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Determination of Ni and V in Crude Oil Samples Encapsulated in Zr Xerogels by Laser-Induced Breakdown Spectroscopy

Mauro Martínez,[†] Ryszard Lobinski,[‡] Brice Bouyssiere,[‡] Vincent Piscitelli,[†] José Chirinos,[†] and Manuel Caetano*,[†]

[†]Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Post Office Box 47102, Caracas 1041a, Venezuela

[‡]Hélioparc, Laboratoire de Chimie Analytique Bio-inorganique et Environnement (LCABIE), UMR 5254, Centre National de la Recherche Scientifique (CNRS)−Université de Pau et des Pays de l'Adour (UPPA), 2 Avenue du Président Pierre Angot, 64053 Pau, France

ABSTRACT: Encapsulation of samples in Zr xerogels has been implemented for the elemental analysis of crude oils using laser-induced breakdown spectroscopy. Pellets produced from xerogels proved to be durable and homogeneous, and they allow for ablation of the samples without splatters. Ni and V present in Venezuelan crude oil were used as probe elements, and Yttrium was used as an internal standard to take into account the fluctuations in the amount of ablated material. All of the calibration curves obtained were described by high correlation coefficients, $r^2 > 0.990$. Detection limits of 7 and 4 $\mu g\ g^{-1}$ for V and Ni were estimated, respectively. V/(V + Ni) quotients showed high values of >0.8. The accuracy of the method was assessed by analyzing standard reference materials (SRM 1084a and 1085b). The measured values of V and Ni in the SRM agreed well with the certified values at the 95% confidence level.

■ INTRODUCTION

Quantitative determination of trace metal concentrations in crude oil has become a critical concern for the petroleum industry.[1] The main reasons are their importance in the geochemical characterization of their source and origin[2,3] and the implementation of remedial, corrective, and preventive programs, for oil production and refining. Ni and V are present in crude oils at concentrations of mg kg^{-1}, generally as mixed-ligand tetradantate, humate complex, and tetrapyrrole metallo-organic complex species.[4] Origin, migration, environment of deposition, and biological, physical, and chemical alterations of kerogen into petroleum could change the absolute concentrations of these two metals; however, once the metallo-organic complexes of V and Ni are established, their high stability assures that their proportionality to one another remains unchanged.[5] It is precisely due to these facts that the V/Ni fraction can be used to infer geochemical information, for example, crude oil origin as well as crude oil source rock correlations.[3,5]

Numerous methods have been developed for trace metal characterization of crude oils and their derivatives;[6−11] however, dispersive X-ray fluorescence spectrometry and inductively coupled plasma optical emission spectrometry (ICP−OES) and mass spectrometry (ICP−MS) techniques are the most commonly used and have the ability to monitor multiple elements simultaneously with high sensitivity and low detection limits. Alternatively, laser-induced breakdown spectroscopy (LIBS) has lately become into a very promising technique that provides full spectral analysis of the laser plasma without the need for a mass spectrometer.[12−14] LIBS is able to provide *in situ*, to any type of sample, elemental and isotopic analyses at high spatial resolution (<5 μm) with minimal sample preparation.

Although laser-induced plasma can be directly obtained on any sample in any location, the splashing, the absence of the appropriate standard, and the choice of a suitable calibration technique may hamper the quantitative analysis. Pretreatment methods for petroleum samples to be analyzed by laser ablation−ICP or LIBS have received considerable attention during recent years. These methods include use of compacted powders,[15] nebulizer-generated dried aerosols combined with the addition of a standard method,[16] petroleum−cellulose mixtures,[17] silica gel plates,[18,19] and ablation cell modifications.[20]

We previously[8] reported a successful method to capture crude oil samples in Zr xerogel matrices for elemental analysis using laser ablation−double focusing sector field inductively coupled plasma−mass spectrometry. This alternative sample pretreatment permits the manufacture of pellets that have shown outstanding durability and homogeneity. Xerogel matrices can also be spiked with solutions of inorganic salts to prepare suitable standards to elaborate calibration curves. The technique is environmentally friendly, with minimum hazardous waste generation, and the samples can be easily preserved. Glassy and ceramic materials can be obtained from the liquid precursors at temperatures much lower than that required for melting techniques.[21,22]

The central purpose of this work was to demonstrate the suitability of the methodology for the determination of Ni and V in crude oil encapsulated in Zr xerogel (COXg) using a simple LIBS experimental configuration. It was optimized that the xerogel drying process and some analytical figures of merits were obtained to assess the analytical performance. The results

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were compared to those obtained with similar sample pretreatments.

■ EXPERIMENTAL SECTION

Instrument. Figure 1 presents a schematic of the experimental layout, and Table 1 shows the experimental conditions. A Q-switched Nd:YAG laser (Surelite II, Continuum) operating a 1064 nm was used as the laser source to generate the plasma. The laser beam was directed to the measurement region using dichroic mirrors and focused using a lens of focal length 50 mm at normal incidence to the sample surface. The sample was placed in a sample holder mounted over a motorized *x*−*y*−*z* precision translation system (elevation stage, PI Micos ES-100, and *xy* linear translation stages, PI Micos LS-65). The LIBS analysis was performed in air at atmospheric pressure, and the light from the resulting plasma plume was collected axially by the same lens used to focus the laser beam and a second lens used to focus the emitted light onto an optical fiber with a 50 μm core. The fiber-optic cable transmitted the light to a high band-pass echelle spectrometer (Andor Mechelle 5000), providing simultaneous recording of a wide wavelength range (200−975 nm) in one acquisition, with spectral resolution $(\lambda/\Delta\lambda)^{-1}$ [corresponding to 3 pixels full width at half maximum (fwhm)] up to 6000. The spectrometer was equipped with a gated, intensified charged coupled device (ICCD) camera (Andor DH734-18F-03), with 1024 × 102 active pixels, 13 × 13 μm effective CCD pixel size, and intensifier diameter of 18 mm. An additional video camera, which views the plasma reflected from a flipper beam splitter placed between the focusing lenses, facilitates bringing the sample into focus. Sampling on xerogel pellets was performed by raster ablation mode by moving the target horizontally, so that each ablation pulse was made on a clean surface. The spectra were processed with the program AndorSolis 4.6.5.0. Figure 2 represents typical average spectra of a crude oil sample pellet in the range of 250−600 nm. Emission lines of the elements were identified using the National Institute of Standards and Technology (NIST) atomic spectral database.

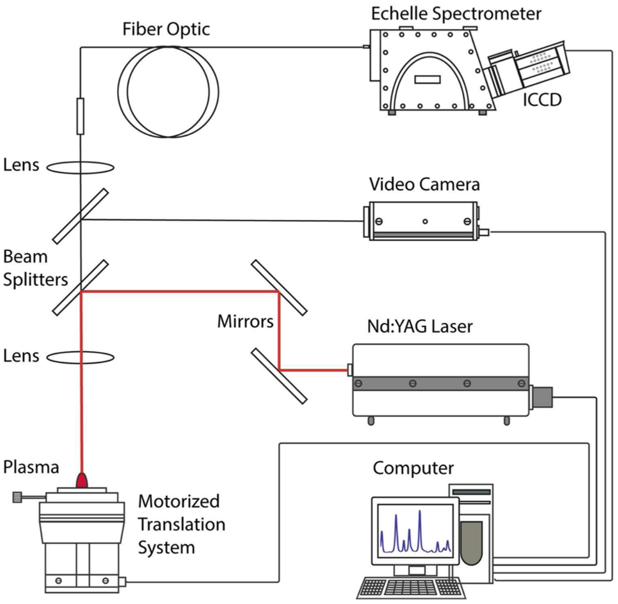

Figure 1. Schematic of the experimental setup for LIBS of pressed xerogel pellets.

Table 1. Experimental Conditions

laser Surelite II	
wavelength (nm)	1064
pulse width (ns)	6
pulse energy (mJ)	75
fluence (J m^{-2})	60
repetition rate (Hz)	10
scan speed (mm s^{-1})	0.6
averaged laser pulses (ICCD integration)	20
Andor Mechelle spectrometer	
gate width (μs)	2.7
gate delay (μs)	0.4
gain	240

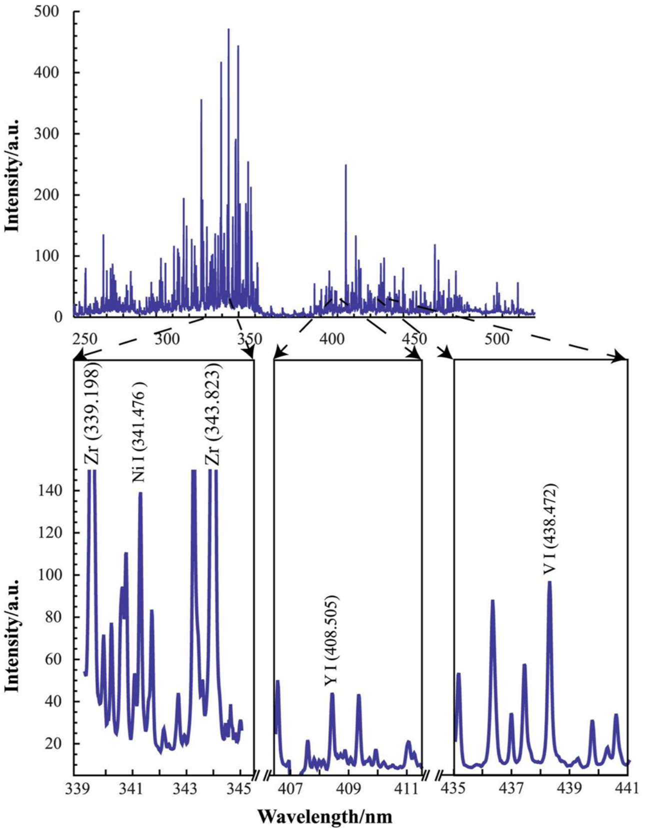

Figure 2. Typical average spectra of a crude oil sample pellet in the range of 250−600 nm.

Reagents and Samples. Xerogel solutions were prepared from zirconium *n*-propoxide (TPOZ) (70% in 1-propanol, Aldrich), trace-metal-grade methanol (Anachemia), anhydrous ethanol, high-purity concentrated nitric acid (Anachemia), and Tergitol solution (70% nonylphenol ethoxylate in H_2O, Aldrich). V, Ni, and Y solutions were prepared from 1000 mg mL^{-1} standard stock solutions (spectrometric grade, SCP Science). Chemical and physical properties of Venezuelan crude oils used are summarized in Table 2. Certified reference materials (SRM) 1084a and 1084b (metals in oil) from NIST were used for validation purposes.

Procedures. *Xerogel Preparation.* The procedure followed was a modification of that used in ref 8. Approximately 0.5000 g of crude oil was suspended in a minimum quantity of dichloromethane and added to 1.8 mL of TPOZ. The mixture was ultrasonic-assisted stirred and added dropwise to a solution formed by 6 mL of methanol, 50 μL of concentrated HNO_3, 20 μL of 2% from Tergitol solution, and 250 μL of a 1000 μg mL^{-1} Y standard solution. A total of 100% of the crude oil becomes trapped inside Zr xerogels. Dilution factors were calculated for each sample (~2.5) and were taken into account in the calculations of the trapped crude oil final concentrations.

Ni and V standards were prepared in capped vials (20 mL, Sarstedt), adding 6 mL of methanol, 50 μL of concentrated HNO_3, 20 μL of Tergitol solution (2%), 250 μL of a 1000 μg mL^{-1} Y standard

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Table 2. Physical and Chemical Properties of the Crude Oil Samples Used in This Work

crude oil sample	API gravity (deg)	resin (wt %)	asphaltene (wt %)	Ni[a] (μg g^{-1})	V[a] (μg g^{-1})
Boscan	10.4	29.4	17.2	107 ± 5	1190 ± 30
Ayacucho (formerly Hamaca)	8.3	43	13	108 ± 5	680 ± 25
Carabobo (formerly Cerro Negro)	8.5	42	13.8	102 ± 5	478 ± 20
Furrial	28.1	7.6	7	68 ± 5	295 ± 20

[a] ICP−OES after wet ashing.

solution, and appropriate quantities of V and Ni solutions to obtain concentrations from 0 μg mL^{-1} to 50 μg g^{-1}. The mixture was ultrasonic-assisted stirred, and gelation was achieved adding dropwise 1.8 mL of TPOZ. Pellets were manufactured following exactly the procedure described in ref 8.

Optimization of the Pellet Preparation. The removal of the remaining liquid (solvent) phase is a critical step in xerogel preparation as a result of the fact that application of the inappropriate drying process may yield no homogeneous product. In our previous work, the xerogels were oven-dried at 100 °C during 8 h, and this was the most time-consuming step. For this reason, different alternatives were studied to reduce the time of the drying process. A one-way analysis of variance design was implemented with the following treatment alternatives: (1) drying the xerogels in an oven at 80 °C overnight (14 h) (standard procedure), (2) evaporation using a rotary evaporator, and (3) vacuum filtration followed by drying in an oven at 160 °C for 2 h. COXg samples (Carabobo) were prepared, using each of the three drying methodologies. Three pellets were made from each COXg sample, for a total of 9 pellets.

Once the appropriate drying process was selected, the repeatability of the pellet preparation process was investigated using another one-way analysis of variance as follows: Three pellets were prepared from the Carabobo crude oil sample. Emission intensities of each pellet were acquired at three randomly selected locations.

Calibration Curves and Analytical Performance. One of the problems commonly related to LIBS analysis is the lack of reproducibility of the emission intensity.[12,23−26] This can be mainly associated with the nature of the laser-induced plasma process, along with shot-to-shot energy variation. Generally, these problems can be addressed using an internal standard and constructing analytical curves from an analyte/internal standard intensity ratio instead of absolute peak heights. Carbon, the major component in the crude oil, was not considered as the internal standard because the possibility of crude oil pyrolysis caused by the laser ablation, giving rise to carbon-based gaseous compounds.[27] In this work, Y was used as an internal standard because this element is not present in the crude oil, can be easily and controllably incorporated into the oil phase, and helps to normalize both the signal fluctuations as a result of the heterogeneity of the pellet and the changes in the emission as a result of laser fluctuations. Zr, a major element in the xerogel matrix, may be another alternative to compensate for the changes in the signal produced by the laser fluctuations but was not consider in this work.

Wavelengths, 341.476 nm (Ni$^{\text{I}}$), 438.472 nm (V$^{\text{I}}$), and 408.505 nm (Y$^{\text{I}}$) were selected as working lines, after providing intense signals and being resolved from other emission lines, meeting the criteria of good sensitivity and linearity, and do not suffering spectral interferences.

The analytical performance of the methodology was evaluated using typical figures of merit: detection limit, short-term precision, long-term stability, and accuracy. Limit of detection (LOD) was determined using the International Union of Pure and Applied Chemistry (IUPAC) definition, as the lowest concentration of analyte that can be detected with reasonable certainty. The criterion for a reasonable certainty used was 3 times the standard deviation of the background signal. Short-term precision was defined as the relative standard deviation (RSD) from 10 replicate measurements. The long-term stability of the COXg was verified by determining Ni and V concentrations in a pellet made from a sample (Ayacucho) prepared at the start of the study, stored at room temperature until measures were taken again 9 months later. The accuracy of the method was validated by determination of V and Ni concentrations in the standard reference materials 1084a and 1084b. Finally, the results of Ni and V were obtained for some Venezuelan crude oils, and the results were compared to previously reported data (see Table 2).

■ RESULTS AND DISCUSSION

Optimization of the Pellet Preparation. Table 3 shows the results of the one-way analysis of variance used to test the drying processes. The p value is 0.012, demonstrating that a real difference exists between the treatment means. Bonferroni and Tukey's tests revealed[28] that the signal from the standard procedure and rotaevaporator were significantly lower than the treatment that considers the solvent removal by filtration. It seems that the former procedure avoids crude oil losses during the drying process. For this reason, this procedure was chosen on further experiments.

Table 3. Analysis of Variance Table for Three Different Xerogel Drying Procedures[a]

	treatments		
	1[b]	2[c]	3[d]
treatment average	18811.6	17765.7	22717.7
grand average	19765.0		
sum of squares	5.83×10^7	3.83×10^7	1.09×10^8
variance	8.33×10^6	5.48×10^6	1.56×10^7
source of variation	sum of squares	degrees of freedom	mean square
between treatments	1.09×10^8	2	5.45×10^7
within treatments	2.06×10^8	21	9.80×10^6
F ratio	5.56		

[a] $p = 0.012$. [b] (1) Drying xerogels overnight in an oven at 80 °C. [c] (2) Evaporation using a rotary evaporator. [d] (3) Filtering followed by drying for 2 h in an oven at 160 °C.

Table 4 shows the results of the experimental design implemented to test the reproducibility of the xerogel pellet preparation. The resulting p value was 0.12 and revealed that there were no statistically significant differences among the treatment (pellets) means; this is, the preparation process can be considered highly reproducible.

Table 4. Analysis of Variance Table of the Xerogel Pellet Preparation Process[a]

	treatment		
	pellet 1	pellet 2	pellet 3
treatment average	25429	18223	22146
grand average	21932.6		
sum of squares	8.16×10^6	2.67×10^7	4.05×10^7
variance	4.06×10^6	1.33×10^7	2.03×10^7
source of variation	sum of squares	degrees of freedom	mean square
between treatments	7.81×10^7	2	3.90×10^7
within treatments	7.54×10^7	6	1.26×10^7
F ratio			3.11

[a] $p = 0.12$.

Calibration Curves and Analytical Performance. Figure 3 presents the calibration curves and their respective residual plots for Ni^I (341.476 nm) and V^I (438.472 nm) spectral lines normalized with Y^I (408.505 nm). Linear models were fitted by a computer program written in the Mathematica language (continuous line). The residuals plots do not reveal any systematic tendency in relation to the estimated values $\hat{y}$. Ni and V calibration plots display high linearity over the whole concentration range, having r^2 over 0.9900.

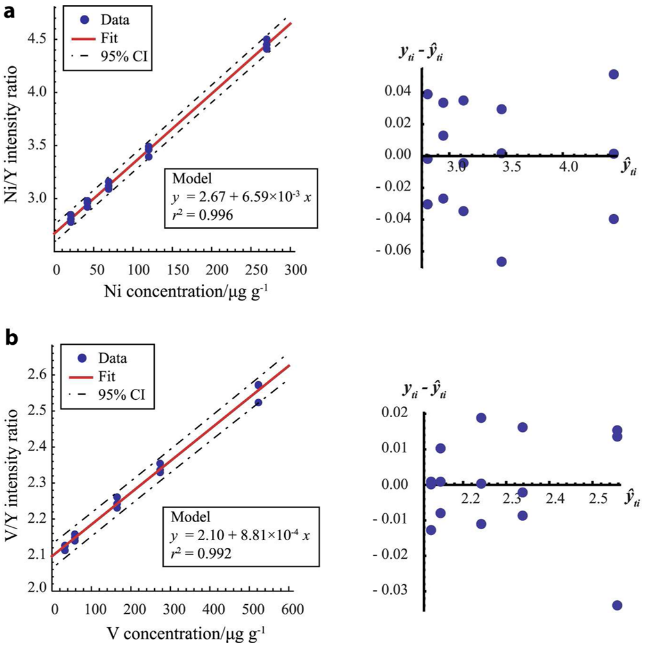

Figure 3. (a) Ni/Y and (b) V/Y LIBS intensity ratios for crude oil xerogels. A linear model was fitted to the data (solid curve), and a 95% confidence two-sided band for it is displayed (dashed lines) along with its respective residual plots.

Table 5 presents LODs and short-term precision obtained for each element, together with those obtained by other authors in the analysis of crude oil residues[15] and a similar matrix, such as asphaltene fractions, using direct ablation and LIBS.[29] Detection limits for V showed no significant differences when compared to that reported by other authors using direct ablation in fractions of asphaltenes.[29] In contrast, the LOD of Ni was significantly better than that exhibited by direct ablation, in both asphaltene fraction and crude oil residues.[15,29]

Table 5. Analytical Figures of Merit Obtained with the Xerogel LIBS Method

	this work		reference[a]		reference[b]	
element	LOD (μg g^{-1})	RSD (%)	LOD (μg g^{-1})	RSD (%)	LOD (μg g^{-1})	RSD (%)
V	7	4.1			8	3.4
Ni	4	4.3	11		10	3.4

[a]Determined in pressed pellets of the crude oil residue using LIBS.[15]
[b]Determined in pressed pellets of the asphaltene fraction using LIBS.[29]

Accuracy and Long-Term Stability of the Method. The accuracy of the method was validated by determination of V and Ni concentrations in the standard reference materials 1084a and 1084b. The results are shown in Table 6, the t test, t(95), reveals a non-significant difference between the analytical values determined by this method and the certified values, for both Ni and V.

The long-term stability values were analyzed in Table 7. Differences in Ni and V concentrations obtained in the pellets 9 months later were not statistically significant (using a two-tailed t test with an α level of 0.05), indicating a good long-term stability under ambient storage conditions.

Table 7. Long-Term Stability (9 Month Interval) of Ni and V Determination Using the Xerogel Method with Ayacucho Crude Oil Samples

	time		
	0 month	9 month	δ[a]
Ni (μg/g)	109 ± 9	114 ± 8	−5 (t = 0.72)
V (μg/g)	550 ± 49	580 ± 41	−30 (t = 0.81)

[a]t critical (α, 0.05; $\Upsilon1 + \Upsilon2$,4) = 2.776.

Crude Oil Analysis. Table 8 shows Ni and V concentrations determined in the crude oil samples. All samples were analyzed in triplicate. The absolute concentrations of vanadium and nickel are in the range of expected values (reported in Table 2). The V–Ni fraction, expressed as the quotient (V/V + Ni), shows high fraction values (>0.8) for all of the crude oil samples, indicating anoxic depositional conditions for their source rock.

Table 8. Results for Ni and V Determined in Crude Oil Samples by the Xerogel LIBS Method

crude oil	vanadium (μg g^{-1})	nickel (μg g^{-1})	V/(V + Ni) ratio
Boscan	1321 ± 110	105 ± 9	0.926 ± 0.007
Ayacucho	550 ± 49	109 ± 9	0.835 ± 0.008
Carabobo	463 ± 41	97 ± 9	0.827 ± 0.009
Furrial	251 ± 23	58 ± 5	0.812 ± 0.010

■ CONCLUSION

In summary, a methodology for the quantitative analysis of metals in crude oil encapsulated in a Zr xerogel by the LIBS technique was successfully implemented. This study clearly demonstrates that the preparation process of the xerogel pellets is reproducible and the filtration of the excess of the solvent before drying significantly reduced the time required for xerogel synthesis. Analytical curves made using Ni- and V-doped xerogels and Y as the internal standard have been shown as an excellent alternative to address the lack of matrix-matched

Table 6. Results for Ni and V in SRM 1084a and 1084b by the Xerogel LIBS Method

	nickel (μg g^{-1})			vanadium (μg g^{-1})		
SRM	this work	certified value	δ	this work	certified value	δ
1084a	101.7 ± 9.3	99.7 ± 9.4	0.2 (t = 0.29))	95.2 ± 8.7	95.9 ± 1.6	−0.7 (t = 0.14)
1084b	300.7 ± 27.6	295.9 ± 7.4	4.8 (t = 0.29)	300.1 ± 25.1	297.8 ± 4.6	2.3 (t = 0.16)

standards available. The analytical figures of merit achieved are similar or even better than LIBS studies with similar substrates. The good accuracy, estimated by comparison to standard reference materials, can be attributed to the homogeneous presence of the internal standard in the pellets, yielding better compensation for signal fluctuations as a result of variations in the amount of ablated material. COXg also exhibited good long-term stability. LIBS can provide high-quality data that can be used for comparative purposes and suitable LODs for some elements of interest.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: +58-212-6051216. Fax: +58-212-6934977. E-mail: manuel.caetano@ucv.ve.

Notes

The authors declare no competing financial interest.

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