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A NOVEL METHOD FOR SEPARATION AND IDENTIFICATION OF SULPHUR COMPOUNDS
IN NAPHTHA (30-200°C) AND MIDDLE DISTILLATE (200-350°C) FRACTIONS OF
LLOYDMINSTER HEAVY OIL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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August 1983

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 83-54 (OP,J)

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ERP/ERL 83-54(OPJ)

Séparation et identification des composés sulfurés dans des coupes de distillation d'huile lourde de Lloydminster par couplage chromatographie en phase gazeuse-spectrométrie de masse

M.A. Poirier et G.I. Smiley

Résumé

On présente une méthode pour la séparation et l'identification des composés sulfurés dans des coupes pétrolières de naphta (30-200°C) et de distillat moyen (200-350°C) provenant du traitement de l'huile lourde de Lloydminster. Il a été possible de concentrer les composés sulfurés (sulfures et thiophènes) par chromatographie liquide en utilisant une colonne remplie de silice et d'alumine. Bien que cette méthode permet l'élution sélective des composés sulfurés, la présence de quelques hydrocarbures aromatiques est inévitable. On a développé cette technique en utilisant un mélange de composés modèles comprenant des sulfures aliphatiques et aromatiques, des thiophènes et hydrocarbures aromatiques ayant des points d'ébullition couvrant l'écart de point d'ébullition 30-200°C et 200-350°C. On effectue préalablement une simplification de la matrice par concentration des composés sulfurés avec les aromatiques par chromatographie liquide sur silice. Les composés sulfurés sont ensuite séparés par chromatographie sur colonne double de silice et d'alumine en utilisant un mélange pentane-acétate d'éthyle (95:5). L'identification des composés sulfurés est réalisée par couplage chromatographie en phase gazeuse-spectrométrie de masse.

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LLOYDMINSTER HEAVY OIL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

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ABSTRACT

A procedure for the separation and identification of organic sulphur compounds from petroleum and related fractions has been investigated and applied to the naphtha (30-200°C) and a middle distillate fraction (200-350°C) of a feed and a processed Lloydminster heavy oil. The method permits the concentration of the sulphur compounds from a distillate fraction, although some aromatic hydrocarbons have been found in the sulphur compound concentrate. The separation method was developed using a mixture of model aliphatic and aromatic sulphides, thiophenes and aromatic hydrocarbons of varied structure covering the investigated boiling range. The procedure employs liquid-solid chromatography, gas chromatography and mass spectrometry. The sulphur compounds were concentrated in the aromatic fraction by chromatography on a silica gel column. The sulphur compound concentrate (sulphides and thiophenes) was obtained by chromatography of the aromatic fraction on a dual packed silica gel/alumina column using a pentane/ethyl acetate (95:5) mixture as eluent. The concentrate was then analyzed by gas chromatography/mass spectrometry. Twenty eight sulphur compounds were tentatively identified by mass spectrometry.

INTRODUCTION

The effect of increasing the severity of hydrocracking on the sulphur-type distribution in Athabasca bitumen has been investigated previously (1). The concentration of sulphur content in the aromatic fraction obtained from the modified API method has received some attention (2). It is well known that sulphur compounds have undesirable effects on processing. They poison catalysts, in particular during the reforming of naphtha to increase octane numbers, on fuel characteristics, and they also have undesirable effects on engine life and performance (3). When sulphur compounds are present noble metal cannot be used as hydrogenation catalysts for the low temperature hydrogenation of middle distillates to diesel fuels. The separation and identification of sulphur compounds is necessary for the development of technologies for their removal for environmental reasons as well as for their use as chemicals or additives.

The objective of this work was to develop a procedure for the separation and identification of sulphur compounds, by gas chromatography/mass spectrometry (GC/MS) from a naphtha fraction (30-200°C) and aromatic fraction from a middle distillate fraction (200-350°C) of a heavy oil and a synthetic fuel. The amounts of mercaptans and disulphides are negligible in these heavy oils and synthetic fuels (1,4). Neither mercaptans nor disulphides were found by GC/MS. Sulphur analyses, mass spectral library search data and gas chromatographic retention time correlations using model compounds constituted evidence for the presence of the identified compounds.

Various methods to separate organic sulphur compounds from aromatic hydrocarbons in petroleum have been reported in the literature (5-13). Some separation methods are based on ligand exchange chromatography using mercury (5,8,14) zinc (11) or copper salts (12) as complexing agents. Another approach is the chemical conversion of sulphur groups in more polar groups by oxidation to sulphones. These compounds can subsequently be reduced to the starting material (9,13). Although these procedures have been well established and provide reliable information, some of the processing steps are time-consuming and require relatively expensive reagents.

This report describes a procedure to concentrate the sulphur compounds in the aromatic fraction by chromatography on a silica gel column. The organic sulphur compounds in naphtha and distillate fractions (200-350°C) are then separated from aromatic hydrocarbons by gradient elution liquid chromatography on a silica gel alumina column.

EXPERIMENTAL

The separation and identification steps described in this report are shown in Figure 1.

Samples

The following samples were investigated in this work:

1. Middle distillate fraction (200-350°C) obtained by distillation of virgin Lloydminster oil.
2. Middle distillate fraction (200-350°C) of hydrocracked Lloydminster oil.
3. Naphtha (30-200°C) of hydrocracked Lloydminster oil.
4. Model compound mixture prepared by dissolving about 1 µL to 1 mg of each individual component in 10 mL of toluene (Table 1). The structures of the sulphur compounds are shown in Figure 2.

Hydrocarbon-Type Separation

About 2 g of each sample (1 and 2) were introduced separately on top of a 4' x 0.5" (120 x 1.3 cm O.D.) stainless steel column packed with 94 g of silica gel Davison Chemical Grade H (100-200 mesh) activated overnight at 240°C. Pentane (250 mL) followed by benzene (250 mL) was used to elute the saturated and aromatic hydrocarbons of the sample respectively. The eluents were delivered to the column under pressure (Lapp Model LS-30 pump) at a flow rate of 2.7 mL/min. The aromatic fraction was used for further separation. Uneluted materials were considered to be polar in nature.

Concentration of Sulphur Compounds from the Aromatics Hydrocarbons

The model compounds mixture, the aromatic fraction and/or naphtha (Sample 3) (0.8 g) spiked with about 0.8 mg of azulene were chromatographed on a 2' x 0.5" (60 x 1.3 cm O.D.) stainless steel column dual packed with 19 g silica gel and 25 g alumina which details have been previously reported (2). The following sequence of eluents was used:

<u>Eluent</u>	<u>Volume used, mL</u>
Pentane	240
Pentane-ethyl acetate (95:5)	300
Benzene	250

Fractions of eluate (12 mL each) were collected in test tubes using an automatic fraction collector. The greenish azulene fractions corresponding to the sulphur concentrate (see results and discussion) were examined by GC-MS.

Sulphur Analysis

A Princeton Gamma-Tech Model 100 X-ray Fluorescence sulphur analyzer was used to determine the percentage of total sulphur in the different samples.

Gas Chromatography and Gas Chromatography/Mass Spectrometry

The analyses of the sulphur compound concentrates as well as the model compounds were carried out using a 27 m x 0.25 mm DB-5 fused silica capillary column. The gas chromatographic profiles were recorded with a Varian 6000 gas chromatograph with precisely controlled oven temperature programmed as follows: initial temperature 50°C, hold 5 min, program rate 10°C/min to 100°C then 2.5°C/min to final temperature 250°C. The head pressure on the capillary column was 120 kPa of helium at 50°C. The flame ionization detector (FID) was maintained at 350°C and the injector temperature at 250°C. The sample was injected directly on-column using a Hamilton 0.5 µL syringe. A Spectra-Physics SP4100 integrator was used for data acquisition.

Mass spectral analyses were performed on a Finnigan 4000 gas chromatograph-quadrupole mass spectrometer (GC/MS) interfaced to an Incos data system. Electron impact spectra were recorded at an ionization energy of 70 eV. Mass spectra were identified through comparison with library data.

RESULTS AND DISCUSSION

Liquid Chromatographic Separation of the Model Compounds Mixture

Development of this procedure was initiated using 29 model compounds followed by gas chromatography and unknowns identified by peak matching mass spectral data.

A mixture of 21 sulphur compounds and 8 aromatic hydrocarbons (Table 1) with boiling points covering the investigated boiling range was chromatographed on a dual packed column as described in the experimental section. The mixture was spiked with azulene, as visual indicator, which eluted with the sulphur compounds, as determined by gas chromatography.

The mono and di-aromatics were eluted with pentane to minimize contamination of the sulphur concentrate.

Compared to the API 60 procedure, our method using a dual packed column uses a much larger sample and solvent to sorbent ratio, 4:1 aromatics to sorbent and twice as much pentane which allows the saturates, mono and di-aromatics to elute with pentane. Elution of aromatic hydrocarbons from a silica gel column using pentane was reported by other researchers (13).

In our procedure, it was found that the pentane/ethyl acetate (95:5) mixture eluted selectively the sulphur compounds independently of their structure and boiling point. All the sulphur compounds were eluted in about 24 mL of the pentane/ethyl acetate eluate.

There was no contamination of the sulphur concentrate from other aromatic hydrocarbons except for 9, 10 dihydroanthracene which eluted with the sulphur compounds. A diagram of the separation and a chromatogram of the model compound mixture are shown in Figures 3 and 4 respectively.

Chromatographic Separation of the Naphtha and Aromatic Fractions

The saturate and aromatic content in the Lloydminster crude oil and two processed products is shown in Table 2. These results were obtained from the hydrocarbon-type separation on the silica gel column described in the experimental section. Polar fractions were calculated by difference. Sulphur distribution in the fractions obtained from the chromatographic separations is shown in Table 3. The naphtha fraction and the middle distillate fractions (200-350°C) have relatively high sulphur content (3-4%). Because most of the sulphur compounds in the virgin oil and processed products are found in the aromatic fractions, the latter fractions of samples 1 and 2 were further separated and analyzed for sulphur. The remaining polar fraction retained on the silica gel column also has a relatively high sulphur content (4-5%) but since the sulphur compounds are associated with other polar groups, they were not investigated further. Although, sulphur content in Lloydminster asphaltenes is high (5-7%), we applied this method only to distillate products.

The naphtha (sample 3) and the aromatic fractions of the middle distillates (200-350°C) (samples 1 and 2) obtained from the hydrocarbon-type separation (see experimental), were spiked with azulene and chromatographed on the dual packed column, previously described for the pure compounds. As indicated by the sulphur analysis results (Table 3), the method allows the concentration of the sulphur compounds in the pentane/ethyl acetate fraction. The polynuclear aromatic hydrocarbons were eluted with benzene leading to a sulphur-free aromatic fraction (Table 3).

Although a relatively small amount of the sulphur concentrate is obtained (sample 3, 168 mg from 1.1 g), the method is suitable for quantification by weight determination. The sulphur compound concentrates (the greenish fractions, about 24 mL) were evaporated and then analyzed by GC/MS. The gas chromatographic separation of the sulphur compound concentrate originating from sample 2 is shown in Figure 5.

Gas Chromatography/Mass Spectrometry

A) Naphtha (30-200°C)

Examination of the sulphur concentrate from naphtha by mass spectrometry shows two series of sulphur compounds: thiophenes and aliphatic sulphides including cyclic and linear sulphides. The compounds which were tentatively identified are listed in Table 4. Single ion monitoring by mass spectrometry permits the identification of a series of compounds but does not differentiate the isomers. Like the thiophenic compounds, aliphatic sulphides show an intense molecular ion (15). Sulphides are readily differentiated from thiophenes by mass spectrometry. The base peak (100% intensity) in the cyclic sulphides corresponds to loss of alkyl substituents by the ejection of the smaller alkyl substituent attached to the sulphur atom. This mechanism gives rise in many cases to the formation of an olefin. The absence of thiophene in a sample might be indicative of their transformation to cyclic sulphides during hydroprocessing.

B) Middle distillate (200-350°C)

The mass spectral data of the material investigated show two series of thiophenic sulphur compounds; benzothiophene and dibenzothiophene. Dialkyl and diaryl sulphides were not detected. Three benzothiophene compounds were identified by a library search routine (Table 4). These are trimethylbenzothiophene (m/e 176), diethylbenzothiophene (m/e 190) and diethylmethylbenzothiophene (m/e 204). Position of the alkyl groups is difficult to determine by mass spectroscopy because of the lack of fragmentation in the spectrum. All of these compounds give an intense molecular ion; m/e 176 (100%), m/e 190 (80%) and m/e 204 (93%) respectively, characteristic of thiophenic compounds. Similarly the dibenzothiophene series undergoes a very simple fragmentation pattern. Dibenzothiophene, methyl and dimethyldibenzothiophenes have been detected. The mass spectra show a molecular ion at m/e 184 (100%), 198 (100%) and 212 (100%) respectively.

The mass spectral data obtained on the sulphur compound concentrate suggests that the sulphur compounds in the hydrocracked Lloydminster oil 200-350°C are mainly substituted benzo and dibenzothiophenes. This is confirmed by our previous work (2).

The feed fraction (200-350°C) contains the same thiophenic series as the hydrocracked sample, as expected from the thermal stabilities of these compounds (Table 4).

CONCLUSION

We have developed a liquid-solid chromatographic procedure for the concentration of sulphur compounds in naphtha and middle distillates using azulene as a visual indicator. This method offers an alternative to the ligand exchange chromatographic methods or those which require chemical treatment of the sulphur compounds. The GC/MS results obtained from the sulphur concentrates have shown that sulphides were only present in the naphtha fraction while the middle distillates contain exclusively thiophenic compounds.

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CAPTIONS

- Figure 1 Separation and Identification Schematic.
- Figure 2 Structure of the sulphur compounds mentioned in this work; see Tables 1 and 4 for key.
- Figure 3 Liquid-solid chromatographic separation of the model compounds mixture on silica gel/alumina column.
- Figure 4 Gas chromatographic separation of the model compounds mixture on a DB-5 fused silica capillary column.
- Figure 5 Chromatogram of the sulphur compounds concentrate obtained from Sample 2 on a DB-5 fused silica capillary column.

TABLE 1 Physical Properties of Aromatic Hydrocarbons and Sulphur Compounds in the Chromatographed Synthetic Mixture

<u>Peak No.</u>	<u>Compound</u>	<u>R.t. (min)</u>	<u>B.P. (°C)</u>	<u>Mol.Wt.</u>
1.	2,5 Diethylthiophene	2.25	-	140
2.	Thiophene	2.35	84	84
3.	Diethyl sulphide	2.79	92	90
4.	Tetrahydrothiophene	5.76	119	88
5.	Ethyl phenyl sulphide	14.80	203	138
6.	Naphthalene	16.15	218	128
7.	Cyclohexyl butyl sulphide	16.46	-	172
8.	n-propyl-2-thienyl sulphide	16.92	-	158
9.	Benzothiophene	19.26	221	134
10.	n-amyl sulphide	19.71	230	174
11.	Azulene	20.78	242	128
12.	1,3-dimethylnaphthalene	24.09	263	156
13.	3-methylbiphenyl	25.18	273	168
14.	2,9-dithiadecane	27.04	-	178
15.	Acenaphthene	28.05	279	154
16.	n-hexyl sulphide	28.05	232	202
17.	Dicyclohexyl sulphide	31.40	-	198
18.	Diphenyl sulphide	32.40	296	186
19.	9,10-dihydroanthracene	36.17	312	180
20.	n-heptyl sulphide	36.71	298	230
21.	Benzyl phenyl sulphide	37.03	310	200
22.	Dibenzothiophene	39.30	332	184
23.	Phenanthrene	40.40	336	178
24.	Dibenzyl sulphide	42.06	m.p. 49	214
25.	Phenyl-β-phenyl ethyl sulphide	42.78	-	214
26.	n-octyl sulphide	44.89	352	258
27.	Phenyl-γ - phenyl propyl sulphide	46.96	-	228
28.	9-methylantracene	47.61	345	191
29.	Thianthrene	47.61	366	216

TABLE 2 Compound-type Distribution (wt%) in the Naphtha (30-200°C) and Middle Distillate (200-350°C) Fractions of the Samples

Sample No.	Saturate	Aromatics	Polars
1	39.7	43.0	17.3
2	46.5	46.3	7.2
3*	48.3	51.7	-

*Determined using FIA method (ASTM D1319-70). The saturate fraction include the olefins. Results report in V%.

TABLE 3 Sulphur Content (wt%) in the Liquid Chromatographic Fractions

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>
Original	4.33	3.78	3.03
Saturates ^a	0.05	0.06	-
Aromatics ^a	7.1	6.5	-
Pentane eluate ^b	0.02	0.04	0.03
Sulphur Compound ^b Concentrates	11.5	10.2	9.2
Aromatics ^b	0	0.01	0.02

^a Obtained from the hydrocarbon-type separation on silica gel column.

^b Obtained from chromatography on dual-packed silica gel-alumina column.

TABLE 4 Sulphur Compounds Identified in the Naphtha and Middle Distillate of Lloydminster Oil

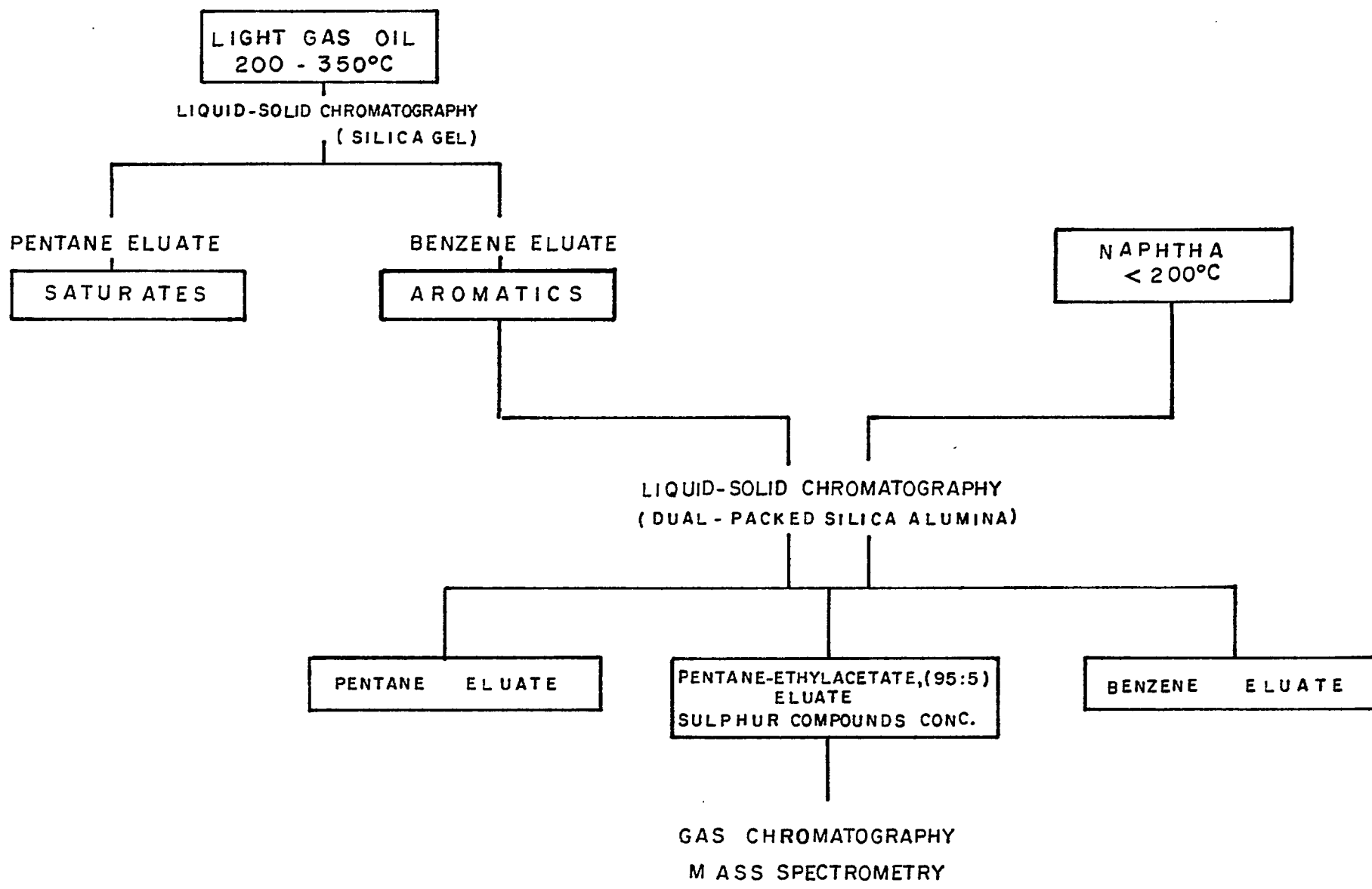
Compound Number	Molecular Types	Possible Compound Types	Samples Estimated Amount		
			1	2	3
9	134	benzothiophene	Trace	Major	Minor
22	184	dibenzothiophene	Major	Minor	
30	102	methyl tetrahydrothiophene			Major
31	116	methyl tetrahydrothiopyran			Minor
32	116	dimethyl tetrahydrothiophene			Major
33	118	ethyl butyl sulphide			Major
34	132	amyl ethyl sulphide			Minor
35	132	propyl butyl sulphide			Minor
36	146	n-butyl sulphide			Major
2	84	thiophene			Minor
-	98	methylthiophene			Trace
37	148	methylbenzothiophene	Trace	Major	
38	162	dimethylbenzothiophene ^a	Minor	Minor	
38	162	dimethylbenzothiophene ^a	Major	Major	
38	162	dimethylbenzothiophene ^a	Major	Major	
38	162	dimethylbenzothiophene ^a	Major	Major	
40	176	trimethylbenzothiophene ^b	Minor	Minor	
40	176	trimethylbenzothiophene ^b	Major	Major	
40	176	trimethylbenzothiophene ^b	Major	Major	
40	176	trimethylbenzothiophene ^b	Major	Major	
40	176	trimethylbenzothiophene ^b	Major	Major	
41	190	diethylbenzothiophene ^c	Major	Major	
41	190	diethylbenzothiophene ^c	Minor	Minor	
41	190	diethylbenzothiophene ^c	Minor	Minor	
42	198	methyldibenzothiophene	Minor	Minor	
43	204	diethyl methylbenzothiophene ^d	Minor	Minor	
43	204	diethyl methylbenzothiophene ^d	Minor	Minor	
44	212	dimethyldibenzothiophene	Trace	Trace	

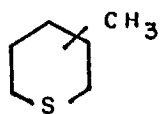
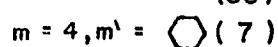
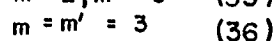
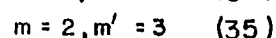
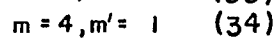
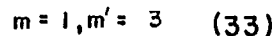
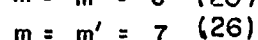
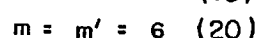
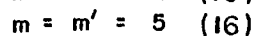
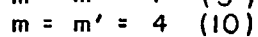
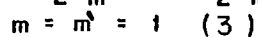
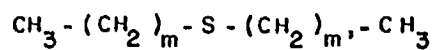
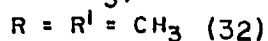
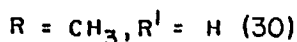
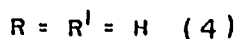
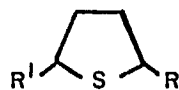
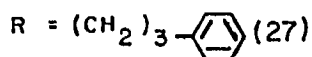
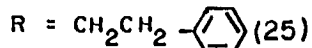
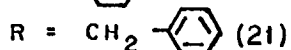
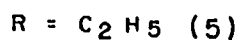
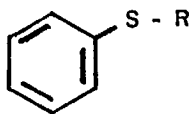
a Could be ethyl

b Could be ethyl methyl

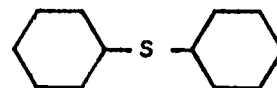
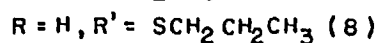
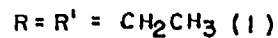
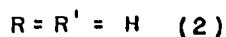
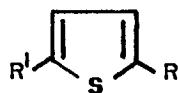
c Could be dimethyl ethyl or tetramethyl

d Could be ethyl trimethyl

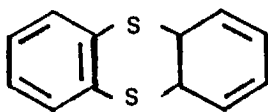




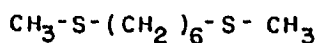
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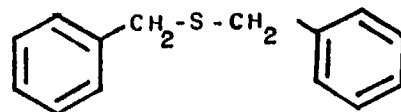
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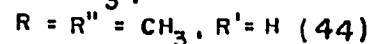
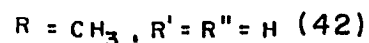
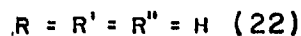
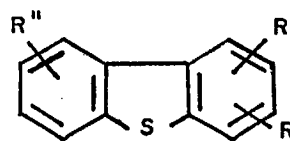
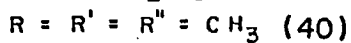
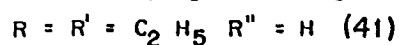
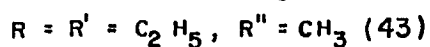
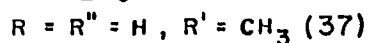
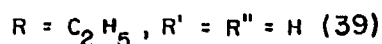
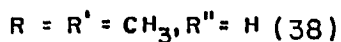
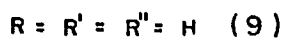
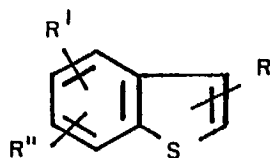
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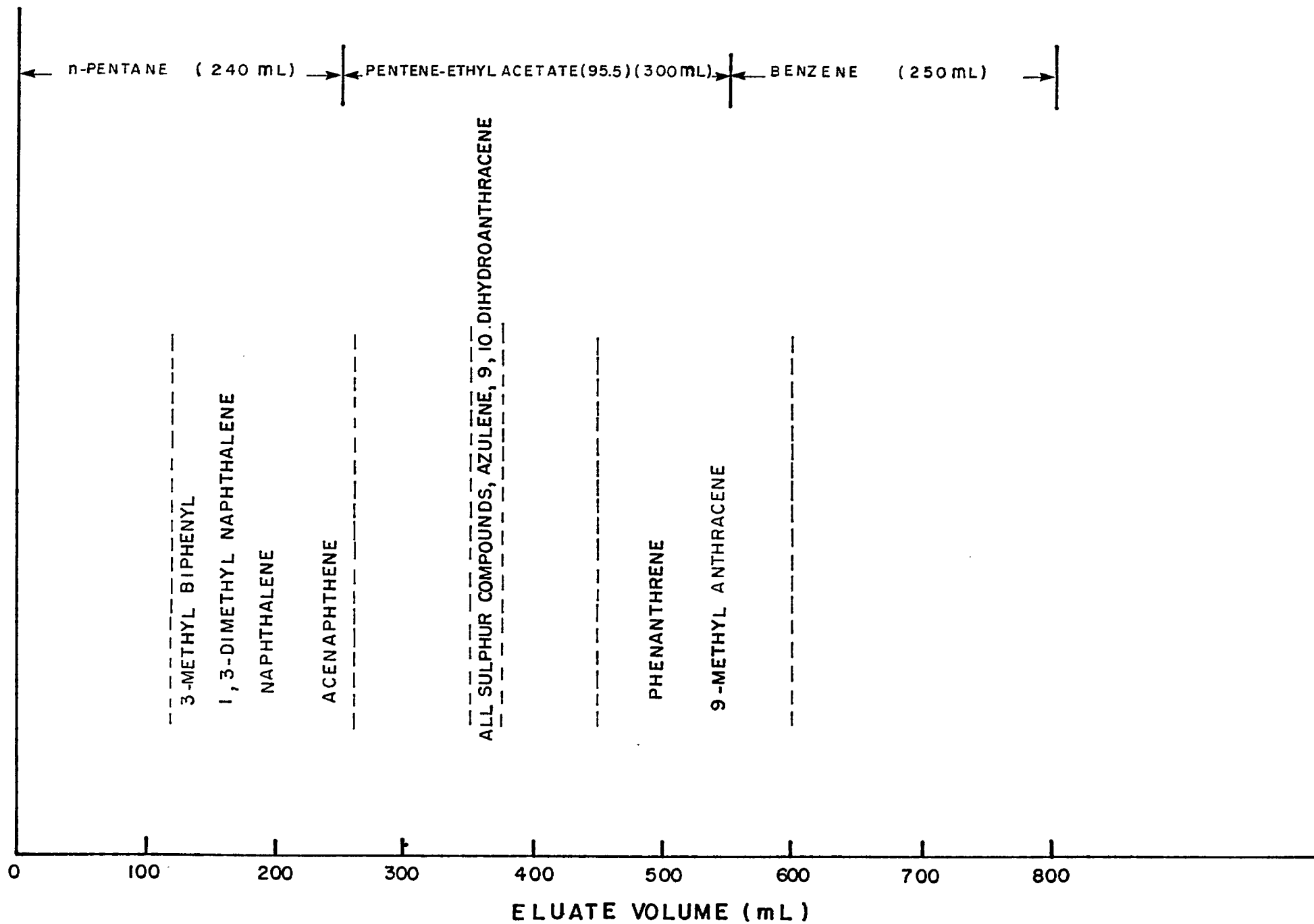


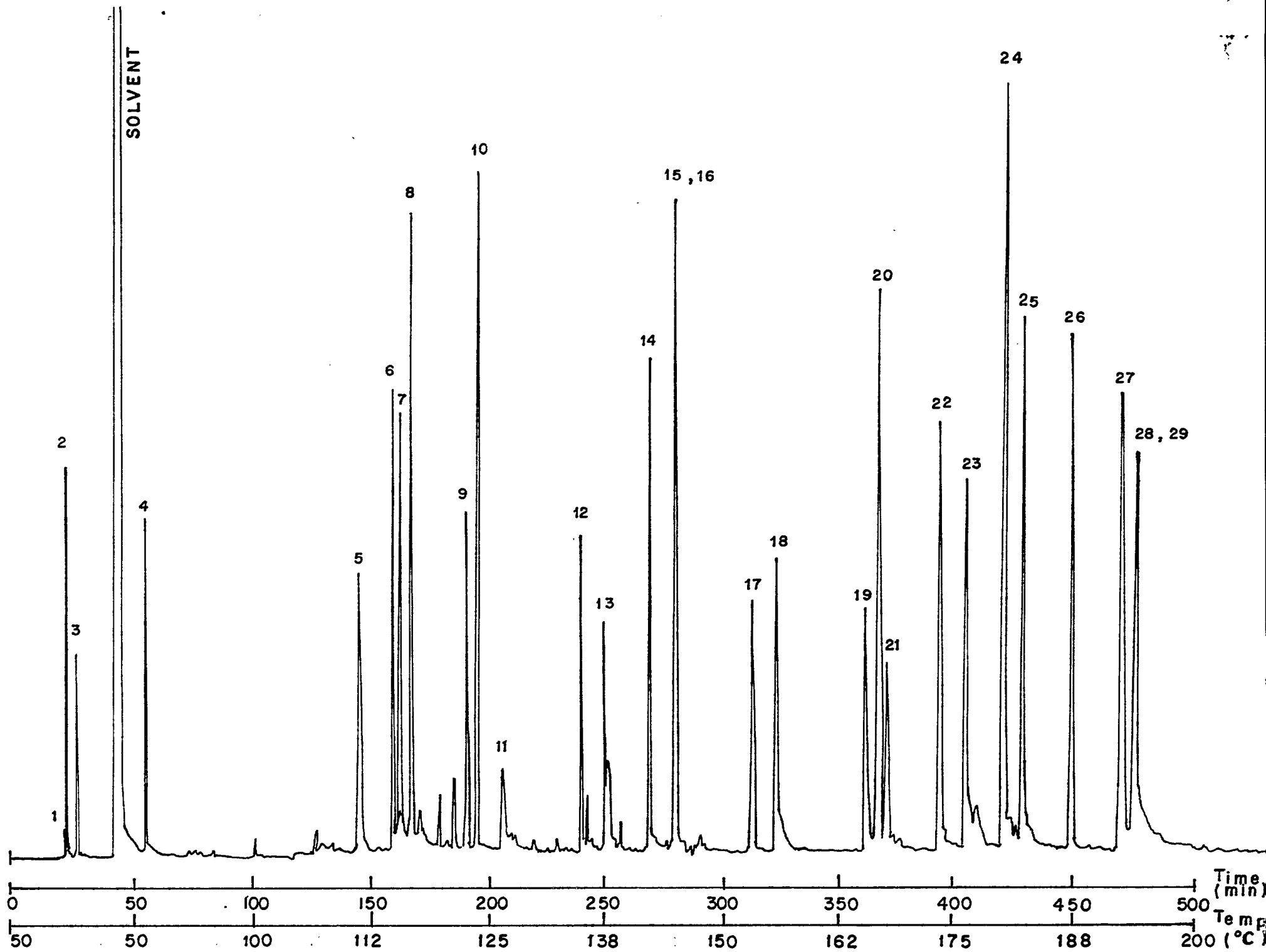
(14)



(24)







ETHER

