

Viewpoint

The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry[☆]

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Abstract

A literature review on the determination of trace elements in crude oil and heavy molecular mass fractions (saturates, aromatics, resins and asphaltenes) by ICP-MS, ICP OES and AAS is presented. Metal occurrences, forms and distributions are examined as well as their implications in terms of reservoir geochemistry, oil refining and environment. The particular analytical challenges for the determination of metals in these complex matrices by spectrochemical techniques are discussed. Sample preparation based on ashing, microwave-assisted digestion and combustion decomposition procedures is noted as robust and long used. However, the introduction of non-aqueous solvents and micro-emulsions into inductively coupled plasmas is cited as a new trend for achieving rapid and accurate analysis. Separation procedures for operationally defined fractions in crude oil are more systematically applied for the observation of metal distributions and their implications. Chemical speciation is of growing interest, achieved by the coupling of high efficiency separation techniques (e.g., HPLC and GC) to ICP-MS instrumentation, which allows the simultaneous determination of multiple organometallic species of geochemical and environmental importance.

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Keywords: Trace elements in crude oil; ICP-MS; ICP OES; AAS; Fractionation; Speciation

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1. Occurrences and importance of metals in crude oil and fractions

Crude oil is a complex matrix composed predominantly of saturated and aromatic hydrocarbons, but also containing

heteronuclear compounds, emulsified water and minerals [1]. Consequently, metals occur in different organic and inorganic forms. The first organic forms identified, the porphyrins, were described in the beginning of the 20th century as tetrapyrrolic complexes of vanadyl, iron (II) [2] and nickel(II) [3] with structures similar to chlorophyll and heme. These compounds were easily identified by simple spectrographic methods because of their relatively high concentration, specifically in heavy crude oils (e.g., Venezuela Boscan oil) [4]. It was soon observed that the V/Ni ratio was constant in crude oils of common source rocks and dependent on the geological age of the rocks (oils from Triassic or older age showing a value higher than unity) [5], and this ratio was used for tracing source effects [6,7]. Presumably, the metalloporphyrins were derived from chlorophyll-*a*, after the loss of Mg^{2+} at the sediment-water interface and the uptake of Ni^{2+} and VO^{2+} under the prevailing Eh and pH conditions [8]. The high chelating constant resulted in high stability of these compounds, distributed between kerogen and bitumen during oil formation [9]. Studies on the thermal evolution of the major vanadyl complex of deoxyphylloerythroetioporphyrin (DPEP) to etioporphyrin indicated a maturity dependence [10,11], thus suggesting the use of these compounds as biomarkers [12]. In contrast to V and Ni, the identification of organic forms of other metals in crude oils was achieved only later, with the advent of hyphenated techniques, e.g., HPLC or GC coupled to AAS or ICP-MS for elemental detection. Porphyrins of Co, Cr, Ti and Zn were identified in oil shales [13] by HPLC-ICP-MS and volatile compounds of alkyl and dialkylmercury were identified by GC-CV-AAS [14] and GC-ICP-MS [15].

Total metal content in crude oils has an extended concentration range, and statistical analysis was the first tool applied to investigate general elemental distribution patterns [16–19].

The analysis of oils worldwide having different viscosities and asphaltene concentrations showed that the more residual the oil, the higher the metal content, being those metal species possibly clustered by heavy molecular mass compounds [18,19]. Alkaline and alkaline earth elements are predominantly associated as carbonates and halides with the emulsified water incorporated into the oil during migration and accumulation in the reservoir [20,21], but their presence can also be the result of contamination from injected water during secondary oil recovery [22]. In sulfate-rich waters, metals are associated with H_2S production through bacterial and thermal reduction of sulfates, which can alter their distributions in crude oils [23].

Crude oil complexity is simplified by separation steps into operationally defined solubility-class fractions. The IP 143 method for asphaltene separation [24] and also a modified ASTM D 2007 method [25] (originally intended for heavy oils above 260 °C) for maltene fractionation into saturates, aromatics and resin (SARA), were applied for the detection of metal partitioning and its implications in crude oil refining and petroleum geochemistry [26–31]. Metals and organometallic compounds distribute roughly in accordance to their volatility. The more volatile species (Hg^0 , MeHg, DMeHg) are found in the more volatile saturated fraction [32] and vanadyl and nickel

porphyrins are observed in intermediate polarity molecular mass fractions of aromatic and N, S, O compounds [4,26]. Most of the non-volatile elements and low volatility species are found in the resin and asphaltene fractions, but mostly in the asphaltenes [31,33,34]. Molecular mass distribution studies using gel permeation chromatography revealed that metals concentrate predominantly in the asphaltene fraction of highest molecular mass and play a major role in asphaltene polarity [35]. The number of trace elements recognized in the asphaltene fraction could be greatly expanded using ICP-MS detection and improved sample introduction methods. It could be shown that this fraction concentrates trace elements up to ten-fold higher than the corresponding crude oil, but still preserving its original elemental fingerprint, allowing new applications in petroleum geochemistry and in environmental studies [18,30].

While advances in refinery processes enable the treatment of high sulfur crude oils, the increasing need for ultra-low sulfur fuels requires the use of low sulfur crudes to reduce the costs of desulfurisation [36]. Metal accumulation in the heaviest polar fractions of crude oils plays a significant role in establishing the refining procedure, since V, Fe, Ni and Mo have both negative and positive effects on product recoveries [37]. High metal content has a general negative effect due to catalyst deactivation by pore clogging, metal deposition, deformation and fissuration of reactors [38]. However, Ni, Co and Mo have a catalytic effect on hydroprocesses and a careful adjustment of the demetallization bed should be made [27]. Most of the metals are separated during deasphaltenation when processes include carbon removal. When hydrotreatment is used, the hydrodemetallization bed and catalyst pore diameter are optimized for a higher recovery and reactor lifetime [39]. Crude oils with high metalloporphyrin content (e.g., Venezuela Boscan oil type) [4,26] are more complicated to treat, since part of it is associated with fractions of intermediate polarity. The process involves hydrogenation prior to demetallization [40], which raises the overall refining costs. Metals and organometallic species are also incorporated during petroleum refining. Nickel, Co, Mo and Ti are constituents of catalysts [41,42]; vanadate and other metal oxides are used during fluid catalytic cracking and SO_2 oxidation/removal [43].

Contamination of soils, water and sediments by crude oil and its derivatives is conventionally evaluated by quantification of toxic hydrocarbons (BTX, poliaromatics). More recently, Ni, V and other metals (Cd, Cu, Pb and others) have been included in the analysis of contaminated soils and organisms by crude oil exudates and results show that they can be an important source of contamination for these elements [44,45]. The final refinery products seem to show a higher toxicity compared to crude oil, since metal speciation is altered and new metals are added to the matrix. Experimental studies on enriched fuel combustion show that Se and Hg tend to form volatile species, whereas other elements are associated with the particulate matter (e.g., V, Ni, Co, Zn, Cd, Pb) [46].

Effects on human health are of growing concern [47]. Tetraethyl lead, which was used as an automotive gasoline additive, is a highly toxic compound now forbidden by legislation [48,49]. Additionally, potentially toxic species like

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