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GAS CHROMATOGRAPHIC CHARACTERIZATION OF SULPHUR COMPOUNDS IN THE 93–162° GASOLINE CUT FROM ROMASHKINO CRUDE OIL USING KOVÁTS RETENTION INDICES

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SUMMARY

Identification of various sulphur constituents in the 93–162° heavy gasoline cut from Romashkino crude oil was effected by using the Kováts retention index system. A concentrate of sulphur compounds was prepared by preparative gas–liquid chromatography on formamide as the stationary phase. The retention behaviour of some of the reference hydrocarbons and sulphur compounds was studied on squalane, dibutyl phthalate and polyethylene glycol 400 as stationary phases on steel capillary columns at two different temperatures (86° and 120°). Retention indices are presented.

INTRODUCTION

It is desirable to know the types of sulphur compounds that occur naturally in petroleum, not only for affecting their removal during refinery operations but also for studies by the chemist and geologist concerned with the origin of petroleum.

SUNNER *et al.*[1] reported the quantitative separation of a number of aliphatic thiols, from propyl to hexyl mercaptan, on a diphenylamine–dioctyl phthalate packed column. RYCE AND BRYCE[2] have investigated the separation of a synthetic blend of volatile organic sulphur compounds. DESTY and coworkers[3,4] included several classes of sulphur compounds in their evaluation of column packings such as aryl alkyl detergents. KARCHMER[5] reported that columns containing β,β'-iminodipropionitrile on Celite are very good for the separation of sulphur compounds. AMBERG[6] separated mercaptans, sulphides and alkylthiophenes on packed tricresyl phosphate columns and reported the relative retention times of eight thiols, five sulphides and eleven thiophenes. SULLIVAN *et al.*[7] reported the separation of a mixture of twelve mercaptans and eleven sulphides in the boiling range 35–235° on a squalane column, while SPENCER *et al.*[8] have reported relative retention data for sulphur gas

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odorants. YAKERSON *et al.*[9] studied the chromatographic behaviour of many synthethized sulphur compounds. COLEMAN *et al.* have identified eleven sulphur compounds in a concentrate of sulphur compounds from Aghazari Iranian crude[10], thiols[11] in Wasson crude oil distillate, and alkylthiophenes[12] and cyclic sulphides[13] in Wilmington, Calif., crude oil distillate. THOMPSON *et al.* described the identification of alkylcycloalkyl sulphides[14] and cyclic sulphides[15] in Wassan crude oil distillates by gas–liquid chromatography (GLC) and reaction gas chromatography (GC). MARTINŮ AND JANÁK[16] described retention indices for a series of lower aliphatic sulphides on isodecyl phthalate and Apiezon L. A few workers[17,18] have used capillary GC columns for the separation of a range of sulphur compounds.

This paper describes the identification of various sulphur constituents in the 93–162° heavy gasoline cut from Romashkino crude oil by using the Kováts retention index system, and systematic GLC procedures used in concentrating and identifying the individual sulphur compounds are discussed.

EXPERIMENTAL

Preparation of sulphur compound concentrate

The separation and identification of individual sulphur compounds from a crude oil distillate is a difficult and tedious problem because of the minute quantities that are usually present. The processing step used for concentrating the sulphur compounds from the heavy Russian Grade gasoline included preparative GLC on a formamide column.

Earlier publications[6,16,17] have reported the separation and identification of various sulphur compounds in different petroleum crudes by using such techniques as isothermal distillation, adsorption, fractionation and infrared and mass spectrometry. Although these procedures have been well established and provide reliable information, some of the processing steps are time-consuming and large quantities of the crude oil are required to produce enough sulphur concentrate for further identification studies. The use of preparatory GLC avoids some of the more time-consuming steps in the preparation of sulphur concentrate.

The 93–162° gasoline cut (d_4^{15} 0.736; total sulphur content 0.037% w/w) was injected into a CHROM-III Commercial Gas Chromatograph (Laboratory Instruments, N.E., Prague, Czechoslovakia) using a formamide column (20% w/w on Celite 545) of length 1.5 m and I.D. 8 mm maintained at a temperature of 47°. The flow-rate of the carrier gas (hydrogen) was 46 ml/min. After examining the chromatogram, the collection of different fractions was planned so as to divide the eluted compounds into four major fractions, which were later trapped in four special glass traps. The four fractions (Nos. 1,2,3 and 4) were obtained in two different sets. In both cases, the total recovery was about 58%.

The evaluation study was undertaken only for fractions 3 and 4, as the first two fractions are composed mainly of hydrocarbons, as seen from the total sulphur content determined by GRANATELLI's method[22]. The total sulphur, as such, was 0.0072 and 0.0290% w/w, and the total sulphur calculated on the basis of the charge (gasoline) was 0.0042 and 0.0029% w/w, for fractions 1 and 2, respectively.

On this basis, fractions 3 and 4 were not analysed for their total sulphur content as it was assumed that over 80% of the total sulphur present in the gasoline

was present in a concentrated form in these two fractions. Attempts were made to avoid evaporation losses by cooling the trapping system effectively.

Analytical studies by capillary gas chromatography

Apparatus. The gas chromatograph was a model Fractovap C (Carlo Erba, Italy), equipped with a flame-ionization detector along a splitter/by-pass device. A 1 mV recorder model Speedomax G was used. Stainless-steel capillary columns of length 50 and 100 and I.D. 0.01 in. were obtained from Perkin-Elmer (U.S.A.), coated with squalane, PEG-400, dibutylphthalate and Apiezon L. Pure nitrogen was used as the carrier gas throughout all the studies.

Reagents. The reference hydrocarbons and sulphur compounds used in the study were analytical reagents obtained either from Lachema, N.E., Brno, or from the Departments of Organic Technology and Synthetic Fuels and Petroleum of the Institute of Chemical Technology, Prague, Czechoslovakia.

The hydrocarbons used were the following: C_6–C_{13} *n*-alkanes, benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene, cyclohexane, methylcyclohexane, hemillitol, pseudocumene, mesitylene, cyclopentane, methylcyclopentane, ethylcyclopentane, *n*-propylcyclopentane, *o*-, *m*- and *p*-methylethylbenzene, cyclopentane, cyclohexane, cycloheptane and cyclooctane.

The sulphur compounds used were the following: *n*-butylthiol, *n*-hexylthiol, *n*-octylthiol, diethyl sulphide, di-*n*-butyl sulphide, thiophene, 2-methylthiophene, 2,6-dimethylthiophene, cyclohexylthiol, thiophenol, *p*-thiocresol and thiacyclopentane and its 2-ethyl, 2-*n*-propyl and 2-*n*-butyl derivatives.

Procedure. After installing the capillary column in the gas chromatograph, the carrier gas flow-rate and other parameters were suitably adjusted as indicated in Table I.

The various standards, *viz.*, the hydrocarbons and reference sulphur compounds, were used to identify the components as well as to ascertain the Kováts retention indices[19] for each individual component in the chromatogram. These compounds were injected individually and also in different combinations into the gas chromatograph. Squalane and PEG-400 columns were operated at two temperatures, 86° and 120°, while the dibutyl phthalate column was operated only at 86° and the Apiezon-L column only at 120°. The gasoline cut (93–162°) was analysed on these columns at two temperatures, 86° and 120°, under the same conditions. Fractions 3 and 4 were analysed on squalane, dibutyl phthalate and PEG-400 columns at 86° only.

TABLE I

CHARACTERISTICS OF VARIOUS COLUMNS USED

Air pressure, 0.55; nitrogen pressure, 0.5–0.6 and hydrogen pressure, 0.25 kp/cm² for all columns.

Characteristic	*Type of column*							
	Dibutyl phthalate	*PEG-400*		*Squalane*		*Apiezon-L*	
Length (m)	100		50		50		100	
Temperature (°C)	86	86	120	86	120		120	
Number of theoretical plates	256,000		55,000		64,000		243,000	

TABLE II

KOVÁTS RETENTION INDICES FOR REFERENCE HYDROCARBONS

Hydrocarbon	*Column*					
	Dibutyl phthalate 86°	*PEG-400* 86°	*Squalane* 86°	*Squalane* 120°	*Apiezon-L* 120°	*PEG-400* 120°
Aromatics						
Benzene	732.9	1023.3	644.4	648.6	673.3	1035.1
Toluene	836.9	1110.1	753.1	756.8	794.2	1119.7
Ethylbenzene	922.8	1176.8	842.6	848.4	886.8	1196.0
p-Xylene	936.5	1182.0				1201.9
m-Xylene	939.5	1189.2	856.6	866.3	904.7	1211.5
o-Xylene	965.2	1234.9	877.4	886.0	930.9	1256.2
n-Propylbenzene	1011.9	1254.9	931.6	939.0	976.7	1274.6
p-Methylethylbenzene	1026.8			952.3	992.3	
m-Methylethylbenzene	1024.9	1267.4		954.6	996.0	1294.0
o-Methylethylbenzene	1046.6	1306.3		970.1	1013.4	1334.9
Mesitylene	1043.9	1284.6	964.4	971.4	1012.7	1304.9
Pseudocumene	1065.8	1323.9	981.3	990.8	1035.7	1348.0
Hemellitol	1097.4	1378.5	1006.7	1018.3	1067.6	1406.5
Cyclohexanes						
Cyclohexane	685.6	737.3	674.0	682.0	685.4	747.5
Methylcyclohexane	746.7	781.5	734.5	741.4	751.2	805.0
Ethylcyclohexane	854.5	910.8	840.0	849.9	867.8	944.3
Propylcyclohexane	946.4	1004.1	931.6	944.2	961.3	1033.5
Cyclopentanes						
Cyclopentane	602.4		572.0			
Methylcyclopentane	650.0	672.4	647.3	650.6	642.8	
Ethylcyclopentane	754.8	750.0	743.1	747.8	754.0	
Propylcyclopentane	848.4	855.0	848.8	848.2	855.4	
Cycloparaffins						
Cyclopentane	602.4		572.0			
Cyclohexane	685.6	737.3	674.0	682.0	685.4	747.5
Cycloheptane	820.9	876.0	802.6	806.8	837.6	914.5
Cyclooctane	945.9	1044.0	924.9	926.6	969.5	1084.1

RESULTS AND DISCUSSION

Kováts retention indices were calculated for all the chromatographic peaks obtained. Values for all the reference hydrocarbons and sulphur compounds used are given in Tables II and III, respectively.

In Table IV, data for the determination of the statistical confidence interval[23] of the estimated Kováts retention indices for the *n*-alkanes used are given. On the basis of these data, retention index values were obtained with a reliability of better than ± 1 unit (ref. 8). In the case of all the standard sulphur compounds, two or three determinations were made for each compound on each column with the same criteria as that for hydrocarbons for the statistical confidence interval. The positions of the peaks were assigned on the basis of the retention indices values obtained for the standards.

The Kováts index values for *n*-pentylthiol and di-*n*-propyl-sulphide were calculated directly while values for 2-ethylthiophene, 2-*n*-propylthiophene, 2-methyl-

TABLE III

KOVÁTS RETENTION INDICES FOR REFERENCE SULPHUR COMPOUNDS

Sulphur compounds	*Column*					
	Dibutyl phthalate 86°	*PEG-400* 86°	*Squalane* 86°	*Squalane* 120°	*Apiezon-L* 120°	*PEG-400* 120°
Thiols						
n-Butylmercaptan	625.8	771.8	693.0	701.0	673.3	944.7
n-Pentylmercaptan (calculated)	701	890	722	729	734	1021
n-Hexylmercaptan	775.7	1019.1	752.0	756.8	749.2	1096.6
Sulphides						
Dimethyl sulphide (graphical)	560	770	497	500	520	775
Diethyl sulphide	750.3	952.6	691.6	694.9	696.5	959.6
Dipropyl sulphide	937.1	1134.8	877.5	882.4	890.1	1144.4
Dibutyl sulphide	1124.0	1316.9	1064.4	1069.8	1083.8	1328.8
Thiophenes						
Thiophene	758.7	1065.5	632.2	643.6	692.9	1088.2
2-Methylthiophene	850.5	1140.2	746.3	747.8	798.2	1159.9
2-Ethylthiophene (graphical)	945	1220	845	850	905	1235
2-Propylthiophene (graphical)	1040	1300	955	960	1010	1310
2,5-Dimethylthiophene	938.3	1262.3	840.0	845.1	894.0	1267.9
Thiocyclopentanes						
Thiacyclopentane	874.4	659.9	771.8	775.0	839	—
2-Methylthiacyclopentane (graphical)	942	830	850	—	—	—
2-Ethylthiacyclopentane (graphical)	1012	995	930	934	—	—
2-Propylthiacyclopentane	1081.0	1167.6	1013.3	1017.0	1072.5	1208.4
n-Butylthiacyclopentane	1151.2	1454.7	1092.7	1098.0	1168.9	1486.8
Aromatic thiols						
Cyclohexyl thiol	827.5	758.0	665.9	686.7	685.4	814.5
Thiophenol	922.4	1076.8	933.4	942.1	965.8	1103.4
p-Thiocresol	1008.0	1454.7	959.9	1116.4	1048.0	1483.6

TABLE IV

CRITERIA FOR STATISTICAL INTERVAL FOR HYDROCARBONS

Values given were obtained on a dibutyl phthalate column.
The Q test was calculated as suggested by DEAN AND DIXON[23] for n-C_7 to n-C_{10} hydrocarbons: n-C_7 = 700.3 ± 0.73; n-C_8 = 800.96 ± 0.68; n-C_9 = 900.0 ± 0.02; n-C_{10} = 1000.0 ± 0.0.

No. of determinations	*Hydrocarbons*			
	n-C_7	n-C_8	n-C_9	n-C_{10}
1	701.4	802.2	900.4	1000.0
2	701.4	801.6	900.0	1000.0
3	700.4	801.0	900.0	1000.0
4	699.8	800.8	900.0	1000.0
5	699.6	800.6	900.0	1000.0
6	699.2	799.6	899.6	1000.0

TABLE V

PRESENCE OF COMPOUNDS IN HEAVY GASOLINE

+ = compound present.

Compound	*Column*					
	Dibutyl phthalate 86°	*PEG-400* 86°	*Squalane* 86°	*Squalane* 120°	*Apiezon-L* 120°	*PEG-400* 120°
n-BuSH			+			
n-Pentyl-SH (calculated)			+	+		
n-Hexyl-SH	+			+		
Di-Et.S			+			+
Di-P-S(calculated)	+		+	+	+	
Di-Bu-S		+				+
Et.-P-S					+	
Et.-Bu-S					+	
P-Bu-S					+	
Th	+				+	
2-M-Th	+	+	+	+	+	+
2-Et.-Th (graphical)	+	+	+	+		+
2 P.-Th (graphical)	+		+	+		+
2,5-di-M-Th	+	+	+			
Th.c-C_5	+				+	+
2-M-Th.cC_5 (graphical)	+		+			
2-Et.-Th.-cC_5 (graphical)		+	+	+	+	
2P-Th-c-C_5		+				+
2Bu-Th-c-C_5				+		
c-C_6-SH	+		+			
Bz.-SH	+		+	+	+	
p.-M-Bz-Sh	+		+			

TABLE VI

PRESENCE OF COMPOUNDS IN FRACTIONS 3 AND 4

+ = compound present.

Compound	*Fraction 3*			*Fraction 4*		
	Column			*Column*		
	Dibutyl phthalate 86°	*PEG-400* 86°	*Squalane* 86°	*Dibutyl phthalate* 86°	*PEG-400* 86°	*Squalane* 86°
n-Bu-SH						
n-P-SH				+		
n-hexyl-SH		+		+		+
D--Et-S	+			+		
Di-P-S		+				
Di-Bu-S		+		+	+	
Th	+			+		
2-M-Th	+		+	+		
2-Et.-Th				+		+
2-P-Th		+				+
2,5-di-M-Th	+	+	+	+	+	+
Th.-cC_5	+		+	+		+
2 M-Th-cC_5				+		+
2 Et.-Th-cC_5			+	+	+	+
2-P-Th-cC_5		+		+	+	
2-Bu-Th-cC_5						
cC_5-SH	+			+		
BZ-SH	+	+		+	+	+
p.-M.-BZ-SH	+		+	+		+

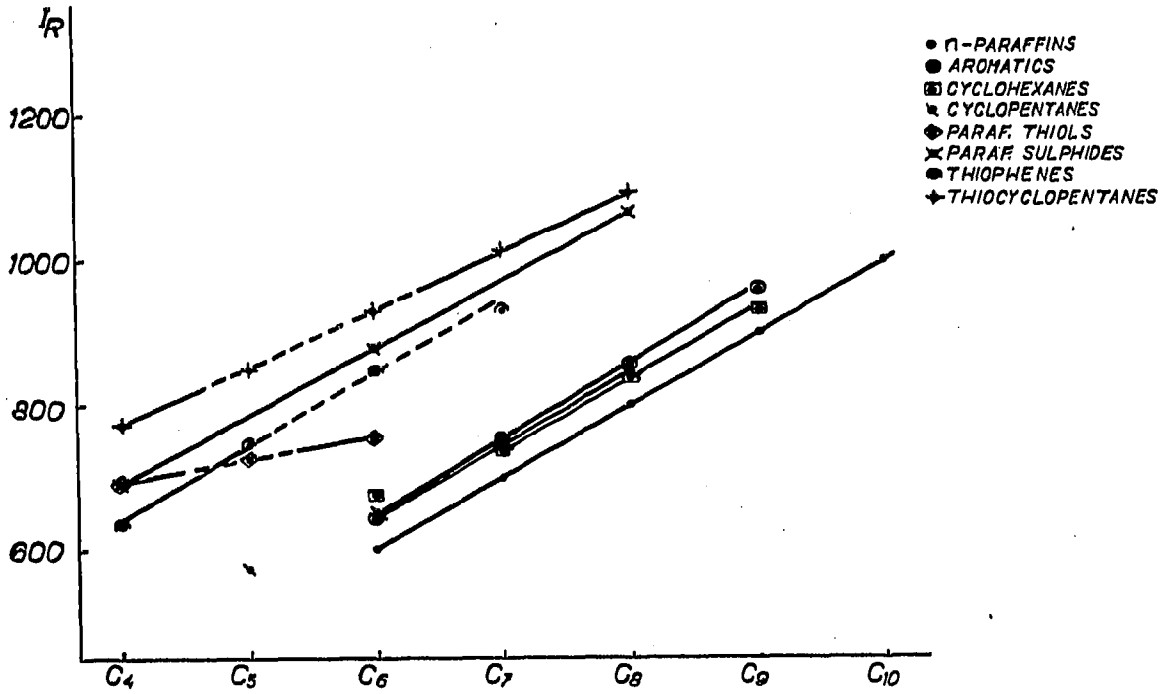

Fig. 1. Correlations between retention indices and carbon number for some homologous series on squalane.

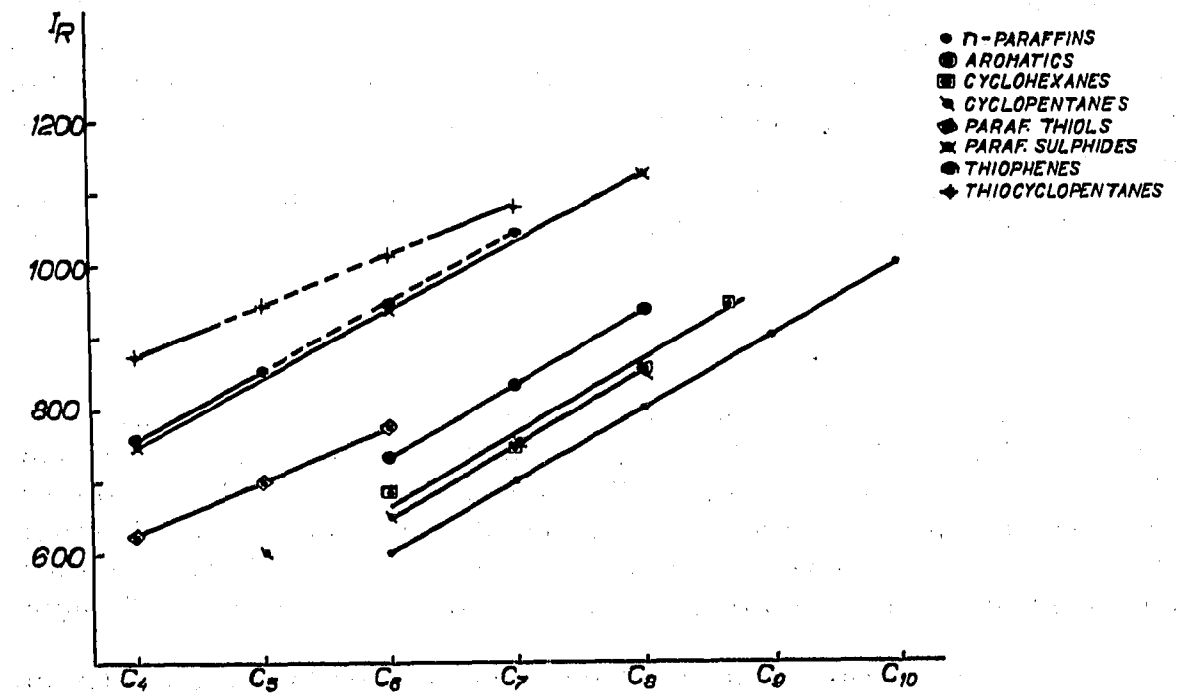

Fig. 2. Correlations between retention indices and carbon number for the same homologous series as in Fig. 1 but on dibutyl phthalate.

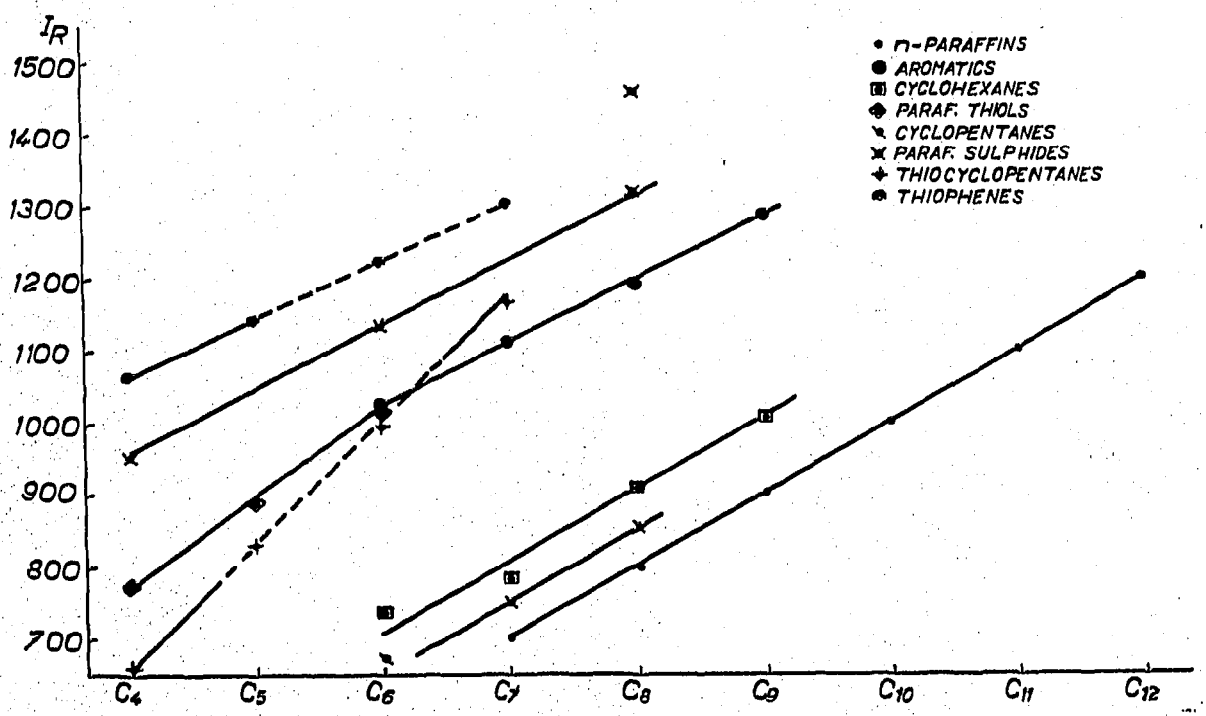

Fig. 3. Correlations between retention indices and carbon number for the same homologous series as in Fig. 1 but on PEG-400.

thiocyclopentane and 2-ethylthiocyclopentane were obtained graphically by using the procedures given in the original KOVÁTS paper[19]. Retention indices for ethyl *n*-butyl sulphide on Apiezon L at 120° were obtained from the earlier study carried out on the same type of substrate at 130°.

The occurrence of an unknown peak in the chromatograms of the gasoline or of the fractions at the same position as that of a standard compound under examination is the basis of the tentative assessment of the presence of compounds as listed in Tables V and VI.

The relation between the Kováts indices and the carbon number for some of the compounds is indicated graphically in Figs. 1–3. The experimental parameters are given in these figures.

CONCLUSIONS

From the present GC studies, some interesting conclusions can be drawn. The following are the major conclusions: lower alkyl thiols are not definitely present; higher alkyl and cyclic thiols are present in all materials; alkyl sulphides are present in the gasoline up to di-*n*-propyl sulphide, but higher alkyl sulphides are not definitely present; alicyclic sulphides showed a predominence in almost all the products studied, and thiophene structures are present, starting with methyl and higher derivatives.

In brief, alkyl thiols are present in small amounts compared with sulphides and thiophenes. The surprising aspect of the study is the indication of the presence of cyclic and aromatic thiols. The major part of the sulphur constituents in gasoline

seems to consist of both aliphatic and alicyclic sulphides. Regarding heterocyclic sulphur compounds, thiophene and its homologues are present in a considerable quantity.

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