

Polycyclic aromatic sulfur heterocycles

IV. Determination of polycyclic aromatic compounds in a shale oil with the atomic emission detector[☆]

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Abstract

A method for the determination of alkylated benzothiophenes and dibenzothiophenes, naphthothiophenes and several other aromatic compounds in a shale oil as an example for a very complex matrix is presented. Fluorinated aromatics were used as internal standards. The isolated aromatic fraction of the shale oil was separated according to the number of aromatic rings. Oxidation of the two-ring compounds led to benzothiophene sulfones which were further separated by liquid chromatography according to the number of side-chain carbon atoms. The three-ring compounds were separated into a sulfur aromatics-free and a sulfur aromatics-containing fraction using palladium chloride/silica gel. The GC stationary phases necessary for the quantification of all compounds of interest are discussed. Quantitative data obtained with an atomic emission detector are given for 22 compounds in the shale oil. Conventional quantification, without the elaborate separations described here, would overestimate the phenanthrene content of the shale oil by ca. 15% and that of dibenzothiophene by nearly 50%.

1. Introduction

One of the main forms of organic sulfur in fossil fuels and many of their industrial conversion products are the thiophenes. A large part of this sulfur is bound in polycyclic aromatic sulfur heterocycles (PASHs) which in oils mainly consist of alkylated benzothiophenes (BTs) and

dibenzothiophenes (DBTs) [1]. Lately an increasing interest in PASHs can be noticed for several reasons, e.g. their potential mutagenic/carcinogenic properties [2], the difficulty of desulfurizing them for the production of low-sulfur fuels [3], their photoreactions in the aqueous phase after oil spills [4], their microbial metabolism [5,6] and their potential as possible indicators for the maturity of crude oils and their source rocks [7,8].

The analysis of PASHs exhibits several problems. For example, there is no known generally satisfactory method of separating them from the polycyclic aromatic hydrocarbons (PAHs) [9]. Additionally, sulfur-selective detection in gas

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chromatography (GC) was until recently essentially limited to flame photometric detection which shows severe drawbacks, particularly for quantifications. The advent of two new detection methods in the last years, sulfur chemiluminescence [10] and atomic emission detection (AED) [11,12] may change the situation, however. A remaining problem will always be the large number of isomers of alkylated PASHs [9] which necessitates complex work-up schemes.

In the present work we tried to find a way to realize the quantification of the C_1 -substituted benzothiophenes and of all the four parent three-ring PASHs (DBT and the three naphthothiophene isomers). The alkylated derivatives are expected to provide information on e.g. the maturity and history of the oil, whereas a reliable determination of the naphthothiophenes is interesting not only in its own right but—as will be shown below—is *necessary* for an accurate quantification of DBT and phenanthrene. In the past, the coelution of naphtho[1,2-*b*]thiophene with DBT and that of naphtho[2,1-*b*]thiophene with phenanthrene on the common GC stationary phases has been ignored, by necessity therefore leading to false quantitative data for all those compounds when the coeluting compounds are present and, for the latter, a universal GC detector is used.

In this work we will demonstrate (a) that the selection of the proper GC stationary phase will permit the separation of the four $C_{12}H_8S$ isomers (dibenzothiophene and the three naphthothiophenes) which is not possible on the columns most frequently used; (b) how a judiciously optimized work-up procedure will make it possible, for the first time, to quantitate all the six methylbenzothiophenes in a complex sample; (c) how the use of fluorinated internal standards can give reliable corrections for losses in the different work-up steps; and (d) how the selective and molar response of the atomic emission detector can be used to great advantage for the quantification of PASHs.

We have chosen a shale oil as sample because of its very complex aromatic pattern which is expected to readily expose the weaknesses of any analytical scheme.

2. Experimental

2.1. Chemicals and standards

All solvents used for the preparation of test or analyte solutions as well as those used for chromatographic purposes were of analytical-reagent grade. The 3-chloroperbenzoic acid was about 55% (Fluka, Germany). The same is true for the palladium chloride, used for preparation of the $PdCl_2$ /silica material (60%, Fluka). PAH reference compounds were commercially available (Aldrich, Germany). PASH reference compounds, with the exception of benzothiophene and dibenzothiophene (Aldrich), were synthesized in our own laboratory or obtained from Astec (Münster, Germany). The following fluorinated PAH and PASH compounds were prepared using synthetic methods: 2-fluoronaphthalene, 3-fluorophenanthrene, 5-fluorobenzothiophene and 2-fluorodibenzothiophene. Additionally, octafluoronaphthalene (Fluka) was used as internal standard. An Austrian shale oil distillate (b.p. < 400°C) from Pertisau/Tirol was chosen as test matrix for the suitability of the work-up scheme.

2.2. Sample work-up

Column chromatography

Isolation of the aromatic fraction was achieved on 10 g aluminum oxide (ICN Alumina B-Super I) in an open glass column of about 1 cm diameter and 25 cm length. Prior to use, the aluminium oxide was stored at 160°C for at least 24 h. The aromatic fraction was eluted with 50 ml benzene after removal of the aliphatics with 25 ml hexane. Separation of three-ring sulfur heterocycles from other three-ring sample constituents was performed on 2 g $PdCl_2$ /silica in a 10×0.5 cm glass column. To destroy the soluble palladium complexes of the PASHs, a small amount of aminopropyl silica was added at the end of each column [13]. PAHs were eluted with 70 ml hexane, followed by 60 ml trichloromethane for the PASHs. The $PdCl_2$ /silica was prepared by stirring silica gel (230–400 mesh) in water together with 5% (w/w) of the $PdCl_2$

powder. After 10 min stirring, the water was removed at 80°C, the remaining material was sieved (100- μ m sieve) and stored at 200°C until use.

The two-ring PASHs were separated from the two-ring PAHs after oxidation with a few mg of 3-chloroperbenzoic acid (stirring the analyte solution in 10 ml dichloromethane with the peroxy-acid at room temperature for 1 h) by chromatography on 5 g aluminium oxide (same type as above) with 40 ml benzene for the elution of the PAHs, followed by 50 ml benzene–methanol (5:1) for the sulfones.

2.3. HPLC separations

All HPLC separations were performed on an HPLC Pump 64 (Knauer, Berlin, Germany), combined with either an Altex UV detector with fixed wavelength at 254 nm, or a GynkotheK SP6 variable-wavelength UV detector. The latter was necessary for detection of the PASH sulfones at 230 nm. The separation of two- and three-ring compounds from the aromatic fraction was done by means of normal-phase HPLC on aminopropyl silica gel. We used a semipreparative 25 cm \times 2 cm column, containing Nucleosil 100-5 NH₂ material purchased from CS Chromatographie Service, Germany. Hexane (10 ml/min) was used as mobile phase. The separation of PASH sulfones according to the number of side-chain carbon atoms was achieved on a Sepralyte diphenyl column, 12 cm \times 0.8 cm (Analytichem/ICT) with methanol–water (1:1) as eluent (2 ml/min). After each work-up step, the sample volume was reduced to about 100 μ l under a gentle stream of nitrogen at room temperature. Reversed-phase HPLC fractions were extracted into dichloromethane, after dilution with water, before the volume was reduced and the fraction analyzed by GC.

2.4. GC separations

Instrumentation

A GC–AED system was mainly used for the GC investigations. It consisted of a gas chromatograph HP 5890 with automatic sampler

HP 7673A, combined with an HP 5921A atomic emission detector. The gas chromatograph was equipped with a splitless/split injection port. The system was controlled by the HP 5895A workstation, using the HP 35920A software package.

Helium 4.6 was used as carrier and plasma gas, after further purification with an HP1-220 helium purifier from VICI Valco Instruments. Other auxiliary gases (hydrogen and oxygen) were used as required by the manufacturer depending on the element detected. Gas selection and detector tuning was computer controlled whereas the plasma gas flow-rate, essential for optimal sensitivity and peak shape in the sulfur trace, was set manually to about 60 ml/min [12].

Columns

The following fused-silica capillary columns were used.

Column 1: SB-Biphenyl-30, Lee Scientific, 25 m \times 0.32 mm, 0.25 μ m film.

Column 2: SP 2331 (100% cyanopropyl), Supelco, 60 m \times 0.32 mm, 0.2 μ m film.

Column 3: DB5, J & W Scientific, 30 m \times 0.25 mm, 0.25 μ m film.

Helium flow-rates were set to about 30 cm/s, samples were injected in the splitless/split mode with a purge delay time of 30 s. Chromatographic conditions are specified in the figures.

Evaluation

Quantitative data were calculated using several internal standards. Due to the linear and molar elemental response of AED [12], neither a correction factor for the different compounds of interest nor a calibration graph was necessary for evaluation. Analyte concentrations were simply calculated by the area ratios of analyte and internal standard (in the elemental traces) multiplied by the amount of internal standard related to C or S.

2.5. Peak numbering

Sulfur-containing compounds were numbered according to their elution order on SB-30-Bi-

phenyl (see Table 1). The PAH numbering is taken from Ref. [14].

3. Results and discussion

3.1. GC separations

First the GC properties of the compounds under study were investigated with reference compounds. Severe coelution is known to occur for many PASHs on the non-polar phases normally used for the separation of aromatics [9]. A biphenyl phase has been shown to provide a useful separation of the important C_1 -DBTs [15] but it does not allow the complete separation of the four-ring parent compounds. On screening several columns we discovered that the very polar cyanopropyl phase is capable of separating the four three-ring PASHs. The retention data on this and on the biphenyl phase are reported in Table 1 which thus complements and extends the data already reported for the C_1 - and C_2 -BTs on three other phases [9]. The retention indices in Table 1 are reported in two forms, depending on whether sulfur selective detection is used or not. The I_C scale is based on benzene, naphthalene, phenanthrene, chrysene and picene as the basis [16,17] and is used for universal detectors and the carbon-selective mode of AED. The I_S scale [9] is used for sulfur-selective detectors and is based on thiophene, BT, DBT and benzo[*b*]naphtho[2,1-*d*]thiophene as reference points.

The retention data listed in Table 1 show that on the non-polar (but polarizable) biphenyl phase the elution is quite similar to that on e.g. DB-5. The same coelutions are observed for C_1 -BTs (3- with 4- and 5- with 6-methylbenzothiophene) as on DB-5, resulting in four peaks for the six isomers. The C_2 -BTs also show considerable coelution problems. A better resolution is obtained for the methyl dibenzothiophenes which are resolved to an analytically useful degree, although no complete baseline separation is reached for 2- and 3-methyldibenzothiophene. Coelution of dibenzothiophene with naphtho[1,2-*b*]thiophene and of anthracene

with naphtho[2,1-*b*]thiophene causes problems for the quantification of both PAH and PASH parent ring systems on this phase.

The cyanopropyl column has a fairly low upper thermal limit of 250°C and therefore does not allow the detection of four-ring aromatics during the temperature program. Consequently, retention indices over 300 cannot be calculated properly. Therefore, in Table 1, indices exceeding this value are given in parenthesis to indicate this deviation from theory and hence should be used with some caution; they are included here mainly in order to show the relative order of elution of the analytes on this phase.

This polar stationary phase discriminates better between PAHs and PASHs than the non-polar phases traditionally used. The introduction of a sulfur atom into the aromatic system of a terminal ring leads to a stronger retention on the cyanopropyl phase compared to other phases. On the biphenyl phase, BT elutes 2.3 index units after naphthalene and thieno[2,3-*b*]thiophene 2.5 units after BT. On the cyanopropyl phase, those differences increase to 7.6 and 7.0 units, respectively (Table 2). For the four three-ring PASHs (dibenzothiophene and the three naphthothiophenes), a similar albeit somewhat less pronounced effect is obtained. Thus their I_C indices change from 295.35, 295.68, 300.94 and 306.29 on biphenyl to 295.45, 297.22, 305.65 and 310.63 on cyanopropyl. Significantly, dibenzothiophene, with an internal thiophenic ring, displays the same index on both phases but the naphthothiophenes, which possess a terminal thiophenic ring, are more strongly retained. As a result, on the cyanopropyl phase, the four three-ring PASHs can be separated from each other and from other interferences and therefore, for the first time, can be quantified individually. In very complex samples however, problems may occur due to the strong retention of the naphthothiophenes and a possible interference from C_1 -dibenzothiophenes and/or C_1 -naphtho[1,2-*b*]thiophenes might be noticed.

The data in Table 1 make it obvious that the polar phase separates the analytes not only according to boiling points but that electronic effects also play a role. The degree of methyl-

Table 1
Retention indices of two- and three-ring sulfur heterocycles on three different stationary phases

No.	Compound	SB-30-Biphenyl		SP-2331		DB-5 I_c
		I_c	I_s	I_c	I_s	
1	Benzothiophene	202.29	200.00	207.59	200.00	201.88
2	Thieno[2,3- <i>b</i>]thiophene	204.83	202.67	214.05	207.33	202.73
3	Thieno[3,2- <i>b</i>]thiophene	205.81	203.78	215.68	209.19	203.92
4	7-Methylbenzothiophene	217.19	216.00	212.98	206.12	
5	2-Methylbenzothiophene	218.46	217.38	213.78	207.03	219.34
6	5-Methylbenzothiophene	220.71	219.79	217.50	211.25	
7	6-Methylbenzothiophene	220.75	219.83	217.50	211.25	
8	3-Methylbenzothiophene	221.86	221.03	219.09	213.06	
9	4-Methylbenzothiophene	222.07	221.25	219.48	213.51	
10	7-Ethylbenzothiophene	230.92	230.79			
11	2-Ethylbenzothiophene	233.06	233.09			
12	2,7-Dimethylbenzothiophene	233.25	233.27	219.32	213.32	
14	6-Ethylbenzothiophene	234.84	235.01			
15	5-Ethylbenzothiophene	234.87	235.04			
16	5,7-Dimethylbenzothiophene	235.72	235.92	224.71	217.34	
17	2,6-Dimethylbenzothiophene	236.13	236.37	223.85	218.46	
18	2,5-Dimethylbenzothiophene	236.36	236.61			
19	3,7-Dimethylbenzothiophene	236.45	236.70	224.29	218.96	
21	2,4-Dimethylbenzothiophene	237.41	237.73	226.68	221.68	
22	4,7-Dimethylbenzothiophene	237.53	237.87	224.71	219.44	
23	3,5-Dimethylbenzothiophene	239.71	240.21	229.76	225.18	
24	3,6-Dimethylbenzothiophene	239.89	240.45	230.04	225.50	
25	4,6-Dimethylbenzothiophene	240.17	240.71	229.40	224.78	
26	2,3-Dimethylbenzothiophene	240.43	240.99	228.87	224.16	
28	6,7-Dimethylbenzothiophene	241.28	241.89	231.02	226.60	
29	5,6-Dimethylbenzothiophene	244.77	245.65	236.36	232.67	
30	4,5-Dimethylbenzothiophene	245.96	246.93	238.01	234.55	
31	3,4-Dimethylbenzothiophene	248.90	250.15	241.50	238.55	
36	Benzo[<i>b</i>]thieno[2,3- <i>d</i>]thiophene	293.21	297.70	295.40	299.73	293.28
39	Dibenzothiophene	295.35	300.00	295.45	300.00	295.35
40	Naphtho[1,2- <i>b</i>]thiophene	295.68	300.40	297.22	(301.88)	295.01
41	Benzo[<i>b</i>]thieno[3,2- <i>d</i>]thiophene	296.02	300.81	(300.43)	(305.22)	295.51
42	[1,2- <i>b</i> ;3,4- <i>b'</i>]Dithienobenzene	297.22	302.27	(304.05)	(308.65)	301.35
43	Naphtho[2,1- <i>b</i>]thiophene	300.94	306.65	(305.65)	(310.16)	300.00
44	[1,2- <i>b</i> ;4,3- <i>b'</i>]Dithienobenzene	303.16	312.22	(312.82)	(316.94)	301.35
45	Naphtho[2,3- <i>b</i>]thiophene	306.29	312.36	(310.63)	(314.86)	303.78
46	4-Methyldibenzothiophene	309.24	315.52	(297.87)	(302.56)	
47	2-Methyldibenzothiophene	213.13	318.60	(303.66)	(308.28)	316.25
48	3-Methyldibenzothiophene	312.94	319.46	(304.46)	(309.03)	
49	1-Methyldibenzothiophene	317.00	323.80	(307.30)	(311.72)	
50	4-Ethyldibenzothiophene	321.09	328.34			
51	4,6-Dimethyldibenzothiophene	323.34	330.74			
52	2-Ethyldibenzothiophene	324.26	331.72			
53	3,6-Dimethyldibenzothiophene	326.79	334.42			
55	2,8-Dimethyldibenzothiophene	326.43	336.16	(313.25)	(317.34)	
56	3,8-Dimethyldibenzothiophene	329.33	337.12	(314.24)	(318.28)	
57	3,4-Dimethyldibenzothiophene	333.12	341.16	(316.24)	(320.17)	
58	1,9-Dimethyldibenzothiophene	334.22	342.33			
59	2,3-Dimethyldibenzothiophene	335.80	344.01	(322.45)	(326.03)	

(Continued on p. 330)

Table 1 (continued)

No.	Compound	SB-30-Biphenyl		SP-2331		DB-5 I_C
		I_C	I_S	I_C	I_S	
62	Phenanthro[4,5- <i>bcd</i>]thiophene	350.38	359.56			
63	Benzo[<i>b</i>]indeno[1,2- <i>d</i>]thiophene	364.33	374.42			
65	Benzo[<i>b</i>]phenanthro[4,5- <i>bcd</i>]thiophene	373.26	383.93			
66	Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	388.35	400.00			
67	Benzo[<i>b</i>]naphtho[2,3- <i>d</i>]thiophene	395.53	(407.67)			
68	Phenanthro[3,4- <i>b</i>]thiophene	396.96	(409.18)			
69	Phenanthro[2,1- <i>b</i>]thiophene	(402.05)	(414.61)			

tion seems to be less important than for the non-polar phase. Thus the earliest-eluting dimethyl-BT elutes faster than the last-eluting monomethyl-BT; in contrast, on the biphenyl phase, a difference of no less than 11 retention index units exists between the same two compounds. As on other phases, the six C_1 -BTs show four peaks so that this phase cannot be used for the analysis of the C_1 -BTs; however, the four C_1 -DBTs are resolved.

3.2. Work-up and separation of PAHs and PASHs

For complex samples such as crude oils, the aromatic fraction is preferentially isolated through adsorption chromatography on alumina or mixtures of alumina and silica gel. The aliphatic compounds are eluted in a first fraction typically with hexane as eluent, and in a second fraction the polycyclic aromatic compounds (PACs) are obtained with a more polar eluent, e.g. toluene. Despite the high selectivity of AED

for sulfur over carbon the large number of alkylated PASHs generally present in such oils makes this aromatic fraction too complex for direct quantification of many compounds.

Traditionally two principally different schemes are used for the further separation of PAHs and PASHs. Oxidation of the sulfur functionality to a sulfone, followed by adsorption chromatographic separation of the polar sulfones from the non-polar unreacted PAHs, is one possibility. Favored oxidant is *meta*-chloroperbenzoic acid (MCPBA), whereas hydrogen peroxide was recently reported as being completely unsuitable [9]. A major drawback of the oxidation approach is the fact that with the exception of BTs and some of its alkyl derivatives, PASHs containing terminal thiophene rings are largely lost, probably through oxidation of other molecular features. Thus the naphthothiophenes cannot be analyzed after oxidation with MCPBA.

The second separation process involves liquid chromatography on palladium chloride deposited on silica gel [18]. In this work we used a small

Table 2
Influence of an aromatic sulfur atom on the retention behavior of some PACs

Column	I_C naphthalene	Increment	I_C benzothiophene	Increment	I_C thieno[2,3- <i>b</i>]- thiophene	Increment	I_C thieno[3,2- <i>b</i>]- thiophene
DB-5	200.00	1.88	201.88	0.85	202.73	1.19	203.92
SB-30- Biphenyl	200.00	2.29	202.29	2.54	204.83	0.98	205.81
SP-2331	200.00	7.59	207.59	6.46	214.05	1.63	215.68

amount of aminopropyl silica to destroy the soluble complexes between palladium and the sulfur aromatics [13]. Problematic is the fact that PASHs with terminal thiophenic rings seem to elute much faster than those with an internal ring, thus being collected in the PAH fraction [13]. The naphthothiophenes can only be collected with the dibenzothiophenes if the cut between PAHs and PASHs is done very accurately; PAHs with more than three rings must not be present since they are somewhat more strongly retained and could elute with the sulfur heterocycles.

In order to make possible the quantification of a large number of PASHs, we decided on the following somewhat elaborate work-up procedure which is a combination of the two principles just discussed and which enabled us to use the mild $\text{PdCl}_2/\text{silica}$ separation also for the naphthothiophenes.

As a first step, the aromatic fraction of the shale oil was separated on an aminopropyl HPLC phase resulting in a two-ring and a three-ring fraction. In the following step the second (three-ring) fraction was subjected to a separation on $\text{PdCl}_2/\text{silica}$. The first one (two-ring fraction) was oxidized with MCPBA (we were unable to get satisfactory results with the suggested replacement for MCPBA, the magnesium salt of monoperoxyperphthalic acid [19]) and the resulting two-ring PASH sulfones (PASHO_2) were separated from the unchanged PAHs on silica. An overview of the complete work-up scheme is presented in Fig. 1.

3.3. Fluoroaromatics as internal standards

Since all sample manipulations are associated with losses of analytes, internal standards (ISs) are preferentially added to the sample before work-up. In PAC work, essentially with mass spectrometric methods, deuterated aromatics have long been used for this purpose [20–22]. We have recently shown [23,24] that fluorinated PACs offer several advantages and thus they were tested here for their suitability for the analysis of PASHs.

Selected as ISs for the two-ring PAHs were

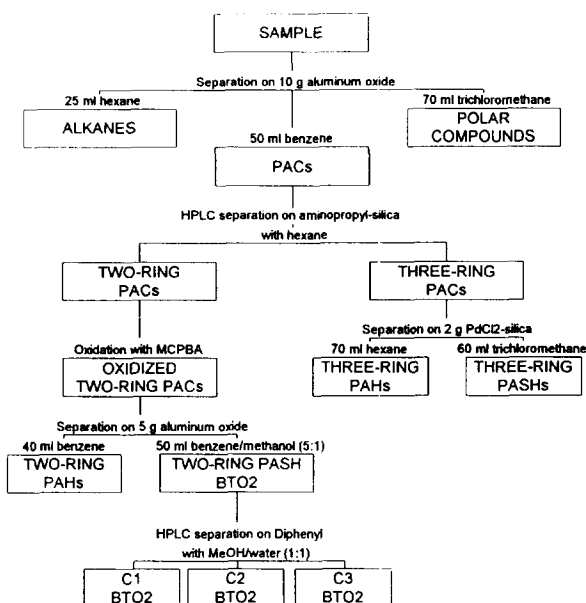


Fig. 1. Flow chart for the separation of two- and three-ring PACs from complex matrices.

2-fluoronaphthalene and octafluoronaphthalene; for the three-ring PAHs, 3-fluorophenanthrene was chosen. The benzothiophenes were quantified using 5-fluorobenzothiophene whereas 2-fluorodibenzothiophene was found to be suitable for the three-ring PASHs. Those fluoro derivatives were chosen because they are well separated from other sample constituents which typically occur in complex oil samples and because they show suitable elution characteristics in the several separation steps of the sample work-up (Fig. 2).

In order to establish the viability of the proposed separation scheme and the use of the internal standards mentioned, a test solution was made up of four benzothiophenes, six three-ring PASHs and six PAHs together with a fluorinated derivative of each of the four parent compounds studied here (BT, DBT, naphthalene, phenanthrene). The test solution was taken through all the steps described above and quantified following each of them. The relative amounts of recovered analytes present after each work-up step, based on a comparison with the fluorinated ISs, are summarized in Fig. 2. It is obvious that

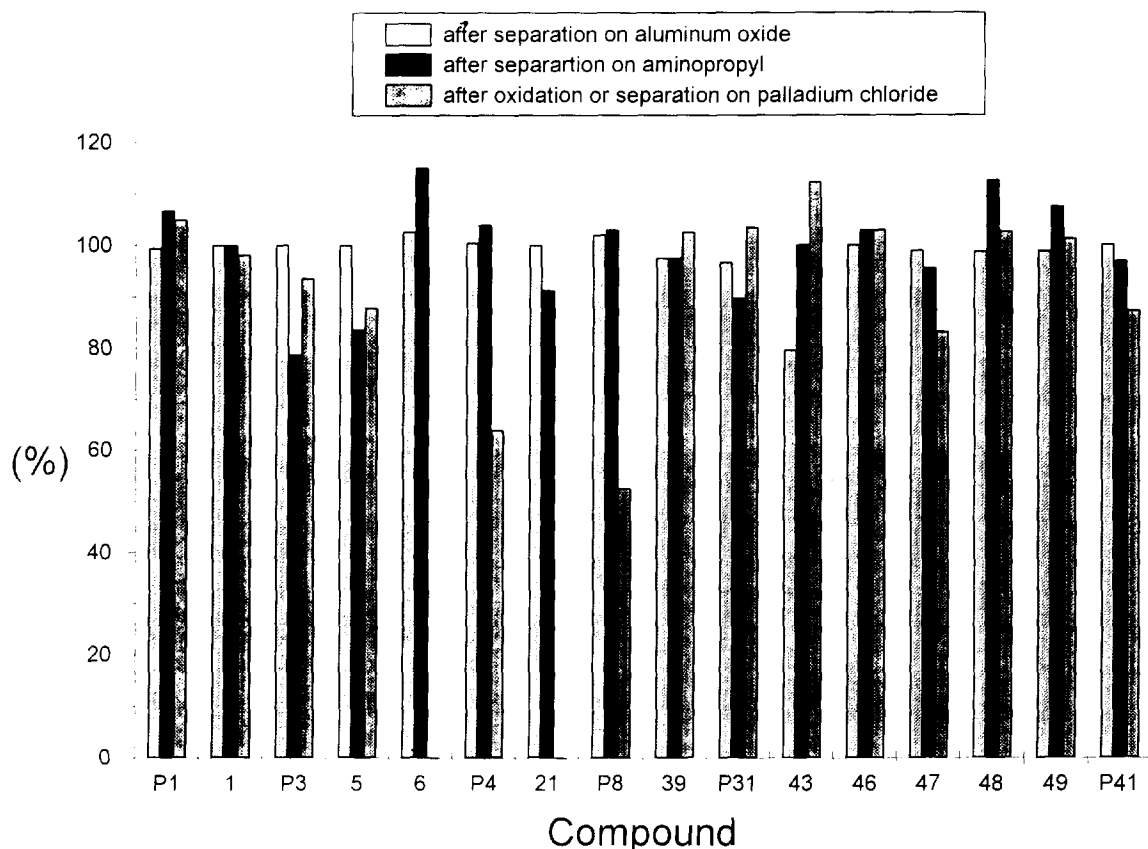


Fig. 2. Recovery of the PACs in the test mixture after each of the several clean-up steps; starting amount = 100%. Compounds: P1 = naphthalene; P3 = 2-methylnaphthalene; P4 = 1-methylnaphthalene; P8 = 2,3-dimethylnaphthalene; P31 = phenanthrene; P41 = 1-methylphenanthrene; 1 = benzothiophene; 5 = 2-methylbenzothiophene; 6 = 5-methylbenzothiophene; 21 = 2,4-dimethylbenzothiophene; 39 = dibenzothiophene; 43 = naphtho[2.1-*b*]thiophene; 46 = 4-methyldibenzothiophene; 47 = 2-methyldibenzothiophene; 48 = 3-methyldibenzothiophene; 49 = 1-methyldibenzothiophene.

most analytes show excellent quantitative data even after several work-up steps and, for the BTs, a chemical reaction.

As demonstrated by the data in Fig. 2, the chromatographic steps on alumina and aminopropyl silica lead to no serious selective losses of any of the compounds. The separation of the PASHs from the PAHs is more problematic. Although the oxidation with MCPBA does not seem to change the pattern of the BTs, considerable losses are recorded for some PAHs, notably 1-methyl- (P4) and 2,3-dimethylnaphthalene (P8). This is in line with the susceptibility of these compounds to oxidation with hydrogen peroxide [9] and stresses that the oxidation of

interfering PASHs in order to remove them for an interference-free determination of PAHs, a fairly common practice, should be avoided. Several large new peaks were detected in the carbon-selective trace as products of PAH oxidation; they were not further characterized (Fig 3).

The losses after chromatography on PdCl₂/silica are less severe. Only 2-methyl-DBT deviates slightly from the other compounds, the cause probably being the very strong retention of this compound on PdCl₂/silica [13], which necessitates a large volume of solvent to wash it quantitatively out of the column. The strong retention of 2-methyl-DBT is further increased by the thermal pretreatment of the PdCl₂/silica

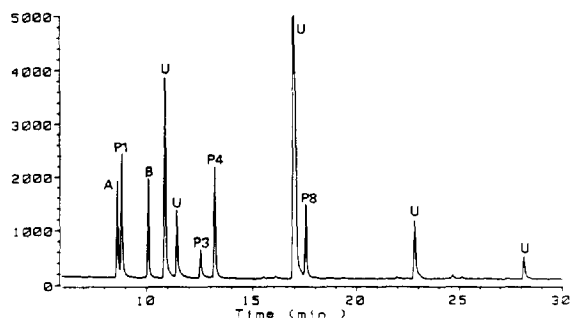


Fig. 3. GC–AED chromatogram of the two-ring PAH fraction obtained from the test mixture after oxidation with 3-chloroperbenzoic acid and LC separation on aluminum oxide, on the SB-30-Biphenyl column. $T_{\text{oven}} = 80^{\circ}\text{C}$ (2 min), then $4^{\circ}\text{C}/\text{min}$ to 280°C . Carbon-selective mode. Peaks: A = 2-fluoronaphthalene; B = octafluoronaphthalene; U = unknown oxidation product; other peaks as in Fig. 2.

(see Experimental), which is necessary for the complete elution of the naphthothiophenes in the PASH fraction. The marginally higher recoveries for several three-ring analytes may be due to the fact that the internal standard used (2-F-DBT) is somewhat more volatile than the analytes and therefore shows slightly higher losses on reduction of the volume of the solution (under a gentle stream of nitrogen) after the last separation.

This initial experiment thus shows that it should be possible to quantify PASHs after several work-up steps, using fluorinated ISs, with very good (relative) recovery, independent of the method used for separating PAHs and PASHs.

3.4. Analysis of shale oil

The distillate of an Austrian shale oil boiling below 400°C was used for the following investigation. The aromatics were isolated through column chromatography on alumina after addition of the same fluorinated IS as were used above. The carbon and sulfur selective traces were recorded using GC–AED (Fig. 4). It is obvious that the complexity of the sample is so high that despite the use of sulfur-selective detection, only BT, 2- and 7-MeBT can be quantified without further work-up.

The HPLC fractionation on aminopropyl led

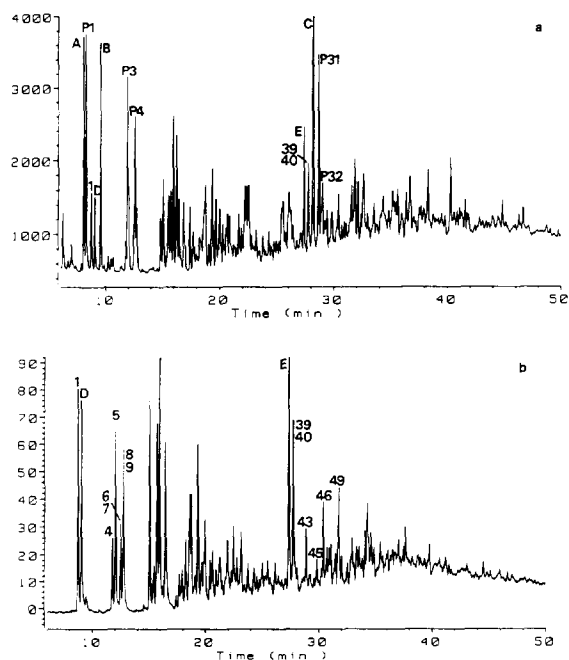


Fig. 4. GC–AED chromatogram of the aromatic fraction obtained from the Austrian shale oil after LC separation on aluminum oxide, on the SB-30-Biphenyl column. $T_{\text{oven}} = 80^{\circ}\text{C}$ (2 min), then $4^{\circ}\text{C}/\text{min}$ to 280°C (15 min). (a) Carbon-selective mode, (b) sulfur-selective mode. Peaks: A = 2-fluoronaphthalene; B = octafluoronaphthalene; C = 3-fluorophenanthrene; D = 5-fluorodibenzothiophene; E = 2-fluorodibenzothiophene; P1 = naphthalene; P3 = 2-methylnaphthalene; P4 = 1-methylnaphthalene; P31 = phenanthrene; P32 = anthracene; 1 = benzothiophene; 4 = 7-methylbenzothiophene; 5 = 2-methylbenzothiophene; 6 = 5-methylbenzothiophene; 7 = 6-methylbenzothiophene; 8 = 3-methylbenzothiophene; 9 = 4-methylbenzothiophene; 39 = dibenzothiophene; 40 = naphtho[1,2-*b*]thiophene; 43 = naphtho[2,1-*b*]thiophene; 45 = naphtho[2,3-*b*]thiophene; 46 = 4-methyl-dibenzothiophene; 49 = 1-methyldibenzothiophene.

to a two-ring and a three-ring fraction. The corresponding gas chromatograms are depicted in Fig. 5.

Even with this fractionation no further two-ring compounds could be reliably quantified. Note the overlap of MeBTs with methylnaphthalenes in the carbon-selective trace which makes a determination of the latter impossible under those conditions. In the three-ring chromatograms (Fig. 5c and d), possibly phenanthrene (C) could be quantified without interfer-

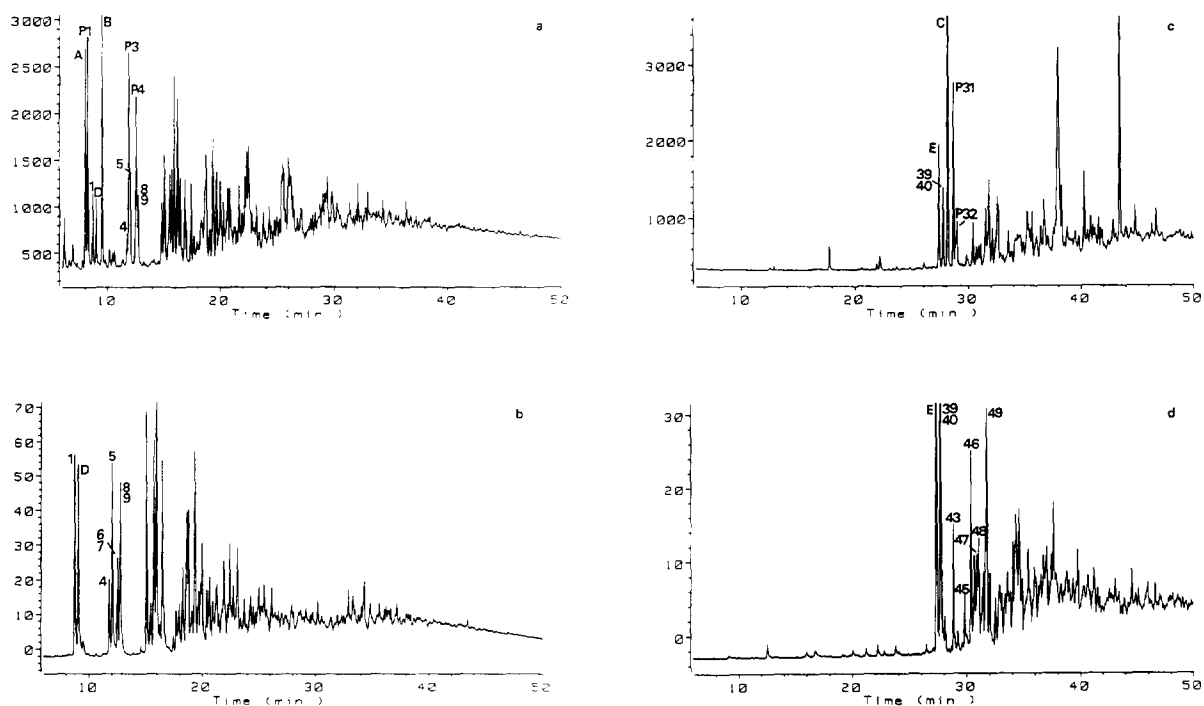


Fig. 5. GC-AED chromatograms of the two-ring PAC and three-ring PAC fraction obtained from the aromatic fraction of an Austrian shale oil after HPLC separation on an aminopropyl column, on the SB-30-Biphenyl column. $T_{\text{oven}} = 80^{\circ}\text{C}$ (2 min), the $4^{\circ}\text{C}/\text{min}$ to 280°C (15 min). (a) Two-ring fraction in the carbon-selective mode, (b) two-ring fraction in the sulfur-selective mode, (c) three-ring fraction in the carbon-selective mode, (d) three-ring fraction in the sulfur-selective mode. Peaks: 47 = 2-methyldibenzothiophene; 48 = 3-methyldibenzothiophene; other peaks as in Fig. 4.

ences. Other parent compounds, for example DBT, naphtho[2,1-*b*]thiophene and anthracene, cannot be determined due to the coelution problems noted above. Likewise the alkylated derivatives are too numerous to be sufficiently resolved, in the carbon- as well as the sulfur-selective trace. Consequently further separations become necessary.

3.5. Two-ring PASHs

The oxidation of the two-ring fraction with MCPBA was performed in the usual way but instead of the traditional liquid-liquid separation of the spent reagent and the products, which is followed by an open column separation of oxidized and non-oxidized compounds, we developed a more convenient and faster procedure combining these two steps into one using chromatog-

raphy of the crude product solution (see Experimental). Although sulfones of PASHs can advantageously be analyzed by GC [9], the oxidized fraction obtained here cannot be used directly. The numerous sulfones do not elute according to the number of carbon atoms in the side chains as do the parent aromatics, thus resulting in serious coelution problems (Fig. 6a). One example among many may be the sulfones of 5-methyl-BT and 2,4-dimethyl-BT which co-elute on non-polar phases although the parent compounds are separated by about 17 retention index units. A mass-selective detector will of course solve this problem since the masses for compounds of different degrees of alkylation can be selectively monitored.

If such a detector is not available, a final separation becomes necessary. An LC step was chosen here. On an octadecyl phase an un-

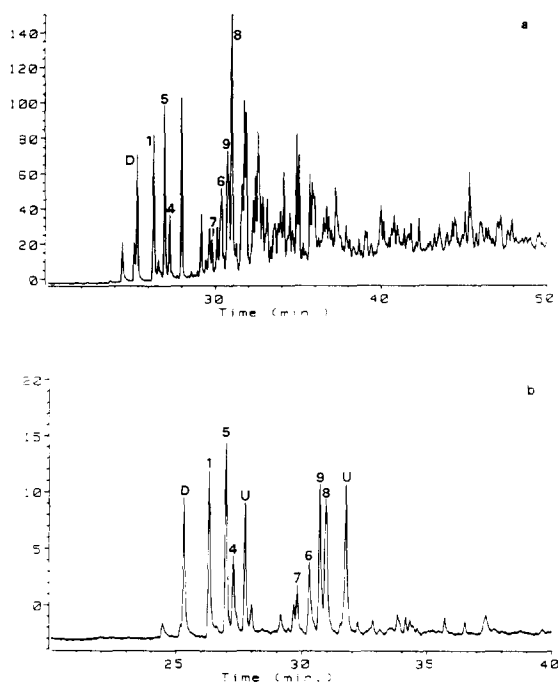


Fig. 6. GC-AED chromatogram of the oxidized PASH fraction obtained from an Austrian shale oil after several separation steps on an SB-30-Biphenyl column (sulfur-selective mode). $T_{\text{oven}} = 80^{\circ}\text{C}$ (2 min), then $4^{\circ}\text{C}/\text{min}$ to 280°C . (a) Oxidized two-ring fraction prior to separation on Sepralyte Diphenyl, (b) first fraction of the Sepralyte Diphenyl separation (see Fig. 7). Peaks: see Fig. 4 (all compounds as sulfones).

wanted resolution of individual sulfones is obtained, whereas a diphenyl stationary phase provided exactly the desired separation according to the number of side-chain carbon atoms (Fig. 7). The $\text{C}_1\text{-BTO}_2$ eluate, marked in Fig. 7, was collected; the corresponding gas chromatogram is reproduced in Fig. 6b and shows complete resolution of all the $\text{C}_1\text{-BTO}_2\text{s}$ although some minor interfering peaks can be seen in the chromatogram. To our knowledge this is the first time that all the six monomethyl-BTs can be quantified simultaneously.

Although it was not done here, it is conceivable to analyze the $\text{C}_2\text{-BT}$, $\text{C}_3\text{-BT}$, $\text{C}_4\text{-BT}$ etc fractions in the same way. A separate internal standard would be needed for each value of x in $\text{C}_x\text{-BT}$. If only the $\text{C}_1\text{-BT}$ ($\text{C}_2\text{-BT}$, etc.) pattern is of interest in a particular sample, there is no

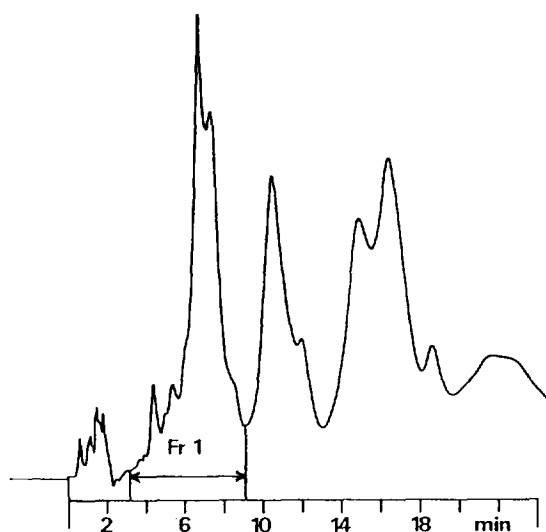


Fig. 7. HPLC chromatogram of the oxidized two-ring PASH fraction obtained from the two-ring fraction of an Austrian shale oil after oxidation with 3-chloroperbenzoic acid, on a Sepralyte Diphenyl column. Flow-rate: 2 ml/min methanol-water (1:1), detection at 230 nm. Fr 1 = First fraction, containing the monomethylbenzothiophene sulfones.

need to perform the separation according to the number of aromatic rings on aminopropyl silica. The whole aromatic fraction can be reacted with MCPBA and the oxidized products fractionated on diphenylsilica as described here. A quantification of three-ring PACs is, however, only possible after this separation step.

3.6. Three-ring PASHs

Following separation on $\text{PdCl}_2/\text{silica}$ (see Experimental), the resulting PAH and PASH fractions were analyzed on the biphenyl column using GC-AED (Fig. 8). A comparison of the carbon trace in Fig. 8a with that of Fig. 5 demonstrates the complete separation of PAH and PASH. Since the naphthothiophenes have now been successfully separated from the PAHs, phenanthrene, anthracene and some methylphenanthrenes can be quantified reliably (i.e., no coelution with PASHs).

The quantification of the unsubstituted sulfur heterocycles was somewhat more complicated.

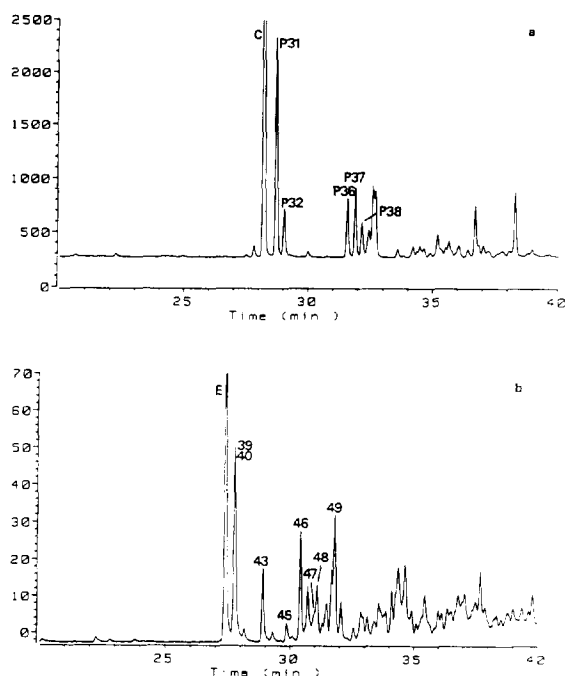


Fig. 8. GC-AED chromatograms of the three-ring PAC fraction obtained from an Austrian shale oil after separation on palladium chloride/silica, on SB-30-Biphenyl. $T_{oven} = 80^{\circ}\text{C}$ (2 min), then $4^{\circ}\text{C}/\text{min}$ to 280°C . (a) Three-ring PAH fraction in the carbon-selective mode, (b) three-ring PASHs in the sulfur-selective mode. Peaks: P36 = 3-methylphenanthrene; P37 = 2-methylphenanthrene; P38 = 2-methylanthracene; other peaks as in Figs. 4 and 5.

Dibenzothiophene and naphtho[1,2-*b*]thiophene were quantified on the cyanopropyl column (Fig. 9), since they coelute on the biphenyl phase. The other two isomers of naphthothiophene were not resolved from alkylated PASHs on cyanopropyl and had thus to be quantified on the biphenyl phase (Fig. 8b). Again, the use of a mass-selective detector in combination with the cyanopropyl column would obviate the use of two different columns for this quantification. In this sample the concentration of the methyl-naphthothiophenes is so high that, due to the coelution, it is impossible to quantify the methyl-dibenzothiophenes with any degree of accuracy. A mass-selective detector would bring no benefit since all these compounds are isomers and show identical mass spectra.

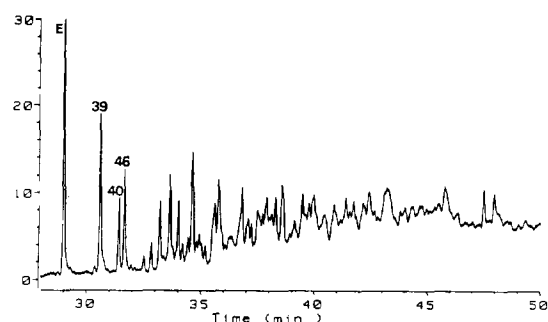


Fig. 9. GC-AED chromatogram of the three-ring PASH fraction obtained from an Austrian shale oil after several separation steps, on a SP 2331 cyanopropyl column in the sulfur-selective mode. $T_{oven} = 90^{\circ}\text{C}$ (3 min), then $10^{\circ}\text{C}/\text{min}$ to 160°C , then $2^{\circ}\text{C}/\text{min}$ to 230°C , then $10^{\circ}\text{C}/\text{min}$ to 250°C (10 min). Peaks as in Fig. 4.

The quantitative data for all compounds determined in this shale oil are collected in Table 3.

Table 3
Quantitative data for some of the aromatic compounds in the Austrian shale oil

Compound	Concentration ($\mu\text{g}/\text{g}$)
Naphthalene	2600
2-Methylnaphthalene	(2003) ^a
1-Methylnaphthalene	(1857) ^a
Phenanthrene	1030
Anthracene	415
3-Methylphenanthrene	363
2-Methylphenanthrene	377
Benzothiophene	768
7-Methylbenzothiophene	405
2-Methylbenzothiophene	974
5-Methylbenzothiophene	341
6-Methylbenzothiophene	197
3-Methylbenzothiophene	515
4-Methylbenzothiophene	662
Dibenzothiophene	445
Naphtho[1,2- <i>b</i>]thiophene	204
Naphtho[2,1- <i>b</i>]thiophene	183
Naphtho[2,3- <i>b</i>]thiophene	65
4-Methyldibenzothiophene	(255) ^a
2-Methyldibenzothiophene	(123) ^a
3-Methyldibenzothiophene	(124) ^a
1-Methyldibenzothiophene	(274) ^a

^a Only semiquantitative values.

4. Conclusions

The shale oil used in this work is extremely rich in alkylated two- and three-ring polycyclic aromatic compounds, making the task of determining individual aromatic sulfur heterocycles a great challenge indeed.

A separation according to the number of aromatic rings was necessary, partly because some highly alkylated benzothiophenes elute with similar retention times as the three-ring compounds on gas chromatographic analysis, and partly because on oxidation with MCPBA, especially the naphthothiophenes are lost and escape quantification.

The oxidation of the two-ring fraction was necessary not for the separation of the benzothiophenes from the naphthalenes, since these compounds could in principle be determined with the sulfur-selective detector but for the excellent GC resolution obtained for the BT sulfones on practically any standard GC phase. It should be stressed again that the non-oxidized BTs coelute to a very much larger extent than the sulfones.

The oxidation also permitted the naphthalenes to be collected as an individual fraction free of interfering sulfur heterocycles. However, several naphthalenes are attacked by MCPBA and show considerable losses. The determination of alkylated naphthalenes in a sample with such high concentrations of C_x-BTs would probably best be done with a mass-selective detector (without oxidation).

The separation on PdCl₂/silica is necessary for the quantification of phenanthrenes and anthracenes; the sulfur heterocycles can in principle be determined using a sulfur-selective detector since there are GC phases available which allow their separation. Here it should be repeated that a universal detector like the flame ionization detector will produce wrong results for phenanthrene (if naphtho[2,1-*b*]thiophene is present) on the so frequently used methyl silicone phases. In the shale oil phenanthrene would be overestimated by ca. 15%. The quantification of dibenzothiophene will likewise be erroneous, here by nearly 50%, because of coelution with

naphtho[1,2-*b*]thiophene unless a phase such as cyanopropyl is used.

Despite a certain complexity, the scheme presented here allows the determination of a relatively large number of PASHs, which have so far not been accessible, and of phenanthrene. The use of fluorinated internal standards was of considerable use, and in future work their role will be expanded since a standard can easily be synthesized for use with each subfraction of interest.

Acknowledgements

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