Sulphur heterocycles in coal-derived products

Relation between structure and abundance

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Sulphur heterocycles in a coal tar and in a coal liquid vacuum residue were isolated by ligand exchange chromatography using $PdCl_2$ on silica gel. Subsequent fractions were analysed by capillary column gas chromatography and gas chromatography–mass spectrometry. Two new selective stationary phases (a smectic liquid–crystalline polysiloxane and a biphenyl polysiloxane), as well as a methylpolysiloxane, were used to resolve the numerous isomers. All major sulphur heterocycles with 3–6 rings were identified by comparison of retention times of mixture components with those of standard reference compounds. The structures and relative abundances of the major sulphur heterocycles were analogous to those of the major polycyclic aromatic hydrocarbons in the same or similar samples.

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Sulphur is present in various forms in all crude fossil fuels. The organic sulphur compounds found in these materials have been categorized according to functionality: thiol (–SH), disulphide (–S–S–), sulphide (–S–), and thiophene. The thiophenes are the major organosulphur compounds in shale oils, coal-derived liquids and heavy petroleum distillates[1,2]. In thermally cracked oils and coal liquids, multi-ring polycyclic aromatic sulphur heterocycles (PASH) are especially abundant[3,4].

The sulphur content in coal and crude oil varies in the range 0.2–12 wt%[5,6]. This sulphur affects the odour and storage stability of petroleum products, the durability of catalysts in catalytic cracking processes, and the corrosion of processing plant equipment. Sulphur-containing gases produced at fossil fuel combustion facilities are major contributors to air pollution. It is also known that many of the PASH are toxic and/or mutagenic in various biological test systems[7–11]. For these reasons, it is important to characterize and identify the sulphur-containing compounds in fossil fuels. In addition, the detailed identification of heteroatom-containing polycyclic aromatic compounds, such as the PASH, in coal-derived products could provide important information relevant to coal structure.

Numerous methods for the isolation and identification of the sulphur-containing compounds in fossil fuels such as thiols, sulphides, and disulphides, have been reported and reviewed[12], while the PASH have not been characterized as extensively. There is a greater number of possible isomers for the PASH than for the corresponding polycyclic aromatic hydrocarbons (PAH). For example, the numbers of cata-condensed 4-ring and 5-ring PASH isomers are 19 and 70, respectively, while the numbers of corresponding PAH isomers are 5 and 12. Highly selective stationary phases are essential to resolve these isomeric PASH, even when using high resolution gas chromatography. Comparison of retention data of mixture components with those of standard reference compounds on these phases makes identification of these PASH possible. However, it is necessary to isolate the PASH from other compound classes even when using highly selective stationary phases. Adsorption chromatography using silica gel and/or alumina has been generally used for the first step for isolating the PASH. However, the isolation of the PASH from the PAH has been difficult. Poirier and Smiley[13] recently reported that a fraction containing 1- to 3-ring PASH could be obtained by adsorption chromatography on silica gel and alumina columns connected in series. However, the 3-ring PASH were not cleanly resolved from other material.

A more selective method for the isolation of PASH is the oxidation/reduction procedure originally reported by Drushel and Sommers[14]. Sulphones formed by oxidation with peroxides could be separated by adsorption chromatography followed by reduction back to the original PASH. This laboratory has used a similar procedure to isolate the PASH fraction from coal-derived liquids and shale oils[15]. Relatively clean fractions were obtained, and many new PASH were identified. However, it was found that the recoveries of selected PASH varied from 0–70%, depending on the structures of the compounds[3]. For example, PASH with fusion on only one side of the thiophene ring (such as naphtho[2,1-*b*]-thiophene, naphtho[2,3-*b*]thiophene, and phenanthro-[3,2-*b*]thiophene) were not recovered.

Recently, thiophenic compounds were separated by ligand exchange chromatography on a silver nitrate-coated silica column[16], however, the separation of only one-ring thiophenes was reported. Salts of metals including mercury, copper, silver and zinc can coordinate with sulphur compounds[17–21]. Procedures using these salts have been effective for the isolation of aliphatic sulphides, but are generally not applicable for the separation of thiophenic compounds. However, phenanthrene and dibenzothiophene were separated on $PdCl_2$-coated silica gel by Gundermann *et al.*[22], and this

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