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Review

Metal speciation analysis of petroleum: Myth or reality?

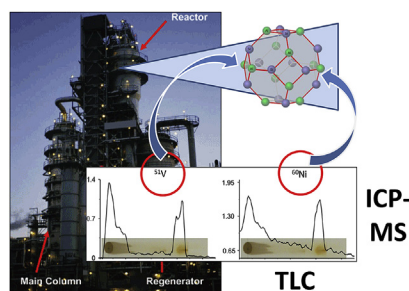
Tatyana A. Maryutina*, Andrei R. Timerbaev

Vernadsky Institute of Geochemistry and Analytical Chemistry, Kosygin St. 19, 119991 Moscow, Russian Federation

HIGHLIGHTS

- There is a lack of information on metal species in crude oil and related fractions.
- The knowledge on metal chemical form requires performing the speciation analysis.
- Analytical methods for determining the metal speciation in petroleum are reviewed.
- The main challenge is related to selective species extraction and determination.
- Speciation of the most important metals, V and Ni, remains difficult to unravel.

GRAPHICAL ABSTRACT



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ABSTRACT

Metals occurring in crude oil in a great variety of complexed forms are minor but important constituents as they affect the refining and production operations, as well as participate in geochemical processes. These roles of metals are thought to be related to their chemical state the knowledge of which requires performing speciation analysis. While exact metal speciation in crude oil still remains obscure, earnest efforts to decipher it based on using up-to-date hyphenated techniques have been attempted in the past decade. With various levels of fractionation of vanadium and nickel species, liquid chromatography with ICP-MS detection allows for an insight into metal distribution in crude oil or its fractions, according to species molecular weight or polarity. Further speciation information on the metal coordination in a variety of porphyrin compounds can be gained by the use of Fourier transform ion cyclotron resonance mass spectrometry. Individual species of mercury are often available for quantification with gas chromatography-ICP-MS as the method of choice. This mini-review is aimed at revealing and giving rise to the development of those speciation strategies and approaches that can achieve the objectives of identification, characterization and determination of metal species in crude oil and its fractions.

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Abbreviations: APPI, atmospheric pressure photoionization; GPC, gel permeation chromatography; ID, isotope dilution; LA, laser ablation; REE, rare earth elements; SARA, saturates, aromatics, resins and asphaltenes.

* Corresponding author.

E-mail address: t_maryutina@mail.ru (T.A. Maryutina).<http://dx.doi.org/10.1016/j.aca.2017.08.036>

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1. Introduction

It is hard (if possible) to contemplate that there is a more complicated sample to carry out metal speciation analysis on than that of crude oil. As with most complex samples [1], the challenge is two-fold. First, an intricate matrix, consisting of a complex mixture of hydrocarbons of various molecular weights and more complex organic compounds such as asphaltenes. On accord of matrix's heterogeneous composition, high viscosity, and difficulty of bringing into solution, crude-oil samples are often incompatible with an analytical technique in use. Second, metal species, though not numerous in terms of a metal variety (mostly Ni, V, and Fe) and fairly abundant in unprocessed crude oil, are distributed among a diversity of ligated forms, both poorly identified and hardly recoverable from the sample. Dealing with crude oil fractions, also the complex mixtures [2], makes speciation analysis not much an easier task. Indeed, some simplification in original matrix composition upon fractionation does not offset lower abundancies of metal analytes in the light fractions, whereas the heavy fractions solubility is problematic.

The complexity of the analytical task in question is not to say that the attempts at identification, characterization and determination of metal species in crude oil and its fractions are scarce [3]. Quite the contrary, a range of combined, chromatography-based techniques were tested to overcome these challenges, as previously reviewed [4]. However, as follows from this excellent coverage, fractionation of the metal species according to their molecular weight or polarity, resulting in specific metal distribution fingerprints, occasionally supplemented by information on the chemical binding of metals in these samples, is virtually only an approximation to real speciation analysis. By definition the latter comprises analytical activities on identifying individual chemical species and measuring their quantities [5], which is currently the Holy Grail for metals in crude oil and its fractions because of (i) interferences from the matrix; (ii) insufficient method's sensitivity; (iii) lack of standards, and perhaps the most troublesome, (iv) species poor recoveries from original samples. It is due to this unwelcome situation that the question in the title of the present review has been raised.

To answer this question, we offer critical analysis of analytical methods available for determining the metal speciation in crude oil and its fractions, with focus on the method's capability to provide reliable speciation information. In order to provide a state-of-the-art picture of the subject and also an update of the benchmark review from 2009 [4], only publications coming out since that year are comprehensively considered here. Reflecting importance of negative effects of metals on the processing of crude oil and its fractions, as well as our current research interests, the discussion is limited to the speciation analysis of these samples, with no concern given to related gaseous and airborne samples (natural gas and gas condensates, emissions from fossil-fuel combustions, fly ash, etc.) or crude oil products. Also, non-metals are excluded from

consideration but those who are interested are referred to recent review work [6–8].

2. Promising methodological developments

2.1. Sample preparation

In the world of analytical chemists, there is a conviction that the more complex the sample, the more intricate is its preparation. This view does not hold true in the case of crude-oil speciation analysis since the strategy based on sample dilution in organic solvents [9] has remained prevalent over the reviewed period. THF is the best solvent for this purpose as this solvent retains the hydrocarbon mixture. However, as can be witnessed below, with such sample treatment, missing the isolation of individual metal species or providing them the specific properties for the following separation, their identification is hardly feasible. In addition, upon dilution of crude oil cut samples time-dependent changes in the size distribution of Ni and V species toward higher molecular weight compounds were observed by Gutierrez Sama et al. [10]. This phenomenon led the authors to the recommendation of preparing the sample on the same day of analysis.

For assessing mercury speciation, a conventional approach is to differentiate the Hg species into particulate, volatile, organic non-ionic, and ionic Hg using consecutively the filtration, gas purge, and liquid-liquid extraction procedures. This sample treatment was recently modified by developing and incorporating a custom-made unit (Fig. 1) and the optimization of conditions involved in all three steps [11]. The developed unit allows for the combination of direct filtration and gas purge operations and, in this way, avoiding sample contamination and analyte oxidation or loss between these two steps. Also importantly, it is applicable for handling crude oil samples on site, directly after collection. This is an advantageous option as the native form of Hg species, mainly elemental mercury, can be easily altered during sample handling. Particular attention is also drawn to the sampling procedure and the type of container used in order to maintain the Hg species integrity between sampling and analysis. Alternatively, mercury in crude oil can be differentiated into extractable (by 4 M HNO₃ under microwave heating) and non-extractable Hg species to evaluate the interconversion within both families [12].

Sample preparation may occasionally require a derivatization step, for instance, to convert the target species into volatile derivatives. For the chemical forms of mercury, this can routinely be achieved by Grignard alkylation through adding BuMgCl directly to a diluted crude-oil sample [13,14]. However, in view of the matrix complexity, special care is to be taken in regard to Grignard reaction conditions and the sample dilution factor [13]. Occasionally, less common operations are implicated prior to speciation analysis. This can be e.g. ultracentrifugation to remove particulate Hg from the sample (via sedimentation) which otherwise impairs the accuracy

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