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Development of an Accurate Method based on MAD-SRC for the Determination of Metals and Sulfur in Crude Oil Atmospheric and Vacuum Residues by ICP OES

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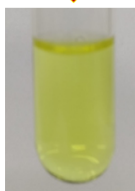
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Microwave-assisted wet digestion in single reaction chamber



Crude oil AR and VR digestion

- ✓ 1000 mg of crude oil Ar and VR were digested
- ✓ Temperature up to 270 °C
- ✓ 40 min of digestion



Determination of metals and S by ICP OES

The present study proposes for the first time a microwave-assisted digestion in an ultra-high pressure single reaction chamber (MAD-SRC) method for the digestion of atmospheric residue (AR) and vacuum residue (VR) from crude oil distillation. The determination of metals and sulfur was performed by inductively coupled plasma optical emission spectrometry (ICP OES). The type of digestion solution (HNO_3 or $\text{HNO}_3 + \text{H}_2\text{O}_2$), the volume of digestion solution (6 to 10 mL), maximum temperature (200 °C and 270 °C), and sample mass (up to 1000 mg) were evaluated. Using 1000 mg of sample, 8 mL of HNO_3 , and 270 °C the final digests presented carbon concentrations lower than 2500 mg L⁻¹ for

both crude oil AR and VR. The accuracy of MAD-SRC was evaluated by using a certified reference material, recovery tests, and comparison with results obtained by using microwave-induced combustion (MIC). No statistical difference was observed between the results obtained after the proposed MAD-SRC method and the certified values and recoveries higher than 95% were obtained for all analytes. Comparing the results obtained by the MAD-SRC method with those obtained by MIC, an agreement higher than 95% was achieved

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for all analytes. The relative standard deviation was always lower than 7%. The quantification limits ranged from 0.06 $\mu\text{g g}^{-1}$ for Ba to 3.13 $\mu\text{g g}^{-1}$ for S enabling metals and sulfur determination in crude oil distillation residues virtually free of interferences. The main advantages of the proposed method is the possibility to digest up to 1000 mg of crude oil AR and VR without the use of relatively long processing time and with lower risks of contamination and volatilization of analytes when compared to an official method using open vessels (about 240 min). In addition, it was possible to obtain digests fully compatible with the determination technique making this method a suitable option for the routine quality control of crude oil AR and VR.

Keywords: atmospheric residue of crude oil, vacuum residue of crude oil, metal determination in crude oil, sulfur determination in crude oil, and MAD-SRC applied to crude oil analysis

INTRODUCTION

In crude oil production, after the desalting step the distillation is the first processing stage, followed by the conversion and finishing stages. In the distillation process, crude oil is separated into complex mixtures (fractions or cuts).^{1,2} Crude oil distillation can be performed through atmospheric pressure and vacuum distillation towers. Both procedures generate residues composed of molecules of high molecular weight at the bottom of the distillation towers. The distillation residues are called atmospheric residue (AR) and vacuum residue (VR). The AR can be used as fuel oil or sent to the vacuum distillation tower, while VR can be used for lubricating oil and coke production, as well as asphalt. However, crude oil AR and VR can contain high amounts of impurities, such as S, Ni, and V (and other metals). Even at low concentrations, some metals (e.g., Ni and V) are responsible for catalyst poisoning and S can cause equipment corrosion. Furthermore, the S can react with O in the atmosphere resulting in SO_x molecules, which are, in combination with NO_x, responsible for the acid rain.³⁻⁵

For metals determination in crude oil and residual fuels, the official methodology is proposed by the American Society for Testing and Materials (ASTM D5863).⁶ In this procedure, the sample is calcined with concentrated H₂SO₄ at 525 °C in a muffle furnace. Further, the ash obtained is solubilized in diluted nitric acid solution (5%) for further determination of metals by flame atomic absorption spectrometry. However, muffle digestion can take a long processing time and can be susceptible to contamination or losses by analyte volatilization.⁷ Regarding sulfur, the ASTM recommends a method based on its direct determination using dispersive X-ray fluorescence (ASTM D2622).⁸ However, using this methodology, the matrix of calibration standards must be similar to the sample matrices and have no standards of AR and VR commercially available. In addition, some heteroatoms present in the matrix (such as Ca, Cl, O, P, Pb, and Zn) can act as interfering elements resulting in erroneous results.⁸

Furthermore, metal and sulfur determination in crude oil AR and VR can be performed by graphite furnace atomic absorption spectrometry (GF AAS),⁹ flame atomic absorption spectrometry¹⁰ (except for sulfur), inductively coupled plasma optical emission spectrometry (ICP OES),^{11,12} and inductively coupled plasma mass spectrometry (ICP-MS),^{13,14} among others. The ICP OES technique has been used due to its multi-elemental capability, better sensitivity, and limit of quantification (LOQ) compared to FAAS.^{7,15} In addition, using ICP OES a relatively high throughput can be obtained compared with GF AAS. Although the ICP-MS technique has better sensitivity and LOQ compared to ICP OES, some elements (such as Ca, Fe, and Mg) are susceptible to interference using conventional determination systems.¹⁶ For ICP OES conventional analysis, samples must be introduced as an aqueous solution by pneumatic nebulization. This is a problem when dealing with crude oil and its heavier distillation residues, which are considered hydrocarbon-based samples that are extremely hard to digest.^{7,17} Thus, it becomes important to develop analytical protocols capable of converting the crude oil AR and VR into an aqueous solution suitable for introduction into the spectrometer.^{7,15} However, this step represents a challenge, since both materials crude oil AR and VR are difficult to decompose by conventional digestion systems, even those operating under high temperature and pressure and using concentrated reagents.^{18,19}

Microwave-assisted sample preparation methods using closed vessels are an important tool for the digestion of samples.^{7,20} Generally, conventional microwave ovens reach temperature and pressure up to 210 °C and 40 bar, respectively.⁷ These systems are used to digest a wide range of samples (botanical, food, biological, among others). However, the maximum temperature allowed is not sufficient for the complete digestion of samples composed of aromatic and high molecular weight organic molecules, such as crude oil AR and VR. It is important to highlight that no studies were found that use these systems to decompose this kind of sample. On the other hand, some studies report the use of systems with quartz vessels, which allow higher temperature and pressure (280 °C and 80 bar, respectively). However, these studies are scarce and often use low crude oil AR and VR sample masses (about 500 mg).^{7,20}

As an alternative, a method based on microwave-assisted digestion using a single reaction chamber (MAD-SRC) was developed²¹ for the further determination of metal and sulfur in crude oil AR and VR. The system allows the application of higher conditions of temperature (up to 290 °C) and pressure (199 bar).²¹ As a result, it makes possible the digestion of larger sample masses when compared to other closed systems. It results in lower LOQ, allowing the determination of metals and sulfur at lower concentrations.²¹ In this study, the proposed method was evaluated by optimizing the type (HNO₃ and a mixture of HNO₃ + H₂O₂) and volume of the digestion solution (6, 8, and 10 mL), the maximum temperature reached during the irradiation program (250 and 270 °C), and the maximum sample mass (500, 750, and 1000 mg). The accuracy of the MAD-SRC method was evaluated by analytes recovery experiments, by the analysis of Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST) – NIST SRM 1634c, and comparison of the results with microwave-induced combustion.

EXPERIMENTAL

Instrumentation

The MAD-SRC method was developed using a microwave oven based on the Single Reaction Chamber (SRC, Milestone, Italy). The rotor used in this work allows 5 quartz vessels (maximum capacity of 40 mL each). More information regarding the system and the instrumental parameters for crude oil AR and VR digestion by MAD-SRC can be found in references.²²⁻²⁵ Before the digestion step, samples were placed for 30 min in an oven (model 400/2ND, Nova Etica, Brazil) at 120 °C for homogenization. For comparison of the results, crude oil AR and VR were also digested by MIC and the instrumental conditions of the Multiwave 3000 system (used in the MIC method) are detailed in reference.²⁶

The determination of metals and sulfur in resultant solutions obtained by the MAD-SRC and MIC methods was performed by using an ICP OES spectrometer (PerkinElmer, Optima 4300 DV, USA). The same equipment was used to determine residual carbon in digests. The operational parameters of ICP OES equipment for metals, sulfur, and carbon determination were based on references^{24,26} and a compilation of the instrumental conditions is shown in Table S1. The results obtained for carbon were used to choose the optimized experimental conditions of the MAD-SRC method.

Residual acidity in all digests obtained by MAD-SRC was determined using an automatic titration system (model 836, Ti stand, Metrohm, Switzerland) and conditions followed as described in reference.²²

Chemicals

Water purified in a Milli-Q system (18.2 MΩ cm, Millipore, USA) was used to prepare all solutions including standards and it was used to clean all materials. Nitric acid (65%, 14.4 mol L⁻¹, Vetec, Brazil) used for crude oil AR and VR digestion and analytes absorption in the MIC method was distilled, as described in reference.²⁶ The 50% H₂O₂ solution (purity of 48 to 52%, Merck, Germany) was used for the MAD-SRC method.

A stock reference solution containing 10 mg L⁻¹ of all metals (SCP33MS, Quebec, Canada) was used to prepare the calibration solutions of ICP OES equipment, by sequential dilutions (2.5 to 100 µg L⁻¹), in 5% (v/v) HNO₃. A Spex CertiPrep solution (1000 mg L⁻¹ of sulfur) was used to prepare the calibration solutions (250 to 10000 µg L⁻¹). The same reference solutions (SCP33MS and Spex CertiPrep) were used for the recovery experiments for the accuracy evaluation of the MAD-SRC method.

To prepare the calibration curve (5 to 2000 mg L⁻¹, in 5% of HNO₃, v v⁻¹) for carbon determination, a solution of 10000 mg L⁻¹ was obtained by dissolving citric acid in water. It is important to comment that for carbon determination, an internal standard (yttrium, 1000 mg L⁻¹, Spex CertPrep, USA) was added at 1000 µg L⁻¹ in all samples and standards.²⁷ Before introducing calibration solutions and samples into the spectrometer, the carbonaceous gases dissolved were removed from all solutions by using Ar flow.²⁷ Argon 99.998% (White Martins - Praxair, São Paulo, Brazil) was used for pressurizing the SRC in the UltraWAVE™ system. The same gas was used for plasma generation, nebulization, and as an auxiliary gas in the ICP OES spectrometer.

Samples

In this study, six samples (three samples of crude oil AR, named A, B, and C and three samples of crude oil VR, named D, E, and F) from PETROBRAS were selected. Sample A and D (crude oil AR and VR, respectively) were arbitrarily chosen for the optimization of experimental conditions of the MAD-SRC method.

MAD-SRC digestion method

The proposed MAD-SRC method was carried out under maximum pressure and temperature of 160 bar and 270 °C, respectively.²¹ The best conditions were chosen based on digestion efficiency (carbon content) and residual acidity in the final solution.

For the optimization of experimental parameters of the MAD-SRC method, sample masses (500 to 1000 mg) of crude oil AR and VR were evaluated. Digestion solutions (HNO₃ or HNO₃ + H₂O₂) and volume of HNO₃ (6, 8, or 10 mL) were studied. In addition, the temperature (250 and 270 °C) was also investigated. It is important to mention that all experiments were performed with concentrated HNO₃ (65%) and H₂O₂ 50%.

The microwave irradiation program used in the present study was performed according to a previous study.²² All the digests obtained from MIC and MAD-SRC methods were transferred to volumetric flasks and were diluted up to 25 mL with water before analyte determination by ICP OES. Details of the system cleaning procedure after each digestion cycle as performed as recommended in reference.²²

Parameters of validation

The accuracy was evaluated by the analysis of NIST SRM 1634c and by recovery experiments in three levels of concentration (5, 50, and 100 µg g⁻¹ for metals and 200, 1000, and 5000 µg g⁻¹ for S). The MIC was used as a reference method. The limits of detection (LOD) and LOQ values of the MAD-SRC method were calculated according to EURACHEM,²⁸ as presented in Equations 1 and 2, respectively.

$$\text{LOD} = a + q \cdot \text{SD} \quad \text{Equation 1}$$

where a is the mean of the blank measurements and $q = 3$

$$\text{LOQ} = a + q \cdot \text{SD} \quad \text{Equation 2}$$

where a is the mean of the blank measurements and $q = 10$

Robustness was taken into account with variations of smaller changes of sample mass (950 to 1050 mg), the volume of digestion solution (7.5 to 8.5 mL), temperature (267 to 273 °C), and time at the maximum temperature (8 to 12 min). Additionally, the robustness was evaluated by changing the radio frequency power (1350 to 1450 W) and nebulizer gas flow rate (0.68 to 0.72 L min⁻¹) of the spectrometer used for analyte determination. Other parameters as intermediate precision (inter-day precision) and repeatability (intra-day precision) were evaluated based on the relative standard deviation (RSD) in three days and three replicated analyses per day.²⁸

RESULTS

Performance of the MAD-SRC method

In general, systems that allow high temperatures (and consequently high pressure) to increase the oxidizing capacity of the acid are required to achieve a suitable digestion efficiency of high carbon content matrices as crude oil AR and VR. In order to be introduced into the equipment, the solutions obtained must have low carbon content as well as low acidity content. These criteria must be carefully evaluated to avoid interference in the measurement stage.²⁹

Studies on crude oil AR and VR digestion are scarce and often use relatively low sample masses (about 500 mg).^{7,20} This is due to the use of medium pressure digestion vessels (50 to 80 bar). However, the proposed MAD-SRC method allows higher pressure (up to 199 bar) and as a consequence, larger sample masses and lower LOQ. It is important if elements in lower concentration must be determined in such kind of matrices. Initial studies were performed using samples A crude oil (AR) and D crude oil (VR). The sample mass and the type of the digestion solution were investigated. Thus, 500 and 750 mg of crude oil AR and VR were digested using two digestion solutions: a) 6 mL of HNO₃ and b) 5 mL of HNO₃ + 1 mL of H₂O₂. The irradiation program applied was: a) hold for 10 min at 85 °C (10 min of ramp); b) hold for 10 min at 250 °C (10 min of ramp), and c) 40 min at 0 W (cooling step). At first experiments, the maximum temperature reached during the irradiation program was set at 250 °C. After, the digests were collected and the decomposition efficiency was evaluated regarding the carbon content and residual acidity. Results can be seen in Table I.

Table I. Carbon content and residual acidity obtained after crude oil AR and VR digestion by MAD-SRC method (mean and standard deviation, n=3).

Conditions	Crude oil AR (sample A)		Crude oil VR (sample D)	
	Carbon, mg L ⁻¹	Residual acidity, %	Carbon, mg L ⁻¹	Residual acidity, %
1. 500 mg, 6 mL of HNO ₃	1235 ± 50	38.3 ± 0.4	1305 ± 135	57.3 ± 1.5
2. 500 mg, 5 mL of HNO ₃ + 1 mL of H ₂ O ₂	1430 ± 85	37.0 ± 0.9	1260 ± 60	55.0 ± 1.8
3. 750 mg, 6 mL of HNO ₃	4080 ± 200	17.0 ± 0.3	3850 ± 180	17.4 ± 0.8
4. 750 mg, 5 mL of HNO ₃ + 1 mL of H ₂ O ₂	4250 ± 100	16.8 ± 0.5	3900 ± 130	16.5 ± 0.8

According to data shown in Table I, using 500 mg of sample and 6 mL HNO₃ (condition 1) the carbon concentration remaining after digestion of crude oil residues was 1235 ± 50 mg L⁻¹ for crude oil AR and 1305 ± 135 mg L⁻¹ for crude oil VR samples. However, using the same sample mass (500 mg) and 5 mL of HNO₃ + 1 mL of H₂O₂ (v v⁻¹) (condition 2), the results for carbon concentration ranged from 1260 ± 60 mg L⁻¹ (crude oil VR) to 1430 ± 85 mg L⁻¹ (crude oil AR). Probably, the results can be explained due to the lower volume used in condition 2 (5 mL) when compared with condition 1 (6 mL). By using the same experimental conditions, the residual acidity obtained in condition 1 (38.3 ± 0.4% and 57.3 ± 1.5% for crude oil AR and VR, respectively) did not show a significant difference when compared with condition 2 (37.0 ± 0.9% and 55.0 ± 1.8% for crude oil AR and VR, respectively).

By using 750 mg of crude oil AR and VR and 6 mL of HNO₃ (condition 3), the carbon concentration was 4080 ± 200 mg L⁻¹ for crude oil AR and 3850 ± 180 mg L⁻¹ for crude oil VR and the residual acidity was 17.0 ± 0.3 and 17.4 ± 0.8%, respectively. When 5 mL of HNO₃ + 1 mL of H₂O₂ (v v⁻¹) (condition 4) was used for 750 mg of sample, the carbon concentration was 4250 ± 100 mg L⁻¹ to crude oil AR to 3900 ± 130 mg L⁻¹ to crude oil VR and the residual acidity was 16.8 ± 0.5 and 16.5 ± 0.8%, respectively. As expected, the results for carbon concentration obtained in conditions 3 and 4 (750 mg) were higher than in conditions 1 and 2

(500 mg) for both crude oil AR and VR samples. On the other hand, in the same conditions, the residual acidity decreased approximately three times. Thus, considering the results obtained, 750 mg using only HNO_3 (6 mL) was selected for subsequent experiments.

Optimization of temperature

In order to achieve a complete digestion of complex a relatively high temperature is required during the digestion. Increasing the temperature of the digestion solution accelerates the oxidation of organic compounds, an essential factor for further determination by atomic spectrometric techniques.⁷ The microwave oven used in the present study allowed to reach a temperature higher than the most conventional digestion systems (210 °C). In this way, this parameter was evaluated for the digestion of crude oil AR and VR samples. Later, the maximum temperature was increased to 270 °C for the digestion of 750 mg of crude oil AR and VR using 6 mL of HNO_3 .

Using 270 °C, 750 mg, and 6 mL of HNO_3 , an increase in the oxidation of both crude oil AR and VR samples was obtained (carbon content was lower than 2800 mg L⁻¹). In addition, the residual acidity decreased significantly (around 7%) for both samples when compared with the residual acidity using 500 mg of samples and 6 mL of HNO_3 at 250 °C (around 17% - Table I). Using higher temperatures (270 °C) the digests obtained were compatible with the ICP OES technique and interferences originating from carbon during the determination of the analytes were not observed.

Considering that the digestion efficiency was significantly better using 750 mg, 6 mL of HNO_3 , at 270 °C, experiments were performed to digest 1000 mg of crude oil AR and crude oil VR using 6 mL of HNO_3 and the same irradiation program, previously applied. However, in this condition, the digests obtained for both crude oil AR and VR samples were not complete. The final solution presented yellowish with particles in suspension (solid residues). Thus, the digestion of 1000 mg of crude oil AR or VR using only 6 mL of HNO_3 was not considered adequate.

An important point to highlight is that no studies report the digestion of crude oil AR or VR with a mass similar or higher than 750 mg. In this way, the obtained results can be considered as promising for such kind of matrices. Additionally, experiments using 1000 mg of sample were performed considering the potentialities of the UltraWAVETM system and the possibility of using larger quantities of HNO_3 .

Influence of HNO_3 volume

It has been known that digestion efficiency depends on the amount and kind of digestion solutions used.^{7,20} For this reason, the amount of HNO_3 was optimized to evaluate the digestion of 1000 mg of crude oil AR and VR. In this sense, 6 to 10 mL of HNO_3 and the same irradiation program previously applied for the digestion of 1000 mg of sample (crude oil AR or VR) were used for the present investigation. The results obtained for carbon concentration and residual acidity are shown in Figure 1.

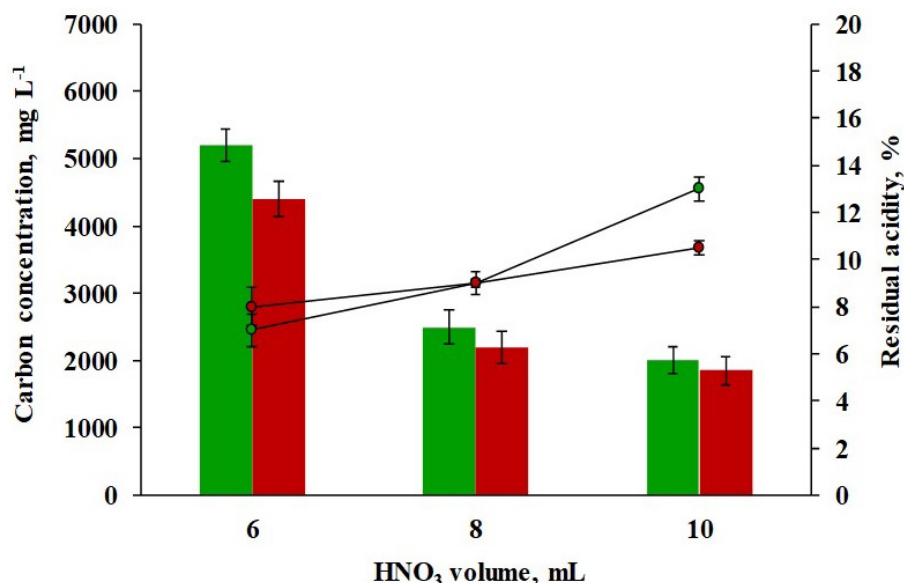


Figure 1. Carbon concentration for (■) crude oil AR and (■) VR and residual acidity for (—●—) crude oil AR and (—●—) VR using 6, 8 and 10 mL of 65% HNO₃, n=3. Conditions: 1000 mg of sample and 270 °C.

According to the results (Figure 1), using 6 mL of HNO₃ to digest 1000 mg of sample at 270 °C, the carbon concentration was 5300 mg L⁻¹ for crude oil AR and 5500 mg L⁻¹ for crude oil VR. Regarding residual acidity, values obtained were around 8% for both samples. As seen in Figure 2A, the digested solution of AR showed a brown appearance with solid residues in suspension. It should be noted that the same aspect was observed for the crude oil VR digests under the same experimental conditions.

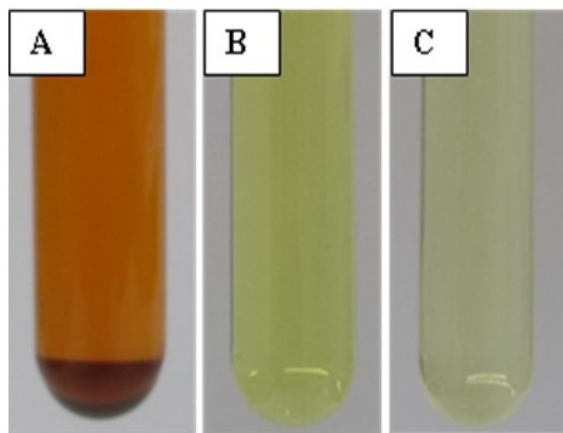


Figure 2. Obtained solutions after digestion of crude oil AR by MAD-SRC using the following digestion solutions: A) 6 mL of HNO₃, B) 8 mL of HNO₃, and C) 10 mL of 65% HNO₃. Conditions: 1000 mg of AR and maximum temperature set at 270 °C.

Using 8 mL of HNO₃ to digest 1000 mg crude oil AR and VR, the carbon concentration was 2200 mg L⁻¹ and 2500 mg L⁻¹, respectively (Figure 1). Regarding residual acidity in final solutions, relatively low values (about 9%) for both crude oil AR and VR digests were obtained. These results are in agreement with those obtained for heavy crude oil using 10 min and 270 °C.²² Furthermore, clean solutions without solid residues were also obtained (Figure 2B). On the other hand, when 10 mL of HNO₃ were used to digest

the same mass of sample (1000 mg), it was observed that the residual acidity in final digests was 13% for crude oil AR and 10% for crude oil VR. The aspect of the solution obtained for the crude oil AR sample is shown in Figure 2C. In this sense, this condition was not chosen for crude oil AR and VR digestion to avoid possible interferences caused by the high amount of HNO_3 during the determination of the analyte by ICP OES. Therefore, considering the relatively low carbon and residual acidity obtained in crude oil AR and VR digests, the digestion of 1000 mg of crude oil AR and VR using 8 mL of HNO_3 was considered an optimized condition. In this condition, no dilution of digests was necessary before analyte determination by ICP OES, and the metal and S were determined free from interferences.

MAD-SRC – Method validation

The accuracy of the proposed method was evaluated by using a SRM of residual fuel oil (NIST SRM 1634c), by recovery experiments and results comparison with MIC. The optimized conditions (1000 mg of sample, 270 °C, and 8 mL of HNO_3) were used for the accuracy evaluation. For recovery experiments, reference solutions containing all metals and sulfur were added to crude oil AR and VR samples to obtain concentrations equal to 5, 50, and 100 $\mu\text{g g}^{-1}$ for metals and 200, 1000, and 5000 $\mu\text{g g}^{-1}$ for sulfur. According to the obtained results, suitable recoveries (ranging from 95 to 106%) were obtained for all analytes. No statistical difference (*t*-test, 95% confidence level) was obtained between the results after MAD-SRC and the certified values of SRM (determined by ICP OES). In comparison with the MIC method (used as a reference), the agreement between the values was better than 95%, as can be seen in Table II (Sample A and D for crude oil AR and VR, respectively). In addition, for all evaluations, the relative standard deviations (RSD) were lower than 7% for all analytes. The LOD and LOQ values were calculated as described in Equations 1 and 2 (*section Method validation*) by using 1000 mg of samples and 25 mL of final volume. For the metals, the values of the LOD ranging from 0.02 (Ba) to 0.16 $\mu\text{g g}^{-1}$ (Ca) and for sulfur was 0.89 $\mu\text{g g}^{-1}$. Relatively low LOQ were also obtained for all analytes (values ranging from 0.06 (Ba) to 0.55 $\mu\text{g g}^{-1}$ (Ca) and 3.13 $\mu\text{g g}^{-1}$ for S). It is important to mention that blank values used to calculate LOD and LOQ were always negligible. The LOD and LOQ for all analytes can be seen in Table S3. A good determination coefficient (R^2) of the calibration curve was observed for all analytes (better than 0.9992), indicating a suitable linear response for the evaluated concentration range (10 to 100 $\mu\text{g L}^{-1}$ for metals and 0.25 to 10 mg L^{-1} for S). The robustness of the MAD-SRC method was evaluated taking into account some changes in the sample mass during digestion of both crude oil AR and VR (950 to 1050 mg), the volume of digestion solution (7.5 to 8.5 mL), temperature (267 to 273 °C), and time at the maximum temperature (8 to 12 min). Additionally, the robustness was evaluated by changing the radio frequency power (1350 to 1450 W) and nebulizer gas flow rate (0.68 to 0.72 L min^{-1}) of the spectrometer used for analytes determination. For these evaluations, the variation of results was less than 5%. In addition, the results for repeatability and precision were considered suitable (RSD lower than 5% for all analytes).

Determination of metals and sulfur in crude oil AR and VR using the MAD-SRC method

After the development of the MAD-SRC method for crude oil AR and VR, the optimized experimental condition (1000 mg, 8 mL of HNO_3 , and 270 °C) was applied for three samples of crude oil AR and three samples of crude oil VR for further metal and sulfur determination by ICP OES. The MIC (reference method) was applied for crude oil AR A and VR D to obtain the reference values in order to compare the results obtained after MAD-SRC. The results obtained are shown in Table II.

Table II. Metals and S concentration after MAD-SRC and MIC methods. Determination by ICP OES. Mean and standard deviation ($\mu\text{g g}^{-1}$, $n=3$).

Analyte	Crude oil AR				Crude oil VR			
	A		B	C	D		E	F
	MAD-SRC	MIC	MAD-SRC	MAD-SRC	MAD-SRC	MIC	MAD-SRC	MAD-SRC
Al	< 0.52	< 1.03	< 0.52	< 0.52	< 0.52	< 1.03	< 0.52	< 0.52
Ba	0.90 ± 0.02	0.88 ± 0.02	0.60 ± 0.01	0.53 ± 0.01	0.61 ± 0.04	0.61 ± 0.01	0.60 ± 0.01	0.40 ± 0.01
Ca	224 ± 4	231 ± 6	18.9 ± 1.0	132 ± 6	27.1 ± 1.3	28.0 ± 3.2	26.8 ± 1.5	3.75 ± 0.21
Co	< 0.25	< 0.54	2.08 ± 0.02	1.55 ± 0.06	3.45 ± 0.07	3.46 ± 0.28	3.30 ± 0.05	1.02 ± 0.03
Cr	< 0.25	< 0.58	< 0.25	< 0.25	< 0.25	< 0.58	< 0.25	< 0.25
Fe	117 ± 2	123 ± 8	28.4 ± 0.4	89.6 ± 5.6	14.4 ± 0.3	14.9 ± 2.5	10.7 ± 0.6	15.0 ± 0.7
Mg	48.6 ± 0.9	49.6 ± 2.8	2.34 ± 0.10	49.6 ± 2.8	3.08 ± 0.16	3.05 ± 0.31	3.52 ± 0.14	4.02 ± 0.28
Mn	2.60 ± 0.15	2.63 ± 0.19	< 0.08	1.22 ± 0.08	0.19 ± 0.01	0.20 ± 0.01	< 0.08	< 0.08
Ni	42.4 ± 0.4	43.3 ± 0.2	24.2 ± 0.6	28.1 ± 0.6	57.0 ± 1.3	58.1 ± 0.8	50.9 ± 1.3	62.4 ± 1.2
V	10.3 ± 0.3	10.9 ± 0.2	28.9 ± 0.8	8.52 ± 0.52	72.7 ± 1.5	74.3 ± 1.0	70.3 ± 1.4	33.8 ± 1.8
S	4390 ± 190	4525 ± 275	5670 ± 240	5535 ± 230	9120 ± 200	9570 ± 295	8660 ± 160	4425 ± 190

Conditions: MAD-SRC: 1000 mg of sample, 270 °C and 8 mL of HNO_3 .
MIC: 500 mg of sample and 6 mL of HNO_3 .

According to the results shown in Table II, Ba, Ca, Fe, Mg, Ni, V, and S are present in all crude oil AR and VR samples. In general, Ba showed the lowest concentrations the results for crude oil AR ranged from $0.53 \pm 0.01 \mu\text{g g}^{-1}$ (sample C) to $0.90 \pm 0.02 \mu\text{g g}^{-1}$ (sample A). For crude oil VR, the Ba concentrations ranged from $0.40 \pm 0.01 \mu\text{g g}^{-1}$ (sample F) to $0.61 \pm 0.04 \mu\text{g g}^{-1}$ (sample D). For Al and Cr, the concentrations were below the LOQ of the method for all samples (< 0.52 and $< 0.25 \mu\text{g g}^{-1}$, respectively). For S, the results ranged from $4390 \pm 190 \mu\text{g g}^{-1}$ (sample A) to $5670 \pm 240 \mu\text{g g}^{-1}$ (sample B). For crude oil VR, the S concentrations ranged from $4425 \pm 190 \mu\text{g g}^{-1}$ (sample F) to $9570 \pm 295 \mu\text{g g}^{-1}$ (sample D). It was possible to observe that S is present in the high concentrations in all evaluated samples (crude oil AR and crude oil VR). In general, these results showed that the concentration of analytes is variable, which possibly is correlated to the geological origin of crude oil.¹

In addition, it is important to mention that no statistical difference (*t*-test, 95% confidence level) was observed between the results by using the MAD-SRC and MIC method (reference method). In Table S2 is possible to observe the agreements between MAD-SRC and MIC methods for all analytes. The RSD values were lower than 7% after MAD-SRC digestion and ICP OES determination.

An advantage of the MAD-SRC proposed method is that was possible to digest 1000 mg of crude oil AR and VR. As a consequence, it was possible to obtain low LOD and LOQ values by ICP OES. Additionally, taking into account the low values of carbon concentration (2200 mg L^{-1} for VR and 2900 mg L^{-1} for AR) and residual acidity (around 9% for crude oil AR and VR), an additional dilution step before the determination step was not mandatory. It is important to mention that a dilution step before the analyte determination is a problem, as this hinders the achievement of low LOQ and makes the determination step time-consuming. For these purposes, the MAD-SRC method can be considered a suitable alternative for the digestion of crude oil AR and VR for further metals and sulfur determination by ICP OES.

Some advantages were observed for the proposed MAD-SRC method in comparison with ASTM D5863 (metals) and ASTM D2622 (S). For the ASTM D5863 method, long processing time, susceptibility to contamination (open system), sample projection, and analyte volatilization are clear disadvantages of the methodology.⁶ Concerning the ASTM D2622 (S), the standard must be similar to the sample matrices to the equipment calibration, which makes it difficult to use this method in laboratory routines.⁷ On the other hand, the MAD-SRC method proposes low digestion time, lower risk of contamination, and analyte losses. Additionally, the analytes are determined free from interferences by ICP OES. Low carbon concentration in final solutions is an undisputed advantage of using this system. Furthermore, the amount of sample that can be digested (1000 mg) is the state of the art for this type of sample. Another point worth highlighting is that it was possible to determine metals and sulfur using the same solution obtained by MAD-SRC. ASTM D5863 is not applicable for the determination of S and ASTM D2622 is not applicable for the determination of metals.

Despite the known advantages of the MIC method, the MAD-SRC method may stand out in comparison to the sample mass that can be digested (1000 and 500 mg using MAD-SRC and MIC, respectively²⁶). The relatively low sample mass when using MIC is due to the limitation of the pressure supported by the system at the time of sample combustion. As a result, the MAD-SRC method provides lower LOD and LOQ, allowing the determination of elements at lower concentrations. This becomes important when elements at the trace or ultratrace level must be determined.

In addition to the advantages already mentioned, the MAD-SRC method presents clear advantages related to the reduction of environmental impacts when compared to the ASTM D5863 method. This method recommends the use of concentrated H_2SO_4 (1 to 10 mL) for crude oil digestion. After that, the use of 10 mL of 50% HNO_3 is also required. However, using the MAD-SRC method, the use of H_2SO_4 is not necessary and only 8 mL of concentrated HNO_3 is enough for a complete matrix digestion. For this reason, the MAD-SRC method presents more environmentally friendly characteristics.

CONCLUSIONS

Using the proposed MAD-SRC method, it was possible to digest 1000 mg of crude oil AR and VR. The carbon concentration obtained in final digests was 2500 mg L⁻¹ for crude oil AR and 2200 mg L⁻¹ for crude oil VR and residual acidity was around 9% for both samples, making it possible to determine metal and sulfur without interferences by ICP OES. Additionally, as an advantage of high sample mass digestion, it was possible to obtain low LOQ values, ranging from 0.06 µg g⁻¹ for Ba to 3.13 µg g⁻¹ for S, for both crude oil AR and VR. Moreover, quantitative recoveries for metals and sulfur were achieved. In this aspect, the proposed method can be considered a good alternative for the complete digestion of crude oil AR and VR providing digests fully compatible with further ICP OES analysis. In addition, the agreement between the values obtained after MAD-SRC with the values obtained by MIC (reference method) was better than 95%. The main disadvantage of the MAD-SRC method is still the use of concentrated HNO₃ (8 mL) but it is important to consider the high difficulty to digest crude oil distillation residues. By using MAD-SRC method it was possible to digest 1000 mg of crude oil AR and VR without the use of long processing time, and with lower risks of contamination and volatilization of analytes when compared with ASTM D5863 method. In this way, the MAD-SRC method can be considered an important tool for crude oil AR a VR digestion for further metals and S determination by ICP OES. As a perspective to the proposed method, its application in routine analyzes in the industry for quality control of crude oil AR and VR is aimed.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SUPPLEMENTARY MATERIAL

Table S1. Operational conditions used for metals and S determination by ICP OES

Parameters	ICP OES
Radio frequency power, W	1400
Gas flow rate, L min ⁻¹	
Plasma	15
Auxiliary	0.2
Nebulizer	0.7
Sample flow-rate (mL min ⁻¹)	2.10
Element wavelength (nm)	
Al	396.153
Ba	233.527
C	193.091
Ca	317.933
Co	228.616
Cr	267.716
Fe	239.562
Mg	285.213
Mn	257.610

(continued on next page)

Table S1. Operational conditions used for metals and S determination by ICP OES (continuation)

Parameters	ICP OES
Element wavelength (nm)	
Ni	231.604
V	290.880
S	181.975
Y ^a	371.029

^aUsed as internal standard for carbon determination.**Table S2.** Agreements between MAD-SRC and MIC for all analytes (results in %)

Parameters	Crude oil AR A	Crude oil VR D
Al	-	-
Ba	102%	100%
Ca	97%	96.8%
Co	-	99.7%
Cr	-	-
Fe	95.1%	96.6%
Mg	98.0%	101%
Mn	98.9%	96.7%
Ni	97.9%	96.6%
V	94.5%	97.8%
S	97.0%	95.3%

Table S3. Limits of detection and LOQ obtained by ICP OES after MAD-SRC (results in $\mu\text{g g}^{-1}$)

Parameters	LOD	LOQ
Al	0.14	0.52
Ba	0.02	0.06
Ca	0.16	0.55
Co	0.07	0.25
Cr	0.08	0.26
Fe	0.07	0.25
Mg	0.04	0.13

(continued on next page)

Table S3. Limits of detection and LOQ obtained by ICP OES after MAD-SRC
(results in $\mu\text{g g}^{-1}$) (continuation)

Parameters	LOD	LOQ
Mn	0.02	0.08
Ni	0.07	0.25
V	0.04	0.13
S	0.89	3.13