

Metal speciation in vacuum residues by LC-ICP MS coupling. Application on hydroconversion processes

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A large amount of metals, such as vanadium (V) or nickel (Ni), is found in the heavy oil matrices with a concentration of several hundred parts per million. These metals are poisons of the catalysts used during refining processes. Information on their speciation are essential for the optimization of their removal and thus of great value for the oil industry.

In this work, we used a new method dedicated for metal complexes characterization, by using an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) coupled to liquid chromatography [1]. Two types of separation have been selected. Size Exclusion Chromatography (SEC) is used to give information on the molecular size distribution of the metal complexes, whereas metal speciation in function of the polarity is obtained by adsorption chromatography. The use of a specific multielementary ICP MS detection allows the detection of several elements simultaneously.

Ni and V repartitions in function of the size distribution have been studied in vacuum residues. Results showed trimodal distributions whose proportions seem to vary with the organic geochemical type. However the size of the aggregates in which are incorporated the Ni and V complexes are not related to the metal content.

A comparison between the Ni and V distributions obtained by SEC-ICP MS for a residue from geochemical type IIS is illustrated figure 1. Profiles indicate that the repartitions of the two metals are not equivalent. Consequently, Ni and V are not complexed to similar structures. Ni seems to be preferentially contained in high molecular weight aggregates, whereas the V is better distributed between low and high molecular weight aggregates.

This type of information is essential regarding residue upgrading since comparison between the aggregates size to which are complexed the metals can be obtained between feed and effluents along the conversion and demetallation. Furthermore, SEC-ICP MS may also be useful in the interpretation of the Ni and V elimination efficiency. Studies have been conducted both in fixed bed and ebullated bed processes.

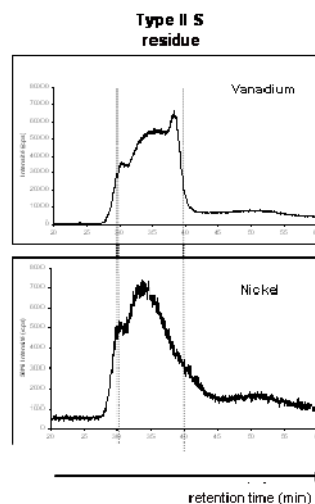


Fig. 1. Vanadium and nickel repartitions of a vacuum residue (Type IIS organic geochemical) determined by SEC-ICP MS coupling.

Besides, metal speciation have been also obtained in function of the polarity by coupling the adsorption chromatography to the ICP MS. Results showed that both Ni and V are distributed in aggregates of different polarities.

To correlate information obtained on both size and polarity, bidimensional liquid chromatography have been coupled to the ICP MS, with a first dimension dedicated to the size separation and the second to the polarity. We have thus determined the polarity properties of each size aggregates to which are complexed both Ni and V.

References

- [1] Caumette G., Lienemann C.P., Merdrignac I., Paucot H., Bouyssiere B., Lobinski R. (2009) *Talanta* 80, 1039-1043.