



# Multivariate optimization of a procedure employing microwave-assisted digestion for the determination of nickel and vanadium in crude oil by ICP OES



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## ABSTRACT

This work presents the optimization of a sample preparation procedure using microwave-assisted digestion for the determination of nickel and vanadium in crude oil employing inductively coupled plasma optical emission spectrometry (ICP OES). The optimization step was performed utilizing a two-level full factorial design involving the following factors: concentrated nitric acid and hydrogen peroxide volumes, and microwave-assisted digestion temperature. Nickel and vanadium concentrations were used as responses. Additionally, a multiple response based on the normalization of the concentrations by the highest values was built to establish a compromise condition between the two analytes. A Doehlert matrix optimized the instrumental conditions of the ICP OES spectrometer. In this design, the plasma robustness was used as chemometric response. The experiments were performed using a digested oil sample solution doped with magnesium(II) ions, as well as a standard magnesium solution. The optimized method allows for the determination of nickel and vanadium with quantification limits of 0.79 and 0.20  $\mu\text{g g}^{-1}$ , respectively, for a digested sample mass of 0.1 g. The precision (expressed as relative standard deviations) was determined using five replicates of two oil samples and the results obtained were 1.63% and 3.67% for nickel and 0.42% and 4.64% for vanadium. Bismuth and yttrium were also tested as internal standards, and the results demonstrate that yttrium allows for a better precision for the method. The accuracy was confirmed by the analysis of the certified reference material trace element in fuel oil (CRM NIST 1634c). The proposed method was applied for the determination of nickel and vanadium in five crude oil samples from Brazilian Basins. The metal concentrations found varied from 7.30 to 33.21  $\mu\text{g g}^{-1}$  for nickel and from 0.63 to 19.42  $\mu\text{g g}^{-1}$  for vanadium.

## 1. Introduction

The determination of nickel and vanadium in crude oil has a great importance in geochemical studies because the vanadium/nickel ratio is one of the most useful parameters to determine the origin of petroleum [1,2]. This relationship tends to be constant because of structural similarities between the organometallic compounds containing these elements [3–6]. Also, vanadium and nickel are the most abundant chemical elements in these matrices [7,8]. In the oil refining industry, these metals act by modifying activities and poisoning the catalysts [6,9,10].

In recent times, several analytical strategies of sample preparation have been proposed for determining metals in petroleum and its

derivatives [11–21]. Flores et al. have proposed various sample digestion procedures employing microwave-induced combustion for the determination of metals in crude oil and its derivatives utilizing spectro-analytical techniques [13–17]. The first work was established for the determination of rare earth elements in crude oil using inductively coupled plasma mass spectrometry (ICP-MS) equipped with an ultrasonic nebulizer (USN) [13]. Subsequently, they developed a method for quantification of rare earth element in heavy crude oil by USN-ICP-MS [14]. For that, the sample digestion was performed using a microwave-assisted single reaction chamber. Additionally, this group also optimized a strategy using microwave-induced combustion for the determination of inorganic impurities in diesel oil employing ICP-MS [15]. Jenny et al. proposed a method utilizing microwave plasma

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atomic emission spectrometry for the determination of nickel, vanadium, iron, calcium, and sodium in crude oil. The sample preparation was established by the dilution of the oil in *o*-xylene [18]. Donati et al. proposed the determination of vanadium in lubricant oils using tungsten coil atomic emission spectrometry. The sample digestion was performed in an aluminum heating block with temperature and time control [19]. Gao et al. proposed a new sample preparation method utilizing a single reaction chamber microwave for determination multi-elemental in crude or fuel oils employing ICP techniques [20]. Shoty et al. determined several chemical elements in bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). High-pressure microwave digestion was employed for sample preparation [21].

Currently, most analytical methods have been optimized using multivariate techniques. Among these, the two-level full factorial is the most used one, even though it preliminarily evaluates the effects of the factors on the processes. This approach provides linear models [22–25]. Response surface methodologies (RSM) are multivariate optimization techniques, which allow for the finding of the critical conditions of the factors (maxima or minima) through the establishment of quadratic models [26]. Doehlert Matrix is one of the RSM that is often employed for optimization of analytical strategies [27,28]. This design has advantages compared to the other RSM because it allows for the obtaining of quadratic models, in which the number of levels of the factors is different, it has good efficiency, and also its matrix does not contemplate experiments with all factors in the positive or negative levels [29–31]. Ngila et al. optimized a preconcentration procedure using solid phase extraction for the determination of silver, aluminum, arsenic, and chromium in gasoline utilizing ICP OES. The optimization was performed using a two level full factorial design [32].

In this work, a sample preparation procedure utilizing microwave-assisted radiation was optimized employing a multivariate technique for the determination of nickel and vanadium in crude oil using ICP OES. Yttrium was efficient as a standard internal to correct the matrix effects during the measurements using ICPOES.

## 2. Materials and methods

### 2.1. Instrumentation

In this study, the wet digestion of the samples was performed using a laboratory microwave oven with 40 closed vessels (Mars 6, CEM, USA). This oven allows the monitoring of the temperature during the implementation of a heating program.

An inductively coupled plasma optical emission spectrometer with axial view (Agilent, model 720 series, Santa Clara, California, USA) was used for the determination of Ni and V in crude oil samples. The gas employed was argon with 99.9999% purity (White Martins, São Paulo, Brazil).

The operation conditions of the ICP OE and the emission lines for the determinations are shown in Table 1. The calibration curves were performed in presence of yttrium as internal standard to correct the matrix effects.

### 2.2. Reagents and standard solutions

The solutions for the calibration curves were prepared from 1000 mg L<sup>-1</sup> mono-element standard solutions (Specsol®, Quimlab, São Paulo, Brazil) of nickel and vanadium in 2.0 mol L<sup>-1</sup> nitric acid solution.

The digested oil samples still contain many organic compounds. Thus, bismuth and yttrium were tested as internal standards in the determination of nickel and vanadium by ICP OES.

**Table 1**

Operational parameters adopted for the determination of Ni and V ICP OES.

Instrument parameter	Operational conditions
RF applied power (kW)	1.2
Argon auxiliary flow rate (L min <sup>-1</sup> )	1.0
Argon plasma flow rate (L min <sup>-1</sup> )	12
Argon nebulizer flow rate (L min <sup>-1</sup> )	0.60
Nebulizer type	Seaspray®
Nebulization chamber	Single-pass cyclonic
Reading time (s)	20
Replicates	3
Sample uptake delay (s)	15
Stabilization time (s)	15

Wavelength Ni (231.604 nm) and V (311.837 nm); Y (371.029 nm); Bi (223.061 nm).

### 2.3. Sample preparation using microwave-assisted digestion

In the pre-digestion step, 0.10 g sample masses were weighed in polytetrafluoroethylene vessels and 3.0 mL of concentrated nitric acid (Merck, Darmstadt, Germany) were added. Then, the systems remained for 30 min at room temperature. Afterward, the vessels were heated on microwave-assisted radiation for 20 min at 180 °C; Subsequently, the vessels were cooled, and 4 mL of hydrogen peroxide (Merck, Darmstadt, Germany) were also added, and another step of irradiation was carried out at 180 °C for 20 min. All the digestion procedure was performed at the power of about 600 W. The digested solutions were diluted with deionized water up to 15 mL, and nickel and vanadium were determined by ICP OES. For each digestion batch, three blank solutions of the reagents were prepared using the procedure described above.

### 2.4. Optimization strategy

The optimization of the sample digestion procedure was performed using a two-level full factorial design involving the followings factors: concentrated nitric acid and hydrogen peroxide volumes and the microwave oven temperature. Table 2 shows the experimental dominions of these factors as real and coded values. The chemometric responses were the nickel and vanadium concentrations found in the digested solutions, which were obtained by employing analytical curves prepared utilizing yttrium as the internal standard. Also, a multiple response was built using a multiple response function, which is established by the average of the sum of the normalized responses for each analyte considering their highest value [33]. The instrumental conditions of the ICP OE spectrometer were optimized utilizing Doehlert matrix [34], in which the factors studied were radio frequency power and nebulizer gas flow rate, having the plasma robustness as the response. The data obtained during the chemometric studies were evaluated using the 6.0 Statistic program.

## 3. Results and discussions

### 3.1. Optimization of the sample preparation procedure using microwave-assisted radiation

A two-level full factorial design was performed to optimize the sample digestion procedure of crude oil for the determination of nickel and vanadium. The individual and multiple responses are shown in Table 2.

Firstly, the factorial design was evaluated individually for each metal. This tool demonstrated that, for nickel, the three factors and all their interactions are not significant for the experimental dominions studied. For vanadium, however, this design showed that the factors digestion temperature and nitric acid concentration are statistically significant with positive and negative effects, respectively.

Afterward, the factorial design was evaluated using the multiple

**Table 2**  
Optimization of the digestion procedure using two-level factorial design.

Experiment	[HNO <sub>3</sub> ]	Temperature	[H <sub>2</sub> O <sub>2</sub> ]	Nickel (µg g <sup>-1</sup> )	Vanadium (µg g <sup>-1</sup> )	MR
1	-1 (3 M)	-1 (160 °C)	-1 (4 M)	27.59	0.64	1.55
2	1 (5 M)	-1 (160 °C)	-1 (4 M)	26.58	0.61	1.49
3	-1 (3 M)	1 (180 °C)	-1 (4 M)	29.44	<b>0.96</b>	<b>1.95</b>
4	1 (5 M)	1 (180 °C)	-1 (4 M)	30.37	0.78	1.79
5	-1 (3 M)	-1 (160 °C)	1 (6 M)	29.28	0.65	1.62
6	1 (5 M)	-1 (160 °C)	1 (6 M)	28.99	0.51	1.46
7	-1 (3 M)	1 (180 °C)	1 (6 M)	28.39	0.77	1.72
8	1 (5 M)	1 (180 °C)	1 (6 M)	<b>31.07</b>	0.64	1.67
9 (CP)	0 (4 M)	0 (170 °C)	0 (5 M)	28.11	0.66	1.59
10 (CP)	0 (4 M)	0 (170 °C)	0 (5 M)	29.34	0.62	1.59
11 (CP)	0 (4 M)	0 (170 °C)	0 (5 M)	28.54	0.59	1.53

M – mol L<sup>-1</sup>, MR – Multiple responses.

response to establish a single condition that allows the multi-element determination [24,35]. The equation employed for calculation of the multiple response is:

$$RM = \Sigma (Ni_{conc}/31.07) + (V_{conc}/0.96)$$

where, Ni<sub>conc</sub> and V<sub>conc</sub> are the nickel and vanadium concentrations found for each experiment of the two-level full factorial design that was performed (Table 2).

The results presented in graphic form are shown in Fig. 1. It can be noted that the digestion temperature and nitric acid volume factors are statistically significant, with positive and negative effects, respectively. Thus, the experimental conditions chosen for the digestion procedure were the following: digestion temperature of 180 °C and nitric acid and hydrogen peroxide volumes of 3.0 mL and 4.0 mL, respectively, which coincides with the experiment 3 of the factorial design, which presented the greatest response to the vanadium as shown in Table 2.

### 3.2. Optimization of the instrumental conditions of the spectrometer

The analysis of digested solutions of crude oil samples using ICP OES requires especial instrumental conditions of the plasma because its matrix is rich in different organic compounds. The performance of an ICP OE spectrometer has been evaluated by the robustness parameter, which describes the excitation and atomization conditions in the ICP. The evaluation of the plasma robustness is performed by measuring the Mg II 280.270-nm/Mg I 285.213-nm line emission intensity ratio, and a plasma is considered robust when this ratio is higher than 8 [36].

So, the radio frequency power and nebulizer gas flow rate were the instrumental parameters optimized using a Doehlert matrix [34] utilizing the plasma robustness as response. The experiments were

**Table 3**  
Doehlert matrix for optimization of the parameters of the ICP OES.

Experiment	Radio frequency power (W)	Argon nebulizer flow rate (mL min <sup>-1</sup> )	MgII/MgI Oil sample doped with Mg(II) ions	MgII/MgI Magnesium solutions
1	1200	1.00	7.965	7.925
2	1400	0.90	8.852	8.853
3	1200	0.60	5.379	5.421
4	1000	0.70	5.735	5.817
5	1000	0.90	7.131	7.133
6	1400	0.70	7.365	7.414
CP	1200	0.80	7.842	7.900
CP	1200	0.80	7.840	7.887
CP	1200	0.80	7.850	7.892

performed employing a digested solution of crude oil doped with magnesium solution and also a magnesium solution in nitric acid media. Table 3 shows the factors studied as coded and real values, and the Mg II/Mg I line emission intensity ratios (robustness obtained) for the two solutions.

The quadratic model obtained employing the emission intensity ratio for the solution of crude oil doped with magnesium solution shows a maximum condition of robustness for the experimental condition of radio frequency power of 1509 W and nebulizer gas flow rate of 0.921 mL min<sup>-1</sup>. However, the quadratic model generated using the intensity ratio for the magnesium solution also shows a maximum condition for a nebulizer gas flow rate of 0.914 mL min<sup>-1</sup> and a radio frequency power of 1504 W. An analysis of these results demonstrates that the radio frequency power required is close to 1500 W, being that the maximum radio frequency power allowed for the spectrometer employed is 1400 W. Yet, considering that 1400 W is not a recommended power for routine analysis, the instrumental condition chosen for the determination of nickel and vanadium were: nebulizer gas flow rate of 0.9 mL min<sup>-1</sup> and radio frequency power of 1200 W. This experimental condition is close to the central point of the Doehlert matrix (Table 3), which shows a robustness value close to 8 as required for axial view spectrometers.

Bismuth and yttrium were tested as internal standards for the determination of nickel and vanadium in digested oil samples using ICP OES. Yttrium was chosen for the method because it ensures a better precision for the method, as seen in Table 4.

### 3.3. Validation studies

The optimized method allowed the determination of nickel and vanadium in crude oil utilizing the external calibration technique, with limits of detection and quantification of 0.24 and 0.79 µg g<sup>-1</sup> for nickel and 0.06 and 0.20 µg g<sup>-1</sup> for vanadium.

These limits were calculated as the IUPAC recommendation,

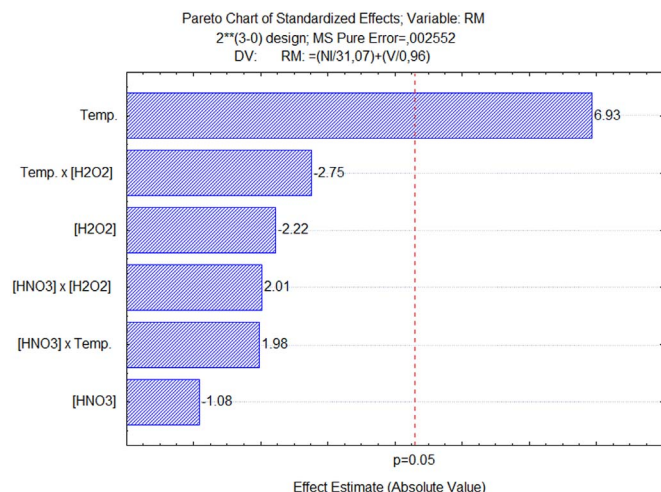


Fig. 1. Pareto chart of the factorial design of the digestion procedure.

**Table 4**  
Effect of the internal standard on the determination of Ni and V using ICP OES.

	Without internal standard		Yttrium as internal standard		Bismuth as internal standard	
	Nickel (mg Kg <sup>-1</sup> )	Vanadium (mg Kg <sup>-1</sup> )	Nickel (mg Kg <sup>-1</sup> )	Vanadium (mg Kg <sup>-1</sup> )	Nickel (mg Kg <sup>-1</sup> )	Vanadium (mg Kg <sup>-1</sup> )
Test 1	28.01	0.68	28.11	0.66	28.12	0.66
Test 1	29.98	0.62	29.34	0.62	30.05	0.59
Test 1	27.66	0.57	28.54	0.59	28.78	0.61
Average	28.55	0.62	28.66	0.62	28.98	0.62
SD	1.25	0.055	0.62	0.035	0.98	0.036
RSD%	4.38	8.84	2.18	5.63	3.38	5.81

**Table 5**  
Determination of Ni and V in certified reference material of trace element in fuel oil.

	Certified value	Concentration found <sup>a</sup>
Nickel (mg Kg <sup>-1</sup> )	17.54 ± 0.21	16.91 ± 0.54
Vanadium (mg Kg <sup>-1</sup> )	28.19 ± 0.40	27.68 ± 0.33

<sup>a</sup> Interval confidence at 95% level.

considering a sample mass digested of 0.10 g. The precision (as repeatability) expressed as the relative standard deviation varied from 1.63% to 3.67% for nickel and from 0.42% to 4.64% for vanadium. These parameters were calculated using oil samples with nickel contents of 10.06 and 7.32 µg g<sup>-1</sup>, and vanadium contents of 19.42 and 9.01 µg g<sup>-1</sup>. There is no certified reference material (CRM) of crude oil, therefore the accuracy method was evaluated utilizing the CRM 1634c Trace elements in fuel oil furnished by National Institute of Standards and Technology (NIST). The results found confirmed the accuracy of the method proposed, as seen in Table 5.

### 3.4. Application

The optimized sample preparation procedure was applied for the determination of vanadium and nickel in five crude oil samples, which came from three Brazilian oil basins. All the analyses were performed in triplicate, using yttrium as an internal standard to improve the method precision. Table 6 shows the results obtained, expressed as confidence interval at 95% level. It can be seen that the metal contents in the five samples analyzed varied from 7.30 to 33.21 for nickel and from 0.63 to 19.42 for vanadium. The concentrations obtained in this work are in agreement with the data obtained for these metals in crude oil samples by other authors [37,38].

The procedures employing microwave-induced combustion [13,15,17] and microwave ultraviolet irradiation [16] have often been employed for sample preparation in the determination of metals and metalloids in crude oil and their derivatives. However, these techniques require a sophisticated instrumentation, which is not widespread in the routine laboratories. The use of pressurized oxygen is another concern. In this work, a simple mineralization procedure using microwave-assisted digestion has been proposed for the determination of nickel and

**Table 6**  
Determination of Ni and V in crude oil samples from different basins.

Sample site	Nickel found <sup>a</sup> (mg Kg <sup>-1</sup> )	Vanadium found <sup>a</sup> (mg Kg <sup>-1</sup> )
Santos City, São Paulo State.	33.21 ± 1.96	1.07 ± 0.74
Campos City, Rio de Janeiro State.	15.76 ± 0.73	0.90 ± 0.28
Potiguar City, Espírito Santos State.	7.30 ± 0.67 10.06 ± 0.41 29.52 ± 1.83	9.00 ± 1.04 19.42 ± 0.20 0.63 ± 0.07

<sup>a</sup> Interval confidence at 95% level.

vanadium of crude oil samples. The reagents and instrumentation required are very common and easily found in routine laboratories.

## 4. Conclusions

A sample digestion procedure for determining nickel and vanadium in crude oil samples using microwave-assisted radiation and ICP OES was proposed.

The multivariate optimization technique demonstrated that the nitric acid and hydrogen peroxide volumes, and digestion temperature (in the conditions established) factors are not statistically significant for the decomposition of nickel organic-compounds for the determination of nickel in crude oil samples by ICP OES. However, for vanadium, the chemometric tool evidenced that the digestion temperature and nitric acid concentration factors are statistically significant with positive and negative effects, respectively, which means that the decomposition of the vanadium organic-compounds requires experimental conditions that are more critical than the nickel organic-compounds.

The employment of yttrium as internal standard improved the precision of the measurements, allowing lower limits of detection and quantification for the method proposed. The analysis of the certified reference material of fuel oil confirmed the method accuracy.

The nickel and vanadium contents found in the analyzed petroleum samples are in agreement with data reported for these metals in other Brazilian petroleum samples.

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