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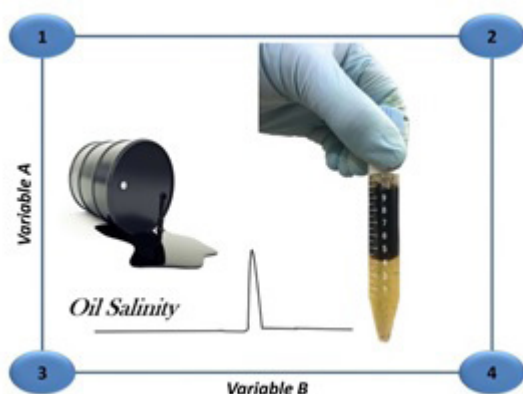
Optimization of Extraction Induced by Emulsion Breaking Variables for Subsequent Determination of Crude Oil Salinity by Ion Chromatography

Anna Carolina de Oliveira Pinheiro Ramos^a, Gabriel Rocha Figueira Caldeira^a, Carolina Ramos de Oliveira Nunes^b, Wagner da Silva Terra^c, Murilo de Oliveira Souza^{a*}  

^aLaboratório de Análises Químicas e Agroambientais (LAQUA). Instituto Federal de Educação, Ciência e Tecnologia Fluminense, Campus Itaperuna, BR 356, km 3, 28300-000, Itaperuna, Rio de Janeiro, Brazil

^bLaboratório de Análise e Monitoramento das Águas. Instituto Federal de Educação, Ciência e Tecnologia Fluminense, Polo de Inovação, 28100-000, Campos dos Goytacazes, Rio de Janeiro, Brazil

^cLaboratório de Petróleo. Instituto Federal de Educação, Ciência e Tecnologia Fluminense, Campus Campos Centro, 28030-130, Campos dos Goytacazes, Rio de Janeiro, Brazil



Due to natural geological oil formation and exploration processes, high amounts of saltwater are emulsified in oil, resulting in high salinity in oil extraction wells. This salinity is due to the presence of non-metals of forming inorganic salt, such as chloride, which, when subjected to high temperatures, tend to react with water vapor to form hydrochloric acid, causing distillation tower corrosion. In this context, extraction induced by emulsion breaking (EIEB) has been as an alternative procedure to the official ASTM D6470 method for chloride extraction and subsequent determination by ion chromatography in oil samples. Thus, the experimental EIEB variables of HNO₃ volume (V) and Triton X-114 mass (T) were optimized using a 2² factorial

design with three central points. The optimal condition obtained for the EIEB and chloride determination was V = 500 µL and T = 0.5000 g. The developed procedure allowed for the assessment of samples presenting different °API (22.9 to 28.8), which originated from the post-salt. Besides, limits of detection of 0.3 – 0.4 mg kg⁻¹ chloride were achieved. The accuracy of the procedure was confirmed by addition/recovery tests (100.4 – 100.7%).

Keywords: Chloride, Ion Chromatography, EIEB, Factorial Design, Corrosion, Refining

INTRODUCTION

Oil is a highly complex mixture consisting of saturated hydrocarbons, aromatics, and polycyclic compounds (resins and asphaltenes), as well as small amounts of organic compounds containing sulfur,

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nitrogen, oxygen and even lower amounts of metal compounds, particularly vanadium, nickel, iron, and copper [1-3]. Its chemical composition may vary from one specific site to another, according to regional and local variations, and the physicochemical processes that occur during its geological origin, thus leading to a wide variety of samples presenting different physicochemical properties [4,5]. Due to this, the determination of certain physicochemical characterization parameters such as density, viscosity, salinity, basic sediment and water contents (BSW); saturated, aromatics, resins and asphaltenes content (SARA), among others, is required in order to propose crude oil transportation and refining strategies [6-8].

Particular emphasis is given to salinity, as high amounts of saltwater are emulsified to the oil through natural oil geological formation processes and exploration and production processes, leading to high salinity values in oil extraction wells [3,9]. This salinity is due to the presence of non-metals that form inorganic salts, with chloride as the main salt-forming anion [9]. In parallel, salts contained in the oil, when subjected to high temperatures, tend to react with water vapor to form hydrochloric acid and, consequently, cause corrosion in oil distillation towers [9,10]. Thus, oil salinity determination should be performed to avoid potential problems during oil distillation and other oil production stages [11].

For the extraction of water in oil, there are several physical techniques, such as gravity or ultrasonic separation, skimming, absorption and filtration [12]. Extraction induced by emulsion breaking (EIEB) can be used for the extraction of emulsified saltwater in oil (aqueous extract), enabling the determination of chloride salts present in this extract. EIEB consists in the formation of oil-in-water emulsions by intense sample agitation (in this case, oil) mixed with an acidified surfactant. After heating, the emulsion ruptures, resulting in an organic phase containing the organic oil fraction and an acidified aqueous phase, the lower portion containing inorganic salts, termed the aqueous extract [13]. EIEB can be an advantageous proposition and an alternative method for the determination of oil chloride salts (salinity). Also, this method presents lower costs and is cleaner, due to the use of smaller sample volumes and organic solvents than the recommended oil salinity determination procedures (ASTM D 6470 [14] and ASTM D 3230 [15]). Besides that, chloride results after EIEB did not differ statistically from those obtained by the most commonly applied official method for the determination of this element in crude oil (ASTM D6470) [16].

Robaina et al. [16] applied the EIEB procedure to transfer the chloride to the aqueous oil phase during the emulsion breaking of oil samples. Chloride determination in the extracts was performed by ion chromatography (IC) using a conductivity detector. Several parameters were evaluated, such as the relation among the oil phase and aqueous phase, crude oil and mineral oil ratio, shaking time, type, and concentration of surfactant that could affect the performance of the method. However, no multivariate statistical procedure was used to evaluate the EIEB variables that could affect the chloride extraction to the aqueous phase and its determination by ion chromatography. Besides that, for extraction of chloride from samples was used mineral oil to solubilize the crude oil. Trevelin et al. [13] developed an analytical procedure for the determination of Ba, Ca, Mg, and Na in heavy oil samples after EIEB. Metal recovery percentages ranged from 99% to 104% and Ba and Na determination results showed good agreement with certified reference material (NIST 1634c) values.

In this context, the present study aimed to evaluate the use of a 2² factorial design with three central points to optimize the variables of extraction induced by emulsion breaking (EIEB) for chloride extraction and subsequent determination by ion chromatography in oil samples. In addition, it is noteworthy that the EIEB was used to extract chloride from four oil samples in order to assess whether studied samples presented salinity exceeding the maximum permissible concentration for oil production refining and processing steps.

MATERIALS AND METHODS

Instrumentation

An ion chromatograph (883 Basic IC Plus, Metrohm, Switzerland) coupled to an autosampler (863 Compact Autosampler, Metrohm, Switzerland) was used for chloride determinations. The calibration curves ranged from 0.1 to 10.0 and 1.00 to 60.00 mg L⁻¹ chloride. Conductivity signals were measured with a heated

DSP conductivity cell and chromatograms were acquired using the MagIC Net 3.1 software. Chloride ion separation was carried out using an analytical column (Metrosep A Supp 5, Metrohm, Switzerland), 150 mm in length with 5.0 μm particle size. A pre-column (Metrosep A Supp 5 Guard, Metrohm, Switzerland), 10 mm in length with 5.0 μm particle size, was used to protect the analytical column. A total of 20 μL were injected for all analyses. The parameters used to perform the analyses are listed in Table I.

Table I. Ion chromatograph operating conditions

Pressure (MPa)	10
Column temperature ($^{\circ}\text{C}$)	25 ± 3
Injected volume (μL)	20
Time (min)	18

A mix stirrer (Phoenix, model AP 56), a heating plate (Centaurus, CAMA-10), and a centrifuge (Edulab, model 80-2B) were used for the EIEB process.

Samples

Different oil samples (S1, S2, S3, and S4) were used, generating aqueous extracts E1, E2, E3, and E4, respectively. All samples were obtained from the Campos dos Goytacazes Basin, in the state of Rio de Janeiro, provided by the Petrobras S.A. Fluid Laboratory, located at the Imbetiba base in the city of Macaé, Rio de Janeiro. Table II presents performed physicochemical characterizations. The physical-chemical characterization parameters were carried out according to the procedure developed by Terra, Martins and, da Cruz (2019) [6].

Table II. Physical and chemical parameters determined in oil samples

Samples	$\rho_{24.2^{\circ}\text{C}}$ (g cm^{-3}) ^a	$^{\circ}\text{API}_{24.2^{\circ}\text{C}}$ ^b	$^{\circ}\text{API}_{15.6^{\circ}\text{C}}$ ^b	μ (mPa s) ^c	BSW (% v v ⁻¹) ^d
S1	0.8825 ± 0.0002	28.8	27.6 ± 0.1	53.3 ± 0.5	0.35
S2	0.8905 ± 0.0002	27.4	26.0 ± 0.1	34.8 ± 0.3	0.25
S3	0.9165 ± 0.0002	22.9	21.6 ± 0.1	127 ± 1	0.10
S4	0.9115 ± 0.0002	23.7	22.5 ± 0.1	304 ± 2	0.10

^a $\rho_{24.2^{\circ}\text{C}}$ specific oil mass in g cm^{-3} , obtained at room temperature (24.2°C); ^b $^{\circ}\text{API}$ (American Oil Institute); ^c μ absolute viscosity determined in a timely and direct manner at room temperature of 24.2°C ; ^d BSW (Basic Sediment and Water).

Material and reagents

Ultrapure water (resistivity = $18.2 \text{ M}\Omega \text{ cm}$) was prepared using a reverse osmosis system with ultraviolet disinfection (OS20LXE, Gehaka, Brazil). Chloride ion standard solutions were prepared by diluting a 1000 mg L^{-1} standard bromide, chloride, nitrate, sulfate, fluoride, and phosphate solution (SpecSol, Sao Paulo, Brazil) with ultrapure water.

Nitric acid 68% m m⁻¹ P.A. (Vetec, Rio de Janeiro, Brazil), sulfuric acid 98% m m⁻¹ P.A. (Dynamics, Sao Paulo, Brazil), sodium carbonate P.A. (Dynamics, Sao Paulo, Brazil), sodium P.A. (Dynamics, Sao Paulo, Brazil), sodium bicarbonate P.A. (Dynamics, São Paulo, Brazil) and Triton X-114 (Nuclear, Sao Paulo, Brazil) were used. Polypropylene tubes (Techno Plastic Products AG, Transadingen, Switzerland) (15.0 mL capacity) were used for the EIEB assessments.

Oil salinity determination

A mass of 3.0000 ± 0.0001 g of each sample was weighed directly into 15.0 mL polyethylene tubes. Then, 500 μ L of concentrated HNO_3 and 0.5000 g of Triton X-114 (optimal conditions) were added to each polyethylene tube – Figure 1(a), which was then made up to 10 mL with deionized water. Subsequently, the tubes were shaken vigorously for 15 minutes using a mix stirrer to form oil/water emulsions. Breaking of the formed oil/water emulsions was achieved by heating for 15 minutes at 80 °C using a water bath. The tubes were then centrifuged for 5 minutes at 3,000 rpm forming two phases, one aqueous containing the extracted chloride and one containing the organic oil portion – Figure 1(b). Finally, a thin-tipped pipette was used; inserting it through the organic phase of oil into the aqueous phase, where the entire aqueous phase formed was removed and weighed. The organic phase was discarded.

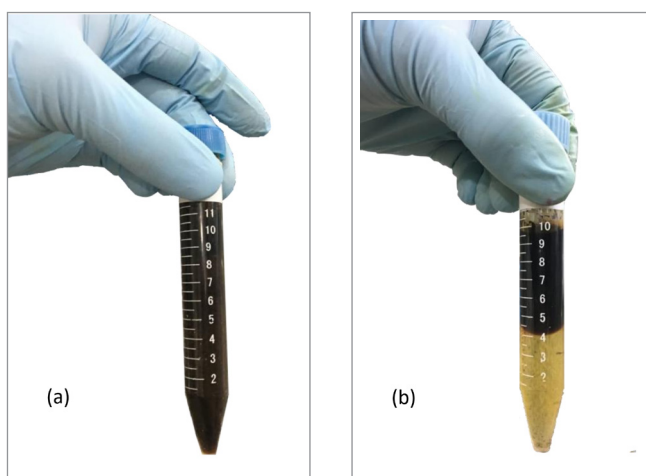


Figure 1. (a) Oil/water emulsion and (b) emulsion breaking (organic phase and aqueous extract E1).

Subsequently, the aqueous extracts were filtered through 0.45 μm cellulose acetate membranes (Filtrilo, Brazil) and diluted 10 times before being injected into the ion chromatography for chloride determination. Oil salinity was reported as mg kg^{-1} NaCl. Preparation blanks of each sample were also analyzed to assess the presence of chloride in water or reagents.

Due to the absence of certified material for oil extract samples, procedure accuracy was verified by chloride addition/recovery tests prior to EIEB. Concerning the recovery tests, a sodium chloride mass (before EIEB) was added to the S1 oil sample to obtain a final concentration of 833 mg kg^{-1} NaCl. Addition/recovery tests aided to ensure the efficiency of the proposed procedure.

Chromatographic conditions

An isocratic method (3.2 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} NaHCO_3) at a flow rate of 0.7 mL min^{-1} was used for chloride separation during the injection stages of the standards for 18 minutes. The chloride peak appeared at 5.610 ± 0.020 min (Figure 2). Sulfuric acid at 0.100 mol L^{-1} was used as a suppressor. Between the injection of each sample, a blank consisting of ultrapure water was injected to clean the column. All aqueous extract (E1 – E4) analyzes were performed in duplicates.

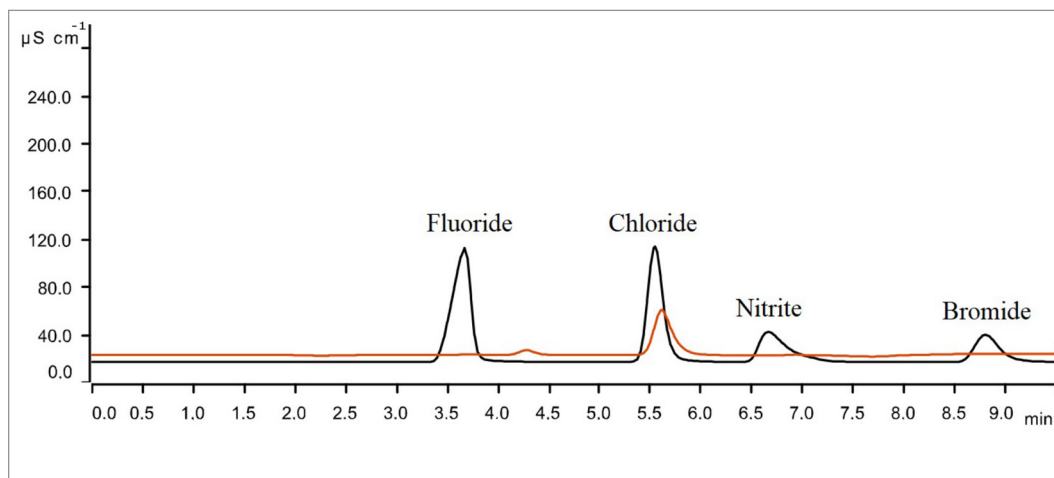


Figure 2. Typical chromatograms of the aqueous extract (E1) diluted 1:10 (red line) and a 60.0 mg L⁻¹ chloride standard solution (black line).

EIEB Variable Optimization

A 2² factorial design with three central points was employed to evaluate the two EIEB variables of the emulsion - breaking extraction procedure: HNO₃ (V) volume and Triton X-114 (T) surfactant mass. A total of seven trials (2^k, k being the number of variables studied in the full factorial design, in this case, 2² = 4; plus three trials at the central point) were performed. The entire optimizing process was performed using Microsoft Excel® 2010 software.

RESULTS AND DISCUSSION

Optimal EIEB conditions

In order to establish the best conditions for chloride extraction from the aqueous oil phase, a 2² factorial design with three central points was employed, evaluating two EIEB variables: HNO₃ (V) volume and Triton X-114 (T) mass. To avoid biased results the experiments were performed randomly. Table III presents the two variables (V and T) and the three studied levels (-1, 0, 1). All factorial design step was performed with oil sample S1.

Table III. Variables and levels assessed in the 2² Factorial Design with three central points

Experiment (sample S1)	Variables		Oil mass (g) ^b	Aqueous extract mass (g) (E1) ^c	Response (mg kg ⁻¹) ^d
	HNO ₃ volume (µL) (V) ^a	Triton X-114 mass (g) (T) ^a			
1	500 (-1)	0.1225 (-1)	3.0253	5.9504	602.4
2	1500 (1)	0.1274 (-1)	3.0127	6.3159	461.7
3	500 (-1)	0.9125 (1)	3.1534	4.2130	478.0
4	1500 (1)	0.8901 (1)	2.9987	5.1196	369.4
5	1000 (0)	0.5362 (0)	3.0153	5.1049	506.9
6	1000 (0)	0.5130 (0)	2.9555	5.0055	513.1
7	1000 (0)	0.5326 (0)	2.9426	4.9038	493.3

^aValues within the parentheses indicate the assessed levels; ^bOil mass (S1) used in each experiment; ^caqueous extract mass (E1) obtained after each EIEB. ^dchloride concentration determined in the aqueous extract (E1), expressed as reported in mg kg⁻¹ oil (S1).

All effects and their experimental errors were then calculated from the responses generated in the complete 2^2 factorial design with three central points. Significant effects were analyzed at 95% confidence by replication at the center point and the t -test with 2 degrees of freedom (t student = 4.303). The significance of each effect was calculated from the multiplication of t student's value of 4.303 by the estimate of the standard error of the effect [5,17]. Figure 3 presents the significant effects of the assessed variables for chloride determination by ion chromatography for sample S1.

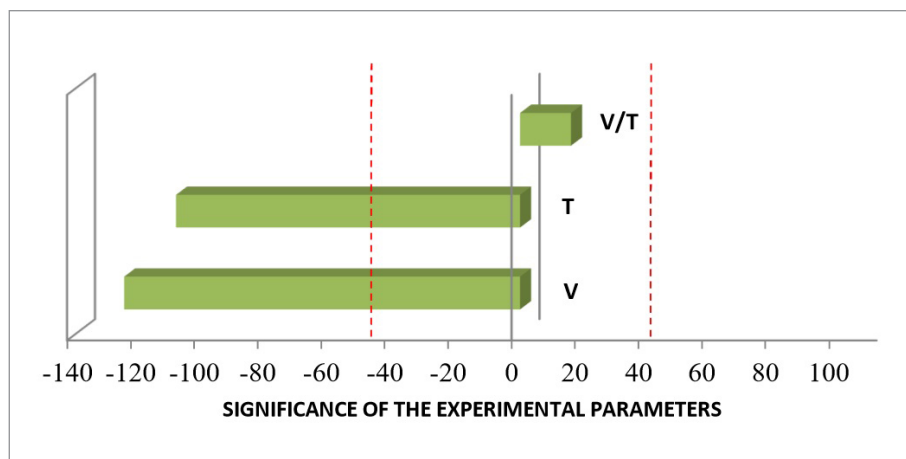


Figure 3. Graphical representation of the significance of the assessed variables: V (HNO_3 volume), T (Triton X-114 mass), and V/T (their interactions) for chloride determination in sample S1 (t student's value \times standard error estimate = ± 43.6).

Variables V and T are significant for oil chloride extraction into the aqueous phase. Triton X-114 (T) is a surfactant used to reduce the surface and interfacial tensions of the medium and facilitate emulsion formation [13,18]. During emulsion formation, the two immiscible liquids (oil/water) are mixed under constant agitation, forming even droplets of one liquid inside the other [19,20]. This oil/water interaction allows inorganic chloride to come into contact with water droplets. During emulsion breaking, these droplets tend to stick together and the liquids separate again, allowing for the chloride to migrate to the aqueous phase. According to Figure 3, better results for chloride extraction would occur with lower Triton X-114 masses, that is, the increase in surfactant concentration decreased the extraction efficiency. Trevelin et al. [13] obtained a maximum extraction for the Ba, Ca, Mg, and Na elements when the surfactant was used at $5\% \text{ m v}^{-1}$ and observed a reduction in the extraction of these elements when were used lower Triton X-114 masses. Robaina et al. [16] used $2.5\% \text{ m v}^{-1}$ of Triton X-114 to the maximum extract of chloride in 0.5000 g of crude oil. Thus, Triton X-114 mass of 0.5000 g ($5\% \text{ m v}^{-1}$), center point, was used in this study to the maximum extract of chloride in 3.0000 g of crude oil, since a mass less than 0.5000 g of this surfactant can make it difficult to form the emulsion (due to the greater mass of crude oil used). In addition, as the V/T interaction was not significant, it is possible to optimize each variable independently and, therefore, only V (HNO_3 volume) was optimized, as it has a more significant effect during EIEB. The variable V (HNO_3 volume) was significant for chloride extraction from the oil sample. In addition, the 2^2 factorial design with three central points indicates that the HNO_3 volume should be decreased to obtain an optimal chloride extraction condition (Figure 3). In this sense, a univariate evaluation was performed, varying HNO_3 volume at five levels (700, 500, 300, 100, and 0 μL), to obtain the ideal volume of this acid for the EIEB (Figure 4).

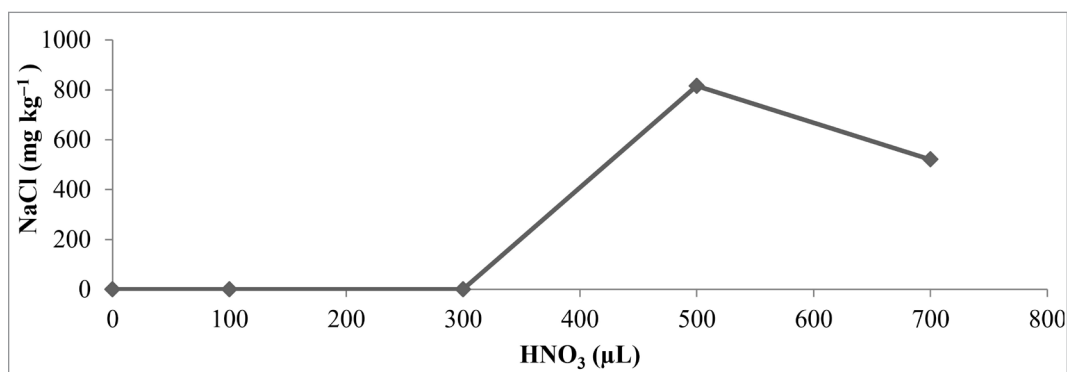


Figure 4. Variation of the extracted chloride to the aqueous phase in relation to the volume of nitric acid used in the extraction for sample S1.

Nitric acid aids in chloride extraction and provides greater stabilization of inorganic species in aqueous media, so that the analyte (chloride) does not precipitate and is not adsorbed to the vial walls [13]. EIEB only occurred at HNO₃ volumes of 500 and 700 μL. The use of the other volumes (300, 100, and 0 μL of HNO₃) did not result in phase separation, indicating that the presence of this acid is important for EIBE. Besides, decreased chloride extraction was observed when using 700 μL of HNO₃, indicating that a volume of over 500 μL is not required for chloride extraction. The high acidity resulting from HNO₃ may increase conductivity during chloride determination by ion chromatography, causing problems during this analysis. Therefore, although a high concentration of HNO₃ may aid chloride extraction, it may also impair its determination during ion chromatography analyses. Thus, V = 500 μL and T = 0.5000 g were used for the EIEB process applied to samples S1 – S4 to establish an ideal condition for chloride extraction and determination.

Oil salinity determination

After optimizing the optimum EIEB condition, chloride concentrations in the S1 – S4 oil samples were determined through chloride determinations in the aqueous extracts (E1 – E4). As chloride concentrations in aqueous extracts from S2, S3 and S4 were much lower than S1, two optimal working ranges (OWR) were obtained for chloride determination by ion chromatography, one with higher chloride concentrations and one with lower chloride concentrations. Table IV presents the performance characteristics of the procedure developed under the optimized extraction condition.

Table IV. Performance characteristics achieved after emulsion breaking induced extraction

Samples	OWR (mg L ⁻¹)	Linearity (r)	Sensitivity	LOD (mg kg ⁻¹) ^b	LOQ (mg kg ⁻¹) ^c	Conc (mg kg ⁻¹) ^d	Rec %
S1	1.0 – 60.0	0.995	0.296	0.3	1.0	829.9 ± 2.9	100.4
S1 rep ^a						827.2 ± 2.0	100.7
S2 – S3	0.1 – 10.0	0.999	0.232	0.4	1.3	ND	ND

^aDuplicate of sample S1 used in the addition/recovery test; ^bLOD limit of detection; ^cLOQ limit of quantification; ^dConcentration recovered from 833 mg kg⁻¹ addition of sodium chloride to oil sample S1 before EIBE. ND, not-determined.

Performance characteristics (linearity, LOD, LOQ, and recovery percentages) for chloride in sample S1 were established from the calibration curves. The concentration of the blank sample was 0.30 ± 0.03 mg kg⁻¹. The LOD was calculated as three times the standard deviation (s) of sample blank noise (s = 0.03 mg kg⁻¹) divided by the slope of the calibration curve (a), i.e. 3s/a, while the LOQ was calculated as 10 times the standard deviation (s) of sample blank noise (s = 0.03 mg kg⁻¹) divided by the slope of

the calibration curve (a), i.e. 10s/a, as defined by the International Union of Pure and Applied Chemistry (IUPAC). Linearity trends were assessed by the curve determination coefficient (r) ($r \geq 0.99$).

Recovery percentages (100.4 – 100.7%) were evaluated to verify the accuracy of the EIEB procedure, indicating a good accuracy (recommended range: 80 to 120%). The obtained concentrations were the result of two equipment determinations (duplicates) and two authentic duplicates (duplicates of the EIEB procedure).

Therefore, after defining the optimal EIEB conditions and performance characteristics, the EIEB process was performed for four oil samples (S1 – S4). Table V presents the chloride results in the aqueous extracts (E1 – E4) using ion chromatography.

Table V. Salinity results obtained (mg kg^{-1} NaCl oil) in oil samples (S1 – S4)

Sample	Oil mass (g)	Aqueous Extract Mass (g)	Chloride (mg L^{-1}) ^a	NaCl (mg kg^{-1})
S1	3.0464	4.5666	333.3 ± 0.8^b	824.6 ± 1.9^c
	3.0489	4.8238	316.8 ± 0.5^b	
S2	2.9600	3.6820	6.8 ± 0.1^b	15.7 ± 2.6^c
	3.0045	5.3150	6.0 ± 0.9^b	
S3	2.9776	5.0511	6.94 ± 0.01^b	16.8 ± 3.7^c
	2.9262	5.1182	4.9 ± 0.1^b	
S4	2.9699	4.9563	6.9 ± 0.1^b	17.3 ± 2.3^c
	2.9503	4.7013	5.95 ± 0.01^b	

^aChloride concentrations in aqueous extracts (E1 – E4) determined in duplicate by the ion chromatograph. ^bStandard deviation of instrument duplicates. ^cAuthentic duplicates of the EIBE procedure.

Samples S2, S3, and S4 presented lower sodium chloride concentrations, although above the LOQ (1.3 mg kg^{-1}), in the extracts (E2, E3, and E4, respectively), ensuring acceptable accuracy and precision. This control is essential, as the maximum salt content, expressed as the sodium chloride mass (mg) dissolved in 1 kg of oil is 570 mg kg^{-1} at the production stage, while refineries establish salt content of below 5 mg kg^{-1} [3,9]. Thus, salinity should be evaluated before refining for all assessed samples S1 – S4. In addition, sample S1 must undergo desalinization processes (NaCl removal) prior to the oil production and refining steps.

CONCLUSIONS

The screening step using a 2^2 factorial design with three central points allowed for the selection of the significant EIEB variables (HNO_3 – V volume and Triton X - 114 mass – T) for chloride extraction for the aqueous oil phase. The optimization of variable V (most significant) was performed in a univariate manner, to obtain the ideal volume of this acid for the EIEB process. High HNO_3 concentrations may facilitate chloride extraction into the aqueous phase. However, residual acidity in the aqueous phase may increase conductivity during chloride determination by ion chromatography, causing problems during the analysis. Interaction (V/T) was not significant for chloride extraction into the aqueous phase. Thus, variables $V = 500 \mu\text{L}$ and $T = 0.5000 \text{ g}$ were established for the EIBE process.

The analytical procedure developed for chloride determination in the aqueous oil phase after EIBE displayed adequate precision and accuracy. Adequate linearity ($r > 0.99$), LOD ($0.3 - 0.4 \text{ mg kg}^{-1}$) and LOQ ($1.0 - 1.3 \text{ mg kg}^{-1}$) guaranteed method precision. Accuracy was confirmed by addition/recovery tests (100.4 – 100.7%). All samples displayed salinity values above the ideal maximum concentration for the oil

refining step (5 mg kg⁻¹). Besides, one of the studied samples presented salinity exceeding the maximum permissible concentration for oil production steps, of 570 mg kg⁻¹. Therefore, as the presence of chloride directly interferes in oil refining and processing, it should be assessed and determined in refineries as a means of obtaining new measures to prevent corrosion processes in the oil industry.

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