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Short communication

Application of TLC and LA ICP SF MS for speciation of S, Ni and V in petroleum samples

Nopparat Vorapalawut^{a,b,1}, Mauro Martinez Labrador^{a,c,1}, Pawel Pohl^d, Manuel Caetano^c, Jose Chirinos^c, Carine Arnaudguilhem^a, Brice Bouyssiere^{a,*}, Juwadee Shiowatana^b, Ryszard Lobinski^{a,e}

^a CNRS/UPPA, Laboratoire de Chimie Analytique Bio-inorganique et Environnement, UMR 5254, Hélioparc, 2, Av. Pr. Angot, F-64053 Pau, France

^b Faculty of Science, Mahidol University, Rama VI Rd., Rajthevee, Bangkok 10400, Thailand

^c Escuela de Química, Universidad Central de Venezuela, Caracas, Venezuela

^d Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspińskiego 27, Wrocław 50-370, Poland

^e Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, Warsaw 00-664, Poland

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ABSTRACT

A coupling of thin layer chromatography with laser ablation ICP SF MS was developed for the fractionation of Ni, V, Fe and S in crude oil and its fractions (saturate, aromatic, resin and asphaltene). The detection limits were 18 ng g⁻¹ and 23 ng g⁻¹ for nickel and vanadium, respectively, and a sample could be characterized in terms of the metal distribution as a function of species polarity within 10 min. The method was used to characterize the metal distribution in crude oils of different origins and their different fractions.

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1. Introduction

Petroleum is a complex mixture of hydrocarbon compounds containing metals (mainly Ni, V and Fe) from few parts per billion to more than hundred parts per billion [1–3]. The metals are mainly concentrated in the heavy fractions of petroleum, such as asphaltenes or vacuum [1,3,4] residue. The most abundant and undesirable metals in petroleum samples are Ni and V because they are responsible for the poisoning of catalysts used in desulfurization process. Ni and V occur mainly in petroleum samples in two different classes of compounds; non-polar porphyrins and polar non-porphyrins. The Ni and V porphyrins have important role as geochemical markers. The sulfur content in petroleum is important because the presence of sulfur can cause problems during storage and processing and affect final quality of petroleum products. The combustion of petroleum products emits sulfur dioxide into the atmosphere which raises environmental concerns. Consequently, the knowledge on the elemental distribution in crude oils is required in view of the development of

refining processes (mainly demetallation) [1,5,6] and the classification of crude oil in term of origin and maturity [7,8]. The couplings of HPLC or GC and an element specific detector, e.g. ICP MS, are widely used for investigation of element species in petroleum samples [9–13]. The asphaltene fraction needs to be removed beforehand because of its low volatility and its low solubility in the HPLC mobile phase.

The fractionation of crude oil into saturate, aromatic, resin and asphaltene (SARA) fractions using silica or aluminum open-column liquid chromatography is the most common method for crude oil characterization [14,15]. Asphaltenes can also be precipitated and separated from the crude oil by addition of *n*-heptane or *n*-hexane. The soluble maltene fraction is usually fractionated on a silica or alumina column using appropriate solvents. In general, saturates are extracted with an *n*-alkane solvent (e.g. hexane) followed by elution of aromatic and polar fractions with the solvents or solvent mixtures of higher eluotropic strength [16]. Non specific quantitative data are obtained by the gravimetric determination of each fraction after evaporation of solvents. However, this method is labor intensive, time consuming and requires large quantities of solvents and samples [17,18].

Thin layer chromatography (TLC) coupled with flame ionization detector (FID) [19–21] and ultraviolet (UV)-fluorescence scanning

* Corresponding author. Tel.: +33 559 407 752.

E-mail address: brice.bouyssiere@univ-pau.fr (B. Bouyssiere).

¹ Both authors worked equally.

densitometer [22] has been applied for hydrocarbon-type analysis in crude oils and its related products in order to avoid the adsorption problems of typical to chromatography. TLC advantages include low cost, simple instrument requirement, high sample throughput and simultaneous fractionation of crude oil into SARA.

Laser ablation—ICP SF MS (LA ICP SF MS) was recently proposed for the single drop analysis of crude oil adsorbed on silica plates [23]. The TLC LA ICP SF MS was proposed for speciation of arsenic [24], chromium [26] and iodine [25] in rice flour, in standard solution, and Iodinated X-ray contrast agents, respectively.

The goal of this work is to investigate the elemental fractionation in crude oil and SARA fractions using TLC LA ICP SF MS as an alternative to the commonly used size-exclusion HPLC ICP SF MS coupling [26,27].

2. Materials and methods

2.1. Instrumentation

A double-focusing sector-field (ICP SF MS) instrument (Element XR, Thermo Fisher Scientific, Bremen, Germany) was used under operating conditions given in Table 1. It was equipped with a Fassel-type quartz torch shielded with a grounded Pt electrode and a quartz bonnet. A Peltier-cold quartz double-pass spray chamber fitted with a MicroMist pneumatic micro-nebulizer was applied for conventional pneumatic nebulization of aqueous solutions. A standard quartz injector (1.75 mm i.d.) was used. A New Wave Research (CA, USA) UP-213 Nd:YAG deep UV system was used for laser ablation.

The LA system was directly coupled to the ICP torch using a 60-cm Tygon tube (5.0 mm i.d.). The ablated material from the LA chamber was swept by a He carrier gas, mixed with an Ar make-up gas immediately prior to introduction to the plasma. No carbon deposition was observed on the cones under these conditions. Standard Ni sampler (orifice diameter 1.1 mm) and skimmer

(0.8 mm orifice diameter) cones were utilized; no additional O₂ gas flow was necessary [23].

2.2. Reagents and samples preparation

500, 1000, 2000 and 5000 ng g⁻¹ multielement standards in organic solutions were prepared by diluting a Conostan (SCP Science, Champlain, NY) multielement oil-based standard S-21 (100 mg g⁻¹) and monoelement oil-based standard of Co (1000 mg g⁻¹), S (100 mg g⁻¹) and Hg (100 mg g⁻¹) solutions in tetrahydrofuran (THF). A 2000 ng g⁻¹ THF solutions of vanadyl 2,11,20,29-tetra-*tert*-butyl-2,3-naphthalocyanine (MW 1004) and standard reference material of wear-metals in lubricating oil (NIST SRM 1085b, V concentration 298 mg g⁻¹) were also prepared. Samples of crude oils were 2-fold diluted in THF.

Silica gel on TLC Al foil, with layer thickness of 200 μm and a particle size 17 μm from Fluka (Steinheim, Germany) was used. ACS reagent grade THF, methanol, dichloromethane, toluene and hexane purchased from Sigma-Aldrich (Steinheim, Germany) were used.

Crude oils A, B, C and D are respectively dead oil from Africa, South America, South Europe and South América.

2.3. Analytical TLC separation

The silica TLC plates (50 × 50 mm, WL) were activated at 80 °C overnight. 1 μl aliquots of sample (multielement standards), vanadyl naphthalocyanine standard, SRM 1085b, crude oils and their fractions (saturated, aromatic, resin and asphaltene) was deposited on TLC plates at start lines (about 5 mm above bottom sides of plates) using a micropipette and dried before separation. Chromatographic separation was performed in 4 chambers filled with hexane (I), toluene (II), dichloromethane (III) and methanol (IV). Each, the TLC plate was removed from a given chamber when the solvent front moved 10 mm; and air dried before to be placed to a subsequent chamber (see Fig. 1).

After completing TLC separation, the TLC plates were divided into 5 stripes (10 × 50 mm, WL). Each stripe was fixed on a glass microscope slide using a two-sided tape, placed in a LA chamber and ablated.

Table 1

Compromised working parameters set to LA ICP SF MS.

Thermo Fisher Scientific Element XR ICP SF MS	
<i>ICP ion source and ion transmission</i>	
Forward power, W	1200
Plasma Ar gas flow rate, l min ⁻¹	16.00
Auxiliary Ar gas flow rate, l min ⁻¹	0.80
Make-up Ar gas flow rate, l min ⁻¹	0.99
Extraction lens, V	-2000
Focus lens, V	-1200
X-deflection lens, V	-2.25
Y-deflection lens, V	1.00
Shape lens, V	105
SEM potential, V	2250
<i>Data acquisition</i>	
Measured isotope	³² S, ³⁴ S, ⁵¹ V, ⁵⁸ Ni, ⁶⁰ Ni
Search and integration window, %	60
Settling time, ms	300 (³² S), 1 (³⁴ S, ⁵⁸ Ni), 34 (⁵¹ V, ⁶⁰ Ni)
Sampling time, ms	10 (³² S, ³⁴ S, ⁵⁸ Ni, ⁶⁰ Ni), 20 (⁵¹ V)
Number of sample per peak	15
Detection mode	Triple (Analog, Pulse, Faraday)
Scan type	E-scan
Integration type	Average
Mass resolution	4000 (Medium)
<i>New Wave Research UP-213 LA</i>	
Wavelength, nm	213
Pulse energy, mJ	0.45 (50%)
Fluence, J cm ⁻²	1.43
Spot size, mm	200
Repetition rate, Hz	20
Scan speed, mm s ⁻¹	80
Carrier He gas flow rate, l min ⁻¹	0.50

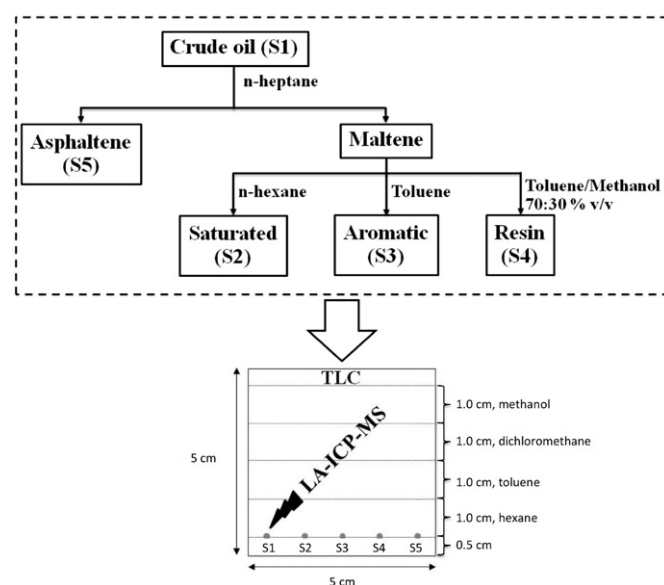


Fig. 1. Analytical procedure for investigation of Ni, V and S fractionations in crude oils and its SARA fractions by silica gel TLC plate for separation and LA ICP SF MS for elemental detection.

2.4. LA ICP SF MS measurement on separated TLC plates

Starting and ending points of the ablation were taken 2 mm below and above, respectively start and end lines of the TLC stripe. The ablation was placed in the center of the sample migration line on the stripe. All the LA ICP HR MS parameter are given in Table 1.

2.5. SARA fractionation

SARA separation of the crude oil was obtained after two main steps. Asphaltenes were separated from crude oil using n-heptane with a ratio 1/40 (v/v) crude oil/n-heptane, with subsequent centrifugation and washing. The maltene fraction (supernatant) was fractionated on silica to separate saturate, aromatic and resin hydrocarbons. The elution with n-hexane allowed the separation of the saturate fraction. The elution with toluene and a mixture toluene/methanol 70/30 (v/v) allowed the separation of the aromatic fraction and resin fraction, respectively [28].

3. Results and Discussions

3.1. Optimization of LA ICP SF MS parameters

Before coupling the LA system with ICP SF MS, the torch position and voltages of ion focusing and transmission lenses of the mass spectrometer were optimized using ClaritasPPT[®] multielement

(SPEX CertiPrep, Metuchen, NJ) aqueous standard solution for the maximum intensities of ⁷Li, ¹¹⁵In and ²³⁸U isotopes.

An important parameter for TLC analysis by laser ablation is the scan speed of laser because this parameter can affect the transient signal profile. Therefore, the effect of laser scan speed on the signal profile and signal intensity was studied at 20, 40 and 80 $\mu\text{m s}^{-1}$. The optimum laser scan speed was found at 80 $\mu\text{m s}^{-1}$ corresponding to the most intense and stable signal. The other parameters of LA including energy and laser spot size were optimized with regard to signal intensities and reproducibility as reported elsewhere [23]. The optimum values were found at 50% (0.45 mJ) of laser energy and 200 μm spot size.

3.2. Analytical performance of LA-ICP-SF MS

10 × 10 mm TLC plates were immersed for 30 min in an organic solution of multielement standards for detection limit and precision investigation and in two standard reference materials of wear metals in lubricating oil (SRM 1084a and SRM 1085b) for method validation. Upon removal, they were dried under laminar hood. The impregnated TLC plates were fixed on a glass microscope slide and analyzed using optimum LA ICP SF MS parameters in line scan mode. The detection limits for nickel and vanadium were 18 ng g^{-1} and 23 ng g^{-1} , respectively, and the relative standard deviation was below 10%. The certified and the

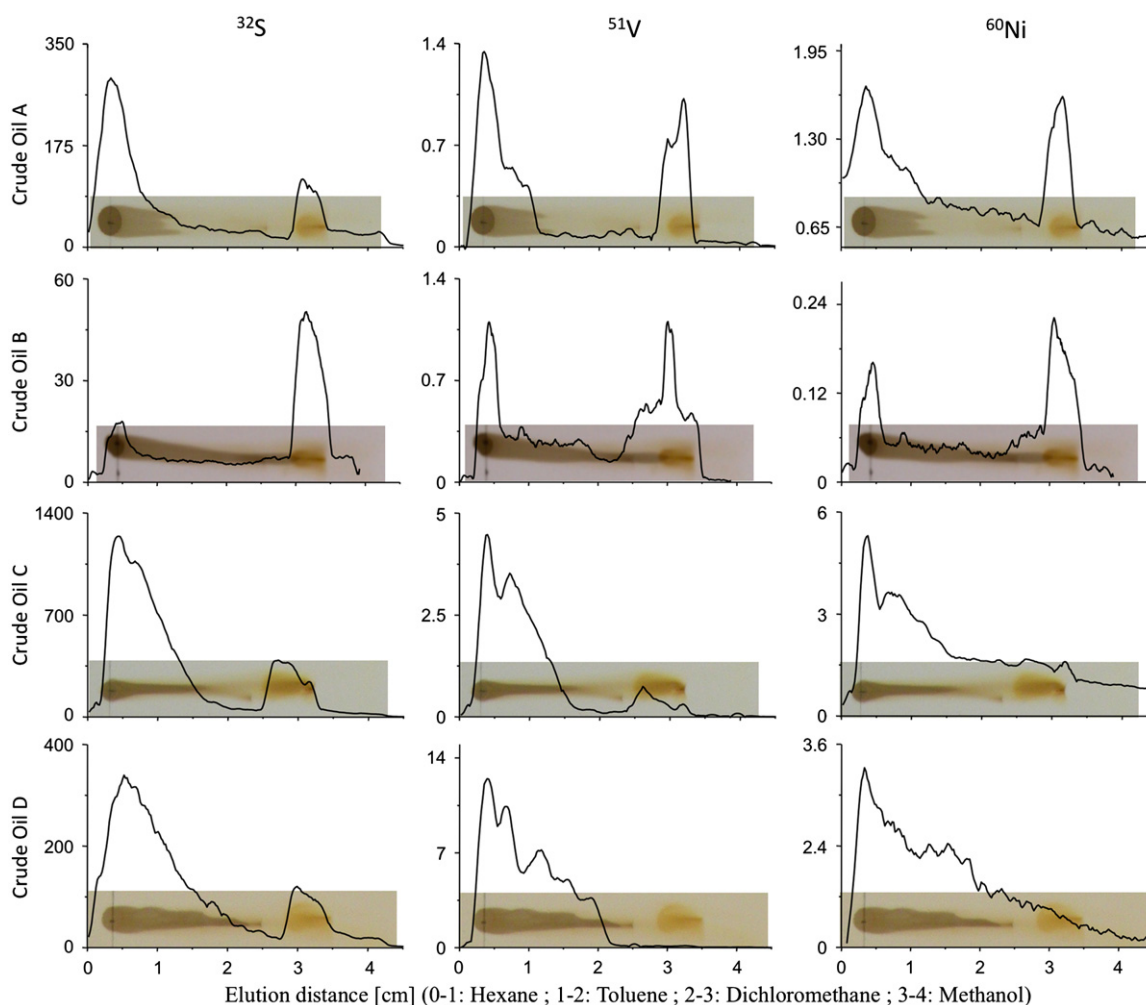


Fig. 2. Thin layer chromatography LA ICP SF MS of crude oils of different origins.

determined concentration of wear metals in lubricating oil (SRM 1084a and 1085b) agreed within 10%.

3.3. Thin layer chromatography of crude oils

The aim of this work was the determination of Ni, V and S distribution in crude oils and its SARA fractions according to their polarity by TLC and LA ICP SF MS. The crude oils and its SARA fractions were separated on TLC plate by increasing the solvent polarity from hexane to methanol. Then, Ni, V and S on the TLC plates were detected by LA ICP SF MS. The best LA scan mode used in this work for Ni, V and S detection on a TLC plate was line scan at the center lane. The analysis time was 10 min per plate.

Four different crude oils were analyzed by the developed technique. Fig. 2 presents photographs of separated TLC plates and thin layer chromatograms of sulfur, nickel and vanadium. The thin layer chromatograms show mainly two separated peaks: one at the highest elution distance (3 cm from the starting line) corresponding to the more polar compounds and the other one at the beginning of

TLC plate corresponding to non-polar compounds. The distributions of nickel and vanadium in polar and non-polar fractions show clearly differences in four crude oils. In crude oil A and B, sulfur, vanadium and nickel species are in the both polar and non-polar fractions whereas crude oil C and D show more intense signals from vanadium and nickel species in the non-polar fractions. Indeed, nickel is entirely found in the non-polar fraction. Sulfur species in crude oil A, C and D are present in the non-polar fraction whereas crude oil B contains most of sulfur in the polar fraction. Consequently, fractionation of sulfur, nickel and vanadium species in crude oil according to their polarity could be accomplished by this proposed method which offers the advantage of lower solvent and time consumption in comparison with liquid column chromatography.

3.4. Comparison of thin layer chromatograms of crude oils and their SARA fractions by TLC LA ICP SF MS

The four crude oils were also separated into saturated, aromatic, resin and asphaltene fractions using SARA method described in

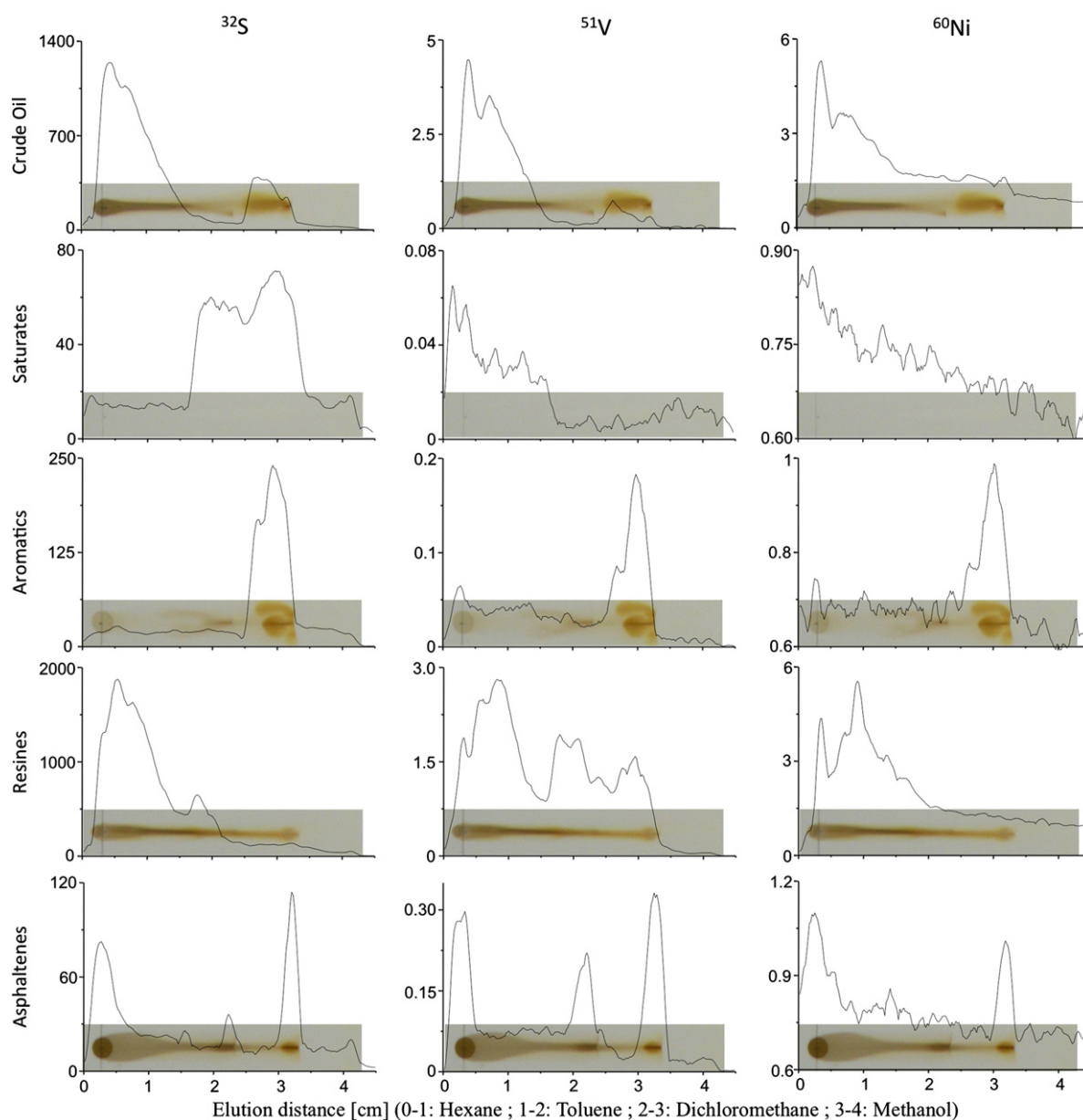


Fig. 3. Thin layer chromatography LA ICP SF MS analysis of a crude oil (Sample C) and its SARA extracts.

experimental. An example of thin layer chromatograms of a crude oil and its SARA fractions for the crude oil C (Fig. 3) shows different distribution patterns of sulfur, nickel and vanadium. As reported by Merino-Garcia et al. [29] during SARA fractionation, the separation was made by solubility adsorption property thus a direct analysis of the entire crude oil can provide information on associating species which were lost during the precipitation of asphaltenes. There are no nickel and vanadium species in saturated fractions of all the crude oils but the nickel and vanadium species occur principally in resin and asphaltene fractions containing polar and non-polar compounds. This is coherent with the observation that nickel and vanadium in the polar fractions are bound to porphyrin compounds.

In all the four studied crude oils samples no relationship between the distribution of nickel and vanadium was found.

4. Conclusion

The use of TLC for the fractionation of crude oils and their SARA fractions combined with LA-ICP-SF MS detection is a convenient tool to probe the distribution of sulfur, nickel and vanadium species according to their polarity. This proposed method has the advantage of lower solvent consumption and higher sample throughput in comparison with liquid chromatography. Moreover, this method can use hexane as a mobile phase for crude oil separation which is impossible in liquid chromatography because of the precipitation of asphaltenes on the column. The parent crude oils and their SARA fractions show different distribution of sulfur, nickel and vanadium species.

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