Fuel 220 (2018) 631–637

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

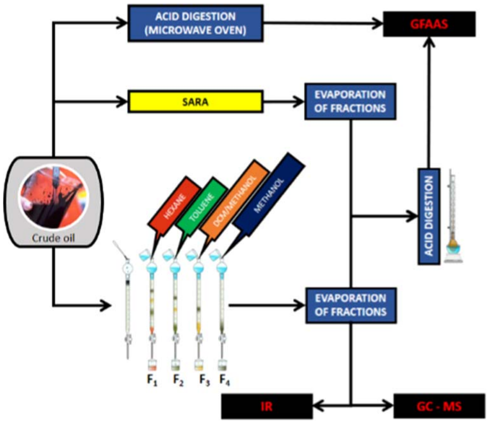
Full Length Article

Sequential extraction procedure for the separation of Ni and V species in crude oil and analysis by ETAAS, GC–MS, and IR

Cleusa Cavalcante, José Paulo de Oliveira, Juliana Hamada, Fernanda Amaral de Siqueira, Angerson Nogueira do Nascimento*

Departamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo, Diadema, SP 09972-270, Brazil

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Crude oil
Vanadium
Nickel
ETAAS
Sequential extraction

ABSTRACT

The determination of nickel and vanadium in crude oil has been evaluated in several scientific studies because these elements can contribute to equipment corrosion, the contamination of catalytic processes, and environmental pollution. Many studies have focused on the evaluation of the total concentration of these elements. However, although it is important to know the total elemental concentration to determine the chemical composition of a sample, this does not yield information about the amount of potentially toxic compounds that may be associated with different macromolecules present in the sample. Here, we report the development of a sequential extraction procedure for the separation of nickel and vanadium species. To determine the total concentration of Ni and V, samples, as well as a certified reference material (NIST – SRM 1634C), were acid digested and analyzed by electrothermal atomic absorption spectrometry (ETAAS). The separation of the species was performed by column chromatography with silica gel as the stationary phase, and hexane (fraction 1), toluene (fraction 2), dichloromethane (DCM) + methanol (fraction 3), and methanol (fraction 4) as the eluents. The extracts obtained in each fraction were analyzed by ETAAS, gas chromatography–mass spectrometry (GC–MS), and infrared (IR) measurements. The experimental results showed that the total concentrations of the elements in the crude oil were between 7.4 and 14.3 $\mu g\ g^{-1}$ for Ni and 9.8 to 14.6 $\mu g\ g^{-1}$ for V. The analysis of SRM 1634C showed that 89% of Ni and 103% of V were recovered. The GC–MS analysis showed the following elution order: saturated compounds and aromatics (fraction 1), aromatic and cyclic compounds (fraction 2), aromatic compounds (fraction 3), and polar compounds (fraction 4). The results obtained by ETAAS showed that 100% of the

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* Corresponding author.
E-mail address: angerson.nogueira@unifesp.br (A.N.d. Nascimento).

https://doi.org/10.1016/j.fuel.2018.02.033
Received 2 September 2017; Received in revised form 4 February 2018; Accepted 6 February 2018

Ni and V contained in crude oil can be separated in three different extracts. However, the IR spectra and GC–MS analysis allowed us to conclude that Ni and V are associated with compounds containing nitrogen and oxygen that were not identified by gas chromatography.

1. Introduction

Crude oil is defined as a complex mixture of saturated hydrocarbons, aromatic and polycyclic compounds, and nitrogen, sulfur, and oxygen-containing compounds [1,2]. This composition provide many organic compounds and considerable quantities of organometallic compounds, which are in the form of inorganic salts dissolved in the emulsified water of the petroleum or concentrated in the heavier oil fractions. These compounds are associated with many elements, but there is a predominance of Ni and V, which range in concentration from 1 to 1200 $\mu g\,g^{-1}$ and are responsible for contamination of catalysts and the corrosion of burner exhaust pipes [3,4].

The mechanisms involved in the processes in which different elementary species are incorporated in the organic fractions depends on the interactions between the chemicals compounds, the temperature, and the catalytic processes involved [5,3]. Therefore, speciation analysis allows us to obtain a fundamental understanding of the changes that have occurred in these systems. To carry out speciation analysis, it is necessary to perform the separation, identification, and characterization of the different forms of these elements in a sample [6]. However, because of the large number of compounds present in oil, it is necessary to perform a fractionation step before the speciation analysis. Fractionation methods can be used to minimize the matrix effects in some instrumental techniques and establish an initial relationship between the molecular compounds (such as asphaltenes and maltenes) and elemental species (such as Ni and V), providing information about the types of compounds formed by these elements, their interactions, and the toxicity of these substances [7–10].

In the literature, there are many methods of petrochemical fractionation; however, the “Saturated, Aromatic, Resin, and Asphaltene” (SARA) method, which separates the analytes into different classes of compounds is widely used. After the fractionation the compounds are analyzed by chromatographic techniques to classify the molecular species present in these matrices [11–15]. However, several studies have criticized the SARA method because of its poor experimental reproducibility [16–19]. Thus, is important to evaluate new fractionation processes that allow the determination of the relationships between the elements and the molecular compounds presents in crude oil. Considering this, it is possible to develop a fractionation procedure and evaluate using two or more instrumental techniques that allow the analysis of organic and inorganic species in petroleum [20–24]. An alternative is to use chromatography techniques (for example, HPLC and GC–MS) because of the high capacity for the resolution of many compounds and the equipment versatility. These techniques can be hyphenated with elemental detectors (spectroscopic techniques, for example) to determine the relationship between the organic compounds and the elements [6,1]. However, the sample preparation step may be problematic because of the required isolation and quantification steps. Furthermore, the results may be accompanied by errors, contamination, and other uncertainties inherent in these methods. Thus, the sample preparation step is a key point to develop a reproducible methodology that allows the quantification of the analytes in speciation analysis [25]. The first step is the sample collection stage, which must avoid sources of contamination or adsorption on the surfaces of the storage bottle [6]. Then, the chemical species should be isolated using techniques such as liquid–liquid extraction, Soxhlet extraction using organic solvents extraction, ultrasound, classical chromatography, and solid phase extraction [26–32]. The compounds obtained by this treatment are then analyzed by instrumental analysis techniques that allow the evaluation of the distribution of elemental/molecular species and the association between each species. In this paper, we report our development of a sequential extraction process for the identification of nickel and vanadium species by spectroscopic and separation techniques.

2. Experimental

2.1. Instrumentation

A graphite furnace atomic absorption spectrometer (GFAAS, GTA 120 model, Varian, Methchen, Australia) equipped with longitudinal deuterium lamp background corrector and a transversely-heated graphite tube (THGA) tube with an integrated pyrolytically coated platform was used. The spectrometer was operated using a hollow cathode lamp for Ni and V (Photron, Australia). Analyses were performed using the instrumental parameters shown in Table 1. A PSD-120 autosampler (Varian) was used to deliver reference solutions and samples from the cup to the graphite tube. Argon 99.998% (v/v) (Air Liquide Brazil, São Paulo, SP, Brazil) was used as the protective and purge gas.

The digestion of the samples and the standard reference material was carried out in a closed-vessel microwave digestion system with a pressure and temperature sensor (ETHOS, Milestone, Sorisole, Italy). This microwave system was equipped with ten vessels made of a perfluoroalkoxy polymer (PFA) with a volume of 100 mL.

The fractions obtained from sequential extraction were evaporated in a rotary evaporator vacuum controller (Buchi, Brazil) and the compounds were analyzed in a gas chromatography mass spectrometer (GC–MS, QP 2010, Shimadzu, Kyoto, Japan) equipped with an automatic injector (Shimadzu, Kyoto, Japan) using a DB-5 capillary column containing 5% phenyl + 95% polydimethylsiloxane and measuring 30 m × 0.32 mm × 0.25 μm film thickness (Restek, USA). The MS scan parameters were an *m/z* range of 40–500, a scan interval of 0.5 s, a scan speed of 1000 $amu\,s^{-1}$, and a detector voltage of 1.1 kV. The carrier gas (He) was delivered at a constant linear velocity of 1.1 $mL\,min^{-1}$. Analyses were performed using an oven with a programmed temperature range of 40–280 °C at 2 $°C\,min^{-1}$ and the samples were held for 30 min at 280 °C.

Table 1
Instrumental conditions and heating program for the simultaneous determination of Ni and V by GFAAS.

Element	Wavelength (nm)	Current (mA)		Slit width (nm)
Ni	232	8		0.2
Step	Temperature (°C)	Ramp (s)	Hold (s)	Air flow ($L\,min^{-1}$)
Drying I	40	0	0.1	0.3
Drying II	110	10	10	0.3
Drying III	130	5	30	0.3
Pyrolysis	1400	10	20	0.3
Atomization	2500	0.8	5	0
Cleaning	2600	0.8	2	0.3
Element	Wavelength (nm)	Current (mA)		Slit width (nm)
V	318.5	10		0.2
Step	Temperature (°C)	Ramp (s)	Hold (s)	Air flow ($mL\,min^{-1}$)
Drying I	40	0	0.1	0.3
Drying II	110	10	10	0.3
Drying III	130	5	30	0.3
Pyrolysis	1400	10	20	0.3
Atomization	2800	0.8	5	0
Cleaning	2800	0.8	2	0.3