



Evaluation and determination of chloride in crude oil based on the counterions Na, Ca, Mg, Sr and Fe, quantified via ICP-OES in the crude oil aqueous extract



Murilo de Oliveira Souza^{a,b}, Maria Aparecida Ribeiro^b, Maria Tereza Weitzel Dias Carneiro^b, Geisamanda Pedrini Brandão Athayde^b, Eustáquio Vinícius Ribeiro de Castro^b, Francisco Luan Fonseca da Silva^c, Wladiana Oliveira Matos^c, Rafael de Queiroz Ferreira^{b,*}

^a Instituto Federal Fluminense, Campus Itaperuna, 28300-000 Itaperuna, Rio de Janeiro, Brazil

^b Departamento de Química, Universidade Federal do Espírito Santo, Laboratório de Pesquisa e Desenvolvimento de Metodologias para Análise de Petróleo, 29075-910 Vitória, Espírito Santo, Brazil

^c Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Campus do Pici, 60000-000 Fortaleza, Ceará, Brazil

HIGHLIGHTS

- Chloride salts contained in crude oil can cause corrosion and encrustation in distillation towers.
- Chloride concentrations can be obtained via ICP-OES through the analysis of its counterions.
- The accuracy of the procedure was confirmed through comparison with the results of FAAS.
- The modified standard test method of ASTM D 6470-99 extraction was compared with microwave-assisted acid digestion.
- The study demonstrated that Na, Ca, Mg, Sr and Fe were mainly associated with chloride.

ARTICLE INFO

Article history:

Received 27 January 2015

Received in revised form 27 March 2015

Accepted 30 March 2015

Available online 4 April 2015

Keywords:

Crude oil
Chloride counterions
ICP-OES
Corrosion
Refining

ABSTRACT

Of the salts present in crude oil, sodium, calcium, magnesium, strontium and iron chlorides are the most abundant and are considered the main cause of corrosion in crude oil refineries. Therefore, the objective of this study was to quantify the main chloride counterions (Na, Ca, Mg, Sr and Fe) using inductively coupled plasma-optical emission spectrometry (ICP-OES) after hot solvent extraction (modified ASTM D 6470-99). The procedure developed in this work allowed samples with different °API values (17.4–30.2) originating from the post-salt to be studied. Under the operational conditions of ICP-OES, robust plasma ($Mg\ II/Mg\ I > 10$ for the axial and radial configurations) was obtained based on evaluation of the ratio of the $Mg\ II/Mg\ I$ intensities. Furthermore, yttrium was used as an internal standard, resulting in as little interference with the analytical signal as possible. This procedure achieved detection limits on the order of $0.99\ mg\ L^{-1}$, $0.025\ mg\ L^{-1}$, $0.33\ \mu g\ L^{-1}$, $0.06\ ng\ L^{-1}$ and $0.26\ \mu g\ L^{-1}$ for Na, Ca, Mg, Sr and Fe, respectively. The accuracy of the procedure was confirmed through addition/recovery tests (91–120%) and through comparison with the results obtained with flame atomic absorption spectrometry (FAAS). The modified standard test method of ASTM D 6470-99 extraction was compared with microwave-assisted acid digestion and was found to achieve extractions higher than 92.44% for Na and 81.06% for Sr from two of the analysed extracts. Finally, the chloride concentrations obtained via potentiometric titration and ICP-OES (through the analysis of chloride with its counterions) in the aqueous extract indicated a high correlation between Na, Ca, Mg, Sr and Fe and chloride (105.10%, 99.33% and 102.12% for the evaluated samples).

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Crude oil is a highly complex mixture composed of saturated hydrocarbons, aromatics and polycyclic compounds (resins and asphaltenes), in addition to trace elements of inorganic origin [1–

* Corresponding author. Tel.: +55 27 40097946; fax: +55 27 40092826.

E-mail address: rafael.q.ferreira@ufes.br (R. de Queiroz Ferreira).

4]. Because of the natural geological processes involved in crude oil formation as well as crude oil exploration techniques, a great amount of salty water is emulsified in crude oil. This water contains large amounts of metals and non-metals, which are responsible for the formation of inorganic salts, causing high salinity in wells [3–5]. Thus, the inorganic composition of crude oil may be associated with its contact with water (due to injection of the water produced during the crude oil exploration process) and the use of chemical compounds, such as additives and catalysts. Additionally, the presence of inorganic elements, such as Na, Ca, Mg, Sr and Fe, is expected, depending on the geology of the reservoir from which the samples are collected [6].

The metals and non-metals contained in crude oil can cause corrosion and encrustation in distillation towers as well as poisoning of catalysts and environmental pollution [6–8]. Special attention is paid to corrosion caused by the presence of inorganic contaminants (chloride salts) in crude oil. It is necessary to control the presence of these salts before crude oil refining and processing without posing damage to the quality of the productive process [9]. This control is fundamental, as the maximum content of salts, expressed as the mass of sodium chloride in mg dissolved in 1 kg of crude oil, is 570 mg kg⁻¹ for the production step; in refineries, the content of salts should be lower than 5 mg kg⁻¹ [4]. In parallel, the high temperatures of distillation towers can promote the hydrolysis of chloride, generating hydrochloric acid as a final product, which is one of the main causes of corrosive processes in crude oil refineries [10–14].

Hence, evaluation of the presence and types of chloride in crude oil, with the purpose of studying corrosion processes, starts with the determination of chloride salt counterions present in the matrix. Among the salts present in crude oil, sodium, calcium, magnesium, strontium and iron chlorides are the most common and, along with carbonate and sulphate salts, are the main cause of corrosion and encrustation [8,12–14]. The counterions (Na, Ca, Mg, Sr and Fe) associated with chloride can be extracted in the aqueous phase of crude oil using the standard ASTM D 6470-99 test method [15]. This methodology employs the solvents xylene, isopropyl alcohol, acetone and water, followed by heating of the extractor flasks, for the extraction of inorganic salts into the aqueous phase of crude oil. After extraction, the chloride content in the aqueous phase is determined via potentiometric titration, and the results are expressed as NaCl in crude oil.

Morigaki et al. [4] modified the experimental procedure of the ASTM D 6470-99 method [15] to achieve efficient extraction of salts from crude oil to the aqueous phase. The results obtained in the recovery tests for intermediary and heavy crude oils using the modified ASTM D 6470-99 method indicated an 89–90% efficiency of chloride extraction, showing higher efficiency than the traditional ASTM D 6470-99 method [4,12]. Thus, aqueous extraction of crude oil using the modified ASTM D 6470-99 method allows the migration of almost all chloride salts to the aqueous phase (aqueous crude oil extract), enabling the use of instrumental techniques for the determination of counterions of the chloride.

The determination of trace elements via inductively coupled plasma-optical emission spectrometry (ICP-OES) is widely applied because of the high sensitivity and low detection limits of this method and, especially, the possibility of performing multi-element analysis [16,17]. However, no available study mentions the use of this technique for the monitoring of chloride via the determination of its main counterions in aqueous crude oil extracts. Most studies emphasise the determination of metals and nonmetals either directly in crude oil and its derivatives [18–21] or after microwave digestion [6,7,10,14,22]. However, destabilisation issues and the extinction of plasma, which are associated with low sensitivity, are frequent occurrences when samples with a high carbon content (e.g., crude oil) are directly introduced

into ICP-OES, affecting the precision and accuracy of the results. Thus, the indirect determination of chloride from its counterions in aqueous extracts of crude oil represents a very advantageous proposed alternative because of the existing difficulties in their direct analysis in the crude oil matrix.

However, the extracted aqueous phase has a high saline content, which interferes significantly with the sensitivity and robustness of ICP-OES [23]. Furthermore, the migration of the organic load to the aqueous phase of the extract, which is caused by the crude oil itself and the organic solvents used for extraction, interferes with the stability of plasma and the sensitivity of the equipment. Thus, the extracts are diluted to minimise the interference of the matrix. In turn, the concentration of the elements decreases as the aqueous extracts are diluted, and an analytical technique with low limits of detection and good sensitivity is therefore required.

In this context, an analytical procedure was developed for the determination of chloride counterions (Na, Ca, Mg, Sr and Fe) via ICP-OES in an aqueous crude oil extract, following hot solvent extraction of crude oil samples (modified ASTM D 6470-99). Additionally, to verify the efficiency of metal extraction into the aqueous crude oil phase (aqueous extract), the results obtained using the developed procedure were compared with those obtained via microwave-assisted acid digestion (total crude oil digestion). Finally, an analysis was conducted to assess the possibility of interfering with the chloride concentration in crude oil by determining its main counterions in the aqueous extract.

2. Materials and methods

2.1. Instrumentation

An inductively coupled plasma-optical emission spectrometer (Perkin Elmer, Model Optima 7000 DV, USA) was used to quantify Na, Ca, Mg, Sr and Fe. The following spectral lines were employed: Na I (589.592 nm), Ca II (317.933 nm), Mg I (285.213 nm), Sr II (407.771 nm) and Fe II (238.204 nm), where I and II refer to the atomic and ionic spectral lines, respectively, of the elements analysed by ICP OES. The radial configuration was used for sodium, and the axial configuration was used for the other elements. For the determination of metals after hot solvent extraction of crude oil samples (aqueous extract) and after microwave-assisted acid digestion (digested), nebulisers connected to a peristaltic pump were employed to introduce samples into a nebulisation chamber. The samples were then introduced into the plasma formed in the quartz torch by an alumina injector (1.2 mm internal diameter (id)).

All measurements were performed in triplicate, and the intensity peak areas were integrated in the respective wavelengths of

Table 1
Operational conditions for ICP-OES (radial configuration for Na and axial configuration for Ca, Mg, Sr and Fe).

ICP-OES operational conditions	Aqueous extract	Digested product
Nebulisation chamber	Twitter cyclonic	Cyclonic
Nebuliser	Mira mist	Seaspray
Alumina injector (mm id)	1.2	1.2
Quartz torch	One slot	One slot
Torch position	+1	+1
Radio frequency generator (MHz)	40	40
Radiofrequency Power (W)	1272	1200
Plasma gas flow (L min ⁻¹)	15	15
Nebulising gas flow (L min ⁻¹)	0.53	0.6
Auxiliary gas flow (L min ⁻¹)	0.5	0.6
Sample aspiration rate (L min ⁻¹)	1.2	1.32 (Na) 1.30 (Others)
Instrument stabilisation delay (s)	55	55

each element. The parameters used for the execution of the analyses are listed in Table 1.

Comparison of the results obtained using the procedure developed for the determination of Na, Ca, Mg, Sr and Fe via ICP-OES in the crude oil aqueous extract was performed using a flame atomic absorption spectrometer (FAAS) model ZEE nit 700 from Analytik Jena® (Jena, Germany).

For the decomposition of crude oil samples, a cavity microwave oven (Anton Paar, Model Multiwave 3000, Austria) equipped with quartz tubes (internal volume of 80 mL, maximum temperature and pressure of 300 °C and 75 bar, respectively) was employed. The pressure and temperature were monitored in each quartz tube by a sensor in the equipment. For the chloride determination, a potentiometer was used (Metrohm, Model Titrand 905, Switzerland).

2.2. Materials and reagents

For the ICP OES, argon (99.9992% purity, Air Products, São Paulo, Brazil) was used as the plasma gas, nebulising gas and auxiliary gas, while nitrogen (99.99% purity, Air Products, São Paulo, Brazil) and nitrogen (99.9992% purity, Air Products, São Paulo, Brazil) were used as the shear gas and purge gas, respectively.

The glass and plastic vessels employed for the ICP-OES analyses were washed with water, placed in a bath with 5% Extran MA 02 neutral v/v (Merck, Darmstadt, Germany) for 48 h, rinsed with deionised water and placed in a 15% HNO₃ bath v/v for at least 24 h.

Suprapur nitric acid (HNO₃; 65%, Merck, Germany) purified in a distillacid™ BSB-939-IR acid distiller (Berghof, Germany), ultrapure water (type 1+, resistivity = 18.2 M Ω cm⁻¹) prepared with a reverse osmosis system (Purelab Ultra Mk2, United Kingdom), isopropyl alcohol pro analysis (pa) (Vetec, Brazil), acetone pa (Vetec, Brazil), xylene pa (Vetec, Brazil) and 30% hydrogen peroxide w/w (Vetec, Brazil) were used for the preparation, extraction and digestion of samples. A mono-elemental Na solution (1000 mg L⁻¹, SpecSol, Brazil) and a multi-elemental standard solution containing Ca, Mg, Sr and Fe (100 mg L⁻¹, PlasmaCal, SCP SCIENCE, Canada) were employed for the preparation of calibration curves. In turn, a mono-elemental solution of 1000 mg of Mg L⁻¹ (SpecSol, Brazil) was used to evaluate the robustness of the plasma. A standard yttrium (Y) solution (1000 mg L⁻¹, Plasma Cal, SCP SCIENCE, Canada) was used as an internal standard. All standard solutions were prepared at an appropriate dilution using 0.2% HNO₃ v/v or ultrapure water in polypropylene tubes with capacities of 15.0 or 50.0 mL (Techno Plastic Products AG, Transadingen, Switzerland).

2.3. Sample preparation: extraction using the modified standard ASTM D 6470-99 method

In the development of this study, different crude oil samples were employed, designated Sample S1 (°API 17.4, salinity 470.2900 mg kg⁻¹ of NaCl), Sample S2 (°API 30.2, salinity 152.1600 mg kg⁻¹ of NaCl), Sample S3 (°API 17.5, salinity 240.9997 mg kg⁻¹ of NaCl), Sample S4 (°API 17.9, salinity 279.4058 mg kg⁻¹ of NaCl) and Sample S5 (°API 17.4, salinity 343.8929 mg kg⁻¹ of NaCl), which generated the extracts E1–E5, respectively.

The crude oil aqueous extract was obtained using the ASTM D 6470-99 extraction method, as modified by Morigaki et al. [4]. For this purpose, 40.0000 ± 0.1000 g of crude oil was homogenised and weighed in a beaker. Then, 70.0 ± 1.0 mL of xylene was added to the same container by slowly pouring it into the sample, followed by manual agitation. The solution was subsequently transferred to a 2-L extractor flask, and 25.0 ± 1.0 mL of isopropyl alcohol and 15.0 ± 1.0 mL of acetone were added to the flask. The

mixture was heated to boiling, and after five minutes of boiling, the heating was interrupted, and 125.0 ± 1.0 mL of deionised water preheated to approximately 80 °C was added. In the next step, boiling of the extractor flask was resumed for 15 additional minutes. After the solution had cooled and the two phases had separated (approximately 20 min), the bottom phase (aqueous extract) was drained using two filter papers (diameter 12.5 cm and porosity 25 µm) to retain the crude oil. Before each extraction, a blank was prepared using the same procedure, but without adding crude oil, to control for contamination.

2.4. Procedure developed for the determination of counterions

Because the salinity of the aqueous extracts of crude oil varies from 152.1600 to 343.8929 mg kg⁻¹ NaCl, aliquots of each one of these samples were added to five 15 mL polypropylene tubes, along with 0.5 mL of yttrium (Y) 10 mg L⁻¹. Then, each tube was diluted with 0.2% HNO₃ v/v to a final volume of 10.0 mL, producing a final salinity of 10 mg kg⁻¹ in the aqueous extract.

The range of the calibration curve for ICP-OES was from 0.05 to 1.00 mg L⁻¹ (for all metals analysed), and for all curve points, the final concentration of the yttrium internal standard was 0.50 mg L⁻¹.

2.5. Performance characteristics for the developed analytical procedure

To ensure the efficiency of the ICP-OES assays, the plasma robustness was tested to assess the efficiency of the plasma in ionising or atomising the metals to be determined. Hence, 25 µL of a standard solution of 1000 mg of Mg L⁻¹ (SpecSol, Brazil) was added to 47.5 mL of aqueous extract of crude oil to obtain a final concentration of 0.50 mg L⁻¹. Then, the Mg(II)/Mg(I) intensity ratio was evaluated.

The salinity of the aqueous extracts was assessed in the range of 5.00–100.00 mg kg⁻¹ of NaCl, for the purpose of verifying whether the presence of sodium chloride would influence the determination of the metals Ca, Mg, Sr and Fe. The presence of the yttrium internal standard was evaluated at a concentration of 0.50 mg L⁻¹ and was added to all extracts and to the calibration curve to compensate for the random and systematic errors that are mainly caused by matrix effects. Additionally, the configuration of the radial and axial ICP-OES torches was evaluated, and five wavelengths were used for sodium. The precision parameters determined were the linearity, background equivalent concentration (BEC), limit of detection (LOD) and limit of quantification (LOQ). For these preliminary tests, the aqueous extracts E1 and E2 were used.

Due to the absence of certified material for the crude oil extract samples, the accuracy of the procedure was verified in addition/recovery tests and through comparison of the results obtained for the metals using the ICP-OES and FAAS techniques. The extracts E1 and E2 were employed for the evaluation of these performance characteristics.

For the recovery tests, different aliquots of the aqueous extracts of crude oil were added to five 15 mL polypropylene tubes, along with 5 µL of the standard solutions of Na, Ca, Mg, Sr and Fe (1000 mg L⁻¹) and 0.5 mL of yttrium (Y) (10 mg L⁻¹). Then, each tube was diluted with 0.2% HNO₃ v/v until a final volume of 10.0 mL was obtained, resulting in a final salinity of 10 mg kg⁻¹ in the aqueous extract. The addition/recovery tests helped to assure the efficiency of the proposed procedure.

For the comparative analysis, the FAAS technique was used. For Ca, Mg and Sr, the procedure for determination in the production water samples [20] was applied, in which the sample was diluted with a 0.2% HNO₃ solution v/v and analysed via FAAS. The

determination was performed with a 100 nm burner head and an air/C₂H₂ mixture, although for Sr, the use of an N₂O/C₂H₂ mixture was indicated. For the determination of Na and Fe, the sample preparation procedure was the same as that employed for Ca, Mg and Sr, and the analyses were performed following the standard protocol of the equipment, using a 100 mm burner head and an air/C₂H₂ mixture. The range of the calibration curve for FAAS was from 1.00 to 7.00 mg L⁻¹.

2.6. Evaluation and determination of chloride in crude oil based on its counterions in the aqueous extract

The total decomposition of the crude oil was performed with the purpose of verifying whether the extraction of metals into the aqueous phase using the modified ASTM D 6470-99 method was efficient, evaluating this technique as a sample preparation procedure for the subsequent determination of Na, Ca, Mg, Sr and Fe in the resulting aqueous extract via ICP-OES. The S3, S4 and S5 crude oil samples were used, which generated the digested products D3–D5. A 0.1000 ± 0.0001 g aliquot of crude oil was first homogenised and weighed in a microwave oven quartz flask. Then, 3.0 mL of 68% HNO₃ w/w and 2.0 mL of 30% H₂O₂ w/w were added to the same container. The sample was rested for 10 min and then microwaved using the crude oil program. The microwave oven steps were as follows: 100–500 W for 10 min, 1000 W for 10 min and 0 W for 15 min (cooling). After cooling, the digested products were diluted with ultrapure water to 25 mL in polypropylene tubes.

Finally, the determination of chloride in the aqueous extracts was performed via potentiometric titration, according to the standard ASTM D 6470-99 method [15] for the samples E3–E5, and the results were reported in mg kg⁻¹ of NaCl in crude oil. The chloride concentrations obtained through potentiometry were compared with the chloride concentrations determined based on the chloride counterions (Na, Ca, Mg, Sr and Fe) according to the procedure developed in this study.

3. Results and discussion

3.1. Developed analytical procedure: aqueous extract

The optimal ICP-OES operational conditions for the quantification of Na, Ca, Mg, Sr and Fe in the crude oil aqueous extract were determined using a central composite design, according to Souza et al. [24]. Then, to evaluate whether robust plasma (in which slight changes in the matrix would not cause significant changes in the analyte signal) was obtained under the optimised ICP-OES operational conditions, the robustness of the plasma was assessed [25]. Under the applied operational conditions, the resulting robustness was 17 for the axial torch configuration and 13 for the radial configuration, thus indicating robust plasma for both configurations. The use of the ionic line (280 nm) to atomic line (285 nm) intensity ratio for magnesium (Mg II 280 nm/Mg I 285 nm) is recommended by some authors for the evaluation of plasma robustness [26,27]. Plasma can be considered robust when the Mg II/Mg I intensity ratio is greater than 10 [25]. This robustness can be explained by the high power (1272 W) and low nebulising gas flow rate (0.53 L min⁻¹) employed, which generate appropriate conditions for an efficient atomisation/ionisation process and for the excitation of analytes, even in the presence of saline samples.

To determine the existence of matrix interference, the range of salinity in the extracts was evaluated, as was the use of the internal standard and the torch configuration. In these tests, two crude oil extracts (E1 and E2) were used.

ICP-OES interference can be caused by matrix effects, compromising the precision and accuracy of the results. The introduction of samples with a high salt content to the plasma can cause interference ranging from disturbances in the formation and transport of the aerosol generated to the excitation of analytes as well as plasma extinction [24]. Hence, the salinity of the extracts obtained via the standard ASTM D 6470-99 method should be at a level at which sodium interference is minimised. In the range of salinities evaluated in this study (5.00–100.00 mg kg⁻¹ of NaCl), it was observed that an increase in the extract salinity extinguished the plasma, whereas a decrease in salinity decreased the quantities of minor chemical elements (such as strontium and iron), producing results below the limits of detection. Hence, the salinity that allowed determination of the elements Na, Ca, Mg, Sr and Fe via ICP-OES with a low deviation and good recovery (Table 2) and no plasma extinction was approximately 10 mg kg⁻¹ of NaCl.

Internal standardisation can be applied to minimise and/or compensate for interference in the signal generated by the equipment. Such interference is generally caused by differences between the characteristics of the analytical solution and those of the sample solution [20,23,24]. Hence, Y was evaluated as the internal standard for the developed procedure because the crude oil extract was highly saline. Table 2 indicates that the presence of Y compensated for the random and systematic errors caused mainly by matrix effects, improving the repeatability and accuracy of the measurements (91–120% recovery).

Therefore, calibration curves were prepared with five points for the concentrations 0, 0.05, 0.50, 0.70 and 1.00 mg L⁻¹ for Na, Ca, Mg, Sr and Fe, using Y as an internal standard. Based on the resulting calibration curves, the performance characteristics of the proposed procedure were established. The limits of detection (LOD) and quantification (LOQ) were calculated using the BEC, as it is more appropriate for the ICP-OES [28] technique. The linearity was evaluated according to the coefficient of correlation (R²) for the curve. The recovery percentage was evaluated by directly adding analytes to the aqueous crude oil extracts, with the purpose of verifying the accuracy of the proposed procedure. Table 2 presents the performance characteristics of the proposed procedure, using 0.5 mg L⁻¹ of Y as an internal standard at a salinity of 10 mg kg⁻¹ of NaCl.

The determination of sodium via ICP-OES is hindered by the saturation of the equipment's integration signal. Therefore, a detailed analysis of this element was necessary. Hence, for the determination of sodium, both torch configurations (axial and radial) in ICP-OES were evaluated. The radial configuration was assessed using five wavelengths for sodium. The quantities detected in the determination of sodium using the radial configuration were

Table 2
Performance characteristics achieved for the developed procedure.

Metals	Extracts	Linearity	BEC ^b	LD ^b	LQ ^b	Conc (mg L ⁻¹) ^c	Rec (%)
Na ^a	E1	0.9999	0.89	0.99	3.29	0.460 ± 0.001	91
	E2					0.480 ± 0.001	96
Ca	E1	0.9998	0.08	0.025	0.08	0.550 ± 0.001	110
	E2					0.580 ± 0.001	116
Mg	E1	0.9999	1.5	0.33	1.09	0.530 ± 0.001	106
	E2					0.600 ± 0.001	120
Sr	E1	0.9996	18	0.06	0.20	0.490 ± 0.003	98
	E2					0.490 ± 0.001	98
Fe	E1	0.9993	0.40	0.26	0.87	0.530 ± 0.012	106
	E2					0.540 ± 0.003	108

^a The results for sodium were obtained with the radial torch configuration.

^b Na and Ca concentrations in mg L⁻¹; Mg and Fe in µg L⁻¹; and Sr in ng L⁻¹.

^c Concentration recovered by adding 0.50 mg L⁻¹ of standard solutions of each metal to the aqueous extracts.

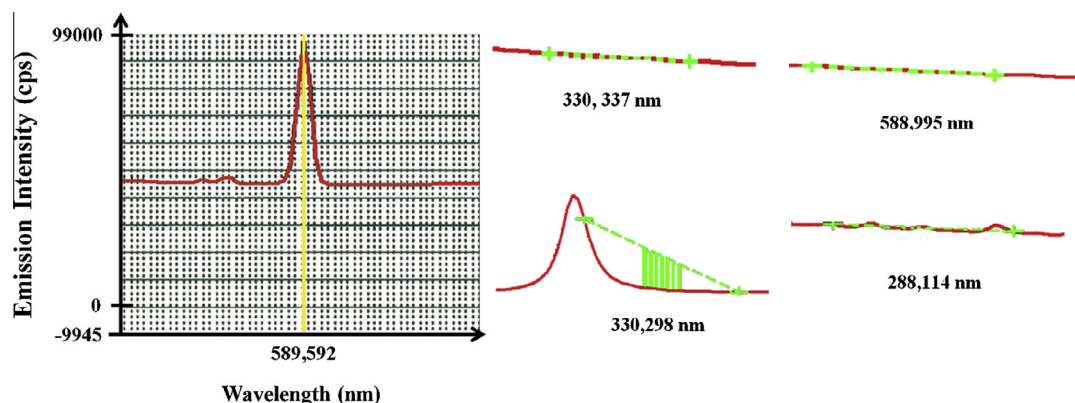


Fig. 1. Spectral line of sodium in the radial view.

significantly higher than those determined with the axial configuration (Table 2). The wavelength of 589.592 nm was chosen because it presented a peak with good integration area and high intensity, as observed in Fig. 1.

The other peaks of the sodium lines did not exhibit sufficient intensity to be used for the determination of this element. Therefore, for the determination of metals, the radial configuration (589.592 nm) was employed for sodium and the axial configuration for the other metals, as shown in Table 2.

Given the absence of certified reference material for the crude oil extract, the accuracy of the proposed experiment was evaluated using a comparative procedure. For this purpose, FAAS was employed to verify the accuracy of the results obtained through the procedure developed in this study. Orthogonal regression was performed for the results of Na and Ca (Fig. 2a) and Mg and Fe (Fig. 2b) determination via ICP-OES and FAAS in the aqueous crude oil extracts E1 and E2.

The determination of metals via ICP-OES and FAAS did not exhibit systematic deviation, with $F = 3.80 < F_{\text{Tab}} = 5.14$ (tabulated), indicating that the metal concentrations determined using the two techniques were in accordance; i.e., the hypothesis of equality of the metal concentrations determined through ICP-OES and FAAS was not rejected.

Orthogonal regression Eq. (1) obtained jointly for Na, Ca, Mg and Fe was as follows:

$$\text{ICP-OES} = 0.143 \pm 0.377 + 1.015 \pm 0.023 \text{FAAS} \quad (1)$$

The correlation coefficient (R^2) of Eq. (1) was 0.9995, indicating a linear trend and high correlation between the results obtained via ICP-OES and FAAS.

The comparison of the results was also evaluated using a two-tailed t test (95% confidence). A total of three ICP-OES readings and five FAAS readings were performed, obtaining $t_{\text{calculated}} < t_{\text{tabulated}}$ for most comparisons between the analytical techniques. Hence, the results of this analysis reinforced the accuracy of the procedure for the determination of Na, Ca, Mg, Sr and Fe through ICP-OES in the crude oil aqueous extract.

3.2. Evaluation of the determination of chloride in crude oil based on its counterions in the aqueous extract

After determining the precision and accuracy of the procedure developed for the determination of the main chloride counterions (Na, Ca, Mg, Sr and Fe) via ICP-OES in the aqueous extract, an analysis was performed to verify the possibility of inferring the chloride concentration in the crude oil from its counterions. Dilution of crude oil samples and its derivatives in organic solvents is the most commonly used traditional method (norms D-4951 [30], D-5185 [31] and D-7260 [32]) for the direct introduction of crude oil samples into inductively coupled plasma equipment (ICP) to determine the metals and non-metals in these matrices. However, the low stability of the analyte after dilution, the carbon deposits formed in the ICP OES plasma (extinguishing it) and the low availability of organometallic standards to plot a calibration curve (which are more expensive and, therefore, less available in laboratories) make the application of this sample preparation procedure unfeasible [21,23]. Thus, microwave-assisted acid digestion has been gaining popularity because it reduces the organic load of crude oil to the maximum, and it is also a fast, efficient procedure (when compared to other decomposition procedures) that can be performed in closed containers, decreasing the loss of volatile analytes and reducing contamination problems [33].

In this sense, the use of microwave acid digestion allows quantitative determination of Na, Ca, Mg, Sr and Fe because the organic matrix is decomposed through this procedure, leaving

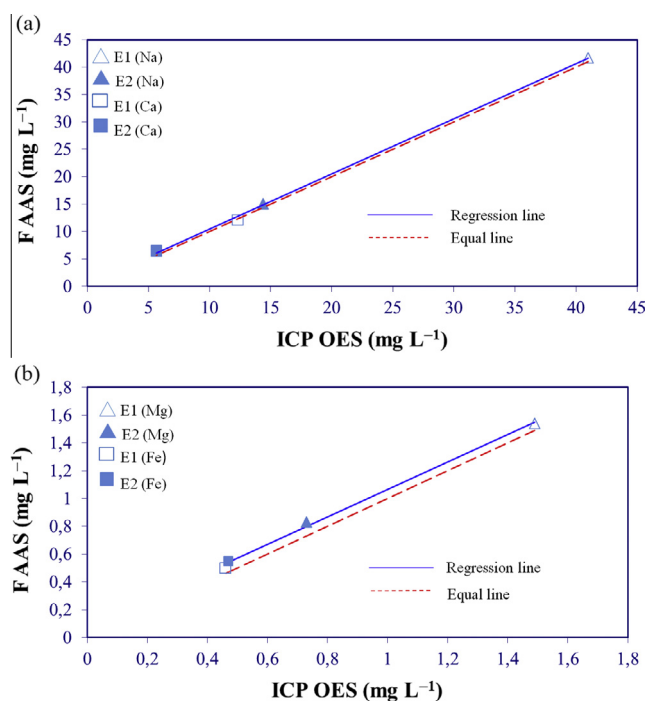


Fig. 2. Orthogonal regression of the results for the determination of (a) Na and Ca and (b) Mg and Fe in the crude oil aqueous extracts via ICP-OES and FAAS. The results for strontium were below the LOD of the FAAS technique, and orthogonal regression was therefore not performed for this element.

Table 3

Na, Ca and Sr concentrations determined via ICP-OES in the E3–E5 aqueous extracts (after extraction using the modified standard ASTM D 6470-99 method) and in the digested products D3–D5 (after microwave acid decomposition of the crude oil).

	Na (mg kg ⁻¹)	Rec (%) ^a	Ca (mg kg ⁻¹)	Rec (%) ^a	Sr (mg kg ⁻¹)	Rec (%) ^a
E3	71.13 ± 2.53	73.16	21.65 ± 1.12	46.74	0.675 ± 0.016	104.17
D3	97.23 ± 1.59		46.32 ± 0.92		0.648 ± 0.001	
E4	79.71 ± 1.17	94.69	22.33 ± 1.65	32.34	0.717 ± 0.044	81.02
D4	84.19 ± 3.01		69.05 ± 2.00		0.885 ± 0.005	
E5	107.60 ± 4.43	92.34	22.21 ± 0.73	26.91	0.972 ± 0.045	77.76
D5	116.52 ± 2.04		82.53 ± 0.98		1.250 ± 0.009	

^a Recovery in relation to the metals determined in the digested products.

the metals available to be determined via ICP-OES in the digested product. The digested product is considered to contain 100% of the metals Na, Ca, Mg, Sr and Fe, whereas in the aqueous extract (obtained using the standard ASTM D 6470-99 method), the presence of metals will depend on their association with the aqueous or organic crude oil phase. Table 3 shows the comparison of the Na, Ca and Sr concentrations determined via ICP-OES in the aqueous extract (after extraction using the modified standard ASTM D 6470-99 method) and in the digested products (after microwave acid decomposition of the crude oil). The digestion of crude oil samples was performed in duplicate. However, the results for Mg and Fe are not presented in Table 3 because these elements exhibited large relative deviations (greater than 10%), indicating a lack of repeatability for these metals.

In general, the elements Na, Ca, Mg, Sr and Fe are present in crude oil as inorganic salts associated with the aqueous phase of oil/water emulsions in crude oil [3–5]. Therefore, it is expected that during extraction using the ASTM D 6470-99 method, these metals will not migrate to the aqueous phase in large amounts. However, Ca, Mg and Fe may be present in crude oil as organometallic compounds, adsorbed either to the oil/water interphase [3,7,29] or to the organic phase of crude oil, preventing their quantitative extraction into the aqueous phase. This characteristic may explain the lack of repeatability observed for Mg and Fe and the low Ca concentration (Ca extraction was below 46.74% in the three aqueous extracts E3–E5 compared with the Ca concentration in the digested products) extracted into the aqueous phase (aqueous extract).

In contrast, Na and Sr were extracted into the aqueous phase in large amounts, especially Na from the extracts E4 and E5 (Na extraction higher than 92.34%) and Sr from the extracts E3 and E4 (Sr extraction higher than 81.06%). This is due to the association of Na and Sr in the aqueous phase of oil/water emulsions in crude oil, such that these metals are extracted into the aqueous phase (aqueous extract) during extraction using the ASTM D 6470-99 method. Comparison of the metal concentrations obtained in the aqueous extracts and digested products revealed that the Na and Sr concentrations in the aqueous extracts were similar to the concentrations of these elements in crude oil. It is not possible to infer the Ca concentration in crude oil based on its determination in the aqueous extract, and total microwave decomposition of the sample is therefore required to obtain a more representative result.

The chloride concentration in the aqueous extract was determined using potentiometric titration. The chloride concentration obtained through potentiometric titration was compared with the chloride concentration inferred from the main counterions present in crude oil (Na, Ca, Mg, Sr and Fe), determined via ICP-OES. Table 4 shows the chloride concentrations determined through potentiometric titration (according to the ASTM D 6470-99 method) and through the indirect analysis of chloride based on its counterions, Na, Ca, Mg, Sr and Fe (results reported in mg kg⁻¹ of NaCl in crude oil).

Based on a comparison of the chloride concentrations obtained via potentiometric titration and through ICP-OES analysis of

Table 4

Comparison of the results obtained through the determination of chloride in crude oil via indirect analysis (through the determination of Na, Ca, Mg, Sr and Fe in the aqueous extract) using ICP-OES and via potentiometry (modified ASTM D 6470-99 method) [4] for samples E3–E5.

Extracts	Crude oil weight (g)	Aqueous extract weight (g)	NaCl (mg kg ⁻¹) ICP-OES	NaCl (mg kg ⁻¹) ASTM D 6470-99	Rec (%) ^a
E3	39.9864	139.5623	253.5550	240.9997	105.10
E4	40.0504	139.6543	277.5432	279.4058	99.33
E5	40.0917	138.9678	351.2033	343.8929	102.12

^a Recovery in relation to chloride, obtained via potentiometry according to modified ASTM D 6470-99 test method.

chloride based on its counterions in the aqueous extract, it was possible to verify that Na, Ca, Mg, Sr and Fe were mainly associated with chloride, forming the salts NaCl, CaCl₂, MgCl₂, SrCl₂, FeCl₂ and FeCl₃. Therefore, because the presence of chloride directly interferes with crude oil refinement and processing, it is an important parameter to be evaluated in refineries as a way to investigate corrosion processes in the crude oil industry.

4. Conclusions

The analytical procedure developed for the determination of chloride counterions (Na, Ca, Mg, Sr and Fe) via ICP-OES in aqueous crude oil extracts following hot solvent extraction of crude oil samples using the modified ASTM D 6470-99 method exhibited adequate precision and accuracy. The obtained robustness (Mg II/Mg I > 10 for the axial and radial configurations), linearity ($R^2 > 0.9993$ for all metals) and LOD (0.99 mg L⁻¹, 0.025 mg L⁻¹, 0.33 µg L⁻¹, 0.06 ng L⁻¹ and 0.26 µg L⁻¹ for Na, Ca, Mg, Sr and Fe, respectively) guaranteed the precision of the developed procedure. The accuracy of the results was confirmed through both the addition/recovery tests (91–120% recovery) and orthogonal regression of the metal concentrations determined via ICP-OES versus FAAS (ICP-OES = 0.143_{±0.377} + 1.015_{±0.023} FAAS, $R^2 = 0.9995$). Additionally, according to the two-tailed *t* test (95% confidence), the hypothesis of equality between the metal concentrations obtained via ICP-OES and FAAS was not rejected.

Na and Sr were extracted into the aqueous phase in a representative manner, especially Na from the extracts E4 and E5 (Na extraction higher than 92.34%) and Sr from the extracts E3 and E4 (Sr extraction higher than 81.06%). This is the result of the association of Na and Sr in the aqueous phase of oil/water emulsions in crude oil, such that these metals are extracted into the aqueous phase (aqueous extract) during extraction using the modified standard ASTM D 6470-99 test method. Finally, comparison of the chloride concentrations obtained via potentiometric titration and ICP-OES (through the analysis of chloride based on its counterions) in the aqueous extract demonstrated that Na, Ca, Mg, Sr and Fe were mainly associated with chloride, forming the salts NaCl, CaCl₂, MgCl₂, SrCl₂, FeCl₂ and FeCl₃. The percent chloride recoveries obtained via ICP OES in relation to the chloride concentrations determined via potentiometry were 105.10%, 99.33% and 102.12% for the extracts E3–E5, respectively. Therefore, because the presence of chloride interferes directly with crude oil refining and processing, chloride should be evaluated and quantified in refineries as a way to obtain new measures to avoid corrosion processes in the crude oil industry.

Acknowledgements

The authors are grateful to Petrobras – Petróleo Brasileiro S.A., ANP – Agência Nacional do Petróleo, Gás Natural e

Biocombustíveis, LabPetro/UFES – Laboratório de Pesquisa e Desenvolvimento de Metodologias para Análise de Petróleo, LEQA/UFC – Laboratório de Estudos em Química Aplicada, CAPES, CNPq and FAPES for supporting this study.

References

- [1] Askea N, Kallevik H, Sjöblom J. Water-in-crude oil emulsion stability studied by critical electric field measurements, correlation to physico-chemical parameters and near-infrared spectroscopy. *J Petrol Sci Eng* 2002;36:1–17.
- [2] Zílio EL, Pinto UB. Identificação e distribuição dos principais grupos de compostos presentes nos petróleos brasileiros. *Bol Téc PETROBRAS* 2002;45:21–5.
- [3] Speight JG. *Handbook of petroleum product analysis*. Hoboken: Wiley-Interscience; 2002.
- [4] Morigaki MK, Chimin RQF, Sad CMS, Filgueiras PR, Castro EVR, Dias JCM. Salinidade em petróleo bruto: otimização de metodologia e proposta de um novo método para extração de sais em petróleo. *Quim Nova* 2010;33:607–12.
- [5] Platteau O, Carrillo M. Determination of metallic elements in crude oil–water emulsions by flame AAS. *Fuel* 1995;74:761–7.
- [6] Maguire-Boyle SJ, Barron AR. Organic compounds in produced waters from shale gas wells. *Environ Sci: Process Impact* 2014;16:2237–48.
- [7] Pereira JSF, Moraes DP, Antes FG, Diehl LO, Santos MFP, Guimarães RCL, et al. Determination of metals and metalloids in light and heavy crude oil by ICP-MS after digestion by microwave-induced combustion. *Microchem J* 2010;96:4–11.
- [8] Pessoa HM, Davis RAH, Campos RC, Castro EVR, Carneiro MTWD, Brandão GP. Determination of Ca, Mg, Sr and Ba in crude oil samples by atomic absorption spectrometry. *J Anal Atom Spectrom* 2012;27:1568–73.
- [9] Barbosa LL, Sad CMS, Morgan VG, Santos MFP, Castro EVR. Time-domain proton nuclear magnetic resonance and chemometrics for identification and classification of Brazilian petroleum. *Energy Fuel* 2013;27:6560–6.
- [10] Pereira JSF, Diehl LO, Duarte FA, Santos MFP, Guimarães RCL, Dressler VL, et al. Chloride determination by ion chromatography in petroleum coke after digestion by microwave-induced combustion. *J Chromatogr A* 2008;1213:249–52.
- [11] Gray MR, Eaton PE, Le T. Inhibition and promotion of hydrolysis of chloride salts in model crude oil and heavy oil. *Petrol Sci Technol* 2008;26:1934–44.
- [12] Sad CMS. Desenvolvimento de metodologia de extração de cloretos em petróleos por aplicação indireta de ultrassom [dissertation]. Brasil: Universidade Federal do Espírito Santo; 2013.
- [13] Chimin RQF. Estudo da evolução de cloretos no processo de destilação de petróleo [dissertation]. Brasil: Universidade Federal do Espírito Santo; 2013.
- [14] Doyle A, Saavedra A, Tristão MLB, Mendes LAN, Aucélio RQ. Spectrometric methods for the determination of chlorine in crude oil and petroleum derivatives – a review. *Spectrochim Acta Part B* 2013;86:102–7.
- [15] ASTM D 6470. Standard test method for salt in crude oils (potentiometric method). West Conshohocken, PA: ASTM International; 2004.
- [16] Vale MS, Lopes GS, Gouveia ST. The development of a digestion procedure for the determination of metals in gum obtained from deposits in internal combustion engines by ICP–OES. *Fuel* 2009;88:1955–60.
- [17] Vogt T, Bauer D, Neuroth M, Otto M. Quantitative multi-element analysis of argonne premium coal samples by ETV-ICP OES – a highly efficient direct analytical technique for inorganics in coal. *Fuel* 2015; <http://dx.doi.org/10.1016/j.fuel.2014.12.057>.
- [18] Souza JR, Santos EF, Duyck CB, Saint-Pierre TD. Comparison of parallel flow and concentric micronebulizers for elemental determination in lubricant oil, residual fuel oil and biodiesel by inductively coupled plasma optical emission. *Spectrochim Acta Part B* 2011;66:356–61.
- [19] ASTM 5863-B. Standard test methods for determination of nickel, vanadium, iron, and sodium in crude oils and residual fuels by flame atomic absorption spectrometry. West Conshohocken, PA: ASTM International; 2005.
- [20] Brandão HMP. Determinação de elementos traço em petróleos e em águas de produção por espectrometria de absorção atômica [dissertation]. Brasil: Universidade Federal do Espírito Santo; 2012.
- [21] Duyck C, Miekeley N, Silveira CLP, Aucélio RQ, Campos RC, Grinberg P, et al. The determination of trace elements in crude oil and its heavy fractions by atomic spectrometry. *Spectrochim Acta B* 2007;62:939–51.
- [22] Pereira JSF, Pereira LSF, Mello PA, Guimarães RCL, Guarnieri RA, Fonseca TCO, et al. Microwave-induced combustion of crude oil for further rare earth elements determination by USN–ICP-MS. *Anal Chim Acta* 2014;844:8–14.
- [23] Souza RM. Desenvolvimento de métodos analíticos para determinação de elementos-traço em amostras oleosas e pastosas por ICP OES e ICP MS [dissertation]. Brasil: Pontifícia Universidade Católica do Rio de Janeiro; 2007.
- [24] Souza MO. Desenvolvimento de um procedimento analítico para determinação dos principais contraíons do cloreto (Na, Ca, Mg, Sr e Fe) em amostras de petróleo por espectrometria de emissão óptica com plasma indutivamente acoplado [dissertation]. Brasil: Universidade Federal do Espírito Santo; 2015.
- [25] Dubuisson C, Poussel E, Mermet JM. Comparison of ionic line-based internal standardization with axially and radially viewed inductively coupled plasma atomic emission spectrometry to compensate for sodium effects on accuracy. *J Anal Atom Spectrom* 1998;13:1265–9.
- [26] Dennaud J, Howes A, Poussel E, Mermet JM. Study of ionic-to-atomic line intensity ratios for two axial viewing-based inductively coupled plasma atomic emission spectrometers. *Spectrochim Acta Part B* 2001;56:101–12.
- [27] Romero X, Poussel E, Mermet JM. The effect of sodium on analyte ionic line intensities in inductively coupled plasma atomic emission spectrometry. *Spectrochim Acta Part B* 1997;52:495–502.
- [28] Thomsen V, Schatzlein D, Mercurio D. Limits of detection in spectroscopy. *Spectroscopy* 2003;18:112–4.
- [29] Matar S, Hatch LF. *Chemistry of petrochemical processes*. 2nd ed. Houston: Gulf Publishing Company; 2001.
- [30] ASTM D 4951. Standard method for determination of additive elements in lubricating oils by ICP-AES. West Conshohocken, PA: ASTM International; 2002.
- [31] ASTM D 5185. Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES). West Conshohocken, PA: ASTM International; 2005.
- [32] ASTM D 7260. Standard practice for optimization, calibration, and validation of inductively coupled plasma-atomic emission spectrometry (ICP-AES) for elemental analysis of petroleum products and lubricants. West Conshohocken, PA: ASTM International; 2012.
- [33] Sánchez R, Todolí JL, Lienemann CP, Mermet JM. Determination of trace elements in petroleum products by inductively coupled plasma techniques: a critical review. *Spectrochim Acta Part B* 2013;88:104–26.