation of an aqueous solution from the chromosorbs. All packings were fired at 700°C for 30 minutes. The columns were made from U-shaped glass tubing, 6 feet x 0.25 inch. The columns were all used simultaneously in a Varian 2100 gas chromatograph fitted with hydrogen flame ionization detectors. The flow rate of the nitrogen carrier gas was 53 mℓ/min. The injections were made with a Hamilton 10-$\mu\ell$ micro-syringe. The sample size affected the retention time. The detector oven was kept 25°C warmer than the column to prevent condensation of the eluates.

The standard injection sample size was 0.9 $\mu\ell$ of a 1 % solution in benzene. However, many such injections had to be made to attain acceptable reproducibility, if the columns had not been in use for over 12 hours. It was found that, by injecting larger samples such as 10 $\mu\ell$ initially, the time required to obtain reproducibility was reduced considerably. All results that were accepted had been reproduced three or four consecutive times. The retention times were corrected for dead volume using methane.

The "pump effect" described by Versino was evident in this work. If the columns were not in use for several hours and the carrier gas continued to flow, then the retention increased. This was quite marked at higher temperatures. Because there was the continuous possibility of column changes, the retention times of the normal alkanes that were used as standards were determined frequently so that reliable Kovat's indices could be derived. Each injection of normal alkanes contained several of them that eluted before and after the compound being evaluated. Ideally the logarithm of the retention times of the normal alkanes should yield a linear plot with their number of carbon atoms. This linear plot could be obtained with the low-molecular-weight alkanes but, for higher-molecular-weight alkanes, there was often substantial deviation if the retention time was greater than 10 minutes. Therefore, at the higher

temperatures, only retention times shorter than 10 minutes were considered. The Kovat's indices were calculated by the formula:

$$I_x = 100 \left[\frac{\log V_{g(x)} - \log V_{g(A_Z)}}{\log V_{g(A_Z + 1)} - \log V_{g(A_Z)}} \right] + 100Z$$

where V_g denotes retention volume and the subscripts x, A_Z, and $A_Z + 1$ refer to the compound investigated, the normal alkane with carbon number Z, and with carbon number $Z + 1$. In this work, the retention times were measured in terms of distances of chart paper measured in cm. The recorder's chart speed was always 2.54 cm per minute.

Regeneration consisted of passing oxygen through the columns at 400°C for at least one hour.

Table I

Mercaptans	B.P. °C	Non-Specific Retention Value *
sec-Butyl	85	650
iso-Butyl	88	660
n-Butyl	97	690
tert-Amyl	119	770
sec-iso-Amyl	122	780
n-Amyl	127	800
1, 2-Ethanedi	146	870
n-Hexyl	151	900
Cyclohexyl	160	930
Phenyl	170	972
n-Heptyl	177	1010
tert-Octyl	160	930
o-Tolyl	194	1100
1-Octyl	199	1120
B-Phenylethyl	217	1207
Pinyl	210	1170
γ-Phenylpropyl	233	1290
n-Decyl	277	1530

Sulphides		
Diethyl	92	670
Tetramethylene	120	775
Diallyl	139	842
Pentamethylene	142	855
Di-n-propyl	143	860
Cyclohexene	180	1020
Di-tert-butyl	149	890

Table I (Cont'd)

Sulphides	B.P. °C	Non-Specific Retention Value *
Di-sec-butyl	165	950
Di-n-butyl	189	1065
Methylphenyl	190	1070
Benzylmethyl	197	1110
Ethylphenyl	203	1140
Di-n-Amyl	230	1275
Di-n-Hexyl	267	1470
Diphenyl	296	1660
Di-n-heptyl	298	1675
Benzylphenyl	310	1750
Di-n-octyl	322	1825
Dibenzyl	324 (est.)	1855
Thioxanthene	350	2050

Thiophenic Compounds		
2-Methylthiophene	113	750
3-Methylthiophene	115	755
2-Ethylthiophene	132	815
2,5-Dimethylthiophene	137	835
2,3-Benzothiophene	221	1225
2,2-Bithiophene	260	1435
Dibenzothiophene	332	1910

Compounds with two sulphur atoms		
1,2-Ethanedithiol	146	870
n-Propyldisulphide	194	1100
Dithiane	200	1122
2,2-Bithiophene	260	1435
Phenyldisulphide	310	1750

Table I (Cont'd)

Compounds with two sulphur atoms	B.P. °C	Non-Specific Retention Value *
Thianthrene	366	2180
4, 7-Dithiadecane	250	1380
3, 8-Dithiadecane		
2, 9-Dithiadecane	260	1448
Benzyldisulphide		

Various Hydrocarbons		
Toluene	111	740
Ethylcyclohexane	132	815
o-Xylene	144	865
m-Xylene	139	845
p-Xylene	138	842
Mesitylene	165	950
Indene	182	1025
Tetralin	207	1160
Naphthalene	218	1205
Bicyclohexyl	238	1320
Phenylcyclohexane	238	1320
β-Methylnaphthalene	242	1335
α-Methylnaphthalene	243	1345
Biphenyl	256	1410
Acenaphthene	278	1540
Fluorene	293	1640
Phenanthrene	340	1960
Anthracene	355	2090
Pyrene	365	2170

* Kovat's Indices.

Table II

Retention Times* of Normal Hydrocarbons at 50°C Over a Period of Time

	T, °C	LiCl-Ch-W-aw **	LiCl-Ch-W	Ch-W-aw	Ch-W
Nonane	50	3.03	2.87	4.20	10.3
		2.95	2.83	4.62	7.45
		2.65	2.67	3.75	6.45
		2.65	2.85	-	-
		2.24	2.32	2.64	3.35
Decane	50	8.70	7.12	12.30	33.10
		8.07	7.60	12.93	22.7
		7.15	6.78	10.20	18.70
		7.24	7.57	10.60	20.60
		7.09	7.26	9.60	-
		5.65	5.80	7.18	-
		5.57	5.55	6.42	8.94
Undecane	50	23.81	20.78	34.84	-
		22.50	21.08	37.40	66.7
		19.63	18.93	28.00	55.5
		20.02	19.92	29.10	-
		19.95	20.17	26.40	-
		15.61	15.41	19.07	-
		14.66	14.43	16.63	24.34

* Distance of recorder chart paper in cm, for time in minutes divide by 2.54.

** LiCl-Ch-W-aw - mixture of lithium chloride and acid washed Chromosorb W.
   LiCl-Ch-W - mixture of lithium chloride and Chromosorb W.
      Ch-W-aw - acid washed Chromosorb W
        Ch-W - Chromosorb W.

Table III

Average Retention Times* of Normal Alkanes at Temperatures Above 50°C

T, °C	Hydrocarbon		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
75	Nonane	B	0.75	0.75	0.78	1.10
	Decane	A**	2.10	2.01	2.50	2.45
		B**	1.68	1.63	1.45	2.35
	Undecane	A	4.72	4.60	5.75	10.4
		B	3.30	3.20	5.25	-
	Dodecane	A	10.5	10.30	-	-
		B	10.6	10.05	-	-
100	Undecane		1.44	1.50	1.45	2.32
	Dodecane		3.07	3.11	3.15	5.3
	Tridecane		6.10	6.20	6.55	11.1
	Tetradecane		13.8	13.25	-	-
150	Tridecane		0.75	0.70	-	0.93
	Tetradecane	A	1.25	1.25	0.9	1.48
		B	-	-	0.4	-
	Pentadecane	A	2.25	2.20	1.55	2.95
		B	-	-	0.70	1.25
	Hexadecane	B	2.25	2.15	-	2.30
175	Heptadecane		1.73	1.83	0.80	1.50
	Octadecane		2.65	2.66	1.0	2.10
	Nonadecane		4.03	3.90	-	-
200	Octadecane	A	1.30	-	-	0.70
		B	0.85	-	-	-
	Nonadecane	A	2.00	2.77	0.75	1.70
		B	1.37	1.35	0.60	1.20
	Eicosane	A	2.90	2.35	-	-
		B	2.25	2.30	-	2.00
	Henecosane	A	4.40	-	1.65	3.75
		B	4.00	3.70	1.3	-
	Docosane	A	8.80	6.50	-	-
		B	-	-	-	5.1

* Distance of recorder chart paper in cm, for time in minutes divide by 2.54.

** The B set of retention times were obtained at least
two weeks after the A set of retention times.

Table IV

Retention Times*for Normal Alkanes After Regeneration

T, °C	Hydrocarbon	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw
50	C_9	3.05		1.0
	C_{10}	4.75	4.2	3.4
	C_{11}	12.55	10.7	12.0
100	C_{13}	5.0	4.6	5.6
	C_{14}	10.3	9.4	11.75
	C_{15}	21.3	19.4	24.5
150	C_{15}	1.9	1.7	2.4
	C_{16}	3.3	3.0	4.2
	C_{17}	5.8	5.2	7 4
	C_{18}	-	9 1	15.1
175	C_{16}	1.3	1.2	1.3
	C_{18}	3.2	3 0	3.5
	C_{19}	5.2	4 9	5.8
	C_{20}	8.6	7.9	9.0
	C_{21}	13.9	12.8	15.4
200	C_{21}	4.4	5.2	4.4
	C_{23}	10.5	10.0	10.1
	C_{25}	25.0	23.6	23.5
225	C_{21}	1.5	1.7	-
	C_{23}	3.2	3.5	-
	C_{25}	6.9	7.3	-

* Distance of recorder chart paper in cm, for time in minutes divide by 2.54.

Table V

Kovat's Indices of Mercaptans

T, °C	Mercaptan	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
50	n-Butyl	977	989	945	934
	iso-Butyl	942	982	905	-
	sec-Butyl	927	952	899	-
	tert-Amyl	946	973	924	955
	sec-iso-Amyl	930	950	894	-
75	sec-iso-Amyl	900	949	989	-
	n-Amyl	1096	1149	1025	1065
	n-Hexyl	1118	1144	1047	1073
	Cyclohexyl	1074	1096	1026	-
	n-Heptyl	1204	1243	1174	-
	1, 2-Ethanedi	1087	1098	941	920
100	n-Hexyl	1136	1172	1090	1131
	Cyclohexyl	-	-	1073	1095
	1, 2-Ethanedi	1050	1120	-	-
	Phenyl	1176	1185	1009	1049
	tert-Octyl	1124	1134	1068	1187
	o-Tolyl	1237	1252	1073	1125
150	2-Pinanyl	1444	1531	1410	1455
	3, 4-Toluenedi	1687	1692	-	1688
	n-Decyl	-	-	1483	1554
175	γ-Phenylpropyl	1781	1758	-	-
	β-Phenylethyl	1588	1611	-	-
200	γ-Phenylpropyl	1894	1901	-	-
	Triphenylmethyl	2018	2002	2067	2089
After Regeneration					
50	n-Butyl	1060	1132	1042	-

Table VI

Specific Retention Values of Mercaptans

Mercaptan	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
sec-Butyl	277	302	249	-
iso-Butyl	282	322	245	-
n-Butyl	287	299	255	244
tert-Amyl	176	203	154	185
sec-iso-Amyl	150	170	114	-
n-Amyl	296	349	225	265
1, 2-Ethanedi	217	228	71	50
n-Hexyl	236	272	190	231
Cyclohexyl	144	166	96	-
Phenyl	204	213	37	77
n-Heptyl	114	253	184	-
tert-Octyl	194	204	138	157
o-Tolyl	237	252	27	25
2-Pinyl	274	361	260	285
B-Phenylethyl	381	404	-	-
γ-Phenylpropyl	491	468	-	-

After Regeneration

n-Butyl	370	442	352	—

Table VII

Kovat's Indices of Sulphides

T, °C	Sulphide	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
50	Tetramethylene	1092	1149	1036	1025
	Diethyl	952	982	881	-
75	Tetramethylene	1117	1181	1029	1031
	Diallyl	1218	1210	1112	1123
	Pentamethylene	1164	1237	1084	1092
100	Cyclohexene	1190	1263	1123	1145
	Di-n-propyl	1194	1282	1092	1087
	Di-tert-butyl	1160	1191	1173	1133
	Di-sec-butyl	1222	1280	1196	1151
	Diallyl	1160	1279	1058	1079
	Pentamethylene	1139	1223	1053	1083
	Ethylphenyl	1315	1356	1205	-
150	Di-n-butyl	1413	1449	1364	1354
	Methylphenyl	1271	1323	-	1214
	Ethylphenyl	1346	1370	1300	1272
	Benzylmethyl	1442	1474	1362	1366
	Di-n-amyl	1596	1630	1546	1544
	Diphenyl	1634	1672	-	1578
175	Benzylphenyl	1915	1962	1741	1888
	Thioxanthene	1800	1881	1800	1843

Table VII (Cont'd)

Kovat's Indices of Sulphides

T, °C	Sulphide	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
200	Dihexyl	1964	2050	-	-
	Diheptyl	2123	2292	1932	1915
	Dioctyl	2280	2470	2115	2106
	Dibenzyl	2000	2050	1986	2021
	Thioxanthene	1854	1900	-	1956

After Regeneration

150	Diphenyl	1910	1995	1858	-
175	Di-n-butyl	2025	2173	1612	-
225	Di-n-octyl	2887	2989	-	-

Table VIII

Specific Retention Values of Sulphides

Sulphide	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
Diethyl	282	312	211	-
Tetramethylene	317	374	261	250
Diallyl	376	368	270	281
Pentamethylene	309	382	229	237
Di-n-propyl	326	314	224	219
Cyclohexene	170	243	3	25
Di-tert-butyl	270	301	283	257
Di-sec-butyl	272	330	246	201
Di-n-butyl	348	384	299	289
Methylphenyl	201	263	-	144
Ethylphenyl	206	230	160	132
Benzylmethyl	332	364	252	256

Table VIII (Cont'd)

Specific Retention Values of Sulphides

Sulphide	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
Di-n-amyl	321	355	271	269
Diphenyl	-26	12	-	-82
Di-n-hexyl	494	580	-	-
Di-n-heptyl	448	617	257	240
Benzylphenyl	165	212	-9	138
Di-n-octyl	455	645	290	281
Dibenzyl	145	195	131	166
Thioxanthene	-196	-150	-	-94

After Regeneration

Di-n-butyl	960	1108	547	-
Di-n-octyl	1062	1164	-	-
Diphenyl	250	335	198	-

Table IX

Kovat's Indices of Thiophenic Compounds

T, °C	Compound		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
50	2-Methylthiophene		920	928	838	859
	3-Methythiophene		915	924	858	837
	2, 5-Dimethylthiophene	A	1050	1061	968	966
		B	996	997	881	880
	Ethylthiophene		1020	1024	936	944
100	2, 3-Benzothiophene		1245	1244	1142	1192
150	2, 3-Benzothiophene		1264	1272	-	-
	2, 2-Bithiophene		1462	1457	1388	1430
175	Dibenzothiophene		1815	1827	1752	1841

After Regeneration

T, °C	Compound		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
100	2, 3-Benzothiophene		1396	1387	1363	-
175	Dibenzothiophene		2101	2147	1955	-

Table X

Specific Retention Values of Thiophenic Compounds

Compound	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
2-Methylthiophene	170	178	87	109
3-Methylthiophene	160	169	103	82
2, 5-Dimethylthiophene	215	226	133	131
Ethylthiophene	205	209	121	129
2, 3-Benzothiophene	20	19	-83	-33
2, 2-Bithiophene	27	22	-47	- 5
Dibenzothiophene	-95	-83	-158	-69

After Regeneration

2, 3-Benzothiophene	171	162	138	-
Dibenzothiophene	191	237	45	-

Table XI

Kovat's Indices of Compounds with Two Sulphur Atoms

T, °C	Compound	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
100	Dithiane	1298	1335	1073	-
175	Dithiane	1336	1386	-	1209
	Propyldisulphide	1264	1249	-	-
	Phenyldisulphide	1800	1817	1789	1800
200	Thianthrene	1950	1962	1986	2057
	4, 7-Dithiadecane	1852	1904	-	1862
	3, 8-Dithiadecane	1950	1938	-	1886
	2, 9-Dithiadecane	2018	1995	-	1877
	Benzyldisulphide	2125	2176	2163	2222
After Regeneration					
200	Thianthrene	2309	2407	2279	-

Table XII

Specific Retention Values of Compounds with Two Sulphur Atoms

Compound	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
1, 2-Ethanedithiol	217	228	71	50
n-Propyldisulphide	164	149	-	-
Dithiane	210	264	-	87
2, 2-Bithiophene	27	22	- 47	- 5
Phenyldisulphide	50	67	39	50
Thianthrene	-230	-242	-194	-127
4, 7-Dithiadecane	472	524	-	482
3, 8-Dithiadecane	-	-	-	-
2, 9-Dithiadecane	578	545	-	437

After Regeneration

Thianthrene	129	227	99	-

Table XIII

Kovat's Indices of Various Hydrocarbons

T, °C	Compound		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
25	Ethylcyclohexane		754	754	754	726
	Toluene		855	851	776	785
50	o-Xylene		1044	1045	912	917
	m-Xylene		1028	1035	900	852
	p-Xylene		1034	1034	900	851
75	Indene		1244	1292	1118	1150
	Mesitylene	1	1153	1240	1069	1105
		2	1248	1288	1076	1116
100	Indene		1190	1220	1089	1108
	Mesitylene	1	1168	1204	1075	1090
		2	1209	1248	1085	1100
	Naphthalene		1296	1301	1231	1272
	α-Methylnaphthalene		1409	1418	1238	1354
	β-Methylnaphthalene		1422	1436	1232	1381
	Dicyclohexyl		1140	1113	1168	-
	Tetralin		1249	1261	1155	-
150	Tetralin		1277	1289	-	1277
	Naphthalene		1313	1300	-	1319
	Phenylcyclohexane		1375	1384	1348	1364
	Biphenyl		1552	1557	1453	1481
	Acenaphthene		1584	1593	1528	1536
	Fluorene		-	-	1568	1681

Table XIII (Cont'd)

Kovat's Indices of Various Hydrocarbons

T, °C	Compound	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
175	Fluorene	1775	1786	1623	1685
	Phenanthrene	1892	1909	1748	1809
	Anthracene	1940	1930	1835	1876
200	Pyrene	2121	2154	2100	2230

After Regeneration

T, °C	Compound	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
100	Dicyclohexyl	1122	1125	1192	-
150	Phenylcyclohexane	1565	1600	1439	-
	Biphenyl	1800	1842	1569	-
200	Anthracene	2287	2335	2229	-

Table XIV

Specific Retention of Various Hydrocarbons

Compound		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
Toluene		115	111	36	45
Ethylcyclohexane		- 61	- 61	- 61	- 89
o-Xylene		179	180	47	52
m-Xylene		183	190	65	7
p-Xylene		192	192	58	9
Mesitylene	1	208	290	119	155
	2	298	338	126	166
Indene		219	267	193	225
Tetralin		89	101	- 5	
Naphthalene		91	96	26	67
Dicyclohexyl		-180	-207	-152	-
Phenylcyclohexane		55	64	28	24
β-Methylnaphthalene		87	101	-103	46
α-Methylnaphthalene		64	73	-107	9
Biphenyl		142	147	43	71
Acenaphthene		44	53	- 12	- 4
Fluorene		135	146	- 17	45
Phenanthrene		- 68	- 51	-212	-151
Anthracene		-150	-160	-255	-214
Pyrene		- 49	- 16	- 70	- 60

After Regeneration

		LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
Dicyclohexyl		-198	-195	-128	-
Phenylcyclohexane		245	280	119	-
Biphenyl		390	432	159	-
Anthracene		197	245	139	-

Table XV

Efficiences of Separation

Compound Type	Efficiencies (plates/ft)			
	LiCl-Ch-W-aw	LiCl-Ch-W	Ch-W-aw	Ch-W
Alkyl Mercaptans	195	183	107	44
After Regeneration	68	72	30	-
All Sulphides	204	186	167	93
After Regeneration	1580	815	172	-
Thiophenic Compounds	313	241	132	116
After Regeneration	880	1050	98	-
Normal Alkanes	288	317	342	324
After Regeneration	1320	1131	427	-
Other Hydrocarbons	386	356	209	187
After Regeneration	719	409	146	-

DISCUSSION

Our approach for the determination of specific retention values is similar to that of Brookman and Sawyer. However, we are expressing our values in terms of differences in Kovat's indices between that of the compound and that of the normal alkane with the same boiling point. A plot has been made of the Kovat's indices of normal alkanes against their boiling points. The Kovat's indices of normal alkanes are by definition the number of carbon atoms multiplied by 100. This plot is shown in Figure 1. The non-specific retention value of a compound is obtained by taking a point on this plot corresponding to the boiling point. The boiling points and non-specific retention values are shown in Table I. Conversion of boiling points under reduced pressure to atmospheric pressure were made with a pressure-temperature alignment chart (25).

Some of the results obtained in this work would appear to indicate that the retention of normal alkanes is not entirely non-specific. This is noted in the case of retention of some aromatic sulphur compounds and aromatic hydrocarbons on columns that have undergone some deactivation. In these cases negative specific retention values were obtained. Such an effect had been noted by Kiselev (22).

The Kovat's indices and specific retentions of the various types of compounds are discussed in the following paragraphs.

<u>Normal Alkanes</u>

The retention times of nonane, decane and undecane at 50°C are shown in Table II. These values are chronological daily averages that were obtained over a period of about one month. It can be seen that there is a gradual decrease in retention with time. The retention values of the various normal hydrocarbons that were obtained above 50°C are shown in Table III. For a few hydrocarbons, there was a time interval of two weeks or more between the times at which they were used. During this time interval, some changes occurred and therefore two sets of time values designated by "A" and "B" are listed. It should be mentioned that before these data were collected, numerous injections including

neat samples were made. Thus, the columns had undergone some change before the repeated results were obtained.

From these tables, it can be seen that the low-molecular-weight hydrocarbons at low temperature are retained more on the uncoated chromosorbs than on the chromosorbs coated with lithium chloride. As the molecular weight of these normal hydrocarbons increases and with it the required column temperature, the retention on the coated chromosorbs increases relative to the uncoated chromosorbs. At 150°C, the retention on the coated chromosorbs is greater than on the uncoated acid washed chromosorb and, at 175°C, the retention on the coated chromosorb is even greater than on the uncoated chromosorb.

The retention values obtained after regeneration are shown in Table IV. It can be seen that, in the case of the lower-molecular-weight alkanes at the lower temperature, the original activity of the columns could not be attained. In fact, the final activity before regeneration was greater than before. For the higher-molecular-weight normal alkane at the higher temperature, greater activity was attained. The uncoated chromosorb after regeneration is a little more active than the coated chromosorb.

Mercaptans

The Kovat's indices and the specific retention values are shown in Tables V and VI. It can be seen that the values from the lithium coated chromosorbs are higher than for the uncoated chromosorbs. In general, the values from the uncoated chromosorb, though lower than those from the coated chromosorbs, follow the same general trend. Though branching does not appear to affect the retention values of the butyl mercaptans, it certainly appears to lower the values for amyl and octyl mercaptans.

The specific retention values of the normal alkyl mercaptans are the largest for the amyl mercaptans and then decrease with increasing molecular weight.

The specific retention for the cyclohexyl mercaptan is lower than that of most other mercaptans. Such an effect was also noted by Sawyer et al (6) and was explained on the basis that carbon atoms not all being on the same plane could not all contact the adsorbing surface.

The specific retention for the thiophenol was lower than for the n-hexyl mercaptan. This was much more marked for the uncoated than for the coated chromosorbs. The specific retention values for the o-tolyl mercaptan was higher than for thiophenol, if obtained from coated chromosorbs, but lower, if obtained from uncoated chromosorbs.

The specific retention values for the phenyl-substituted alkyl mercaptans were higher than those of most other mercaptans. Here, both the aryl and mercapto groups contribute to the retention. In these cases, the results obtained from the uncoated columns were considered unreliable because it was believed that these mercaptans were decomposing during chromatography.

The specific retention of the 1, 2-ethanedithiol was not as great as expected probably because the ethylene group cannot provide the required electron density to the thiol groups.

Sulphides

The Kovat's indices and specific retention values are shown in Tables VII and VIII. In general, the specific retention values for the alkyl sulphides are large. There appears to be a general increase of specific retention with increasing molecular weight. Possibly this might be ascribed to greater column activity at the higher temperatures. As for the mercaptans, the values from the coated columns are greater than from the uncoated chromosorbs. This difference became more marked after regeneration.

The cyclic tetramethylene and pentamethylene sulphides have higher specific retention values than the corresponding dialkyl sulphides probably because the sulphur atom is more exposed. Branching of alkyl groups reduces specific retention as the sulphur atoms become more shielded.

The diallyl sulphide shows the effect of unsaturation in that it has higher specific retention than the dipropyl sulphide. The specific retention of the cyclohexene sulphide is lower than those of corresponding alkyl sulphides on the coated chromosorbs and almost non-existent on the uncoated chromosorbs. This might be due to non-planarity and/or to ring strain in the thiacyclopropane molecule.

If the sulphur atom is attached directly to an aromatic group, the specific retention is lowered substantially. Thus, the specific retention for ethylphenyl sulphide is much lower than for methylbenzyl sulphide. In the cases of diphenyl sulphide and thioxanthene, negative specific retention values were obtained.

After regeneration, the specific retentions of both aryl and alkyl sulphide increased markedly as can be seen from the values obtained for diphenyl and dioctyl sulphides. However, the difference in specific retention between the alkyl and aryl sulphides become even more marked. On the regenerated chromosorbs that had been coated with lithium chloride, specific retention of both the high- and low-molecular-weight normal alkyl sulphides was between 1000 and 1100.

Thiophenic Compounds

The Kovat's indices and specific retention values for thiophenic compounds are shown in Tables IX and X. The specific retention of these compounds is much lower than of the mercaptans and alkyl sulphides. Alkyl substitution on the thiophenes enhances retention. It is unfortunate that alkylated benzothiophenes and dibenzothiophenes were not available for comparison. As in the case of the sulphides, direct attachment of a sulphur atom to a phenyl group appears to cause low specific retention as in benzothiophene. When the sulphur atom is attached to two phenyl groups like in dibenzothiophene, a negative specific retention was obtained. However, regeneration raised the specific retention values to positive levels.

The dimethylthiophene values were redetermined after an extended period of time and, therefore, two sets of values are given. It is obvious that the columns had undergone change during the time interval.

Compounds with Two Sulphur Atoms

The Kovat's indices and specific retention values of these compounds are listed in Tables XI and XII. All the specific retention values are low except those of the dithiadecanes. These dithiadecanes have values similar to those of alkyl sulphides but the additional sulphur atom does not appear

to increase the retention very much. The specific retention for thianthrene was quite negative and, after column regeneration, was quite low. Again, it appears that sulphur attached to aryl groups causes low specific retention.

Various Hydrocarbons

The specific retention values for the hydrocarbons are generally low compared with some sulphur compounds like alkyl sulphides. In most cases, higher values are obtained from the coated than the uncoated chromosorbs. Negative specific values were obtained for several of these hydrocarbons.

An interesting series of hydrocarbons is biphenyl and its reduction products. The specific retention values decrease as the phenyl groups are saturated. The specific retention values for the dicyclohexyl are negative and the ones obtained on the coated chromosorbs are more negative than the uncoated chromosorb. Regeneration of the columns raised the specific retention of the biphenyl and phenyl cyclohexane but not of the dicyclohexyl. Hydrogenation also lowers the specific retentions as can be seen in the case of naphthalene and tetralin.

It appears that quite low specific retention values are obtained from saturated cyclic hydrocarbons as can be seen from the values of ethylcyclohexane and bicyclohexyl. Sawyer (4) made similar observations and described this phenomenon to non-planarity.

Methyl substitution appears to increase specific retention of the benzene ring as can be seen from the values for toluene, xylene, and mesitylene. However, this effect cannot be observed for naphthalene. In this case, monomethyl substitution lowered specific retention.

The sample of mesitylene that was used was claimed to be of high purity. Only a single symmetrical peak was obtained during gas chromatography on silicone rubber SE-30 and only a single parent ion was obtained during mass spectroscopy. However, two main and some minor peaks were obtained in this work. The two main peaks were well separated on the lithium chloride chromosorbs but not on the uncoated chromosorbs. The retention values of the main peaks are reported but the mesitylene peak could not be identified.

The specific retention values of phenanthrene, anthracene and pyrene were all negative. The value for anthracene was the lowest. Regeneration of the columns raised the specific retention value for the anthracene to a fairly positive level.

Before regeneration, the retention values obtained for the hydrocarbons were very similar to the values obtained by Vernon (20) on alumina that had been modified with sodium hydroxide and impregnated with sodium chloride. His retention indices of the polycyclic aromatic hydrocarbons were obtained at 400°C, though in this work the value for pyrene was obtained at 200°C and the values for the others were obtained at lower temperatures.

Efficiencies

The efficiencies were obtained from the formula: $16 \left(\dfrac{\text{retention time}}{\text{peak width}} \right)^2$ in which the peak width is determined as the distance between the intercept of the tangents to the points of inflection on either side of the peak. The averages of the various types of compounds are shown in Table XV. It can be seen that Chromosorb W that has been coated with lithium chloride leads to the best separation efficiency, especially after regeneration. The uncoated chromosorbs have low efficiency and acid washing appears to have increased the efficiency on both the coated and uncoated chromosorbs. Acid washing removes some of the oxides of aluminum and iron and thus increases efficiency by reducing the tailing.

The efficiency of separation for the alkyl mercaptans was low and regeneration of the columns reduced the efficiency. This is not too surprising because these compounds are highly polar and have an acidic group. The peak width for thiophenol was greater than the retention time. The presence of significant amounts of mercaptans in the high boiling petroleum fractions is unlikely, therefore, there is not much concern about the low efficiency for separation of the mercaptans at this time.

In our bitumen work, it also appeared that the Chromosorb W that had been washed with acid and coated with lithium chloride was the most efficient column packing material that had been tested. Also, it was found that the column

deteriorated with use but that it could be regenerated to restore efficiency. In Figure 2, it can be seen how the column had deteriorated. In the upper chromatogram, it can be seen that a sulphur-free material eluted before a sulphur-containing material and that there was a fair separation between them. In the lower chromatogram it can be seen that the separation was very poor. After regeneration, the original chromatogram could be reproduced. The high Melpar sulphur peak in the lower chromatogram is the result of faster rise in oven temperature that caused faster elution of the sulphur containing components.

There are very few references as to the efficiencies of columns. However, Vernon (21) found that the efficiency of his 45-cm column increased from 230 to 284 plates/ft while the temperature was increased from 200 to 300°C. We calculated efficiencies of from 171 to 218 plates for the chromatograms he shows of some polycyclic aromatic hydrocarbons. Our columns were about four times the length of Vernon's column, though efficiency does not vary linearly with column length. The lithium-coated, acid-washed Chromosorb W column compares favourably with that of Vernon's, especially after regeneration. As mentioned earlier in this report, Vernon's retention values in terms of Kovat's indices were similar to ours before regeneration. However, after regeneration our values were much larger indicating that the separation of saturated from aromatic material would be greater. Vernon required a temperature of at least 200°C to chromato- graph benzene, whereas at this temperature we obtained our retention values for pyrene and benzene elutes at room temperature.
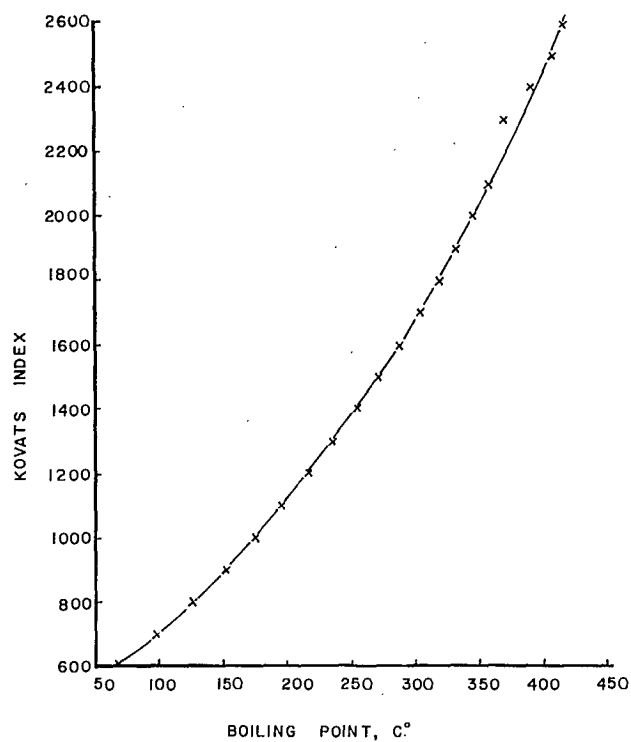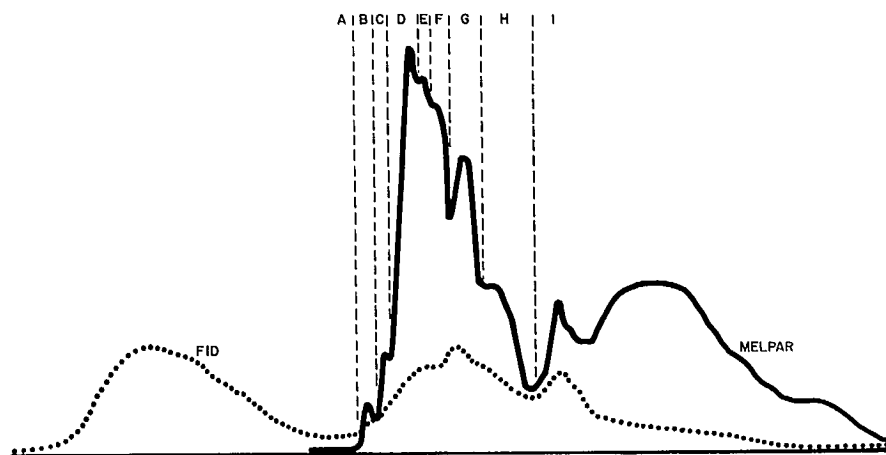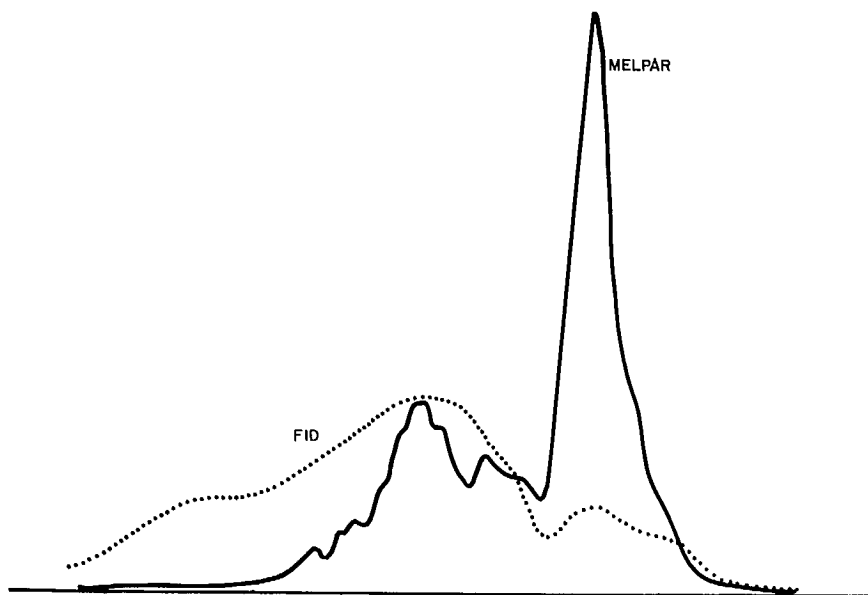

ACKNOWLEDGEMENT

Fig.(I) PLOT OF KOVATS INDICES AGAINST
BOILING POINTS OF n₋ALKANES.

Fig. (2) Bitumen Fraction No. 80, boiling at
348°C, Chromatographed on LiCl - Chromosorb W
Preparative Column.

(1) Original analysis and analysis after
regeneration with oxygen at 400°C.

(2) Analysis on degraded column after several
months use.

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