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Speciation of alkylphenols after labeling with ferrocene

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Phenols form a group of polar components of many fossil materials like crude oils. They are toxic and fairly reactive, thereby potentially causing stability problems of technical products. They are also studied in petroleum exploration and measured in many environmental situations. Despite these wide-ranging applications, there is still need for rapid, accurate and sensitive analytical methods for phenols that will allow the different species to be individually quantified.

We have found that ferrocenecarboxylic acid chloride is an excellent derivatization regent for phenols (and, to a lesser extent, alcohols) (1, 2). The reaction is rapid and sample work-up following the derivatization is limited to filtration through a short column. The determination of phenols is done using gas chromatography with either an atomic emission detector (AED) or a mass selective detector (MSD). Gas chromatography has a high separation power which is fundamental to resolve the complex mixture of isomers typically found in crude oils and products thereof. The AED relies on the iron atom which can be measured with an excellent sensitivity (2.5 fmol iron compound injected) and with a selectivity versus carbon of over 3.5 million. With the MSD, the typical fragmentation pattern of the esters can be used to obtain a phenol-selective gas chromatogram (and, in addition, an alcohol-selective chromatogram using a different ion). The prominent molecular ion can be used for speciation of differently alkylated phenols.

Examples of the analysis of alkylphenols in heating oil before and after desulfurization will be presented. A speciation of the differently alkylated phenols is desirable to distinguish between sterically hindered phenols, which contribute to the lubricity of the fuel, and unhindered phenols, which can be problematic when they form polymeric oxidation products. Changes of phenol patterns during desulfurization of fuels can give important information about the reaction mechanism on the catalyst surface. We have analyzed heating fuel, desulfurized with two different methods, at different stages of the desulfurization process. The results show that the desulfurization methods lower phenol concentrations to a different extent and vary in their effect on phenol patterns.

References:
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(2) N. Kolbe and J.T. Andersson, *J. Agric. Food Chem.*, 54 (2006) 5736-5714