Method for the quantification of vanadyl porphyrins in fractions of crude oils by High Performance Liquid Chromatography–Flow Injection–Inductively Coupled Plasma Mass Spectrometry ☆

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ARTICLE INFO

ABSTRACT

High performance liquid chromatography hyphenated by flow injection to inductively coupled plasma mass spectrometry (HPLC–FI–ICP-MS) was used to investigate V linked to porphyrins present in fractions of crude oil. First, the crude oil sample was submitted to fractionation by preparative liquid chromatography with UV detection, at the porphyrin Soret band wavelength (400 nm). The obtained porphyrin fractions were then separated in a 250 mm single column, in the HPLC, and eluted with different mobile phases (methanol or methanol:toluene (80:20; v:v)). The quantification of V-porphyrins in the fractions eluted from HPLC was carried out by online measuring the ^{51}V isotope in the ICP-MS, against vanadyl octaethylporphine standard solutions (VO-OEP), prepared in the same solvent as the mobile phase, and injected post-column directly into the plasma. A 20 µg L^{-1} Ge in methanol was used as internal standard for minimizing non-spectral interference, such as short-term variations due to injection. The mathematical treatment of the signal based on Fast Fourier Transform smoothing algorithm was employed to improve the precision. The concentrations of V as V-porphyrins were between 2.7 and 11 mg kg^{-1} in the fractions, which were close to the total concentration of V in the porphyrin fractions of the studied crude oil.

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1. Introduction

The investigation of petroleum composition in studies related to prospection and refinery of heavy and biodegraded crude oils, has gained interest because of the recent advances on heavy fuel hydroprocessing [1,2]. It is well known that heavy oils concentrate sulfur and metals, with high contents of Ni and V linked to porphyrins [3,4]. The porphyrins commonly found in crude oils are homologous series of two well documented primary structures, the deoxophylloerythroetioporphyrin (DPEP) and the etioporphyrins (Etio), with possible naphtenic or aromatic substitutions [5]. The substitution groups of the porphyrin nucleus and the concentration and distribution of the series are related to the origin, maturity and biodegradation of the crude oils, making them potential biomarkers in biodegraded fields where isoprene and terpene derivatives give limited information [6–9]. In addition, the knowledge of vanadium porphyrin concentrations in crude oils is important for the oil industry, regarding the processes known as downstream (refining-related) [10]. These compounds are detrimental to most refinery operations, causing catalyst poisoning and corrosion in cracking units and furnaces [11].

Studies in the 1980's on vanadium porphyrins in oil and shales used High Performance Liquid Chromatography (HPLC) for their separation and mass spectrometry for their identification [12–14]. The employed methodologies used extensive liquid chromatographic separations for purification that required high amounts of sample (10 g of oil and up to 10 kg of shale). The use of UV–Vis detection during HPLC analysis gave a quantitative estimate of the DPEP and Etio global content in a crude oil, however vanadium porphyrin content could not be informed, due to the low specificity of the technique for the determination of V compounds in the presence of other porphyrin compounds. As a result, it was observed that the DPEP series was more abundant than the Etio series, the latter being formed during maturity processes [15,16].

Vanadium porphyrins present in petroleum can be quantified by their metal content. To this end, the authors have hyphenated HPLC or Gas Chromatography to Inductively Coupled Plasma Mass spectrometry (ICP-MS) [17–24], but the hyphenation of HPLC with ICP-MS appeared as a more adequate technique, due to the high boiling point and heavy masses of the investigated compounds. The hyphenation is quite straightforward and HPLC flow rates are compatible with ICP-MS, however the introduction of organic solvents into ICP techniques present particular difficulties. Even with a proper operational setup of the spectrometer for organic compound introduction, the determination of elements in solvents is prone to interferences due mainly to polyatomic

ions of Ar with O, C and H: in particular, $^{51}V^+$ is interfered by $^{38}Ar^{13}C^+$. In order to reduce those interferences, the presence of oxygen in the plasma is necessary for carbon removal as CO and CO_2. The first study using HPLC coupled to ICP-MS was reported in the 1990's and used a reversed phase C_{18} column as the stationary phase, resulting in the separation of nickel and vanadium porphyrins in shale extracts [18]. The study employed methanol, an oxygenated solvent, in the mobile phase and used 3.5% oxygen in the argon nebulizer flow. The concentrations of Ni porphyrins were reported, however no data about precision and accuracy of the HPLC–ICPMS methodology was included with the reported results and the quantification of vanadium compounds was not attempted.

Size Exclusion Chromatography (SEC) has been recently employed for the determination of V and Ni porphyrins in low and high molecular weight and boiling point fractions of petroleum [19–21]. A specific coupling system was developed by Caumette et al. [19] which allowed splitting of the mobile phase before its introduction into the ICP-MS, for the use of solvents with high vapor pressure, such as tetrahydrofuran (THF) that resulted in a low oxygen percent (about 5.6%) in the argon nebulizer flow. The use of this solvent was necessary for the complete elution of the V and Ni compounds that concentrate in the high molecular weight fractions of crude oils (asphaltenes). Quantitative results were reported as percentage of the total metal collected. Normal phase HPLC was used with the SEC as bi-dimensional separations and the vanadium compounds detected were suggested to be non-porphyrinic, however no additional information regarding UV–Vis or mass spectrometry, supporting this suggestion, was presented. Recently Desprez et al. overcame spectral interferences using high resolution ICP-MS and reported a study on the size distribution of V, Ni and S compounds in petroleum and petroleum products during thermal processes [22].

The quantification of vanadium porphyrins in crude oils using reversed phase HPLC hyphenated to ICP-MS was recently proposed by Duyck et al. [23,24]. The authors used the Saturated Aromatic Resin and Asphaltene (SARA) separation step in Preparative Liquid Chromatography for the pre-concentration of porphyrins [23]. Vanadium porphyrins were eluted with methanol while Ni porphyrins elution needed a mixture of chloroform-methanol that could not be used for vanadium, due to the $^{35}Cl^{16}O^+$ interference on $^{51}V^+$. A flow injection system was used between the HPLC and the ICP-MS for inorganic standard compound introduction and quantification by HPLC–FI–ICP-MS with 6.5% precision in calibration [24]. Recovery was evaluated for one porphyrin fraction injected but the elemental mass balance between the oil and the fraction was not investigated.

The present study made changes in the HPLC–FI–ICP-MS quantification previously cited, by introducing an online internal standard and a mathematical treatment of both signal and noise by Fast Fourier Transform (FFT) smoothing, in order to improve the transient signal/noise ratio for ^{51}V, which is the principal limitation for vanadium porphyrins quantification in crude oil fractions. The mobile phase composition was also investigated for resolution and recovery of compounds, supported by elemental mass balance between vanadium porphyrins concentrations and total vanadium concentration in oil and oil fractions as determined by an independent methodology recently developed by the group [25].

2. Experimental

2.1. Samples, standards and reagents

A Brazilian internal reference crude oil (O1) and the Venezuelan certified crude oil, NIST 8505 (Gaithersburg, MD, USA) were used in this study.

The solvents methanol, toluene, chloroform, n-heptane and dichloromethane were of HPLC grade (JT Baker, USA) and xylene (Vetec, Brazil) was PA grade. Deionized water was used for preparing the buffer and other aqueous solutions. The buffer solution (pH = 4.1), employed in the mobile phase to test the separations of the V-porphyrins, was prepared with acetic acid (1 mol L^{-1}) and sodium acetate (1 mol L^{-1}) solutions, in water.

Monoelemental organometallic Ba, La and In (Conostan, Conoco, Ponca City, OK, USA) standards solutions, at 20 µg kg^{-1} in xylene, were used for the optimization of the ICP-MS equipment. An organic multielemental standard (SPC 21, Conostan, Canada) diluted in xylene from 5 to 50 ng mL^{-1} of V, approximately, was used for the determination of total V in crude oil samples and their fractions, by direct introduction in ICP-MS, according to the method developed by Souza et al. [24].

The use of a V-porphyrin standard, vanadyl octaethyl porphine (VO-OEP) (Sigma Aldrich, MI, USA), was necessary because of the low stability of inorganic V in mixtures of methanol and toluene. About 3 mg of it was diluted in 100 mL methanol and the exact concentration of V as VO-OEP in this solution was determined by ICP-MS through external calibration with inorganic multielemental standard solutions in methanol (PerkinElmer, 29 elements in 5% HNO_3). This solution was further diluted in the same solvent composition as the HPLC mobile phase, at approximate concentrations of 50–100–200–400 µg L^{-1} and used for V-porphyrins determination in the fractions by HPLC–FI–ICP-MS.

Inorganic monoelemental Ge, Sc, Y, Nb, Rh and Ta, at 20 µg L^{-1} in methanol (PerkinElmer), and the organic monoelemental In at 50 µg L^{-1} in xylene (Conostan), were tested as internal standards.

Argon 99.996% (Linde Gas, Brazil) was used in the ICP-MS. Oxygen 99.5% purity (White Martins, Brazil) was used to avoid carbon deposits and interference in the introduction of organic solvents into the plasma.

2.2. Sample preparation — oil fractionation

The oil samples were fractionated by preparative chromatography, involving two steps: first, about 0.6 g of crude oil was fractionated on a gravimetric column (50 cm × 2.5 cm) filled with silicagel® (63–200 mm, Merck, Germany). A sequence of n-heptane, toluene and dicloromethane and their mixtures was used to obtain the PAP (Paraffins, Aromatics and Polar compounds) and resin fractions, as described by Duyck [23,24]. In the second step, a medium pressure LC system was used, in which a peristaltic pump forced the mobile phase into the column (250 mm × 25 mm, Omnifit Supelco, Cambridge, USA). The PAP or the resin were manually injected and a sequence of methanol, methanol:toluene (50:50; v:v) and toluene was used. When the eluent at the exit of the column absorbed at 400 nm, which is the porphyrin's Soret band, it was separately collected. Two concentrated porphyrins fractions were obtained from PAP and three from the resin, as presented in Fig. 1. The obtained fractions (Fr 1 to Fr 5) were filtered (0.45 µm, Teflon, Millipore, USA), evaporated and stored in a refrigerator at 2 °C until analysis by HPLC–FI–ICP-MS for the determination of V-porphyrins.

2.3. Instrumentation

In all the analysis (HPLC–FI–ICP-MS and ICP-MS direct analysis), V concentrations were determined using a NexIon 300X ICP-MS spectrometer equipped with collision/reaction cell (PerkinElmer, Toronto, Canada). The device for organic analysis was constructed using an introduction system composed of nebulizer (chosen according to the kind of analysis, as described below) and an Isomist™ cylonic spray chamber (Glass Expansion, Pocasset, MA, USA), which temperature was fixed according to the solvent. The injector i.d. was 0.8 mm and oxygen was added at the injector entrance. Oxygen flow was regulated by means of a mass flow controller (MKS Instruments Inc., USA).

For the direct analysis of xylene solutions by ICP-MS, the nebulizer was a microconcentric PFA-100 (Elemental Scientific, USA) adequate for organic solvents, because it allows lower solvent load into the