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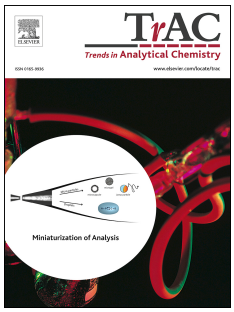

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Recent trends in element speciation analysis of crude oils and heavy petroleum fractions

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Abstract

Medium and heavy crude oils and high-boiling distillation fractions which are increasingly used in petroleum industry contain high concentrations of sulfur and metals. Their behavior in refining processes is critically dependent on the speciation. Recent analytical developments, especially on the level of coupled techniques and high-resolution mass spectrometry, start allowing the speciation of individual metal compounds in crude oil known for its extreme complexity. These developments include: (i) GC stationary phases of high thermal stability and the high-temperature interfaces with ICP-MS and TOF-MS; (ii) high-efficiency microcolumn gel-permeation chromatography with detection by sector-field ICP-MS; (iii) thin layer chromatography coupling with laser ablation ICP-MS detection; and (iv) two-dimensional separation protocols increasing the purity of heteroelement containing fractions. Progress in electrospray and atmospheric-pressure photoionization Fourier Transform MS allows resolutions of above 1,000,000 to be achieved making it possible to identify by accurate mass measurement individual sulfur and metal species directly in crude oils.

Introduction

The shrinking supply of light crude oils results in the interest, temporarily slowed down by the drop of the price of the barrel, in the use of medium and heavy crude oils as feeds in petroleum industry [1, 2]. They are characterized by the high concentrations of heteroatoms, such as sulfur and metals, which are incorporated, by covalent or non-covalent bonds, into molecules with high boiling points and high polarity [3-6].

Crude oil is a complex hydrocarbon mixture where carbon and hydrogen represent 83-87% and 10-14% of the mass, respectively. It also contains low percentage of hetero-elements, such as sulfur (0.04-8%), oxygen (0.1-5%), nitrogen (0.1-2%) and metals, mainly vanadium and nickel with concentrations of up to a few hundred parts per million (ppm) [7, 8]. The presence of sulfur and metals is detrimental in refining processes as they promote corrosion, reduce the efficiency of car catalytic converters by poisoning effect, and contribute to the environmental pollution [9-13]. Consequently, the legislation reduces the admissible sulfur content in transportation fuels and fluid catalytic cracking (FCC) feeds. Directive 98/70/EC of the European Parliament and of the Council and