Metal ion containing liquid chromatographic stationary phases for the analysis of polycyclic aromatic sulfur heterocycles in fossil fuels

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Refiners worldwide are facing a tough challenge to produce increasingly cleaner fuels to comply with current low legal limits for sulfur in fuels. The catalytic hydrodesulfurization (HDS) is highly efficient in removing the sulfur in thiols, sulfides and disulfides. Thiophenic compounds can be more difficult to desulfurize and thus some polycyclic aromatic sulfur heterocycles (PASHs) survive the reaction. The ultimate objective of this work is to define the structural features of those PASHs which are recalcitrant to the desulfurization process. Such information is of great help in the development of new catalysts and improved refinery processes.

The very high complexity of higher-boiling petroleum fractions demands a prefractionation of the recalcitrant PASHs prior to mass spectrometric characterization. Here we investigate the liquid chromatographic properties of several sulfur aromatic model compounds on stationary phases containing Pd(II) and Ag(I) ions. Pd(II) has previously been used in different forms to separate sulfur-free and sulfur-containing aromatics but in higher-boiling samples many PASHs are poorly retained. The present study with several sulfur aromatic model compounds shows that compounds containing non-annealed thiophenes display poor retention and elute faster compared to thiophenes condensed with other aromatic rings. Compounds containing a non-aromatic sulfur atom are irreversibly retained by the Pd(II) ions.

A comparable Ag(I)-loaded stationary phase was similarly investigated; it shows that PASHs are retained based on the number of p electrons in the aromatic rings. The interaction of Ag(I) with sulfur in PASHs is weaker than that of Pd (II); however, the degree of alkylation plays a certain role for the retention properties. This phase was used for further separation of PASHs into compound classes like benzothiophenes, dibenzothiophenes, benzonaphthothiophenes and so on. The several fractionations according to defined criteria allow us to simplify the enormously complex samples so that high-resolution mass spectrometric analysis can be applied to great advantage.