

Investigating Metal Containing Aggregates in Crude Oil with ACQUITY APC

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GOAL

To understand the chemical environment (speciation) and size profiles of undesirable metal macromolecular aggregates in petroleum products, necessary for their characterization and treatment.

BACKGROUND

Several chromatographic techniques have been developed for the fractionation of complex petroleum samples according to various physico-chemical properties, such as molecular size, the degree of aromaticity, or polarity. Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) separates molecules based on their size or, more precisely, hydrodynamic volume. SEC is widely used in the crude oil industry and its use continues to increase with the new analytical challenges posed by heavy crude oil. This technique preserves the metal-ligand bond in speciation studies and also allows the study of some aggregation states. SEC has also been hyphenated to inductively coupled plasma mass spectrometry (ICP-MS) for mapping and process improvement studies, or to obtain aggregate information with specific detection of metals. A significant barrier to this technique is the lengthy analysis time (a traditional SEC analysis can take 1 to 2 hours for a single sample), as well as the solvent consumption (cost of the solvents used, cost of disposal, and associated environmental concerns).

APC allows size profiles of undesirable metal aggregates in petroleum products to be determined in less than 10 minutes.

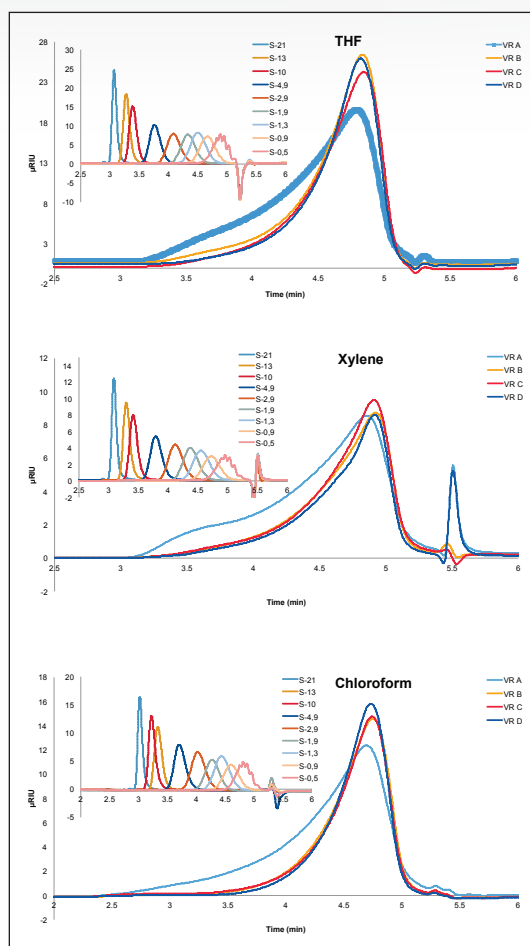


Figure 1. ACQUITY APC RI chromatograms of four VR samples obtained using different solvents with the separation of polystyrene standards from 0.5 to 21 kDa inset.

THE SOLUTION

Waters® ACQUITY® Advanced Polymer Chromatography® (APC™) System provides a breakthrough in SEC technology that defines the ultimate in size-based chromatographic separations, delivering more information about your products faster than ever before. The APC System provides unparalleled macromolecular peak resolution, particularly for low molecular weight species, accurate and repeatable molecular weight information that is up to 5 to 20 times faster than traditional SEC methods, lower analysis costs through reduced solvent consumption and waste disposal volumes, and the ability to run diverse macromolecule applications on a single system.

Four Vacuum Residues (VR), heavy petroleum cuts with boiling point over 560 °C, were studied: VR A. from South America; VR B. from Africa; VR C. from Russia; and VR D. from Northern Europe. Separations were completed with two ACQUITY APC XT Columns of 125 Å and 450 Å (4.6 x 150 mm, 2.5 µm). 10 µL sample solutions were injected with a dilution factor of 160. The ACQUITY APC System enabled different solvents to be used and tested for sample preparation and elution without extended solvent swap out procedures. The APC-ICP-MS profiles obtained are presented in Figure 1.

Samples from different origins could be differentiated in only 6 minutes, especially for the heaviest VR A., presenting early eluting, higher molecular weight compounds. In addition, the different profiles obtained for each solvent could arise from different aggregation states.

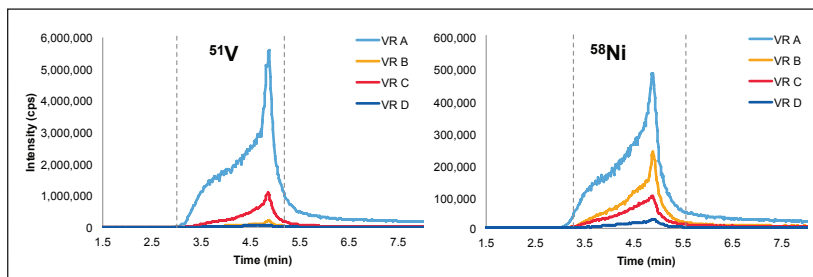


Figure 2. APC-ICP-HR-MS chromatograms obtained for V and Ni aggregates using THF for sample preparation and mobile phase. Exclusion time at 2.95 min, corresponding to the retention time of the PS standard of 43,700 Da and permeation time (5.13 min) are shown as dotted lines.

An ICP-HR-MS instrument (ELEMENT XR, Thermo Scientific), fitted with a modified total consumption micronebulizer mounted with a laboratory-made single pass spray chamber, was coupled to the ACQUITY APC. The APC-ICP-HR-MS profiles obtained are illustrated in Figure 2.

V- and Ni-containing compounds followed a bimodal distribution, indicating the presence of different types of compounds of different molecular weight. Multimodal profiles have been previously observed with classical SEC columns, although with more than six times longer analysis times than with ACQUITY APC.

SUMMARY

- According to the results obtained, the ACQUITY APC System allows the mapping of petroleum samples faster than SEC in order to establish the structure/properties relationship, enabling optimization of crude oil refining.
- Hyphenation of the APC System to ICP-HR-MS was completed for four VR samples. The size distribution profiles of V- and Ni-containing compounds showed different types of aggregates of different size.
- Significant differences of the profiles were found dependent on the origin of the sample as well as the solvent used, which seem to have an influence on the aggregation state.

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