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SULPHUR-CONTAINING POLYNUCLEAR AROMATIC HYDROCARBONS FROM PETROLEUM

EXAMINATION OF THEIR POSSIBLE STATISTICAL FORMATION IN SEDIMENTS

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SUMMARY

Two procedures are described for the determination of sulphur-containing polynuclear aromatic hydrocarbons (SPAHs) in petroleum and in its derived industrial products. As a general clean-up procedure, the total aromatic fractions were obtained after partition of the sample between dimethyl sulphoxide (DMSO) and pentane, followed by liquid–liquid extraction of the DMSO layer. In the first method, SPAHs were oxidized to sulphones, isolated selectively and back-reduced to SPAHs. The second approach was the direct determination of SPAHs in the aromatic fractions from the clean-up, by gas chromatography with selective detection using a flame photometric detector and gas chromatography–mass spectrometry with selected ion monitoring.

The determination of SPAHs in four crude oils and a coker gas oil is reported. The various isomers are assumed to have been formed in sediments by random alkylation and degradation mechanisms, although specific substances with an increased stability compared with that of other isomers accumulated preferentially.

For dibenzothiophene congeners, the number of GC peaks observed in a capillary column chromatogram is close to the maximum number of peaks that could be observed, as predicted by the statistical theory of Giddings. For benzothiophene congeners, the observed number is smaller. SPAHs are concluded to result from severe transformation mechanisms of the organic precursors occurring in sediments.

INTRODUCTION

Sulphur compounds are well known constituents of crude oils and industrial products from petroleum processing. The sulphur content is 0.5–3% in most samples[1], but is up to 8% in the vacuum residue of heavy crude oils[2]. It is distributed over a wide range of molecular structures: aliphatic thiols, mono- and disulphides

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are sometimes present[3,4], but a large amount of sulphur occurs in aromatic structures, especially as alkylated thiophene benzologues.

Sulphur-containing polynuclear aromatic hydrocarbons (SPAHs), like nitrogen-containing polynuclear aromatic hydrocarbons (NPAHs), are generally associated with adverse effects on the quality of petroleum products, such as catalyst poisoning, corrosion or pollution. They are removed from heavy petroleum distillates, coal tars, synthetic fuels, etc., by hydrotreatments, and accurate analytical methods are required for the development of these upgrading techniques. The determination of specific toxic or potentially carcinogenic compounds is also important for environmental impact studies[5]. Finally, the elucidation of their molecular structures is also of interest for geochemical investigations and is an approach to the elucidation of polycondensed structures, *e.g.*, asphaltene and kerogen, as the sulphur atom is suspected to play a key role in polycondensation processes leading to these macrostructures[6].

Because of their occurrence in low concentrations and in complex mixtures, sulphur molecules are in general not determined directly in starting materials, but after several pre-concentration steps or selective extractions[7–16], although recent selective identification methods to be discussed below are sometimes applicable to starting mixtures.

SPAHs are frequently isolated by purification of the polynuclear aromatic hydrocarbon (PAH) fractions obtained from a given starting mixture by narrow-cut short-path distillation[2] and/or column liquid chromatography over silica or alumina adsorbents[7,8]. The old chromatographic method has now been updated by using high-performance liquid chromatography, and various systems of solvent and adsorbents have been suggested for reducing analysis times and improving the separations[15,16].

The other set of pre-concentration methods often applied to SPAH analyses are based on reversible complexing reactions with aromatic rings. These include liquid–liquid extraction after partition of the sample between a hydrocarbon, *e.g.*, *n*-hexane or cyclohexane, and a pi-complexing solvent, such as nitromethane[12] or dimethyl sulphoxide (DMSO)[13], and precipitation of insoluble adducts such as picrates[14] or mercury (II) complexes[15].

Attempts have also been made to isolate a pure SPAH fraction after several chemical modification steps. SPAH fractions can be oxidized to sulphoxides and sulphones[13] and the resulting polar derivatives are then easily separated by liquid chromatography from less polar PAHs that have not been affected by the oxidation step. However, sulphones are high boiling and heat-sensitive molecules and are difficult to characterize by gas chromatographic techniques[16]. In theory, reduction of the sulphones gives back the SPAHs, which are more volatile and less fragile, but incomplete reaction or reduction of C–C bonds in aromatic nuclei may introduce undesirable artifacts.

These various extraction procedures have been applied to crude oils, coal tars and refined petroleum fractions[17–21], but the resulting sulphur-containing fractions are generally still contaminated by PAHs, which complicate the characterization of individual SPAHs. The difficulty is circumvented by selective detection and identification methods such as capillary column gas chromatography (GC) with flame photometric detection (FPD)[22,23], high-resolution mass spectrometry under a low

ionization voltage[24], chemical ionization using reagent gases, for instance ammonia, that do not react with PAHs but combine with SPAHs[25], selective ion monitoring using gas chromatography–mass spectrometry (GC–MS)[20], Shpol'skii spectrophotometry[26] or photoelectron spectroscopy[27].

The first objective of this work was to investigate the relative merits of these different enrichment procedures, in particular the efficiency of extractions based on liquid–liquid partition, or on the oxidation–reduction procedure, for isolating a pure SPAH mixture. The second objective was to develop a general scheme for the rapid separation and identification of SPAHs using analytical techniques available in this laboratory, *i.e.*, GC using FPD and GC–MS.

Finally, SPAHs were investigated in a few selected samples to compare their repartitions with those of PAHs and NPAHs studied previously in this laboratory[28–35]. The purpose was to delineate possible structural similarities between substances in each family of polynuclear aromatic compounds and to evaluate their possible significance in geochemical studies of sedimentary organic matter.

EXPERIMENTAL

Reagents and samples

Four crude oils of different origins were obtained from the Société Nationale Elf Aquitaine (SNEA) and the Compagnie Française de Raffinage (CFR). Geological data on the samples can be found elsewhere[28]. A coker gas oil was obtained from the French Institute of Petroleum. These five samples had been investigated previously in this laboratory for isolation of nitrogen molecules[28–31].

All solvents (analytical-reagent grade from Merck, Darmstadt, F.R.G., or Carlo Erba, Milan, Italy) were glass-distilled before use. Adsorbents (silica and alumina from Merck) were Soxhlet-extracted with dichloromethane and activated at 150°C for several hours. Other reagents were obtained from various sources and were used as received. Model thiophenes were purchased from Fluka (Buchs, Switzerland) or were gifts from SNEA (Boussens, France).

Extraction

Polynuclear aromatic fractions were isolated according to the procedure reported by Natusch and Tomkins[13]. A 50-ml volume of crude oil was partitioned between 200 ml of DMSO and 20 ml of *n*-pentane at ambient temperature. After shaking, phase equilibrium was attained after 1 h. The dark orange and fluorescent DMSO layer was separated, and the pentane layer was again extracted twice with equal volumes of fresh DMSO. The three resulting DMSO fractions were combined and back-partitioned once with 50 ml of pentane.

Occasionally, depending on the investigated sample, significant amounts of asphaltenes were precipitated by pentane. In these instances, the pentane layer was filtered before being further extracted with DMSO.

Recovery of polycyclic organic compounds from the 600-ml DMSO fraction was accomplished by adding 600 ml of pentane, then slowly adding 600 ml of distilled water as the mixing with DMSO is strongly exothermic. After 1 h the aqueous layer was discoloured and the dark pentane fraction was separated and concentrated in a rotary evaporator. The aqueous fraction was re-extracted twice with 600 ml of pen-

tane. After combining the organic extracts, pentane was removed *in vacuo* with the rotary evaporator, yielding *ca.* 500 mg–1 g of total polynuclear aromatic fractions.

Oxidation

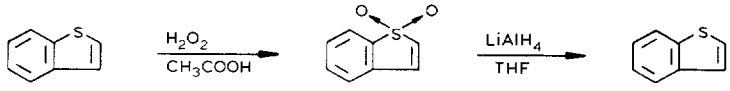
In a 100-ml reactor, *ca.* 500 mg of polyaromatic fraction were dissolved in 30 ml of dichloromethane and 20 ml of glacial acetic acid were added. The solution was stirred and heated to dichloromethane reflux, then 10 ml of 20-volume hydrogen peroxide solution was slowly added and the solution was kept at dichloromethane reflux temperature for 2 h. After allowing the mixture to cool to room temperature, the solution was partitioned between equal volumes (50 ml) of water and dichloromethane. The organic layer had a red-orange colour, probably due to quinones in solution. After separating the two phases, the aqueous layer was washed once with 20 ml of water and concentrated in a rotary evaporator.

Purification was achieved by column liquid chromatography over 1 g of silica. Polyaromatic hydrocarbons and unreacted molecules were eluted with dichloromethane; sulphones were eluted with methanol–chloroform (1:1).

Reduction

Sulphones were dissolved in 20 ml of dry tetrahydrofuran (THF). The solution was transferred into a 100-ml reactor and heated to THF reflux, then 500 mg of $LiAlH_4$ were slowly added. The reaction mixture was refluxed overnight. After cooling to ambient temperature, 50 ml of dichloromethane were added, then 50 ml of water was slowly introduced in order to destroy the excess of the hydride. The resulting precipitate of aluminium hydroxide was filtered and the two liquid phases were decanted. The organic layer was separated and evaporated to dryness in a rotary evaporator to remove THF.

The residue was dissolved in dichloromethane and purified by liquid chromatography over a silica column; reduced fractions were eluted with dichloromethane.



Direct extraction of thiophenic molecules from polyaromatic fractions

About 500 mg of polyaromatic fractions were deposited on top of a column filled with 1 g of neutral alumina prepared in *n*-hexane. Four fractions were collected. Monoaromatic hydrocarbons (fraction1) were eluted with 200 ml of *n*-hexane and the other fractions were eluted with toluene. Fraction 2 (200 ml) contained di- and triaromatic hydrocarbons and some weakly retained alkylbenzothiophenes, fraction 3 (200 ml) contained benzothiophenes and fraction 4 (100 ml) contained dibenzothiophene derivatives. Further determinations showed that fractions 3 and 4 contained sulphur molecules exclusively.

Gas chromatography

The gas chromatograph was a Varian Model 3700 equipped with both a flame ionization detector and a Varian dual flame photometric detector with a 394-nm

filter. Capillary columns coated with OV-73 stationary phase (5.5% phenyl, 94.5% methylsilicone) were prepared in the laboratory[32]. Parallel recordings of traces from the two detectors were obtained by splitting the capillary column effluent with low-dead-volume connections.

Gas chromatography–mass spectrometry

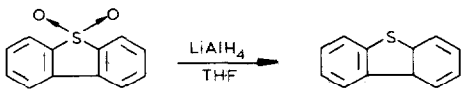
A Varian Model 2700 gas chromatograph was coupled directly to a DuPont Model 21-492B mass spectrometer. Spectra acquisition and data processing were under the control of a DuPont Model 094B-2 data system.

RESULTS AND DISCUSSION

Selective extraction of SPAHs by isolation and reduction of their sulphone derivatives

The method was examined for potential application to the determination of SPAHs in petroleum. The oxidation reaction and the selective extraction of sulphone derivatives appeared easy to achieve, as checked by analytical thin-layer chromatography, although no control of the relative distributions of the sulphones was attempted because of their thermal fragility under GC conditions[16]. After reduction, the resulting mixture contained only sulphur derivatives, so chromatograms obtained with flame ionization detection (FID) or flame photometric detection (FPD) were completely identical (Fig. 1). However, the FPD trace did not represent the original distribution of SPAHs in the petroleum sample, because it was impossible to control completely the reverse reduction of sulphones back to thiophenes.

When the reduction was carried out at 92°C, *i.e.*, at THF reflux, partial reduction of the aromatic ring was unavoidable. Comparison of SPAHs obtained with FPD during analysis of the total aromatic fractions prior to oxidation and reduction and of the reduced sulphones (Fig. 2) showed that additional peaks were present in the second mixture. GC–MS revealed that several of them corresponded to derivatives with their original aromatic nuclei partially hydrogenated. For instance, benzothiophenes could be reduced according to the following reaction:



These drawbacks could be minimized by lowering the reaction temperature, for instance by replacing THF with diethyl ether. However, the conversion yield was reduced dramatically and the reaction time became prohibitive.

Finally, a serious loss of sample was observed, especially for low-boiling substances during solvent reflux, and for trace substances, owing to adsorption on the aluminium hydroxide formed during the destruction of the excess of reducing hydride.

No specific advantage is offered by the oxidation–reduction method for the elucidation of SPAH distribution patterns. The result can be obtained more directly by FPD monitoring during GC analysis of the total polynuclear aromatic fractions obtained after partition of the sample over DMSO and pentane, followed by

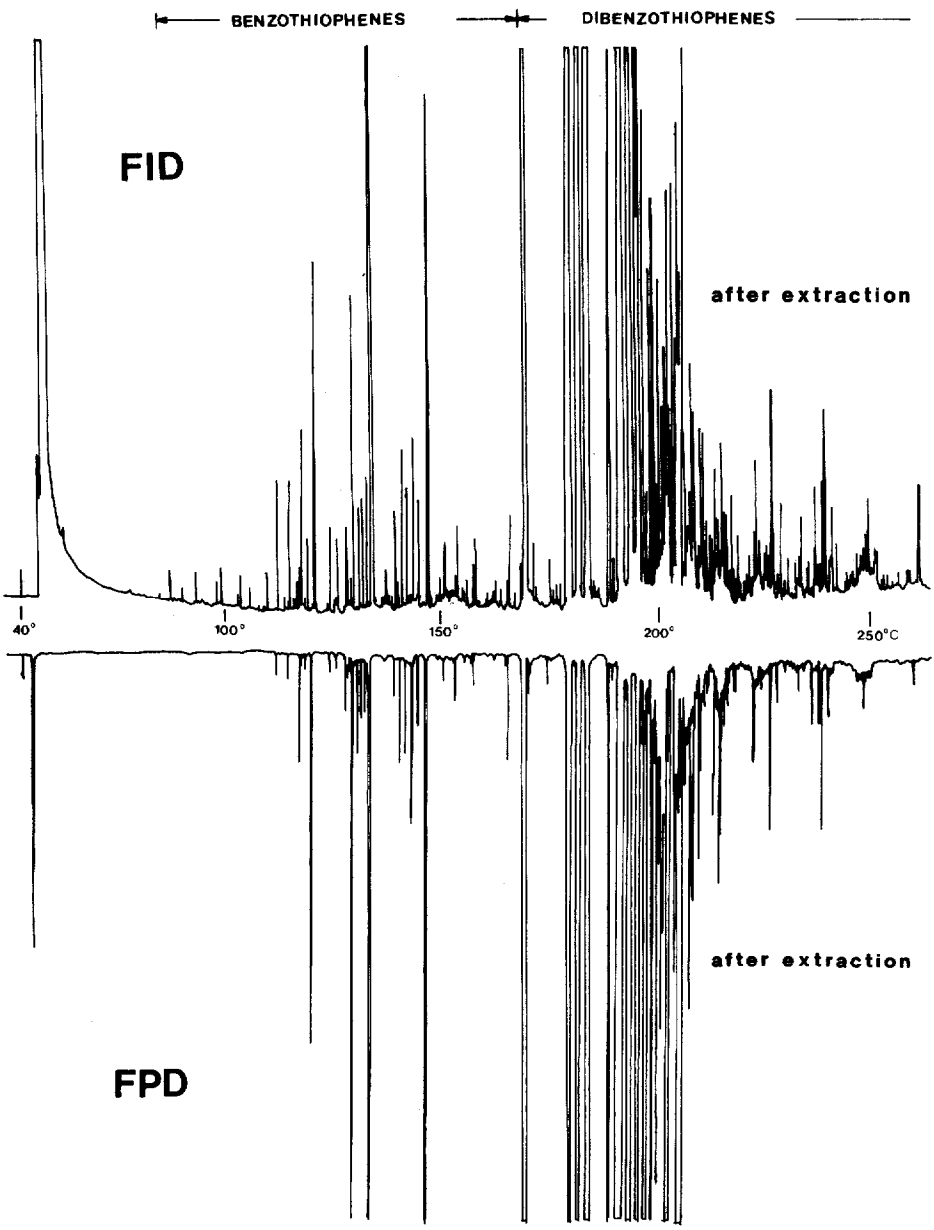


Fig. 1. Capillary gas chromatogram with parallel FID–FPD monitoring of a Khursaniya SPAH fraction resulting from the oxidation–reduction protocol via sulphone derivatives. Glass capillary column coated with OV-73, 68 m × 0.28 mm I.D., 0.15 μm film thickness, temperature programmed at 1.5°C/min.

liquid–liquid extraction of the DMSO layer. Extraction via the sulphone intermediates, which is difficult to achieve for trace substances, could be of some interest if a preparative separation of a given SPAH was attempted in order to submit the substance to another spectroscopic method. Another potential application has been

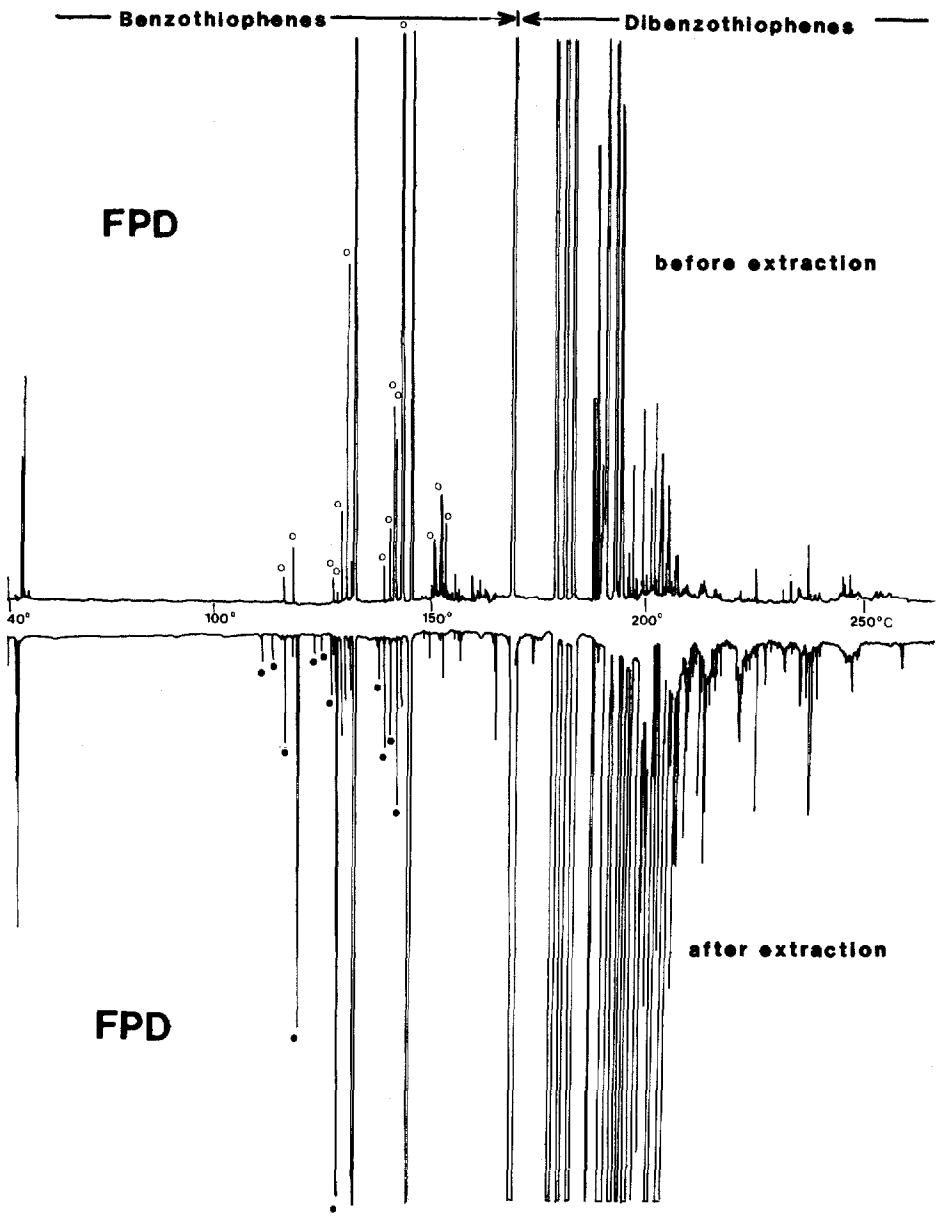


Fig. 2. FPD capillary gas chromatograms (OV-73) of the same crude oil fraction as in Fig. 1, obtained before and after the oxidation–reduction protocol. Peaks labelled with open circles in the top chromatogram correspond to peaks that disappeared during the treatment and were not found in the bottom chromatogram. Peaks labelled with closed circles in the bottom chromatogram correspond to hydrogenated artifacts not present in the starting mixture.

demonstrated for total sulphur determination, using photoelectron spectroscopy[27]. Because of its limitations and the uncontrolled introduction of artefacts, the method was not used further in this study.

Combination of solvent partition and SPAH selective detection

The saturated and the aromatic fractions from middle-east Khursaniya crude oil were efficiently separated by liquid–liquid extraction after partition of the sample over pentane and DMSO (Fig. 3), using the procedure described under Experimental.

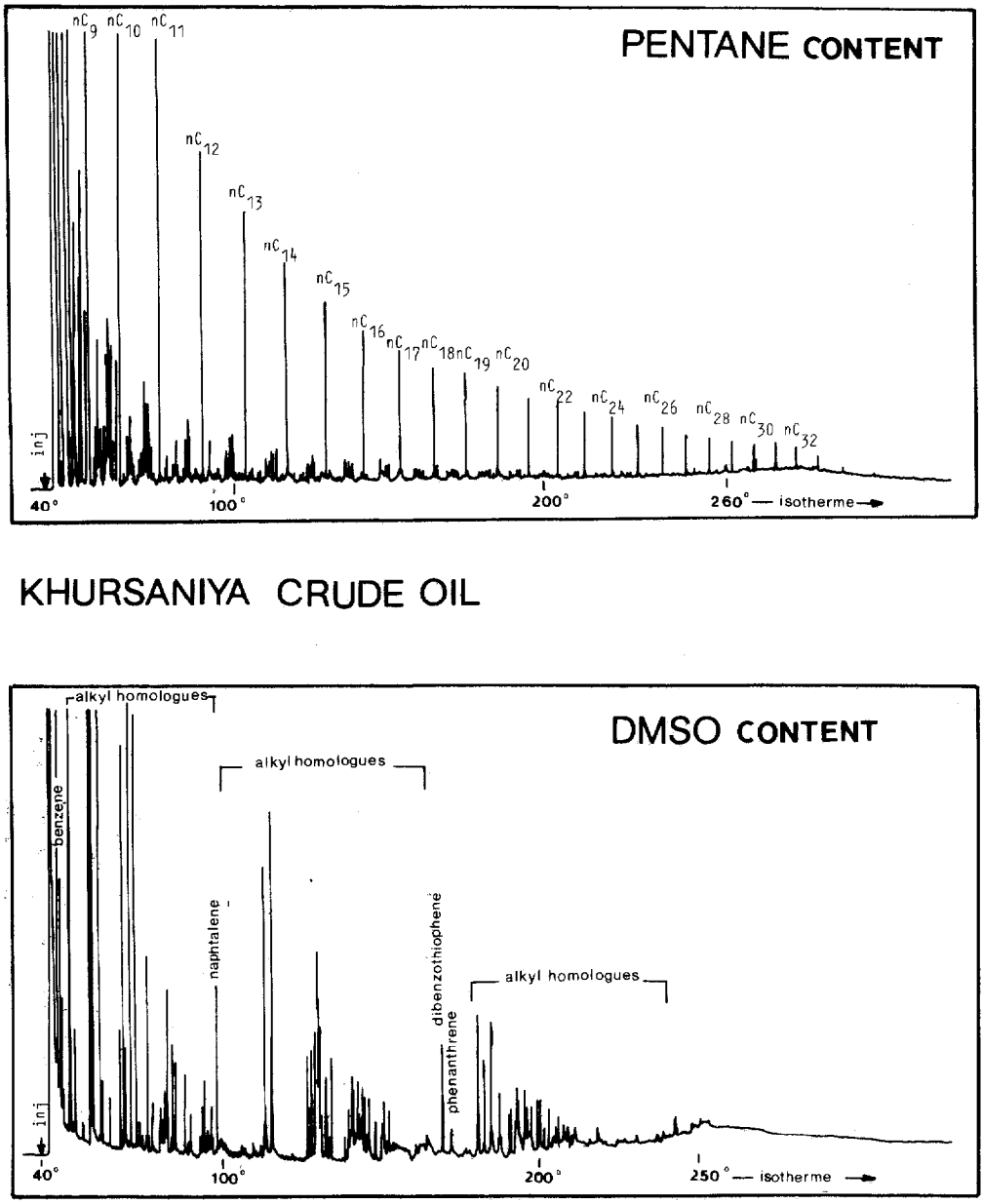


Fig. 3. Capillary gas chromatograms (OV-73) of saturated and aromatic fractions from a Khursaniya crude oil resulting from liquid–liquid extraction after partition over DMSO and pentane. The aromatic fraction represents *ca.* 3% of the total sample.

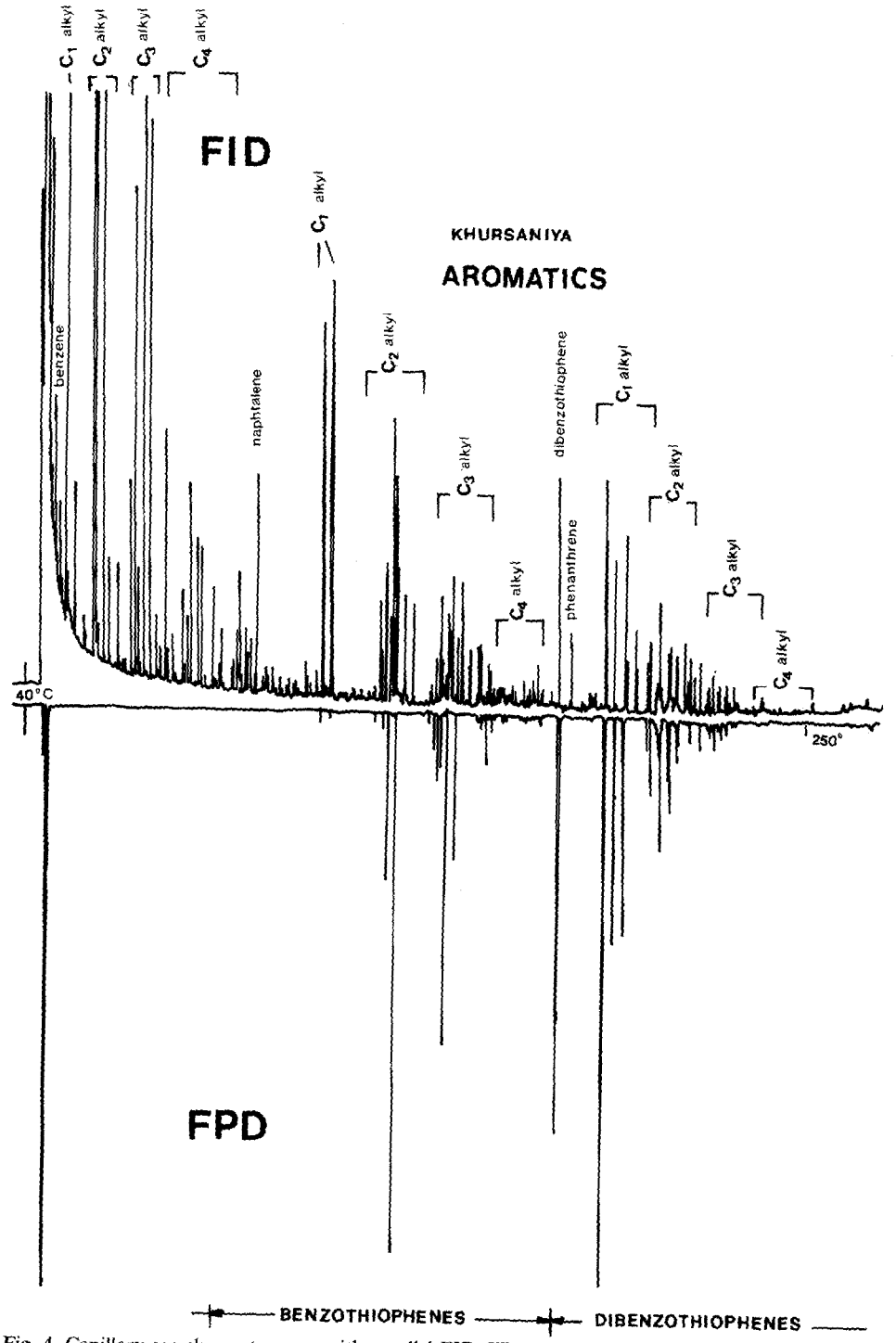


Fig. 4. Capillary gas chromatograms with parallel FID–FPD monitoring of the same aromatic fraction as in Fig. 3. Relative compositions of the aromatic fractions are alkylbenzens 33%, alkylnaphthalenes 23%, alkylphenanthrenes 13%, higher PAHs 7% and 1–4-ring SPAHs 24%.

The mixture of aromatic substances mainly contained PAHs, but selective detection of sulphur-containing molecules by GC using FPD or by GC–MS with selective ion monitoring displayed the relative distributions of SPAHs shown in Figs. 4 and 5.

SPAH response and retention parameters in capillary column GC

The response of the flame photometric detector does not vary linearly with the

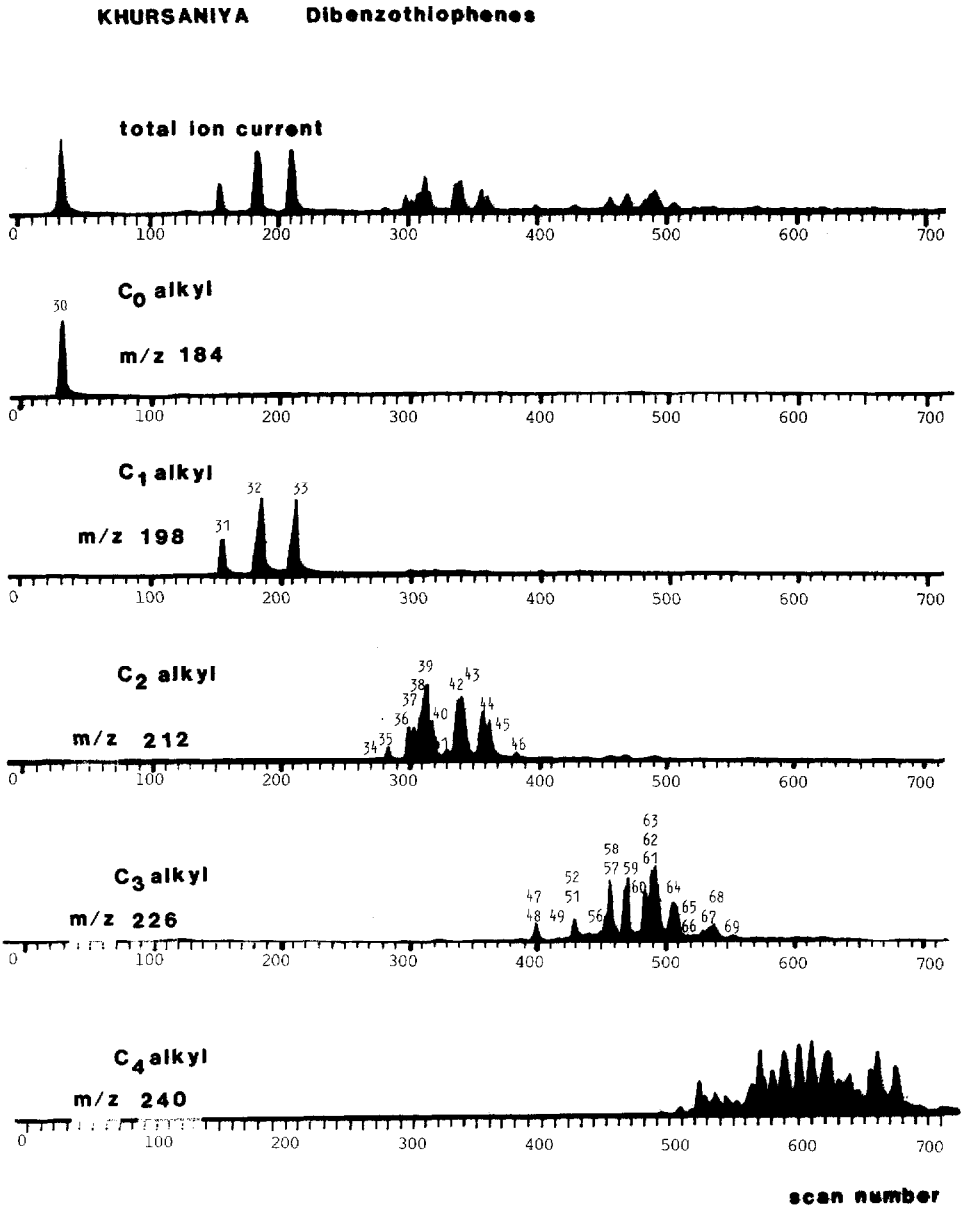


Fig. 5. Selected mass chromatograms from the capillary column GC–MS analysis of the Khursaniya aromatic fraction, showing selective detection of C_0–C_4 alkyl homologues of dibenzothiophene.

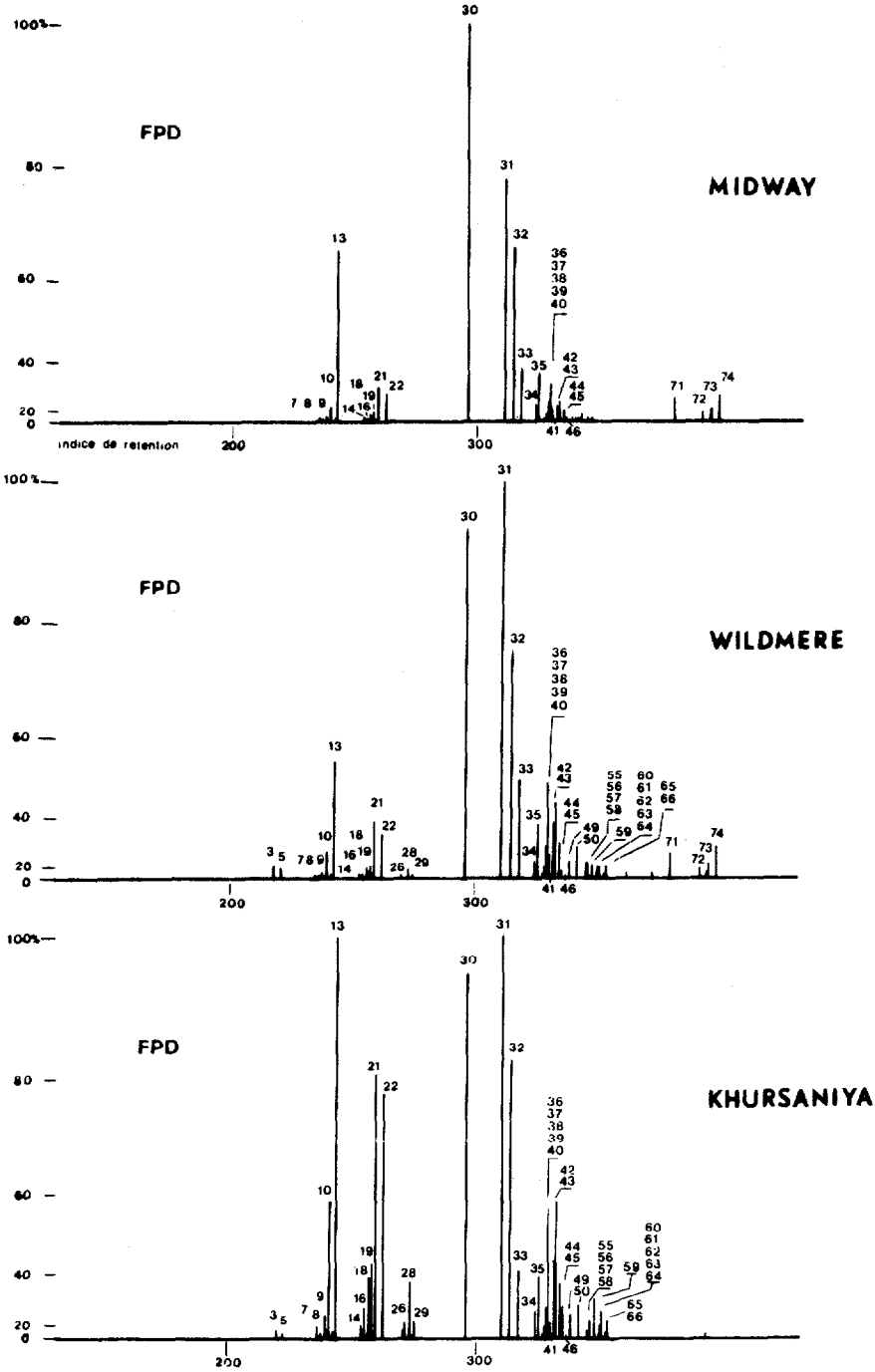
mass of the sulphur-containing analyte, but it is approximated by the equation $y = kS^n$, where n is close to 2, although it varies with the nature of the substance. Values of $n = 1.88$ and 1.92 for benzothiophene and dibenzothiophene, respectively, were determined by injecting known amounts of standards. Quantitative determinations were therefore arbitrary in the absence of accurate response factors for all compounds.

TABLE I

LIST OF THE SPAH DERIVATIVES IDENTIFIED IN FIVE SAMPLES AND RETENTION INDICES (MEANS OF FIVE MEASUREMENTS) MEASURED ON OV-73

Peak No.	*Compound*	*Retention index*	*Peak No.*	*Compound*	*Retention index*
1	*Benzothiophene*	201.6	33	1-Methyl-	319.3
2	7-Methyl-	219.2	34	Ethyl-	328.3
3	2-Methyl-	221.0	35	Dimethyl-	329.7
4	5-Methyl-	222.0	36	Ethyl-	331.6
4	6-Methyl-	222.0	37	Dimethyl-	331.8
5	3-Methyl-	223.1	38	Ethyl-	332.5
5	4-Methyl-	223.1	39	Dimethyl-	333.0
6	Ethyl-	235.0	40	Ethyl-	333.5
7	Ethyl-	237.4	41	Dimethyl-	336.0
8	Dimethyl-	238.7	42	Dimethyl-	336.1
9	Dimethyl-	240.3	43	Dimethyl-	336.5
10*	2,7-Dimethyl-	241.5	44	Dimethyl-	338.6
11	Dimethyl-	242.5	45	Dimethyl-	339.2
12*	3,5-Dimethyl-	243.4	46	Dimethyl-	341.4
13*	2,3-Dimethyl-	244.2	47	*n*-Propyl-	341.0
14	Ethylmethyl-	257.8	48	*n*-Propyl	342.4
15	Ethylmethyl-	258.5	49	Ethylmethyl-	343.8
16	Ethylmethyl-	259.1	50	Ethylmethyl-	345.5
17	Trimethyl-	259.4	51	Ethylmethyl-	345.7
18*	2,3,4-Trimethyl-	260.3	52	Ethylmethyl-	346.1
19	Trimethyl-	261.4	56	Trimethyl-	348.2
20	Trimethyl-	262.0	57	Trimethyl-	348.6
21*	2,3,5-Trimethyl-	263.0	58	Trimethyl-	349.1
21*	2,3,6-Trimethyl-	263.0	59	Trimethyl-	350.4
22*	2,3,7-Trimethyl-	266.4	60	Trimethyl-	352.3
23	Isopropylmethyl-	266.7	61	Trimethyl-	352.4
24	*n*-Propylmethyl-	270.3	62	Trimethyl-	352.9
25	Ethyldimethyl-	272.1	63	Trimethyl-	353.1
26	Ethyldimethyl-	272.9	64	Trimethyl-	354.7
27	Ethyldimethyl-	274.5	65	Trimethyl-	355.3
28	Ethyldimethyl-	275.7	66	Trimethyl-	357.1
29	Tetramethyl-	277.6	67	Trimethyl-	357.5
30	*Dibenzothiophene*	295.9	68	Trimethyl-	358.4
31	4-Methyl-	312.5	69	Trimethyl-	358.9
32	2-Methyl-	315.8	70	Trimethyl-	359.0
32	3-Methyl-	315.8			

* Identified by co-injection with the standard.


FPD
MIDWAY
indice de retention
200
300
FPD
WILDMERE
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KHURSANIYA
200
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Fig. 6.

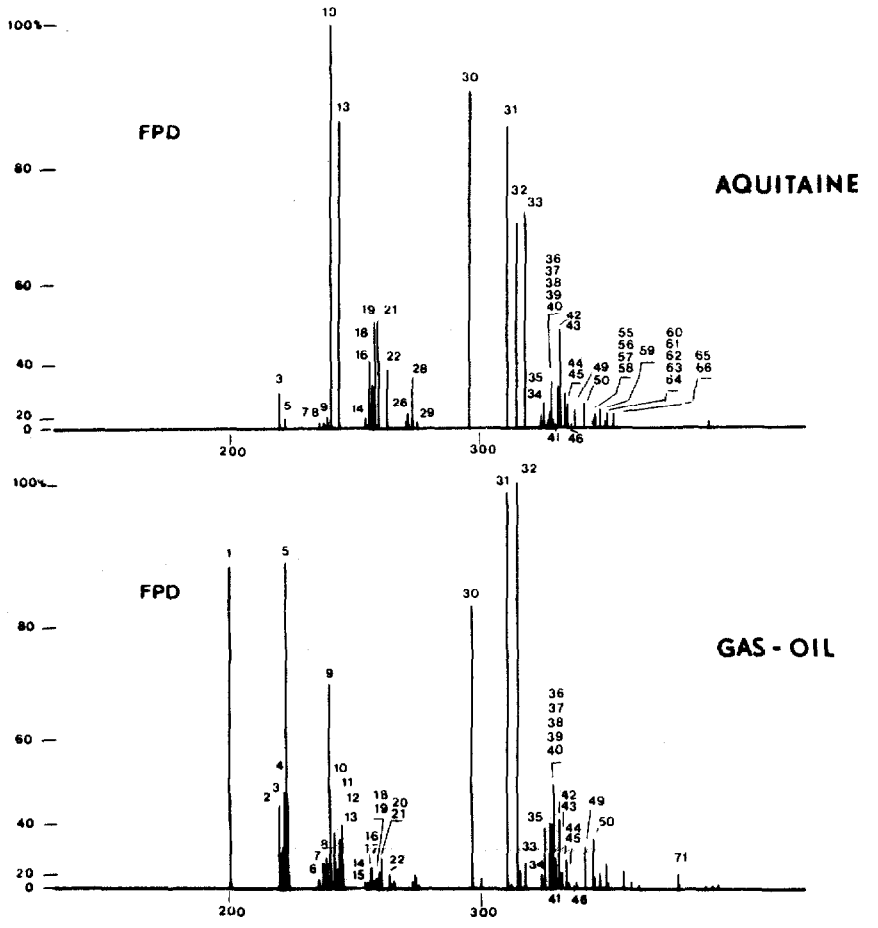

Fig. 6. Diagrammatic representation of the SPAH distribution patterns in four crude oils and one coker gas oil, derived from capillary column GC analysis with FPD monitoring of the total aromatic fractions. Numbers correspond to substances listed in Table I.

The other known problem with FPD is quenching of the response by other co-eluting non-sulphur products when analysing complex mixtures[5]. The double flame in the Varian instrument was designed to eliminate this difficulty, and possible quenching problems were in fact not observed in this study.

The reproducibility of the responses for equal amounts of SPAHs was satisfactory. The relative intensity for the different SPAHs was taken as the square root of the detector response, ignoring any variation in the response factors. They were measured by an electronic integrator (Hewlett-Packard Model 3390A) connected to the signal output. The relative standard deviation for peak-area determinations was 0.5%.

Retention indices were measured on OV-73 stationary phase (Table I) during temperature-programmed analysis. They are based on the retention index system

described in ref. 36, *.i.e.*, relative to the series of benzene benzologues (benzene = 100, naphthalene = 200, phenanthrene = 300, chrysene = 400, etc.). SPAHs are identified by the same numbers in Table I and in Figs. 5 and 6.

Identification of the number of carbon atoms in the alkyl substituents was achieved by GC–MS; an example for Khursaniya crude oil is shown in Fig. 5. Computer-generated ion current profiles for m/z = 184 (dibenzothiophene) and for $m/z = 184 + n \cdot 14$, n = 1–4, (alkyldibenzothiophenes) displayed the distribution patterns of the isomers within a given class of homologues.

The exact nature and location of the alkyl chains on the aromatic ring could not be deduced unambiguously from the electron-impact mass spectra because of a lack of specificity of the spectra. Identifications were based on co-injection with reference compounds, when available, and on comparison of the measured retention indices with those published by Vassilaros *et al.*[36].

This operating protocol was applied to four different crude oils and to a coker gas oil. The relative distributions of SPAHs are presented schematically in Fig. 6. The relative abundance, normalized to 100 for the most abundant peak, is plotted against the substance retention index on OV-73.

As observed for PAHs and NPAHs in geological samples, most SPAHs are alkylated by hydrocarbon chains. They consist of benzothiophene, dibenzothiophene and their alkylated homologues, with preference for polymethyl substituents. The histogram in Fig. 7, derived from the results in Fig. 6, emphasize the fact that abundant substances have substituents with only two or three carbon atoms. Substances substituted with more than five carbon atoms are rare or absent. The histograms for the investigated crude oils are similar and non-characteristic, considering the fact that these samples were chosen at random and have different geological histories; their differences can be measured by a large set of physico-chemical parameters (elemental analysis, biomarker distributions, etc.), but not by the distributions of their polyaromatic substances (PAHs, NPAHs, SPAHs).

The investigated SPAHs are probably thermodynamically stable end-products, formed after a series of complex transformations that affected the organic precursors during petroleum diagenesis and evolution in sediments. The transformation of kerogens and crude oils of different origins over long periods of time could produce similar distributions of randomly synthesized SPAHs. However, the specific thermodynamic stability of a few isomers could make the evolution process converge towards the accumulation in crude oils of a number of substances smaller than the maximum number of possible isomers.

Hypothesis on the random synthesis of SPAHs in geological samples

Considering that SPAHs could be synthesized at random in sediments, some simple and arbitrary assumptions have been made as an attempt to predict the maximum number of carbon substituents attached to the aromatic system that should be observed in SPAHs of geological origin.

We first assume that the observed alkylated aromatic molecules have been produced by random alkylation of aromatic precursors or random degradation of higher homologues. We consider the total number of active sites within a molecule by ignoring differences in reactivities induced when a heteroatom is present, *e.g.*, both benzene and benzothiophene have six locations that could be branched by alkyl

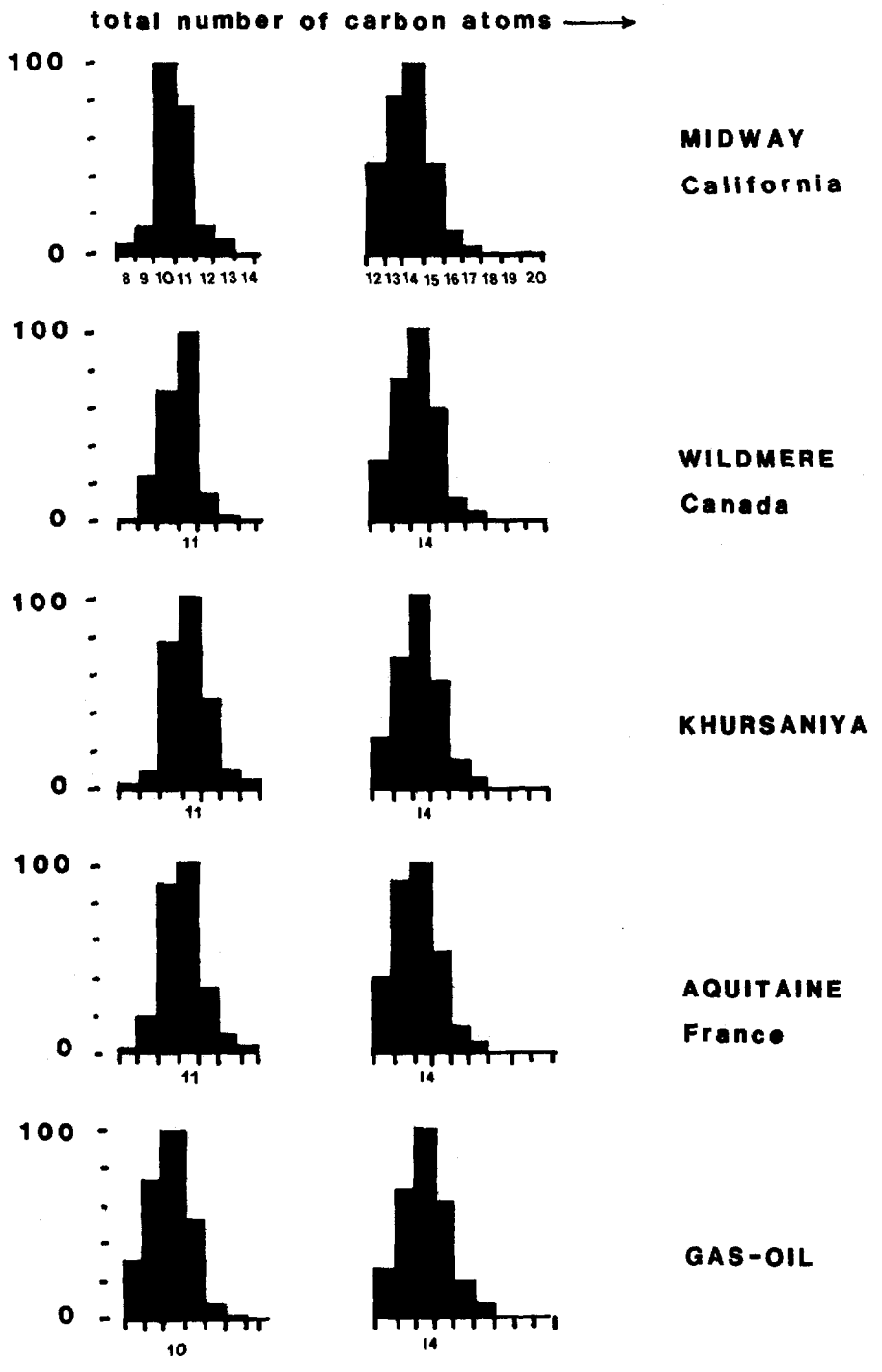

Fig. 7. Experimental histograms for the relative abundances of alkylbenzothiophenes and alkyldibenzothiophenes in the same samples as in Fig. 6.

substituents. Finally, the probability for a fragmentation (substitution of an alkyl radical by a hydrogen radical) is estimated to be double that for an alkylation. Under these conditions, benzene or benzothiophene with six centres should lead to prominent alkyl derivatives with at the maximum three carbon atoms; naphthalene and dibenzothiophene, which have eight centres, should lead to species substituted with four carbon atoms. The hypothetical histograms that one should observe have been plotted in Fig. 8.

The experimental histograms (Fig. 7) are not very different, although they maximize at C-2 instead of C-3 for benzothiophene, and at C-3 instead of C-4 for dibenzothiophene. This could be accounted for in our simple theory by taking the probability for a cleavage to be higher than double the probability for an alkylation.

The assumptions made for the calculation are simple. They do not reflect the probably extreme complexity of the alkylation and degradation mechanisms that may occur in sediments. For instance, molecules can be chemically attached to polycondensed structures, *e.g.*, the kerogen, and further released by bond cleavages. However, the predicted distributions are not very different from the experimental results. For the moment, the calculation should be taken as a simple rule of the thumb, to be tested further for a large set of samples of different origins. However, it substantiates the idea that SPAHs could be randomly synthesized, and that a large number of possible isomers should be present in SPAH distribution patterns obtained by GC.

Statistical repartition of SPAH isomers in GC chromatograms

If one assumes that SPAHs are random substances from the transformation of organic matter in sediments, then a large number of possible isomers should be present in the different samples. The theoretical maximum numbers of isomers with 0–4 carbon atoms in the alkyl substituents of ubiquitous SPAHs in geological organic mixtures are listed in Table II.

The numbers of peaks that were obsered in the different chromatograms were much lower than the expected computed numbers. Nevertheless, if every possible

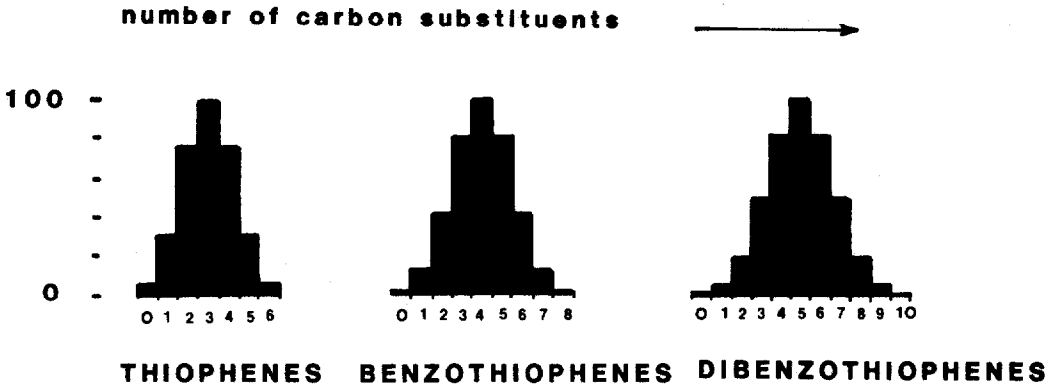

Fig. 8. Theoretical histograms for polyalkyl SPAHs with 2–4 fused aromatic rings based on the assumption of a series of random alkylation–fragmentation mechanisms.

isomer were present in the samples, then it is interesting to deduce the maximum number of them that could be separated under our chromatographic conditions, in the light of the statistical theory of the repartition of isomers in a chromatogram.

Davis and Giddings[37], Rosenthal[38] and Nagels *et al.*[39], have shown that in a given interval of retention indices, assuming a random distribution of GC peaks, the number of probable distinct GC peaks can be estimated. As an example, there are 20 possible C_2-alkyldibenzothiophenes with retention indices ranging between 328.3 and 341.4 (Table I). Assuming that the peak capacity of our column was 30, then the theory predicts that the maximum number of equally abundant peaks that could be observed is 12.

More generally, the expected number of GC peaks was calculated for each family of isomeric SPAHs and compared with the experimental number of observed peaks (Table III). Both numbers compare favourably for alkyldibenzothiophenes, whereas the experimental figure is much lower for alkylbenzothiophenes.

The most abundant substances among the alkylbenzothiophenes (peaks 3–29 in Figs. 5 and 6) correspond to congeners with a methyl group at position 2 and/or 3 on the aromatic ring. The prominent peaks numbers 13, 21 and 22 correspond to disubstituted molecules at positions 2 and 3. An increased abundance of polyaromatic molecules with methyl groups at a precise site on the aromatic ring has been observed previously in this laboratory, for instance for NPAHs with azaarene[30] or carbazole[31] structures. This could be explained by an increased stability of the isomers towards geological maturation, causing a preferential accumulation, thus introducing a bias in the statistical mechanism suggested above.

TABLE II

MAXIMUM NUMBER OF ISOMERIC C_0–C_4 ALKYL SPAHs WITH 2–4 AROMATIC RINGS

C_n	*Substituent*	*Thiophene*	*Benzothiophene*	*Dibenzothiophene*
C_0	–	1	1	1
C_1	Methyl	2	6	4
C_2	Ethyl	2	6	4
	Dimethyl	4	15	16
C_3	Isopropyl	2	6	4
	n-Propyl	2	6	4
	Methyl + ethyl	6	30	28
	Trimethyl	2	20	26
C_4	*sec.*-Butyl	2	6	4
	tert.-Butyl	2	6	4
	Isobutyl	2	6	4
	Methyl + isopropyl	6	30	28
	Methyl + *n*-propyl	6	30	28
	n-Butyl	2	6	4
	Diethyl	4	15	16
	Dimethyl + ethyl	6	60	78
	Tetramethyl	1	15	39
	Total	52	264	292

TABLE III

COMPARISON BETWEEN THE TOTAL NUMBER OF C_1–C_3 ALKYL DERIVATIVES OF BENZO- AND DIBENZOTHIOPHENES, THE TOTAL NUMBER OF PREDICTED GC PEAKS (37–39) AND THE NUMBER OF EXPERIMENTALLY OBSERVED PEAKS

Derivative	*Maximum No. of possible isomers*	*Theoretical No. of GC peaks*	*No. of observed peaks*
C_0 alkylbenzothiophene	1	1	0
C_1	6	5	2
C_2	21	10	5
C_3	62	11	6
C_0 alkyldibenzothiophene	1	1	1
C_1	4	3	3
C_2	20	12	11
C_3	62	12	12

For the group of alkyldibenzothiophenes, the observed number of GC peaks was close to the theoretical maximum number predicted by the statistical theory. The results suggest that these SPAHs were randomly synthesized in sediments, and that their chemical stabilities, under the geological conditions, were comparable.

CONCLUSION

The pre-concentration and isolation procedure for SPAHs based on liquid–liquid partition over DMSO–pentane followed by GC with FPD is suitable for the rapid determination of SPAH distribution patterns in crude oils and derived industrial mixtures. Conversely, the selective oxidation–reduction protocol is not recommended for this purpose as incomplete reaction products interfere with genuine mixture constituents.

The chemical structures and the relative abundances of major SPAHs and of a large set of less abundant constituents from samples of unrelated origins are identical. SPAHs are assumed to be terminal products of sedimentary transformation mechanisms that affect the organic matter incorporated into the sediments. Gas chromatograms of benzo- and dibenzothiophene congeners show nearly statistical patterns of all the possible isomers. Consequently, the abundant SPAHs are not usable as biomarkers or correlation markers for geochemical and petroleum exploration studies.

Geologists have known from a long time that fossils of great interest are always isolated from a mud of commonplace mineral and organic degradation products. The ubiquitous SPAHs determined in this study may conceal other interesting sulphur-containing molecular fossils, for instance the methylene thienyl hopane identified by Valisolalao *et al.*[40]. Immature crude oils and sediments still contain intermediate molecules between constituents of living organisms and the terminal polyalkyl SPAH[41], for instance thiophanes and tetracyclic structures with several saturated rings[42] and long-chain alkylthiophenes with 7–10 carbons[43]. However, they tend to disappear rapidly under geological transformation conditions, to converge toward the more stable short-chain polyalkyl SPAHs.

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