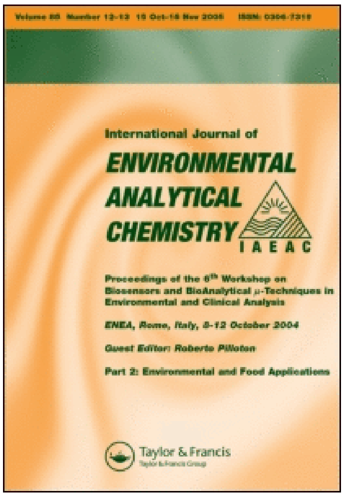

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Polycyclic Aromatic Sulfur Heterocycles. I. Use of Hydrogen Peroxide Oxidation for the Group Separation of Polycyclic Aromatic Hydrocarbons and Their Sulfur Analogs

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POLYCYCLIC AROMATIC SULFUR HETEROCYCLES. I. USE OF HYDROGEN PEROXIDE OXIDATION FOR THE GROUP SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR SULFUR ANALOGS[1]

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Some of the reasons for the difficulty of devising a generally valid analytical procedure for polycyclic aromatic sulfur heterocycles (PASHs) are discussed. A procedure for the separation of polycyclic aromatic hydrocarbons and PASHs which has been used for many years is investigated. It is shown that the oxidation with hydrogen peroxide in acetic acid/benzene produces not only the desired sulfones of the PASHs but that also the aromatic rings of polycyclic compounds of all types are oxidized. Low or zero recovery of the analytes is therefore often found. A large number of reagents was tested for the reduction of aromatic sulfones to PASHs in order to find a substitute for lithium aluminum hydride. None was discovered that cleanly affects this conversion. It is strongly recommended that oxidation with hydrogen peroxide not be used for any samples in which aromatic compounds are to be analyzed.

KEY WORDS: Polycyclic aromatic heterocycles, polycyclic aromatic sulfur heterocycles, sulfur-selective detection, crude oil.

INTRODUCTION

The analysis of polycyclic aromatic sulfur heterocycles (PASHs) has attained a certain degree of importance. These compounds occur as wide-spread as and, as a matter of fact, nearly always together with the polycyclic aromatic hydrocarbons (PAHs) which they resemble in many respects. Thus, they are present in most petroleum and coal products, combustion products, sediments, air particulates, tobacco smoke, organisms inhabiting polluted water, etc. In addition to the sulfides and thiols which can also be present, several hundred sulfur-containing aromatic compounds had been identified in petroleum up to 1983 when a list of them was compiled[1]. For air quality reasons there is a considerable interest in the removal of sulfur from fossil fuels in order to decrease sulfur dioxide emissions. The presence of sulfur compounds in fuels is undesirable also from the point of view of catalyst poisoning during refining and,

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consequently, desulfurization processes are a very active research area. Since many experiments suggest that the aromatics are the most difficult compounds to desulfurize, analytical attention has been focussed on them.

Furthermore, many PASHs share the carcinogenic and/or mutagenic properties of the PAHs[2] and are therefore of relevance for health reasons. It is well-known that subtle changes in the skeleton or alkylation pattern of aromatic compounds can drastically alter their carcinogenic potential. This observation has led to a demand for improved identification and quantitation of such compounds in fuels and in the environment. Other applications of PASH analysis include geochemical studies which i.a. have revealed that the relative concentration of alkylated benzothiophenes and dibenzothiophenes can give information on the maturity of a crude oil[3] and on its source rock[4].

Although attempts have been made to analyze PASHs for more than half a century, efforts have been hampered by several problems. Since the following factors have a profound influence on the possibility of accurately analyzing PASHs, they will be discussed in some detail in this paper:

1) The PASHs nearly always occur as minor constituents together with related PAHs;

2) Their chromatographic properties are very similar to those of the PAHs;

3) There is a larger number of isomeric parent structures among the PASHs than among the PAHs;

4) There is a larger number of alkylated isomers among the PASHs than among the PAHs.

Different approaches have been taken in order to formulate an analytical scheme but none has proved to be completely successful. One of them will be considered in some detail here. Although it has been shown that the reactions employed destroy many of the compounds to be analyzed, this scheme continues to attract attention both with respect to PASH analysis and for the removal of sulfur aromatics seen as interfering compounds in PAH analysis. It will be demonstrated here that this procedure should be avoided for both purposes and the reasons for its failure will be discussed.

EXPERIMENTAL

The gas chromatograph was a PYE 4500 from Philips, equipped with a split-splitless injector, a flame ionization detector and a flame photometric detector. Hydrogen at a linear flow of 60 cm s^{-1} was used as carrier gas. The columns and conditions used are indicated in the legends. The work with the atomic emission detector (AED) was performed on an HP 5890 gas chromatograph with the detector 5921A and with purified helium at 30 cm s^{-1} as carrier gas. The injector and detector temperatures were 275°C. The compounds were either commerical samples or synthesized according to published procedures.

The oxidations with H_2O_2 (and the following reduction with $LiAlH_4$) were performed according to directions in Ref. 21. For these experiments 0.5–2 mg of each compound were dissolved in 10 ml of a 1:1 mixture of acetic acid and benzene and refluxed overnight together with 2 ml 30% H_2O_2. The products were extracted with chloroform after addition of water. After being dried over magnesium sulfate, this solution was either directly analyzed by GC or, if pertinent, reduced with lithium aluminum hydride.

The reduction experiments were carried out using a solution of about 4 mg each of the sulfones of benzothiophene, 2,3-dimethylbenzothiophene, dibenzothiophene and benzo[b]naphtho[2,1-d]thiophene in 10 ml acetic acid. 0.5 ml of this solution was added to 2 ml acetic acid and, if applicable, a mineral acid. For those cases where a metal (zinc, tin, magnesium, aluminum, iron, nickel) was used as reducing agent, 0.2–0.5 g of the metal was added. After reflux for periods between 1 and 6 hrs, extraction with toluene produced a solution for GC analysis. Variations included the use of ultra-sound and the addition of toluene to form a two-phase system. Other reducing agents used under the appropriate conditions included palladium on carbon with hydrazin, stannous chloride, lithium triethylborohydride, diphenylsilane, sodium borohydride, boron trifluoride, dicyclohexylcarbodiimide, triethylphosphite, dimethyl dichlorosilane with $LiAlH_4$, diphenylsilane and triphenylphosphine with iodine.

DISCUSSION

The four points listed in the introduction as contributing to the difficulty of designing a general analytical procedure for PASHs will be considered in this section:

1) In almost all samples the PAHs dominate over the PASHs, although the ratio between the two classes of compounds varies widely depending on sample type and sample identity. Examples from the literature on SRMs (Standard Reference Materials) of the National Institute of Science and Technology, U.S.A., include a coal tar (SRM 1597) in which the ratio between the 3-ring PAHs (molecular weight 178) to the 3-ring PASHs (MW 184) was 24.5[5]. In an air particulate (SRM 1648) the ratio for the 4-ring isomers (MW 228 and 234, resp.) was 6.8[6].

In Figure 1 an example of an element-selective gas chromatogram of the pre-isolated non-polar aromatic fraction is shown for a typical shale oil sample (SRM 1580). The atomic-emission detector (AED) was used in the carbon- and the sulfur-selective modes. This fraction contains a large number of both PAHs and PASHs with the former dominating. In order to illustrate the relative dominance of the PAHs, some of the more abundant PASHs have been marked in both traces.

PASHs are abundant in crude oils but in general it would not be very meaningful to state a general PAH/PASH ratio for them since the amount of PASHs varies very much between different oils. Although the total sulfur content usually lies in the range of 0.3–3%, the extremes are 0.05 and 14%[7]. One unusual case investigated in this laboratory involved a crude oil—containing about 10% sulfur—from northern Germany in which nearly every aromatic compound was found to contain sulfur (Figure 2). Note the near identity of the carbon- and the sulfur-selective traces.

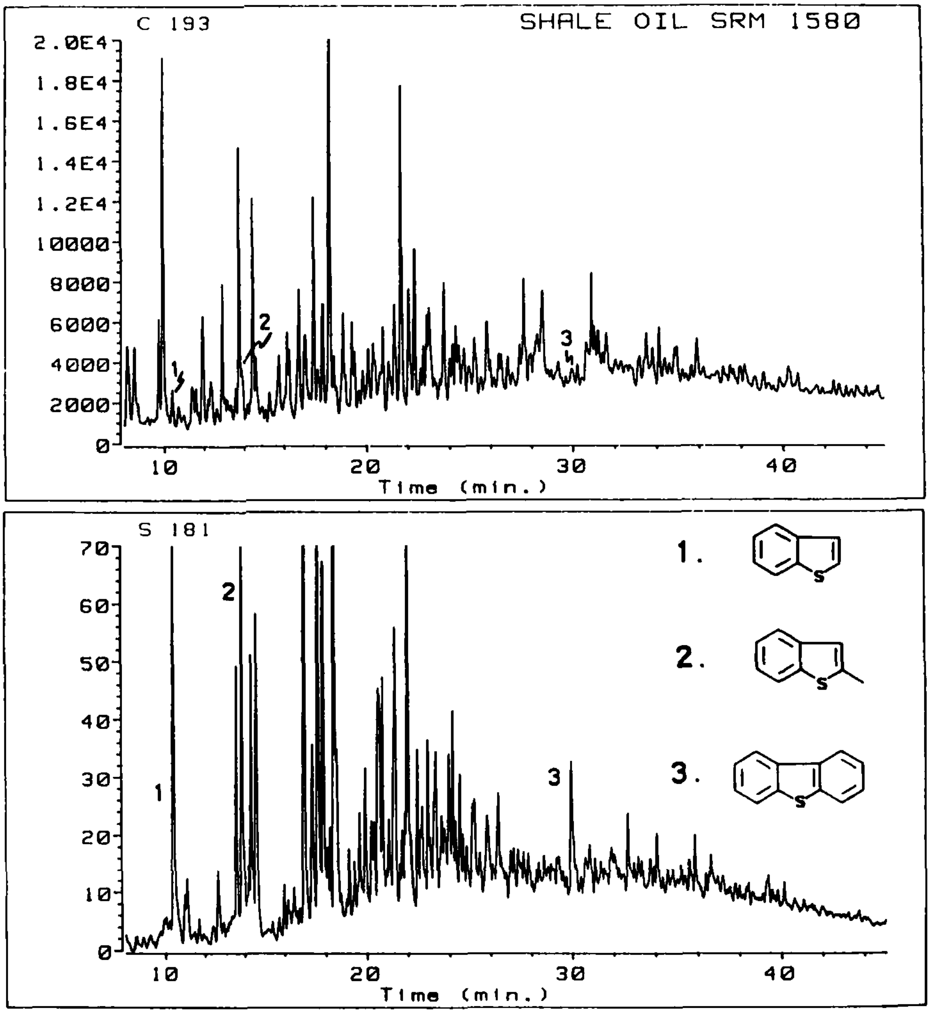
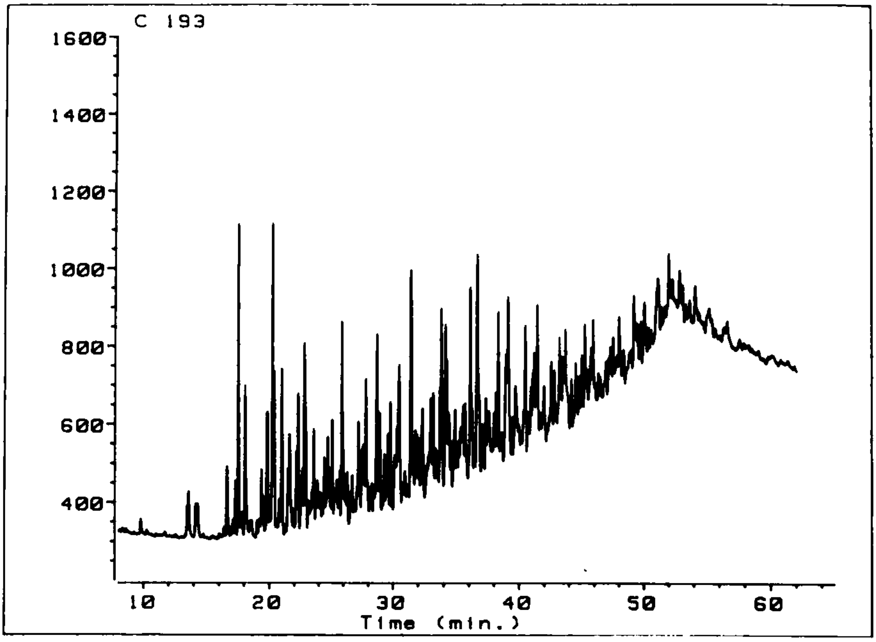


Figure 1 Aromatic fraction of a shale oil (SRM 1580) on a 20 m, 0.32 mm, 0.25 μm SB-30 biphenyl phase. 80°/2 min, 4°/min to 280°C. Atomic emission detection of (top) carbon at 193 nm, (bottom) sulfur at 181 nm.

2) It is well-known that unlike the more polar nitrogen heterocycles, PASHs cannot be separated from PAHs through chromatography on adsorbents like silica gel or alumina[8]. Since sulfur shows a pronounced affinity for heavy metals, an attractive alternative might employ a complexing chromatographic support, such as a salt of a heavy metal. Such phases work well for acyclic sulfides with salts of zinc, mercury, copper, silver and cadmium, but dibenzothiophene as a representative of the class of PASHs was found to be as weakly retained as anthracene[9]. Similarly, silver ions added to the liquid-chromatographic eluent complex with olefins, causing them to elute in a shorter time. The retention of DBT remained uninfluenced by the silver



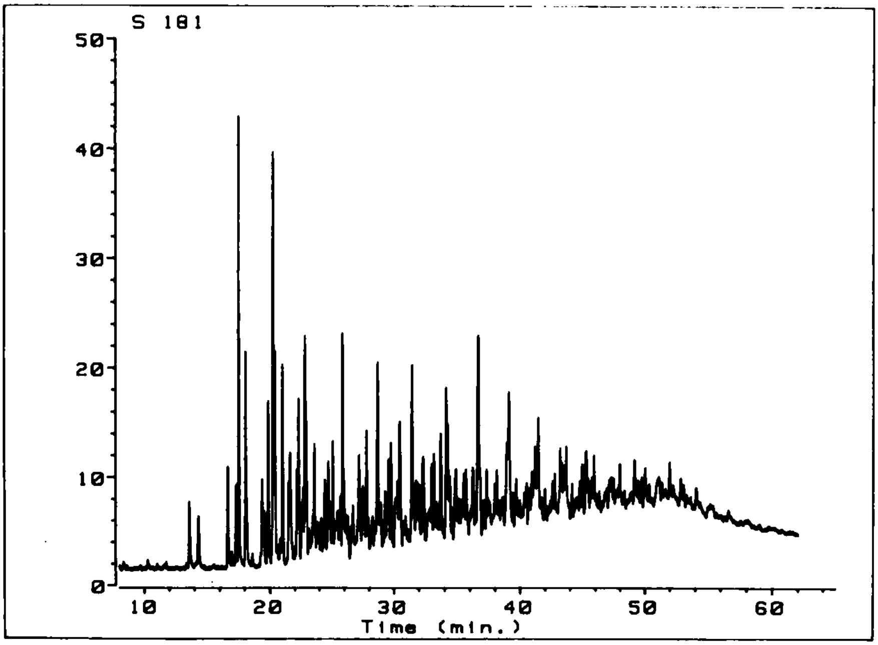


Figure 2 Aromatic fraction of a crude oil from Lower Saxony, Germany. The same conditions as in Figure 1.

ions[10]. One report advocates silver nitrate on silica[11] for the separation of PAHs and PASHs of an oil sample. However, a closer examination concluded that this system was unsuitable for the class separation of PAHs and PASHs[12]. A phenylmercuric acetate phase likewise did not show a selectivity for PASHs over PAHs[13]. Work in this laboratory on the use of ion-exchange resins containing heavy metals has also consistently failed to show a stronger retention for PASHs than for PAHs.

Partial success was achieved with palladium chloride on silica[14] but only such PASHs are separated from the PAHs in which the sulfur atom is in an internal ring[15]. If it is located in a terminal ring, as in the simplest member of the whole class, benzothiophene, then the compound elutes together with the sulfur-free aromatics unless it bears several methyl groups which increase the electron density on the sulfur atom and thus its complexing ability.

In conclusion, no chromatographic method is known yet that is capable of a clean class separation of PAHs and PASHs.

3) Although a sample may contain a significant amount of sulfur bound in aromatic rings, the larger number of PASH parent structures for a given ring number has two consequences: firstly that each parent may be present in a lower concentration and thus be more difficult to analyze correctly, and secondly that the risk of coelution from the GC column increases. Furthermore, isomers belonging to the different types of sulfur aromatics (containing either terminal or internal thiophene rings) may show quite different physical (e.g. complexation with palladium chloride, see above) and chemical behavior (e.g. the oxidation procedure, see below). Until a general procedure is devised that does not discriminate on grounds of the position of the thiophene ring in the molecule, this distinction will remain a factor to be considered in all PASH analysis.

There exist four 3-ring PASHs (see below), although often dibenzothiophene (DBT), usually predominant, is the only one determined. One reason may be that naphtho[2,1-b]thiophene coelutes with phenanthrene and naphtho[1,2-b]thiophene with DBT on SE-54, the most popular stationary phase in the analysis of aromatics. A case illustrating the quantitation of three of the four possible isomers is an anthracene oil[16] in which three resolved peaks for the four 3-ring PASHs indicated concentrations of 12200, 5400 and 1400 $\mu g\, g^{-1}$. Since no retention data for the compounds were listed for the SP-2250 phase used, it is not clear if there is a coelution of one naphthothiophene with DBT in this case, too, and therefore the value of 12200 $\mu g\, g^{-1}$ is not in fact the sum of two isomers.

In Table 1 a comparison between the number of parent structures of PAHs and PASHs is made for cata-condensed systems containing from two to five rings. The sulfur atom in the thiophene ring is considered to be analogous to an ethylene bridge in a PAH[13]. Only such PASHs have been counted which do not share the c-edge of the thiophene ring with another ring since such compounds are not likely to be encountered in environmental samples because of their quinoid structure. Furthermore, heteroaromatics containing more than one sulfur atom are not included although it is known that in samples like shale oils[17] there are many of such PASHs.

The tabulated numbers for the sulfur compounds of course apply equally well to the corresponding oxygen and nitrogen heterocycles.

Table 1 Number of cata-condensed parent structures and alkylated isomers of PAHs and non-quinoid PASHs (containing one sulfur atom per molecule) as a function of the number of aromatic rings and the number of carbon atoms in the side chains.

Number of aromatic rings	*Number of C-atoms in the side chains*	*Number and formula of isomers possible*	
		PAH	*PASH*
2	0	1 $C_{10}H_8$	1 C_8H_6S
	1	2 $C_{11}H_{10}$	6 C_9H_8S
	2	12 $C_{12}H_{12}$	21 $C_{10}H_{10}S$
	3	32 $C_{13}H_{14}$	62 $C_{11}H_{12}S$
3	0	2 $C_{14}H_{10}$	4 $C_{12}H_8S$
	1	8 $C_{15}H_{12}$	28 $C_{13}H_{10}S$
	2	48 $C_{16}H_{14}$	128 $C_{14}H_{12}S$
	3	176 $C_{17}H_{16}$	448 $C_{15}H_{14}S$
4	0	5 $C_{18}H_{12}$	13 $C_{16}H_{10}S$
	1	29 $C_{19}H_{14}$	130 $C_{17}H_{12}S$
5	0	12 $C_{22}H_{14}$	51 $C_{20}H_{12}S$
	1	117 $C_{23}H_{16}$	594 $C_{21}H_{14}S$

4) In many samples the alkylated derivatives dominate over the parent structures. Both as a result of the larger number of parent structures and because of the asymmetry introduced into the molecule by the hetero-atom, a very much larger number of isomers is possible for the alkylated heterocyclic compounds than for the PAHs, despite the fact that the sulfur atom effectively replaces two carbon atoms which could bear alkyl substituents. The chromatograms in Figure 1 illustrate this for the smaller PASHs. The large number of isomers of alkylated PASHs makes a complete separation of them difficult. There is for instance no capillary gas-chromatographic column known that resolves all the six monomethyl isomers of the simplest PASH, benzothiophene[18]. Their behavior on a liquid-crystalline phase does not seem to be reported.

The data in Table 1 are not only a game with numbers; an analysis of alkylated derivatives can have a high information content. The carcinogenic properties shown by methylated aromatic compounds can vary dramatically in dependence of the position of the methyl-group[19]. The maturity of a crude oil is reflected in the distribution of alkyl isomers of different aromatics, including dibenzothiophene[3]. The ratio between different methyldibenzothiophenes in crude oils has been correlated with the nature of the source rock of the oil well[4].

The data in Table 1 illustrate the great difference in the number of alkylated isomers for all possible PAHs and PASHs of the same ring number.

Strategies for the analysis of PASHs

The first two problems discussed above may in principle be overcome in one of the two ways: either through the use of a sulfur-selective detection system or a complete separation of the two classes of compounds. Both ways have been attempted. Because of the high resolution necessary, capillary gas chromatography is routinely used.

Sulfur-selective detection is most commonly carried out with the flame-photometric detector (FPD). However, it shows many peculiarities such as being sensitive to most experimental conditions, having a linear response over only about two orders of magnitude, having a (more or less) quadratic dependence on the sulfur concentration, showing quenching of the sulfur signal due to coeluting sulfur-free compounds in the single-flame configuration, and showing different response to different compounds. This detector has found many applications in qualitative sulfur analysis but its drawbacks make it less useful for quantitative purposes.

The Hall conductivity detector shows promising characteristics for sulfur but has never gained much popularity, probably because of experimental inconvenience. Recently, two new commercial detectors have been introduced on the market which appear to be superior to the FPD, namely the atomic emission detector (AED) and the sulfur chemiluminescence detector (SCD). They are free of the drawbacks listed above for the PDF, however, the ability of the chromatographic column to separate the PASHs (points 3 and 4 above) will remain a serious problem.

The other strategy for the analysis of PASHs involves their separation as a class from the PAHs. The separation on palladium chloride was referred to above, as noted, this salt does not seem to be able to cleanly separate PASHs as a class from PAHs. Another procedure, described in 1967[20], will be discussed in detail here since it has found frequent use. Originally it was developed for the analysis of petroleum aromatics. Reendorsement of it in 1981[21] has led to its use for samples like coal gasification tar[22], emissions from coal-fired furnaces[23], synthetic[24] and fossil fuels[25] and crude oil[26,27].

The idea behind it is based on the polarity of the oxidized products of PASHs. Oxidation of the PASHs in the sample with hydrogen peroxide in a mixture of acetic acid and benzene, chromatographic separation of the polar sulfones from the non-oxidized PAHs and reduction of the sulfones back to the PASHs with lithium aluminum hydride (LAH) is supposed to give a solution containing only the sulfur aromatics of the sample[21].

The oxidation procedure has also been used to remove PASHs which interfere in the determination of PAHs in regenerated oils[28], in crude oils[29] and kerogen samples[30]. Some of the following remarks apply to the use of the procedure for such purposes as well.

Oxidation of aromatic compounds with hydrogen peroxide

To test the suitability of the procedure on smaller PASHs, mainly alkylated benzothiophenes (BT) and dibenzothiophenes, a mixture of nine pure compounds ranging from BT to 6H-benzo[b]indeno[1,2-d]thiophene was made and taken through the whole sequence of reactions and chromatographic separations. The GC traces[31] of the mixture before and after the procedure are shown in Figure 3.

The only compound that seems to survive the reactions to a major extent is 2-methyl-DBT, in agreement with the recovery of 67% reported for DBT[32]. Three of the methylated benzothiophenes are present in amounts corresponding to between 11 and 31% of their concentrations in the starting mixture (calculated relative to

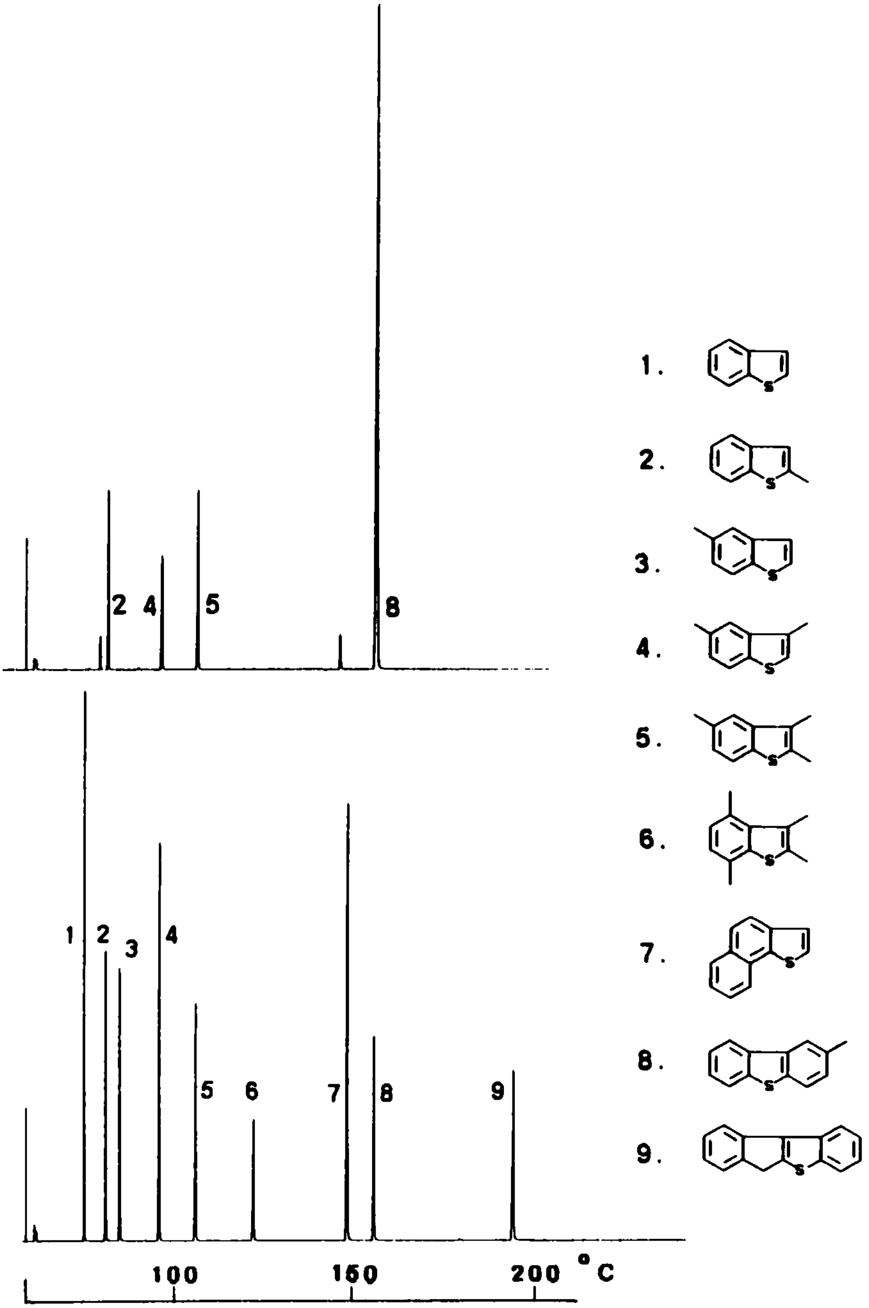
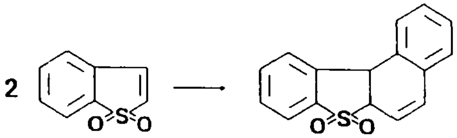


Figure 3 Standard mixture of polycyclic aromatic sulfur heterocycles before (bottom) and after (top) oxidation with hydrogen peroxide in acetic acid, followed by reduction with lithium aluminum hydride. column, 26 mx, 0.20 mm Carbowax 20M, 80°C during 5 min and 4°C min^{-1} to 225°C.

2-methyl-DBT). Five of the PASHs disappeared completely, while traces of some new compounds appeared which might be 2,3-dihydrothiophenes which are known to be formed on the reduction of benzothiophene sulfones with $LiAlH_4$[33].

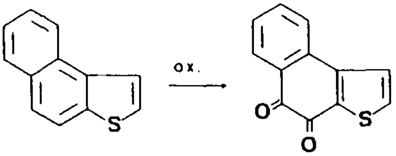
This result parallels the findings of the original authors who on reinvestigating their separation found a recovery of various 3- to 5-ring PASHs of between 0 and 41% when these were added to a sulfur-free oil and worked up according to the oxidation-reduction procedure[32]. They interpreted the low yield in terms of different ease of oxidation of various structural details of the aromatics, other than the sulfur atom, but concluded that the procedure is still useful.

The problem of terminal thiophenes is not only that their 2,3-double bond can be hydrogenated in the reduction step. The sulfones of terminal PASHs are known to react in a Diels–Alder reaction in which the compounds serve both as diene and dienophile:



Examples include benzothiophene[34], methyl-BTs[35] and naphthothiophenes[36,37]. Although the reaction conditions selected for this dimerization usually are more severe than in the analytical scheme discussed here, benzo[b]naphtho[1,2-d]thiophene has been reported to be formed when benzothiophene is oxidized under conditions comparable to those here[34]. If this reaction takes place in the sample, the result will not only be that a portion of the compounds is not recovered but that new PASHs are synthesized which in the extreme case may be mistaken for components of the sample. This risk is probably diminished by the fact that in most samples there is a very large number of terminal PASHs which can react with each other, forming a vast number of dimers, each of which is present in minute amounts only.

The yellow coloration which arises when colorless standard compounds are subjected to the peroxide oxidation is an indication that larger aromatic systems and/or quinones are formed (the sulfones are colorless). That quinones are present, which on reduction with $LiAlH_4$ form hydroquinones, is indicated by the fact that on chromatography on silica of the reduced samples, a colored band stays at the top of the column and is not eluted with the PASHs. Such a side reaction is known to occur not only with compounds containing an anthracene system[32] but also with, e.g., naphtho[2,1-b]thiophene, which is described to give the 4,5-quinone on oxidation with hydrogen peroxide[37] or chromium trioxide[38].



Furthermore, even very similar compounds may react in side-reactions to different extents. When a mixture of BT, 2-methyl- and 7-methyl-BT was oxidized, the GC peak ratio of 1:2.2:1.5 for the three compounds before the oxidation changed to 1:1.1:0.9 for the sulfones after the oxidation (equal response factors are assumed for the flame ionization detection of the three compounds). Obviously, even with such simple and closely related compounds, uncontrollable side-reactions distort the PASH pattern during the oxidation.

It therefore seems that not only the thiophene ring is affected by the oxidation but also the sulfur-free part of the molecule. If that is the case, then the procedure is invalid also for such cases where PASHs are removed in order to facilitate the study of the PAHs in the sample. The following experiment was designed to test whether this is true.

A solution of nine PAHs, ranging from naphthalene to 4H-cyclopenta[def]phenanthrene (see identification of the peaks in Figure 4), was subjected to the oxidation procedure. Hexadecane was added as a marker on the assumption that it will not react, at least not as readily as the aromatics. In Figure 4 the GC traces of the mixture before and after the reaction (without column chromatographic separation of oxidized material) are shown.

Even a superficial comparison shows that hardly anything is left of the original compounds. Of the peaks in the resulting chromatogram only three peaks could be assigned to a compound through their retention times, namely 1-methylnaphthalene, hexadecane and 1,4-naphthoquinone. Only 6% of 1-methylnaphthalene remained (based on a comparison with hexadecane). 9,10-Phenanthroquinone and acenaphthenone were absent. Other similar experiments indicated a less severe but still substantial loss of PAHs under the present conditions.

The reactions leading to this loss of aromatics are known but seem not have been considered properly by analytical chemists. Already in 1910 the reaction between hydrogen peroxide in acetic acid and naphthalene, anthracene and phenanthrene at ordinary temperature or on gentle heating was described[39]. The products were identified as phthalic acid, anthraquinone and phenanthrone, respectively. A further product of phenanthrene oxidation is diphenic acid, and anthracene may yield 9,9′-dianthrone[40]. The same workers reported the oxidation of naphthalene and methylnaphthalenes to the corresponding quinones through heating with hydrogen peroxide in acetic acid for periods between 45 minutes and 10 hours (in the analytical procedure described above, the reflux time is 16 hours). The 9,10-double bond of acenaphthylene is easily oxidized, first to the epoxide which readily rearranges to acenaphthenone[41] which probably can react further. No doubt it should be possible to find examples of similar behavior of other PAHs if a systematic search of the literature has been done. The heavy losses of aromatics in the experiment shown in Figure 4 are probably related to the further oxidation to very polar material, including carboxylic acids like phthalic acid, which are lost in the work-up of the reaction product.

An example of this was recently reported[25]. Mass spectral evidence from samples taken through the oxidation/reduction scheme described above suggests that phthalides can be formed from naphthalenes through oxidation to phthalic anhydrides followed by $LiAlH_4$ reduction of these to the phthalides. It may be pertinent to add here that it was observed quite early in the research on petroleum aromatics that

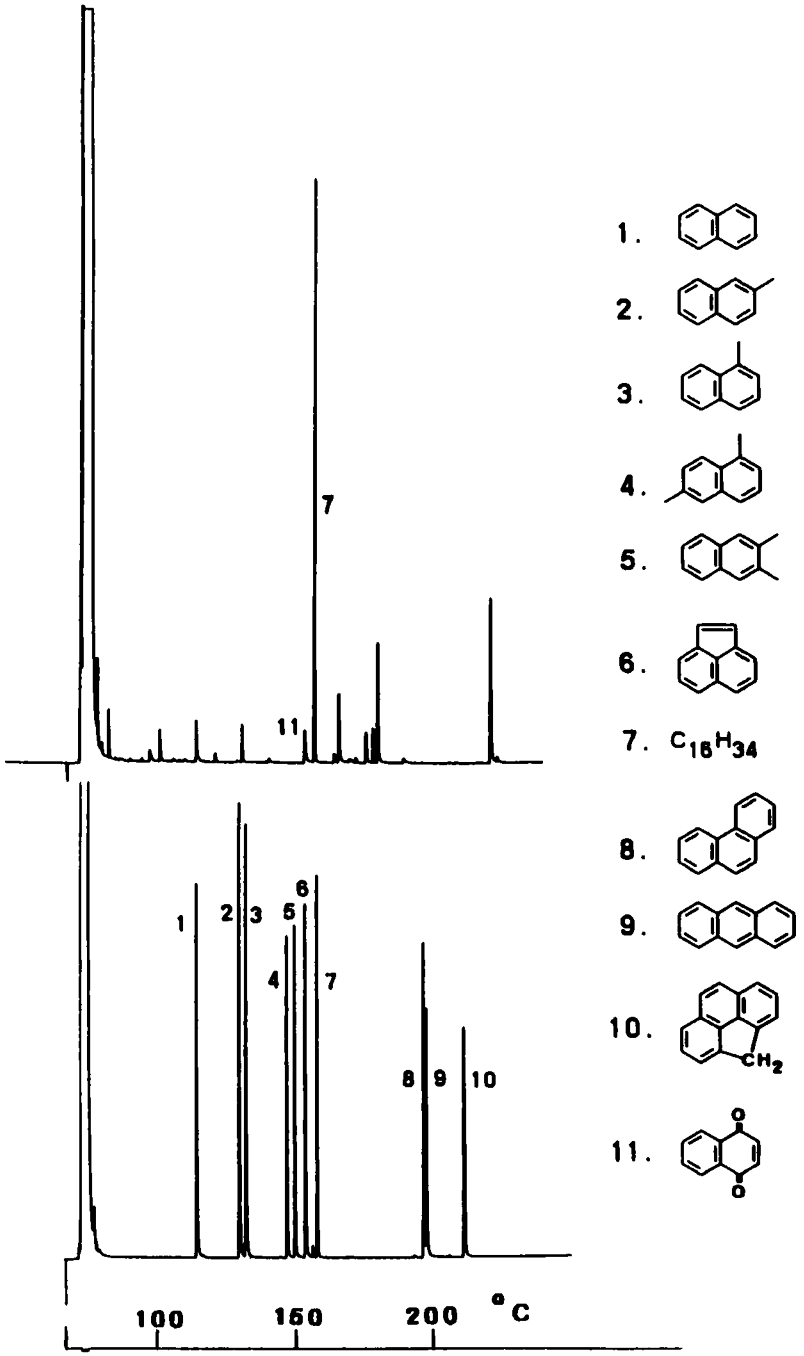


Figure 4 Standard mixture of polycyclic aromatic hydrocarbons before (bottom) and after (top) oxidation with hydrogen peroxide in acetic acid. Column 30 mx, 0.25 mm, 0.2 μm DB-17101. 80°C for 2 min and 6°C min^{-1} to 225°C.

naphthalene was oxidized to naphthoquinone during peroxide oxidation[42] and that this observation was thought sufficient ground to abandon the procedure.

Why is it possible to synthesize the sulfones of many PASHs by reacting them with hydrogen peroxide and why do "sturdy" sulfur aromatics such as DBT and benzonaphthothiophene show fairly low losses and are recovered in about 70% yield[32] following the oxidation and reduction? A reasonable answer may be that the sulfur atom is the most oxidation-prone feature of these molecules and rapidly reacts to the sulfone. The strongly electron-attracting property of this functional group lowers the reactivity of the aromatic system toward further oxidation. In larger compounds, the effect of the sulfone group is smaller on the aromatic rings furthest away from the sulfur atom and they can then be oxidized in the usual manner. This could explain why some of the larger PASHs investigated[32] were for all practical purposes completely lost.

Reduction of sulfones

The reduction of the sulfones has not been as intensely investigated here since already the oxidation step profoundly changes the aromatic pattern. It has been known for a long time that the sulfone of benzothiophene (BTO_2) is hydrogenated at the carbon-carbon double bond catalytically[43] as well as electrochemically[44] to dihydrobenzothiophene dioxide and that $LiAlH_4$ first reduces the carbon-carbon double bond and then the sulfone group[33]. The occurrence of dihydrobenzothiophenes[21] in samples worked up with $LiAlH_4$ therefore comes as no surprise.

Since it is known that zinc in acetic acid reduces BTO_2 to BT[43], we looked into this and similar reductions to see if they offer an alternative to the LAH reduction. For this survey a mixture of the sulfones of BT, 2,3-dimethyl-BT, DBT and benzo[b]naphtho[2,1-d]thiophene was treated with different metals in acetic acid with hydrochloric acid added as well as with hydride and deoxygenation reagents under the appropriate conditions. Altogether more than 25 different reagents were investigated. In no case was a reduction of all the sulfones apparent. In several products there appeared a GC peak which corresponded to dihydrobenzothiophene sulfone. In other cases unidentified side-products were formed. The reduction with zinc succeeded well only for BTO_2. The 2,3-dimethyl dioxide was partly reduced, whereas the 3- and 4-ring dioxides were stable.

It must therefore be recognized that the sulfur–oxygen bond in aromatic sulfones is a surprisingly difficult bond to cleave cleanly.

CONCLUSION

This investigation has studied the oxidation/reduction procedure[21] with hydrogen peroxide in acetic acid, recommended for the isolation of a PASH fraction from complex mixtures. Since this procedure has been used quite frequently both with the intention of obtaining a PAH-free solution of the PASHs and of obtaining a PASH-free solution of the PAHs, the suspicion that the reactions used in the procedure may transform the analytes in undesirable ways had to be investigated. It is known that several side-reactions can take place, namely

1) oxidation of aromatic rings,
2) ring opening of quinones thus formed, leading to carboxylic acids,
3) Diels–Alder dimerization of terminal sulfones,
4) hydrogenation of the 2,3-double bond in sulfones.

These reactions lead to massive losses of many analytes and possibly to the formation of new PASHs. Even closely related PASHs which are reasonably cleanly oxidized to the sulfones undergo different side-reactions, leading to a changed distribution of them in the oxidized fraction. This makes the procedure unusable also for pattern studies of such compounds.

All those factors taken together lead to the conclusion that the procedure should be avoided both in the study of PAHs and of PASHs.

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