

Discussion

Comments on the Note “Liquid chromatographic determination of planar aromatic sulphur compounds in crude oil”, *J. Chromatogr.*, 475 (1989) 421

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In a Note by Sinkkonen [1], some efforts were reported on the attempted separation of polycyclic aromatic sulphur heterocycles (PASHs) from polycyclic aromatic hydrocarbons (PAHs). This is not a trivial problem, and efforts have been made for several decades to accomplish this separation in many laboratories, but no completely satisfactory procedure is known to date. In the Note, three methods were tested, all of them having been described previously in the literature, and no new results of use were presented.

The three methods mentioned are (1) thin-layer chromatography (TLC), (2) ligand-exchange chromatography (LEC) and (3) “oxidation of dibenzothiophenes to sulphones and analysis by high-performance liquid chromatography (HPLC)”.

Thin-layer chromatography. Biphenyl and dibenzothiophene were used on silica and alumina as test substances to check whether a PAH and a PASH can be separated by normal-phase chromatography. It is well known that this separation does not succeed and in general that PAHs and PASHs of the same number of aromatic carbon atoms cannot be usefully separated on silica [2].

It was stated that they are separable on alumina; however, this is not necessarily very significant for the ultimate goal of the work, which is the separa-

tion of the two *classes* of compounds from each other from a very complex mixture such as a crude oil. In such a mixture there may be, *e.g.*, fluorenes and acenaphthylenes present which elute in the similar range to the above compounds. Further, such samples consist of mixtures of a large number of alkylated derivatives of all parent structures, obscuring any small separation that may be observed using parent compounds. Those limitations were not mentioned.

Normal-phase chromatography on silica or alumina is widely used (also in the Note) for the separation of aromatic compounds from alkanes in mixtures such as crude oils. Obviously no useful class separation of PAHs and PASHs has ever been observed by the literally hundreds of workers who have used this separation method.

Ligand-exchange chromatography. That dibenzothiophenes can easily be separated from PAHs, as reported in the Note, is already well documented in the literature (see, *e.g.*, the four references to LEC in the Note and ref. 2 here). This result is therefore far from new.

It is now well known that LEC on palladium(II) chloride–silica discriminates against those PASHs which contain a terminal thiophene [3], such PASHs elute in the PAH fraction. This method

therefore does not provide a general method of separating PASHs from PAHs. This fact was not mentioned in the Note.

It is stated that the PASHs "partly eluted as PASH-PdCl₂ complexes which cannot be analysed by conventional means". A very simple remedy for this problem, involving the use of a small amount of aminopropyl-substituted silica, was described in 1987 [3].

The use of silver nitrate-silica was mentioned as an alternative; a closer examination has already shown it not to be a very useful alternative for the desired separation [4].

Oxidation. The statement that sulphones of PASHs cannot be analysed by gas chromatography is not true, there is absolutely no problem in doing this [5,6]. Hundreds of such sulphones have been routinely analysed by gas chromatography. The oxidation-reduction procedure is singularly ill-suited for the analysis of PASHs as the finally isolated PASH fraction frequently shows very little similarity to the starting mixture [7]. This was also indicated by the workers who introduced the procedure [8].

It is difficult to say whether the reversed-phase HPLC of the oxidized fraction of a Russian crude oil, described in the Note, is relevant or not, but as it is known that the oxidation method used in producing the sample for this chromatographic step so drastically alters the sample components (and not only effects the oxidation of PASHs to their dioxides), it is not very plausible that it is of any use for the determination of the aromatic sulphur components, which was the aim of the whole work.

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