

Determination of Vanadium/Nickel Proportionality in the Asphaltene Fraction of Crude Oil Using Thin-Layer Chromatography with Femtosecond Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry

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ABSTRACT: A method that integrated thin-layer chromatography (TLC) with femtosecond laser ablation–inductively coupled plasma–mass spectrometry (fs-LA–ICP–MS) was developed for the determination of the proportionality of vanadium/nickel in the asphaltene fraction of crude oils. TLC is easy and fast to implement for separation of crude oil components requiring minimal amount of solvents, and fs-LA–ICP–MS allows for direct analysis of the TLC plates without any additional sample preparation. This method was tested on Venezuelan crude oil samples and their isolated asphaltenes. The results correlated well to those obtained using a traditional method for asphaltene analysis involving separation and digestion with measurements by inductively coupled plasma–optical emission spectroscopy (ICP–OES). The combination of TLC with fs-LA–ICP–MS provided fast and reliable measurements of V/Ni proportionality in asphaltene and directly from the crude oil without solvent-exchange processes.

■ INTRODUCTION

Crude oil is a complex mixture of hydrocarbon compounds that can be grouped into four chemical classes based on differences in solubility and polarity: saturates, aromatics, resins, and asphaltenes (SARA).^{1,2} Metals also are found in crude oils; however, these are “predominantly associated (~80%) with the asphaltenes portion”. Asphaltenes correspond to the heaviest, polar, and aromatic portion of the crude oil, and they are defined in terms of solubility as the fraction that precipitates when an excess of low-molecular-weight paraffin, such as *n*-heptane, is added to the crude oil.³ Ni and V are the most abundant metals in crude oil at concentration levels from ng kg⁻¹ to mg kg⁻¹, and they are mainly present as mixed-ligand tetradentate species, humate complexes, and tetrapyrrole metallo-organic complexes.⁴

The proportionality of vanadium/nickel can be used to infer geochemical information, for example, crude oil origin as well as crude oil source rock correlations.^{4–7} The proportionality of V/Ni in crude oils is controlled by environmental conditions of the source rock. Once the metallo-organic complexes of vanadium and nickel are established, their high stability assures that they will remain during lithification and at high levels of diagenesis. Their stability also suggests that generation, migration, and entrapment of crude oil are not likely to affect these metallo-organic structures. Variations exist in V and Ni concentrations, but the proportionality of the two elements likely remains constant.^{4–6}

Inductively coupled plasma–mass spectrometry (ICP–MS) and inductively coupled plasma–optical emission spectrometry (ICP–OES) are commonly used for the analysis of Ni and V in petroleum products. Several sample preparation methods have been reported for the analysis of crude oils and their products.^{8–17} Particularly for asphaltene analysis, the traditional method consists of asphaltene separation and purification from the maltenes with *n*-heptane,³ followed by digestion in strong

oxidative conditions or dilution in organic solvents. These procedures are labor-intensive (3–5 days) and require large quantities of sample and solvents.

Laser ablation (LA) of petroleum allows for direct analysis without these pretreatment preparation methods. Previous studies of crude oil samples using LA have been reported but described limitations because of sample splashing and lack of standards for quantification.^{18–23} Several studies have been reported to eliminate the splashing, for example, immobilization of the crude oil using powders formed by fusion or pelletization,¹⁸ dried aerosols produced by ultrasonic nebulization,¹⁹ isotope dilution quantification with the use of petroleum-impregnated cellulose,²⁰ silica gel plates,²¹ specially designed chambers,²² and use of xerogels.²³ Although these approaches reduce or eliminate splashing, large amounts of the ablated sample still deposit inside the chamber and on the ICP–MS sampling cones. Controlling the amount of ablated sample is a key issue in the analysis of crude oil samples using this direct laser sampling approach.

Thin-layer chromatography (TLC) with laser ablation–inductively coupled plasma–sector field–mass spectrometry (LA–ICP–SF–MS) was recently reported for the analysis of S, Ni, and V in crude oil.²⁴ This method has the analytical advantage of small sample and solvent consumption and high sample throughput. The aim of this work was to further develop the use of TLC for semi-quantitative analysis of petroleum samples using femtosecond laser ablation–inductively coupled plasma–mass spectrometry (fs-LA–ICP–MS). Specifically, the goal was to develop a fast procedure to measure the proportionality of V/Ni in the crude oil, thereby avoiding the labor-intensive method of

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asphaltene separation. Using a crude oil with known Ni and V concentrations as a reference, the V/V + Ni ratio was measured with good precision and without the traditional time-consuming separation method generally required for asphaltenes. The direct LA measurements are compared to the traditional methods for asphaltene separation and analysis.

EXPERIMENTAL SECTION

Instrument. The instrumental system consisted of a fs-LA system (J100 Applied Spectra, Inc., Fremont, CA) coupled to quadrupole-based ICP–MS (VG PQ3, VG Elemental). The laser (Amplitude Systems, model S-Pulse) is a ytterbium diode pump technology with a fundamental wavelength at 1030 nm and frequency tripled to obtain the 343 nm wavelength. Experimental conditions for the laser and ICP–MS are listed in Table 1. LA was performed in a helium atmosphere, adding

Table 1. Experimental Conditions

ICP–MS VG PQ3	
ICP Ion Source and Ion Transmission	
forward power (W)	1400
plasma Ar gas flow rate (L min ⁻¹)	14.00
auxiliary Ar gas flow rate (L min ⁻¹)	0.80
make-up Ar gas flow rate (L min ⁻¹)	0.90
extraction lens (V)	-309
collector (V)	-0.7
L1 (V)	-00
L2 (V)	-3.2
L3 (V)	-5.7
L4 (V)	-160.9
Data Acquisition	
measured isotope	²⁷ Al, ²⁹ Si, ⁵¹ V, and ⁶⁰ Ni
LA system J100 Applied Spectra	
wavelength (nm)	343
pulse energy (μJ)	120
fluence (J cm ⁻²)	5
spot size (μm)	30
repetition rate (Hz)	100
scan speed (μm s ⁻¹)	0.05–0.5
carrier He gas flow rate (L min ⁻¹)	0.90

argon after the sample chamber as a makeup gas. The J-100 ablation system is equipped with an ablation chamber that could accommodate samples up to 100 mm in diameter with flexibility in volume and wash-out time.

Reagents and Samples. Ni and V standards were prepared by diluting a 300 mg g⁻¹ standard reference material of wear metals in lubricating oil [National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) 1085b] in chloroform. The samples were Venezuelan crude oils having different V and Ni concentrations or [V/Ni] ratios. Table 2 list properties and characteristics of the crude oil samples. The SARA composition was obtained by

Table 2. Properties and Characteristics of Crude Oil Samples

crude oil samples	API (deg) ^a	saturates (% w/w) ^a	aromatics (% w/w) ^a	resins (% w/w) ^a	asphaltenes (% w/w) ^a	Ni (mg kg ⁻¹) ^b	V (mg kg ⁻¹) ^b	V/Ni
Hamaca	9	19	25	43	13	423	1934	4.572
Carabobo	8	19	28	42	11	442	2057	4.654
Boscan	10	12	36	38	14	406	4958	12.21
Monagas	24	52	26	16	6	253	1124	4.44
DM8	26.8	59	20	13	6	261	3698	14.02
DM63	15.8	43	34	19	3	247	3712	15.02
DM115	15.8	40	23	17	17	360	5297	14.71

^aFrom refs 6, 17, and 33. ^bDetermined using the microwave digestion method with ICP–OES. *n* = 3. RSD = 4%.

precipitating the asphaltenes with *n*-heptane.³ The maltenes (resins, aromatics, and saturates) were analyzed by thin-layer chromatography with flame ionization detector (TLC–FID) using an Iatroscan MK5 instrument (Iatron Laboratories, Inc., Tokyo, Japan).^{25–28} Approximately 25 mg of crude oil and 2 mg of their respective precipitated and purified asphaltenes were diluted in 1 mL of 1:1 toluene/chloroform mix for TLC analysis. Silica gel 60F₂₅₄ on Al foil, with a layer thickness of 200 μm and a particle size of 17 μm, 20 × 20 cm plates from Merk (Darmstadt, Germany) was used for TLC. American Chemical Society (ACS)-reagent-grade toluene, chloroform, *n*-heptane, and isopropanol were purchased from Sigma-Aldrich (Steinheim, Germany). Ni and V in the asphaltene fraction were measured by a validated microwave digestion method and ICP–OES to compare the TLC results.¹⁷

Analytical TLC Separation. The silica Al foils were divided into strips (25 × 50 mm). Aliquots of the sample, oil SRM 1085b, Venezuelan crude oils, and their respective asphaltenes, were deposited on the TLC strips at about 7 mm above the bottom using a microdispenser (Drummond Scientific) and dried before separation in the development chamber.

RESULTS AND DISCUSSION

Conditions for TLC Samples. Thin-layer chromatographic conditions for fast separation of the aromatic and saturate

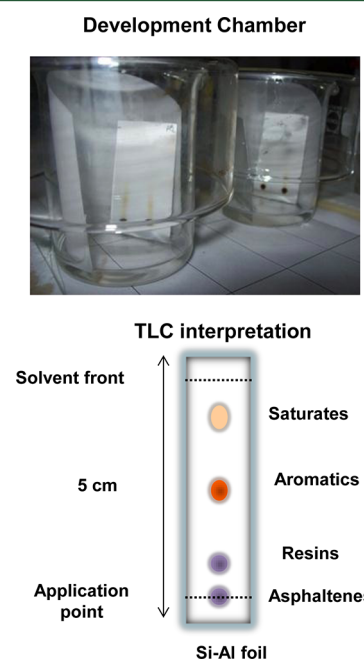


Figure 1. TLC methodology: the development chamber and schematic of the TLC elution process.

fractions from the asphaltenes and resins were optimized following similar conditions of an established method with

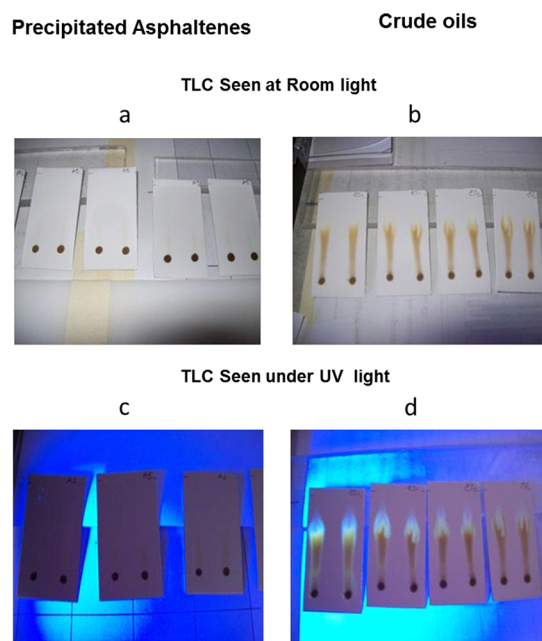


Figure 2. Example of TLC elution: (a) asphaltenes, (b) crude oils, (c) asphaltenes under UV light, and (d) crude oils under UV light.

TLC–FID.^{25–28} It was found that 2 μL of the crude oil sample dissolved in toluene/chloroform deposited on the TLC plate provided excellent separation. Figure 1 shows the development chamber and schematic of the TLC separation. Each silica Al plate with the sample was placed in the development chamber to elute in 95:5 *n*-heptane/isopropyl alcohol for separation of saturate, aromatic, and resin fractions. This solvent combination provides similar results to a dichloromethane/methyl alcohol mix commonly used to separate polar and nonpolar fractions of crude oil, with the benefit that no halogen solvent was used.^{25,26} Asphaltene was not mobile in this mixture of solvents and, therefore, remained at the application point. TLC plates were removed from the development chamber when the solvent front moved about 39 mm. The plates were left to air-dry and placed on a metal support. The total separation process time was approximately 4 min. Panels a and b of Figure 2 show the resulting TLC plates with crude oils and precipitated and purified asphaltenes.³ A low sample aliquot was used to minimize lateral

diffusion of the fractions, which is an important parameter in a TLC process. The TLC separation of crude oil produced a thin line, leaving a small asphaltene spot at the bottom of the plate (less than 3 mm² diameter) that concentrated the metals. As seen in the TLC plates, asphaltene did not move from the application point. Four TLC replicates were prepared for all samples. Observation of the crude oil samples under ultraviolet (UV) light clearly shows the separation of the four fractions (asphaltenes, resins, saturates, and aromatic compounds) (panel d of Figure 2). Observation of the TLC plates with the asphaltenes under the UV light does not show the presence of the other fractions; they were efficiently removed by the precipitation and purification processes.

LA–ICP–MS Conditions for TLC Samples. Optimization of the fs-LA sampling process involved establishing conditions for fast removal of the silica layer containing the asphaltenes, without ablating the substrate (Al foil). Laser energy, repetition rate, spot size, and raster speed were adjusted to ablate an amount of sample that did not deposit inside the chamber or produce residue on the ICP sampling cones. The conditions for TLC ablation sampling were laser energy of 100 μJ , repetition rate of 100 Hz, and 30 μm spot size. Figure 3 shows ²⁹Si and ²⁷Al average signal intensities, as function of the raster rate from 0.05 to 0.50 mm/s. ²⁷Al was highest at 0.05 mm/s (slowest raster rate tested). At this slow raster rate, the Al foil was ablated because of the high number of laser pulses overlapping (approximately 60 pulses per location). In contrast, silicon signal intensity was highest between 0.3 and 0.4 mm/s when approximately 10 pulses overlapped. Therefore, 0.3 mm/s was selected as the raster rate for these studies.

A raster pattern that includes parallel lines covering an area of about 3 mm² was used for the analysis. Figure 4 shows the ablation sampling pattern on the TLC plate over the asphaltene zone. An area of 2.7 mm was analyzed using 10–15 parallel lines. The image shows the good spatial resolution achieved using a small laser-beam spot size (30 μm), without any damage to the Al foil. No accumulation of carbon was found inside the ablation cell, on the ICP torch, or on the interface cones. These advantages are attributed to the use of fs-LA sampling, which produces a small amount of mass per laser pulse, negligible thermal heating in the TLC plate, small particles, and less particle agglomeration compared to nanosecond laser ablation.^{29–32}

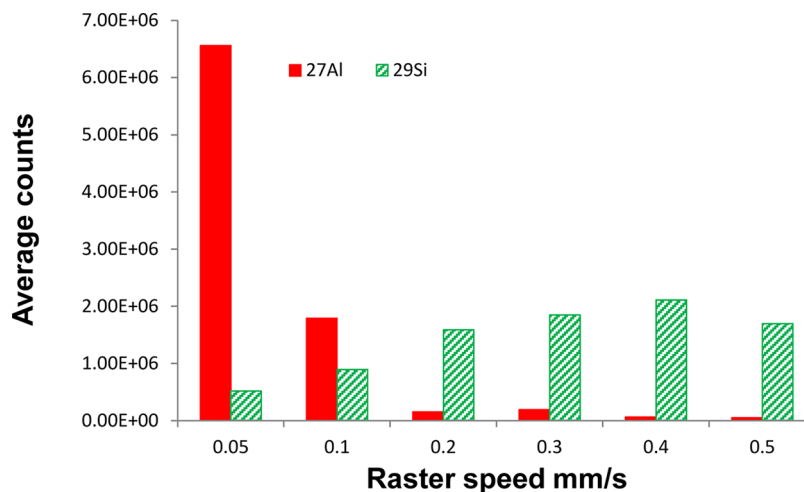


Figure 3. Si and Al average signal intensity as a function of the laser-beam raster speed.

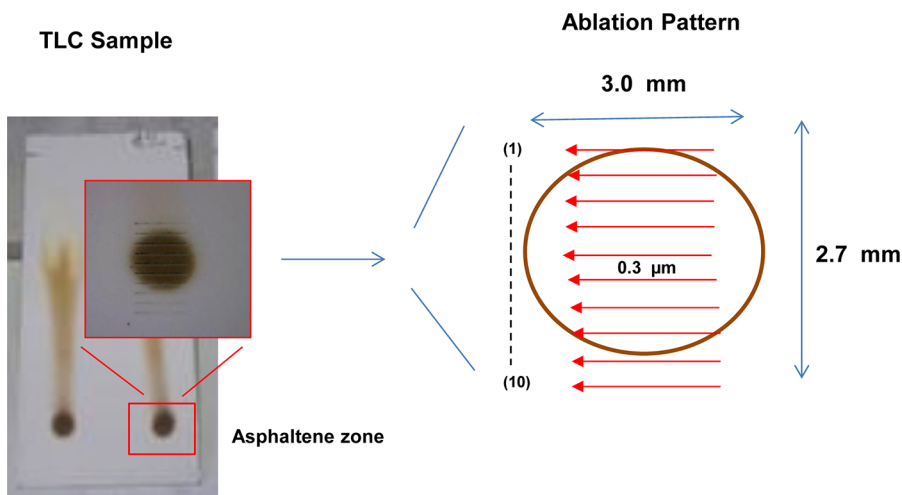


Figure 4. Sampling pattern on the TLC plate over the asphaltene region.

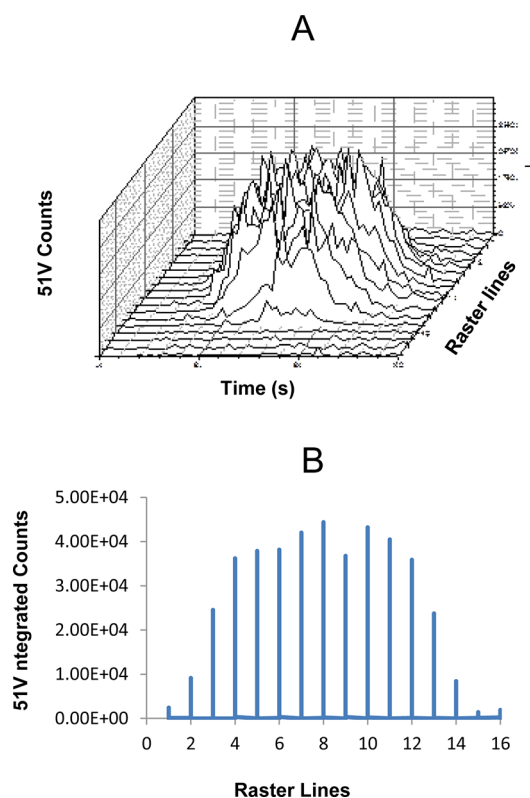


Figure 5. ICP-MS results from the raster line ablation pattern obtained from the TLC of Hamaca crude oil: (A) raw vanadium signal and (B) integrated vanadium signal.

Table 3. Precision for the Proportionality of Vanadium/Nickel Using TLC-fs-LA-ICP-MS

crude oil sample	[V/V + Ni]	precision (RSD %)
Hamaca	0.849	0.5
DM8	0.916	0.5
Boscan	0.931	0.4
Carabobo	0.861	0.3
Monagas	0.814	0.4
DM63	0.910	0.4
DM115	0.934	0.4

Table 4. Proportionality of V/Ni in the Asphaltene Fraction Obtained with TLC-fs-LA-ICP-MS and the Traditional Separation Method Using *n*-Heptane

crude oil sample	[V/V + Ni] asphaltene	[V/V + Ni] TLC crude oil	bias (%) ^a
DM8	0.906 ± 0.005	0.916 ± 0.004	1.1 (<i>t</i> = 0.329)
Boscan	0.933 ± 0.004	0.931 ± 0.003	-1.3 (<i>t</i> = 0.074)
Carabobo	0.865 ± 0.004	0.861 ± 0.003	-0.4 (<i>t</i> = 0.149)
Monagas	0.801 ± 0.002	0.799 ± 0.003	-0.2 (<i>t</i> = 0.074)

^a*t*_{critical}(α , 0.05; $\gamma_1 + \gamma_2$, 6) = 2.450.

Table 5. Proportionality of V/Ni Measured in the Asphaltene Fraction Using TLC-fs-LA-ICP-MS and a Reference Wet Digestion Method

crude oil sample	[V/V + Ni] reference ^a	[V/V + Ni] TLC crude oil	bias (%) ^b
DM8	0.934	0.916 ± 0.004	1.9
Boscan	0.924	0.931 ± 0.003	0.8
Carabobo	0.823	0.861 ± 0.003	4.6
Monagas	0.816	0.799 ± 0.003	2.1
Hamaca	0.820	0.849 ± 0.004	3.5
DM115	0.936	0.934 ± 0.004	0.2

^aReference values were obtained from Table 2. ^b*t*-paired test = 0.647. *t*_{critical}(α , 0.05; 5) = 2.57.

Data in Figure 5 show the V ICP-MS data from the TLC plate containing “Hamaca” crude oil. This heavy crude oil was selected as a reference because its V and Ni concentrations are well-known and frequently used as a reference in our laboratory.¹⁷ The raster line pattern provides a profile distribution of V in the asphaltene spot (A) (same behavior was observed for ⁶⁰Ni). The signal intensity from each raster line was integrated and used to calculate the V and Ni ratio (B). A blank TLC plate was sampled and analyzed to check for Ni and V background; none was found.

Proportionality of Vanadium/Nickel in Crude Oils. The proportionality of V/Ni is usually expressed as a decimal fraction of the concentrations, and it is defined as the quotient of vanadium divided by the sum of Ni plus V [V/V + Ni]. This expression is referred to as the V-Ni fraction and has been found to be more useful for geochemist compared to the V/Ni ratio^{4,5}

The proportionality of vanadium/nickel reported in this work was obtained by normalizing the integrated intensities by a

calculated factor that uses the ratio of sensitivity of $^{51}\text{V}/^{58}\text{Ni}$ (eq 1)

$$F = \frac{S_V}{S_{\text{Ni}}} = \frac{I_V[\text{Ni}]}{I_{\text{Ni}}[\text{V}]} + e \quad (1)$$

$$\begin{aligned} \frac{[\text{V}]}{[\text{V}] + [\text{Ni}]} &= \frac{I_V/S_V}{(I_V/S_V) + (I_{\text{Ni}}/S_{\text{Ni}})} + e \\ &= \frac{I_V/S_{\text{Ni}}F}{(I_V/S_{\text{Ni}}F) + (I_{\text{Ni}}/S_{\text{Ni}})} + e = \frac{I_V/F}{(I_V/F) + I_{\text{Ni}}} + e \end{aligned} \quad (2)$$

where I is the intensity of the element, S is the sensibility of the element, $[\]$ is the concentration of the element, and e is the error. The experimental factor F can be obtained if V and Ni concentrations are measured using a certified standard and applied to all of the samples using eq 2.

The standards used for the determination of the F factor were prepared by diluting different concentrations of NIST oil (1085b), Hamaca crude oil, and its precipitated asphaltene. From these standards, the following sensitivity factors were obtained: 1.62 ± 0.05 , 1.01 ± 0.05 , and 1.02 ± 0.05 , respectively. There is a significant difference in the sensitivity factor obtained from the NIST oil standard versus those obtained from the crude oil and the purified asphaltene standards; the sensitivity factor calculated from the NIST oil cannot be used to obtain the proportionality of V/Ni in the crude oil or the precipitated asphaltenes. However, the F factor obtained from the precipitated asphaltene can be used to analyze the asphaltene fraction directly from the crude oil sample. The calculated factor is close to unity using the Hamaca crude oil, and their previously precipitated asphaltene indicates that the proportionality can be easily obtained using the integrated signal ratio of $^{51}\text{V}/^{58}\text{Ni}$ using eq 2.

Table 3 presents the V/Ni proportionality in the asphaltene fraction for several crude oil samples using this TLC–fs-LA–ICP–MS method. Four replicates of each sample were analyzed. Excellent precision, expressed as the relative standard deviation (RSD), below 1%, was obtained for the ratios.

The proportionality of V/Ni was measured from two types of samples: (a) asphaltene fraction after TLC separation from the crude oils and (b) precipitated asphaltene (using the separation method with *n*-heptane) deposited on the TLC plate (Table 4). A statistical t test does not show any significant differences between the two average measurements. In general, changes around ~ 0.2 indicate significant differences in the crude oil.^{4,5} These data demonstrate that it is not necessary to separate the asphaltene fraction from the crude oil by conventional methods to obtain $[\text{V}/\text{V} + \text{Ni}]$. Table 5 compares the results using a validated microwave digestion method of the precipitated asphaltenes to those results obtained from the TLC–fs-LA–ICP–MS method developed in this study. There is no significant statistical difference when the t -paired test was applied with reference values. This approach demonstrates that the TLC method can be used for the fast determination of V/V + Ni with similar accuracy to that provided by the traditional digestion method.

CONCLUSION

The method employing TLC with fs-LA–ICP–MS for the rapid determination of V/Ni proportionality in the asphaltene fraction of the crude oil was successfully demonstrated in this work. This ratio was measured with good precision and without the

traditional time-consuming separation method required for asphaltenes. The use of a femtosecond laser allows for precise control of the ablation sampling conditions. The TLC method is fast and easy to implement and provides similar results to conventional wet method digestion procedures, with the additional advantage of being a low waste method because only 2 μL of the sample was necessary.

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Notes

The authors declare no competing financial interest.

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