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A Simple and Green Analytical Alternative for Chloride Determination in High-Salt-Content Crude Oil: Combining Miniaturized Extraction with Portable Colorimetric Analysis

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Abstract: A simple and miniaturized protocol was developed for chloride extraction from Brazilian pre-salt crude oil for further salt determination by colorimetry. In this protocol, the colorimetric analysis of chloride using digital images was carried out in an aqueous phase obtained after a simple and miniaturized extraction carefully developed for this purpose. A portable device composed of a homemade 3D-printed chamber with a USB camera was used. The PhotoMetrix app converted the images into RGB histograms, and a partial least squares (PLS) model was obtained from chemometric treatment. The sample preparation was performed by extraction after defining the best conditions for the main parameters (e.g., extraction time, temperature, type and volume of solvent, and sample mass). The PLS model was evaluated considering the coefficient of determination (R^2) and the root mean square errors (RMSEs)—calibration (RMSEC), cross-validation (RMSECV), and prediction (RMSEP). Under the optimized conditions, an extraction efficiency higher than 84% was achieved, and the limit of quantification was 1.6 mg g^{-1}. The chloride content obtained in the pre-salt crude oils ranged from 3 to 15 mg g^{-1}, and no differences (ANOVA, 95%) were observed between the results and the reference values by direct solid sampling elemental analysis (DSS-EA) or the ASTM D 6470 standard method. The easy-to-use colorimetric analysis combined with the extraction method's simplicity offered a high-throughput, low-cost, and environmentally friendly method, with the possibility of portability. Additionally, the decrease in energy consumption and waste generation, increasing the sample throughput and operators' safety, makes the proposed method a greener approach. Furthermore, the cost savings make this a suitable option for routine quality control, which can be attractive in the crude oil industry.

Keywords: petroleum; salt determination; green analytical chemistry; miniaturized detection system; colorimetric analysis

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1. Introduction

Corrosion in pipes, valves, and pumps is the most common form of damage in petroleum refineries. This is related to corrosive compounds such as the hydrochloric acid produced from the thermal decomposition of chlorinated compounds (even at low concentrations). These compounds can naturally be present in crude oil in organic or, most commonly in inorganic form (as a salt). In addition, saline deposits can cause clogging, which can hamper heat exchange units and reduce thermal efficiency, resulting in a series of related problems such as energy consumption increase. Furthermore, if salts remain until catalytic cracking, they can poison catalysts reducing their efficiency [1]. The concentration of corrosive salts in crude oil, such as sodium, magnesium, and calcium chloride, is mainly related to the oil origin [2], and the knowledge of salt concentration in samples from different reservoirs are of concern.

While the determination of salt in crude oil is mandatory, it is considered a challenge to the industry. Some official standard methods by the American Society for Testing and Materials (ASTM) can be used for this purpose, such as ASTM D 6470 and ASTM D 3230 [3,4], and some literature protocols also offer options. The most common protocol (ASTM D 6470) is based on extraction of chloride using a mixture of organic solvents (isopropyl alcohol, xylene, and acetone) under heating, with final chloride determination by potentiometric titration. In spite of the assured accuracy and precision, the low throughput, the consumption of large amounts of toxic reagents, the waste generation (more than 350 mL per run), and the safety risks associated with heating toxic solvents [5] constitute clear disadvantages of this protocol. ASTM D 3230 states that oil conductivity is related to the presence of sodium, calcium, and magnesium salts (mostly in the chloride form). Conductivity is thus measured after dissolving crude oil in xylene and adding a mixture of alcohols and water [4]. Although the analysis time is shorter compared to the ASTM D 6470 standard method, the use of organic solvents and the smaller application range are the main disadvantages of this protocol. In addition, calibration standards similar to the samples must be used to avoid matrix interference, making it difficult to use this method in laboratories, which routinely work with oils with different properties and salinity [5].

Several techniques can be used to perform chloride determination, such as ion chromatography (IC) [6–9], inductively coupled plasma-based spectrometric techniques such as optical emission (ICP-OES) [9,10] and mass spectrometry (ICP-MS) [9,11], conductivity [4,12–14], potentiometric titration [5,15], energy-dispersive X-ray fluorescence spectrometry [16], as well as precipitation [12]. Undoubtedly, the most extensive sample preparation approach investigated is based on the extraction of chloride from crude oil prior to quantification. Some reports suggest carrying out salt extraction using hot water after oil solubilization in a range of organic solvents (acetone, xylene, 2-propanol, toluene, ethanol), with quantification by potentiometric titration [5] or by the Volhard method [17]. Indirect estimation can also offer an alternative method to determine the chloride concentration, by determining the contents of Na, Ca, Mg, Sr, and Fe by ICP-OES [18]. Emulsion breaking was also investigated, resulting in an aqueous extract for direct injection into the IC [7,19]. However, some inherent disadvantages limit the choice of such protocols depending on the circumstances, such as the equipment and its high maintenance cost (ICPs and IC), the time-consuming sample preparation protocol required, and the manipulation of large amounts of toxic solvents (extraction).

Alternative protocols have been proposed to avoid or minimize these problems. The ideal protocol must align with the 12 principles of green analytical chemistry (GAC), which promote the minimization of waste generation and the reduction of sample amount. It is similarly recommended that toxic reagents be eliminated or replaced, that reagents from renewable sources be prioritized, and that derivatization be avoided. The selection of direct analytical techniques, the integration of analytical processes and operations, never wasting energy, and the enhancement of operator safety are also included in the GAC principles. In addition, the reuse or recycling of materials are also desirable [20–30]. In the context of the petroleum industry, some principles of green chemistry are hard to achieve, especially following the traditional procedures as described by ASTM. These methods require, in general, a large number of steps and use large sample amounts, are carried out using toxic reagents, and generate large quantities of waste, and the sample throughput is low for most of them.

Some alternatives have been reported in the literature, such as digital image-based methods. These methods, mainly using colorimetry with a smartphone for image acquisition, can offer an excellent approach to overcome the disadvantages and provide low-cost and time-saving analyses. In addition, the potential for on-site analysis, automation, miniaturization, a reduced amount of sample for analysis, and reduced generated residues agree with GAC. Also, real-time results and operators' safety are general characteristics of such methods, which present easy-to-use protocols for the crude oil industry and are aligned with GAC aspects [31].

These image-based methods are based on color changes due to the analyte's presence, and their intensity depends on the concentration. Printing new devices (with different geometries) and evaluation of chemical reaction parameters (ratio of reagents, time, temperature, and others) are the most common optimizations. The parameters for image acquisition (e.g., focal length, image illumination, acquisition time, and others) are also commonly investigated [32–34]. When using equipment from different manufacturers, some optimization may be necessary to overcome hardware limitations and differences in the image acquisition devices.

As colorimetry with digital images depends on color changes, some drawbacks arise from its application with more complex matrices or those with pronounced coloration (the colorimetric reaction may not be distinguished in colored samples) [35]. In this context, in most cases, it is necessary to perform a sample pretreatment (such as extraction, pre-concentration, or clean-up), converting the sample to an aqueous solution suitable for the colorimetric chemical reaction. These limitations can impair the application of this approach for crude oil because this is an organic-based matrix and presents a very pronounced color [33]. Thus, to separate the analyte from the matrix and allow the colorimetric reaction, sample preparation becomes necessary [36]. In a previous report, the suitability of colorimetric determination of salt in aqueous extracts from crude oil using a PLS model, with an endoscopic camera and PhotoMetrix UVC app, was demonstrated [37].

This work was aimed at the development of a miniaturized protocol for chloride extraction from high-salt-content crude oil for further determination by colorimetric analysis. Sample preparation parameters were optimized, such as the sample mass, the solvent volume, the temperature, and the extraction time, by means of univariate and multivariate experiments by the response surface methodology (RSM). The PhotoMetrix PRO app was used for obtaining, processing, and converting digital images into analytical models using chemometric tools.

2. Materials and Methods

2.1. Instrumentation

For extraction and phase separation, an orbital shaker (model TE-420, Tecnal, Piracicaba, Brazil) and a centrifuge (model 3K30, Sigma, Osterode am Harz, Germany) were used. An analytical balance (model AG 245, Mettler Toledo, Polaris Pkwy, OH, USA, 0.0001 g of precision) was used. Reference values for the salt content in crude oil were determined according to the ASTM D 6470 standard method with an automatic titrator (model 6.0502.180, Metrohm, Herisau, Switzerland).

The total chloride content for results comparison was determined using an elemental analyzer [38] (Multi EA® 5000, Analytik Jena, Jena, Germany) equipped with a combustion furnace (multi-purpose combustion tube, part number 402-889.510), a quartz boat (40 mm × 9 mm, part number 402-889.674), and a sampler (Multi-matrix sampler MMS 5000) with an automatic introduction module (Automatic Boat Drive, ABD, Analytik Jena). A module for micro coulometric detection of chloride (Analytik Jena) was used. Analytical signals were monitored as the peak area with a maximum integration time of 1200 s. A quartz fiber membrane (part number 402-889.039) was placed on the quartz boat for calibration with standard solutions.

Colorimetric analysis was carried out using a miniaturized and portable device previously designed (Solidworks® 3D Premium 2008, Waltham, MA, USA) and 3D printed (Core A3 V2, GTMaX 3D, Americana, Brazil) in thermoplastic polylactic acid. A transparent polypropylene flask (2.0 mL Eppendorf type, round bottom, Cralplast, Cotia, Brazil) was positioned in the center as in previous reports [34]. This homemade apparatus was used for the colorimetric analysis using a USB camera (SmartCam, endoscope model, 640 × 480-pixel resolution, B-MAX, São Paulo, Brazil) and a light-emitting diode (LED, 6 W).

2.2. Reagents

All reagents were PA-grade unless specified. Ultrapure water (Milli-Q system, resistivity of 18.2 MΩ cm, Millipore, Burlington, MA, USA) was used to prepare standards and calibration solutions for potentiometric and colorimetric determination. Mineral oil, kerosene (Guanabara, São José dos Pinhais, Brazil), and toluene (Synth, Diadema, Brazil) were used to clean materials. Different solvents were evaluated for chloride extraction, such as xylene (Neon, Suzano, Brazil), toluene (≥99.5%, Sigma-Aldrich, Burlington, MA, USA), kerosene (≥98%, ACS Científica, Sumaré, Brazil), isopropyl alcohol (≥99%, Vetec, Rio de Janeiro, Brazil), acetone (≥99.5%, Dinâmica, Indaiatuba, Brazil), and ethyl acetate (≥99.7%, Merck, Darmstadt, Germany).

An aqueous chloride standard solution (1000 mg L^{-1}) was prepared by dissolving sodium chloride (≥99%, Vetec, Rio de Janeiro, Brazil) in ultrapure water, and other solutions for calibration were prepared by sequential dilution with water. Reagent-grade $AgNO_3$ (≥99.9%, Vetec) and K_2CrO_4 (≥99.5%, Merck) were used for colorimetric reaction.

For the determination by DSS-EA, a 30:70% ($w\ w^{-1}$) ethanol:toluene (both with purity ≥99.5%, Merck) mixture was used for crude oil solubilization. A 1000 µg g^{-1} standard solution (ASTM-P-0092-10X in 75 cst mineral oil, AccuStandard, New Haven, CT, USA) was diluted in toluene (≥99.5%, Merck) to obtain a 100 µg g^{-1} chloride solution and used to prepare the calibration curve (ranging from 10 to 100 µg g^{-1} chloride), also in toluene. An electrolyte solution (65 mL; 0.03 mol L^{-1} sodium acetate (≥99%, Vetec) and 13.9 mol L^{-1} glacial acetic acid (≥99.7%, Vetec) in water) was used in the coulometric cell with sulfuric acid (95–98%, Sigma-Aldrich) for drying.

2.3. Samples

To optimize the colorimetric chloride determination in aqueous extracts, natural crude oil emulsions were used, and two oil samples were arbitrarily selected to optimize the extraction protocol: CO1 and CO2. Robustness and accuracy were evaluated using other natural crude oil samples (CO3, CO4, CO5, CO6, CO7, and CO8), which were obtained from Brazilian crude oil producers for research purposes. Samples were characterized by standard protocols, either the ASTM D 4377 standard method by Karl Fischer titration for the water content, or the ASTM D 4807 standard method for the sediment content (with a 0.45 µm porosity membrane). The water and sediment contents for the set of samples evaluated in this work are presented in Table 1, as well as the salt content obtained according to ASTM D 6470, as described in Section 2.4.1.

Table 1. Water, sediment, and salt contents in crude oil investigated in this work.

Sample	Water, % ($w\ w^{-1}$)	Sediment, % ($w\ w^{-1}$)	Salt, % ($w\ w^{-1}$) [a]	Chloride, mg g^{-1}
CO1	2.52 ± 0.05	1.15 ± 0.12	0.685 ± 0.067	4.16 ± 0.41
CO2	2.77 ± 0.16	0.96 ± 0.17	0.915 ± 0.084	5.56 ± 0.51
CO3	8.22 ± 0.02	0.558 ± 0.032	nd	nd
CO4	5.55 ± 0.03	0.864 ± 0.014	nd	nd
CO5	8.74 ± 0.14	3.42 ± 0.14	2.78 ± 0.09	16.8 ± 1.9
CO6	3.48 ± 0.01	0.708 ± 0.073	0.539 ± 0.038	3.27 ± 0.23
CO7	6.49 ± 0.10	2.33 ± 0.19	0.950 ± 0.09	5.77 ± 0.56
CO8	2.15 ± 0.01	0.168 ± 0.012	0.560 ± 0.132	3.40 ± 0.80

[a] expressed as NaCl, according to ASTM D 6470. nd = not determined (insufficient amount of sample).

2.4. Determination of Chloride in Crude Oil for Comparison Purposes and Accuracy Evaluation

2.4.1. Salt Determination by ASTM D 6470

Salt determination was carried out to obtain reference values for chloride according to ASTM D 6470. Briefly, 40 ± 0.1 g of oil was dissolved in 70 mL hot xylene (65 ± 5 °C) and transferred to a round-bottomed flask fitted with a reflux condenser, in a heating mantle under magnetic stirring. After the complete dissolution, 25 mL of isopropyl alcohol, 15 mL of acetone, and 125 mL of ultrapure water were added, and this mixture was boiled for 15 min. After separating the phases (between 5 and 10 min), the aqueous fraction was filtered, and chloride was determined by potentiometric titration.

2.4.2. Chloride Determination Using DSS-EA

Reference values for chloride were also obtained by DSS-EA. After a simple evaluation of sample solubility and its influence on the results, a mixture of ethanol:toluene (30:70%, $w\ w^{-1}$) was used for crude oil solubilization. Samples were directly weighed in a 1.5 mL glass bottle, and some of the solvent mixture was added. The flasks were placed in the analyzer's auto-sampler, and the sampling was carried out using the automatic system.

2.5. Sample Preparation and Colorimetric Chloride Determination

To carry out a simple and miniaturized extraction procedure, a simple shaker with moderate heating was used. For the first set of experiments, 0.25 to 1 g of sample CO1 and CO2 was extracted in polypropylene vessels (15 or 50 mL) with water (5 mL) at 50 °C, by 30 min, at 200 rpm. The influence of adding an organic solvent to improve extraction was evaluated by mixing 2 mL of toluene or, alternatively, the other solvents. At the end, the extracts were centrifuged to separate the aqueous phase (5 min, 6000 rpm) for chloride determination. To optimize sample preparation conditions, a central composite design (CCD) with 27 experiments covering the range of sample masses, extraction times, temperatures, and solvent volumes was carried out (see Table S1). The CCD was performed using sample CO1, included 8 axial points and 3 repetitions (central point). StatSoft Statistica Enterprise Software (version 10.0, 2010 Oklahoma, OK, USA) was used for data treatment. Additionally, statistical evaluations were performed by ANOVA testing with a 95% ($p > 0.05$) confidence level. The confidence level of 95% offers a reasonable degree of assurance that the data represent the true population, while reducing the probability of rejecting a true hypothesis.

To obtain the calibration curve ranging from 0 to 500 mg L^{-1}, successive dilutions were performed using a chloride standard solution (1000 mg L^{-1}, previously prepared). The RGB histograms were used to obtain the partial least square (PLS) chemometric model directly from the app. For image acquisition, the aqueous sample extract or standard (0.5 mL) was mixed with $AgNO_3$ (100 mmol L^{-1}, 85 µL) and K_2CrO_4 (5% $w\ v^{-1}$; 30 µL) in the microtube (Figure 1, in detail). All images were taken immediately after the mixture of reagents, with a, ROI of 64 × 64, 80 lux, and 2.19 cm focal distance following a previous report [37]. The portable homemade 3D-printed device used in this work was equal to that developed by Costa et al. (2021) and used for the determination of four adulterants (chloride, hypochlorite, hydrogen peroxide, and starch) in raw milk as a proof of concept [34]. Figure 1 shows a view of the portable device and a schematic representing the image acquisition step, and Figure S1 shows a complete flow chart of the protocol.

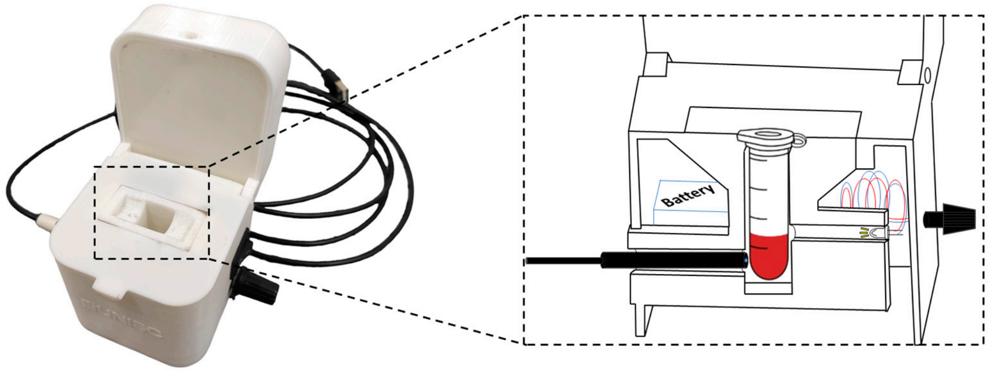


Figure 1. Schematic showing the apparatus optimized in this work for colorimetric analysis of chloride in crude oil aqueous extracts obtained by a miniaturized sample preparation protocol.

3. Results and Discussion

3.1. General Optimization of Sample Preparation for Colorimetric Chloride Determination: Optimizing the Conditions for an Aqueous Extract

The possibility of obtaining an aqueous extract by mixing and heating the sample with water and solvents, as recommended in ASTM D 6470, was the starting point from which we set out to optimize a miniaturized protocol. Previous work demonstrated that this can be feasible with water and a demulsifier, but without a solvent, the extraction efficiency can be poor, depending on the sample characteristics [37]. Then, extraction using water and a small portion of the toluene was briefly investigated, based on the solvents used when following ASTM-D 6470. Despite acetone and isopropyl alcohol are mixed to toluene in the standard method, this work seeks for a condition in agreement with GAC thus avoiding the use of toxic solvents or at least minimizing the amount and the complexity of the generated laboratory waste. The extraction efficiency was evaluated using different extraction setups: 15 or 50 mL polypropylene flasks and a sample amount from 0.25 to 1 g, at fixed extraction conditions. For all investigations, the chloride content was quantified in the aqueous phase (after the extraction) by potentiometric titration using $AgNO_3$. The chloride content obtained was then compared to reference values (by ASTM D 6470), and the extraction efficiency was calculated.

Extraction efficiencies were about 55% and 83% for crude oils CO1 and CO2, respectively, using the lowest sample mass (0.25 g) and the 50 mL extraction flask. In addition, using a higher sample mass (1 g) with the smaller flask (15 mL) resulted in lower extraction efficiencies (7 and 35% for crude oils CO1 and CO2, respectively). Those results demonstrated that extraction efficiency was impaired, probably because the analyte distribution was affected. Then, the larger flask (50 mL) and an intermediate sample mass (0.5 g) were selected to evaluate the effect of using toluene or other solvents for sample dilution.

Mineral oil, kerosene, xylene, ethyl acetate, acetone, and isopropyl alcohol were investigated (2 mL for 0.5 g of crude oil), considering that the influence of the solvent could circumvent the poor extraction of chloride for some samples. As the addition of an organic solvent can affect the harmful impacts of the procedure on the environment and the analyst, some options were investigated, looking for a greener approach. After diluting the sample with the solvent, the extraction was performed with water (5 mL), for 30 min at 50 °C and 200 rpm. Finally, chloride was determined in the aqueous phase by potentiometric titration. The best results were obtained using ethyl acetate, acetone, and isopropyl alcohol, as shown in Table 2, which includes results for other solvents.

Table 2. Extraction efficiency of chloride from crude oil for several organic solvents investigated for sample dilution (results in %, mean ± standard deviation, n = 3) using water for extraction (2 mL of solvent, 0.5 g of sample, 5 mL of water, 50 °C, 30 min, 200 rpm).

Condition	Extraction Efficiency, %	
	Crude Oil CO1	**Crude Oil CO2**
Mineral oil	69.1 ± 4.7	10.5 ± 1.7
Kerosene	43.4 ± 3.3	30.7 ± 4.5
Toluene	71.0 ± 4.2	53.0 ± 0.1
Xylene	93.7 ± 4.4	48.2 ± 6.0
Ethyl acetate	97.6 ± 3.8	98.1 ± 0.8
Acetone	99.2 ± 5.0	106 ± 5
Isopropyl alcohol	108 ± 4	97.4 ± 3.7
Without solvent	23.3 ± 4.0	0.964 ± 0.015

It is possible to see from the results in Table 2 that the extraction efficiency was poor when no solvent was used (only water). Considering safety aspects, ethyl acetate was revealed to be a suitable choice. According to the Solvent Selection Guide (SSG) [39], ethyl acetate is considered "preferred" by AstraZeneca and GlaxoSmithKline. Its use is "recommended" by the Sanofi institute, and it is "usable" according to the American

Chemical Society Green Chemistry Institute Pharmaceutical Roundtable® (ACS GCI-PR). These institutes consider the Safety, Health, and Environment (SH&E) criteria for the classification of solvents. Additionally, the CHEM21 guide classifies ethyl acetate as "recommended". This guide was proposed to align with the Global Harmonized System (GHS) and European regulations [40]. Therefore, based on the extraction efficiency and the mentioned classifications, ethyl acetate was chosen as the solvent for the next experiments.

The influence observed in the first set of experiments suggested that an appropriate experimental design could be carried out. Analysis of variance (ANOVA) was used for a general optimization of the miniaturized extraction protocol with the simple sample plus solvent mixed with water approach. The Fisher test (F-value) and the probability (*p*-value) statistical significances were considered. The standardized Pareto chart (see correlations in Figure S2) shows that no independent variable significantly influenced the chloride extraction (even with $p = 0.1$).

However, when evaluating the chloride content (mg g^{-1}, shown in Table S2, determined by potentiometric titration), it was observed that the chloride extraction efficiency was higher than 70% ($w\ w^{-1}$) in 16 experiments (that means about 60% of all experiments). The best condition, resulting in 87% efficiency, was used to extract chloride from other oils (CO1 to CO8, n = 3) and evaluate the protocol's accuracy. No statistical differences (95% of confidence level, ANOVA) were observed between the results when using this optimized extraction method and the reference results produced by DSS-EA (Figure 2).

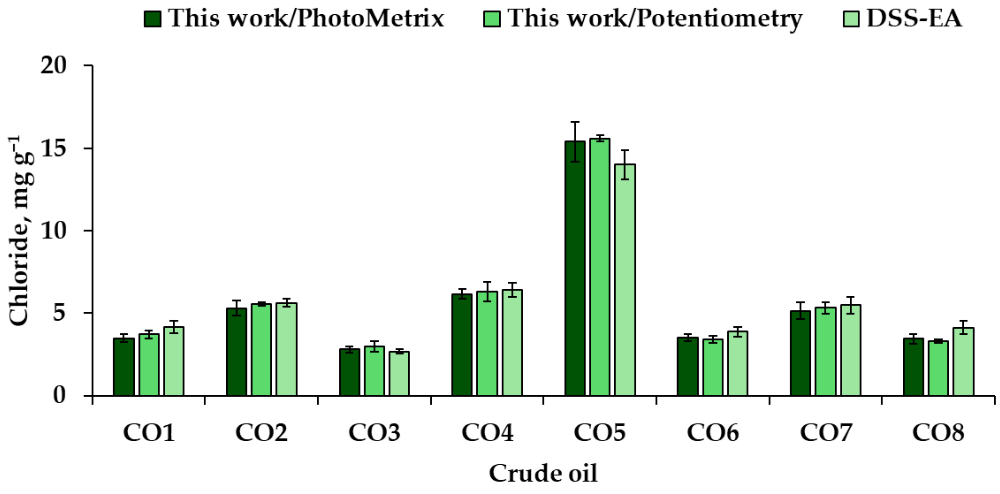


Figure 2. Results for chloride in aqueous extracts from crude oils produced by colorimetric analysis with the portable device or by potentiometry (0.7 g of sample, 35 min at 55 °C, with 1 mL of ethyl acetate as the solvent and 5 mL of water as the extraction solution), and reference values produced by DSS-EA (results in mg g^{-1}, mean ± standard deviation, n = 3).

In comparison to classical extraction methods, as with the conditions of ASTM D 6470 that require heating crude oil with a mixture of organic solvents, the miniaturization of the proposed extraction method by more than 1500 times clearly contributed to minimizing the waste generation. Although a small amount of organic solvent (1 mL of ethyl acetate) was required, according to Tobiszewski [39], this solvent is less toxic than the xylene used in ASTM D 6470.

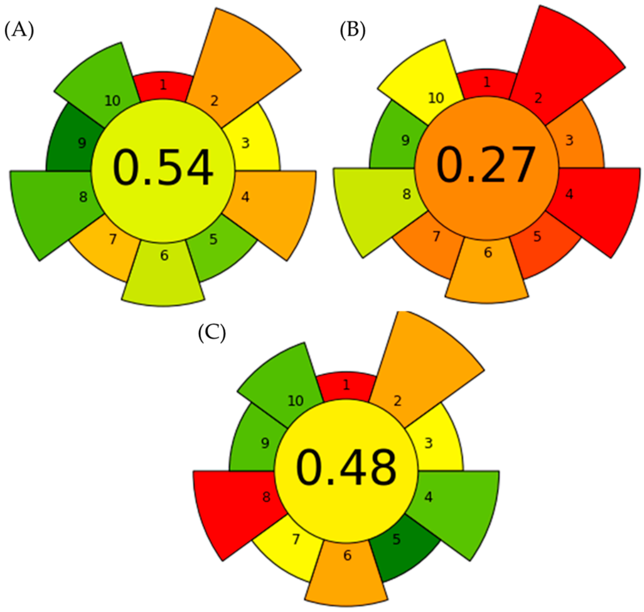
3.2. Colorimetric Analysis of Chloride in Crude Oil Aqueous Extracts: Combining Miniaturized Extraction Protocol and the Portable Device for Detection

Colorimetric analysis was carried out for a set of samples after extracting chloride under optimized conditions. The calibration curve was obtained using more than 30 samples for calibration, with the PLS chemometric model obtained directly from the PhotoMetrix app. An R^2 of 0.999 (with five factors), an RMSEC of 9 mg L^{-1}, an RMSECV of 51 mg L^{-1}, and an RMSEP of 22 mg L^{-1} were obtained. The results were compared with those produced by DSS-EA as well as with chloride, considering the salt content obtained by ASTM D 6470 (Table 1). Furthermore, to evaluate the accuracy of the colorimetric analysis of chloride using the PhotoMetrix app after extraction, chloride determination in extracts was also carried out by potentiometric titration with $AgNO_3$ (reference technique), and the results were compared. These results are shown in Figure 2.

As shown in Figure 2, the chloride content in crude oil ranged from 3 to 15 mg g^{-1}, and no statistical differences (95% confidence level, ANOVA) were observed among methods for all the samples. Although the chloride concentration is higher than those normally reported in the literature (sometimes lower than 1 mg g^{-1}) [7,11,15,41,42], other reports have already demonstrated chloride concentrations higher than 5 mg g^{-1} in some crude oils [6,9,10,37]. While there are no reports in the literature covering chloride determination in high-salt-content crude oils such as those analyzed in this study, some reports describe its determination in general Brazilian crude oils. However, in these studies, the use of specialized and more expensive techniques (in comparison with the proposed portable method) is demonstrated, such as ion chromatography [7,19], high-resolution atomic absorption spectrometry [42], and energy dispersive X-ray fluorescence spectrometry [16]. The salt concentration in crude oil depends on the reservoir's origin [2], and one of the characteristics of oils derived from the pre-salt region is the high salt content [37]. This is unfavorable for the crude oil industry due to corrosion of pipes, pumps, and valves [1]. For this reason, the chloride salts must be removed before distillation, and the content must be monitored during refining steps in accordance with industry trends and green analytical chemistry [1,2]. This demonstrates the applicability of the optimized method for samples with different salt contents and different physicochemical properties (water content ranging from 2 to 8%, and sediment content ranging from 0.17 to 3.4%). The extraction efficiency was better than 84%, considering the results obtained using the PhotoMetrix app and DSS-EA. In addition, the relative standard deviation (RSD) using the PhotoMetrix app was lower than 9.7%, the limit of detection (LOD) was 0.5 mg g^{-1}, and the limit of quantification (LOQ) was 1.6 mg g^{-1}.

Finally, green sample preparation (GSP) aspects based on the AGREEprep calculator [43] were evaluated taking into account the aspects of the proposed method (miniaturized extraction plus colorimetric determination) and those from the ASTM D 6470 standard method or DSS-EA. This tool is based on ten principles of GSP, in total agreement with GAC. Each of the ten individual steps presents a default weight ranging from 0 to 1. Through this approach, these scores are combined to yield the overall score (also ranging from 0 to 1), with the value 1 attributed to the best performance. The color of each criterion (red, yellow, or green) provides an easy way to identify the weak and strong points of each protocol, and the central score allows for a value that can be suitable for comparison between procedures. The proposed method presented the highest overall score (0.54), demonstrating a better performance in comparison with the other methods (ASTM D 6470 or DSS-EA), as shown in Figure 3.

The proposed method resulted in the best score, performing from good to excellent in six principles of green sample preparation (principles 3, 5, 6, 8, 9, and 10). An overall score of 0.27 (Figure 3B) was obtained for the ASTM D 6470 standard method, which showed a good performance (green score) only for principles 8 and 9. It is easy to recognize that the high amount of toxic organic solvent and the sample amount used in this protocol contributed to this worse score. For the DSS-EA method, a good performance was observed in four principles: principle 4 (waste generation—about 0.5 mL of sample diluted in ethanol:toluene mixture), principle 5 (stages in sample preparation—just weighing and placing in the equipment), principle 5 (size economy of the sample—around 20 mg), principle 9 (micro coulometric detection), and principle 10 (operator's safety—the sample must be diluted in a mixture of solvents containing toluene). However, in terms of sample throughput, energy consumption, and post-sample preparation configuration for analysis (principles 6, 8, and 9, respectively), the proposed method presented a better performance.



10 Green Sample Preparation principles:

1 – Sample preparation placement
2 – Hazardous material
3 – Sustainability, renewability, and reusability of materials
4 – Waste
5 – Size economy of the sample
6 – Sample throughput
7 – Integration and automation
8 – Energy consumption
9 – Post-sample preparation configuration for analysis
10 – Operator's safety

Figure 3. Scores for the methods for chloride determination in crude oil by AGREEprep analysis [43]. (**A**) Proposed extraction–colorimetric method, (**B**) ASTM D 6470 standard method, and (**C**) DSS-EA.

When comparing with ASTM D 6470 or DSS-EA, the proposed method offers some advantages. Large amounts of organic solvents were unnecessary (only ca. 1 mL of ethyl acetate plus 5 mL of ultrapure water can be used), and the sample throughput was increased from 4 to 12 samples per hour, in comparison with the ASTM standard method or in comparison with DSS-EA. DSS-EA presented a better score than ASTM D 6470, despite its worse score in contrast with the proposed method. However, DSS-EA requires specific equipment that has an energy consumption of about 1800 W h (around 450 W h per replicate—without considering the calibration procedure). Considering the costs, the analyzer can be considered a relatively high-cost piece of dedicated equipment (high-purity argon and oxygen gases are necessary for the instrument operation and a specific standard is used for calibration), in comparison to the proposed method and even to ASTM. Moreover, it must be considered that the proposed protocol requires only a homemade 3D-printed device and a smartphone to obtain the images and carry out quantification through chemometrics, in a miniaturized and portable apparatus. The proposed method can offer a suitable alternative that allows us to consider the principles of GSP for the determination of chloride in crude oil, combining time and energy savings and providing safety to the operator, in an easy-to-use system, with a reduced amount of waste being generated [21–28].

4. Conclusions

The impact of the crude oil salt content in refinery processes highlights quality control as an important step in the petroleum industry. However, the protocols available and their drawbacks in analyzing chloride and in dealing with crude oil samples make this a challenge to analytical chemistry laboratories. Accuracy for samples with different properties is a matter of concern. Moreover, the development of methodologies aligned with the precepts of green analytical chemistry is important. Among the key aspects of the new methodologies, it can be seen that their miniaturized methods, high throughput, low generation of toxic waste, and eco-friendly protocols agree with the trends of green analytical chemistry. The optimized method developed in this work is simple, robust, and low-cost, with suitable accuracy and precision. In this protocol (using 0.7 g of crude oil plus 1 mL of ethyl acetate and 5 mL of water, at 55 °C, with 30 min of extraction), the efficiency of extraction was higher than 84% for all oils. A relative standard deviation (RSD) lower than 9.7% was also obtained for all experiments. No statistical differences in comparison with reference values were observed (ANOVA, 95% confidence level). In addition, the proposed protocol allows for the analysis of 12 samples per hour, with low energy consumption (constituting advantages over the ASTM D 6470 and DSS-EA methods). Therefore, this work developed a miniaturized protocol generating compatible extracts for the rapid determination of chloride by colorimetric analysis using the PhotoMetrix app, with a suitable LOD (0.5 mg g^{-1}) and a portable device. These aspects demonstrate the compliance of the proposed method with green analytical chemistry, as shown using the AGREEprep calculator.

Finally, though the proposed method agrees with GSP principles, there are opportunities for further enhancements. Future research could focus on method validation using different crude oils (e.g., heavy crude oils) or other organic matrices, such as crude oil fractions and related fuels, to ensure its applicability. Further miniaturization and better LOQs must always be contemplated in analytical chemistry improvements. The development of automated or semi-automated systems for sample processing could improve sample throughput, enabling further implementation in routine laboratories. In addition, some economic benefits when applying this method in the crude oil industry can also be highlighted. Among them, the sample throughput may be shown to reduce labor and operational costs. The miniaturized approach decreases the waste generated, potentially reducing the costs associated with waste disposal and regulatory compliance. Also, time-saving and the low energy consumption make it economically attractive in comparison with conventional methods such as ASTM D 6470. Portability and colorimetric analysis using the PhotoMetrix app reduce the costs with complex instrumentation, further lowering capital investment and maintenance costs. Collectively, these factors suggest that the implementation of this method could lead to significant cost savings, making it a viable option for routine quality control in the crude oil industry.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr12112425/s1, Table S1: Experimental variables used in the CCD for the optimization of the miniaturized extraction method; Table S2: Experimental conditions and results for chloride in crude oil CO1 used in the CCD for the optimization of the miniaturized extraction method, real and coded values (between parentheses) of each experiment; Figure S1: Representative flow chart of optimized conditions of this work including the extraction and the colorimetric quantification step; Figure S2: Standardized Pareto chart results from experimental design for chloride extraction from crude oil by a miniaturized extraction method.

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References

1. Groysman, A. *Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry*, 1st ed.; Springer: Cham, Switzerland, 2017.
2. Speight, J.G. *The Chemistry and Technology of Petroleum*; CRC Press: Boca Raton, FL, USA, 2006; Volume 5, p. 953.

3. *ASTM D 6470*; Standard Test Method for Salts in Crude Oil (Potentiometric Method). American Society for Testing Materials: West Conshohocken, PA, USA, 2015.
4. *ASTM D 3230*; Standard Test Method for Salts in Crude Oil (Electrometric Method). American Society for Testing Materials: West Conshohocken, PA, USA, 2019.
5. Morigaki, M.K.; Chimin, R.Q.F.; Sad, C.M.S.; Filgueiras, P.R.; Castro, E.V.R.; Dias, J.C.M. Salinity of crude oil: Optimization of methodology and new method for extraction of salt in petroleum. *Quim. Nova* **2010**, *33*, 607–612. [CrossRef]
6. Moraes, D.P.; Antes, F.G.; Pereira, J.S.F.; Santos, M.D.F.P.; Guimarães, R.C.L.; Barin, J.S.; Mesko, M.F.; Paniz, J.N.G.; Flores, E.M.M. Microwave-assisted procedure for salinity evaluation of heavy crude oil emulsions. *Energy Fuels* **2010**, *24*, 2227–2232. [CrossRef]
7. Robaina, N.F.; Feiteira, F.N.; Cassella, A.R.; Cassella, R.J. Determination of chloride in brazilian crude oils by ion chromatography after extraction induced by emulsion breaking. *J. Chromatogr. A* **2016**, *1458*, 112–117. [CrossRef] [PubMed]
8. Campos, A.F.; Cassella, A.R.; Cassella, R.J. Microwave-Assisted Extraction of Chloride Followed by Ion Chromatography as an Alternative to the ASTM D6470 Method for the Determination of Crude Oil Salinity. *Energy Fuels* **2020**, *34*, 6844–6850. [CrossRef]
9. Antes, F.G.; dos Santos, M.D.P.; Guimaraes, R.C.L.; Paniz, J.N.G.; Flores, E.M.M.; Dressler, V.L. Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination. *Anal. Methods* **2011**, *3*, 288–293. [CrossRef]
10. Pereira, J.S.F.; Mello, P.A.; Moraes, D.P.; Duarte, F.A.; Dressler, V.L.; Knapp, G.; Flores, É.M.M. Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion. *Spectrochim. Acta Part B At. Spectrosc.* **2009**, *64*, 554–558. [CrossRef]
11. Nelson, J.; Poirier, L.; Lopez-Linares, F. Determination of chloride in crude oils by direct dilution using inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). *J. Anal. At. Spectrom.* **2019**, *34*, 1433–1438. [CrossRef]
12. Fortuny, M.; Silva, E.B.; Filho, A.C.; Melo, R.L.F.V.; Nele, M.; Coutinho, R.C.C.; Santos, A.F. Measuring salinity in crude oils: Evaluation of methods and an improved procedure. *Fuel* **2008**, *87*, 1241–1248. [CrossRef]
13. Higa, K.M.; Guilhen, A.; Vieira, L.C.S.; Carvalho, R.M.; Poppi, R.J.; Baptistão, M.; Gobbi, A.L.; Lima, R.S.; Hantao, L.W. Simple solid-phase extraction method for high efficiency and low-cost crude oil demulsification. *Energy Fuels* **2016**, *30*, 4667–4675. [CrossRef]
14. Sad, C.M.S.; Santana, Í.L.; Morigaki, M.K.; Medeiros, E.F.; Castro, E.V.R.; Santos, M.F.P.; Filgueiras, P.R. New methodology for heavy oil desalination. *Fuel* **2015**, *150*, 705–710. [CrossRef]
15. Diehl, L.O.; Moraes, D.P.; Antes, F.G.; Pereira, J.S.F.; Santos, M.F.P.; Guimarães, R.C.L.; Paniz, J.N.G.; Flores, E.M.M. Separation of heavy crude oil emulsions using microwave radiation for further crude oil analysis. *Sep. Sci. Technol.* **2011**, *46*, 1358–1364. [CrossRef]
16. Doyle, A.; Saavedra, A.; Tristao, M.L.B.; Nele, M.; Aucélio, R.Q. Direct chlorine determination in crude oils by energy dispersive X-ray fluorescence spectrometry: An improved method based on a proper strategy for sample homogenization and calibration with inorganic standards. *Spectrochim. Acta Part B At. Spectrosc.* **2011**, *66*, 368–372. [CrossRef]
17. Hajian, R.; Oroojloo, A.H.; Mousavian, S.S.; Shams, N. Determination of Sodium Chloride in Crude Oil of Gachsaran County Oil Wells. *Asian J. Chem.* **2011**, *23*, 4223–4224.
18. de Oliveira Souza, M.; Ribeiro, M.A.; Carneiro, M.T.W.D.; Athayde, G.P.B.; de Castro, E.V.R.; da Silva, F.L.F.; Matos, W.O.; de Queiroz Ferreira, R. 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. *Fuel* **2015**, *154*, 181–187. [CrossRef]
19. Ramos, A.C.O.P.; Caldeira, G.R.F.; Nunes, C.R.O.; Terra, W.S.; Souza, M.O. Optimization of extraction induced by emulsion breaking variables for subsequent determination of crude oil salinity by ion chromatography. *J. Braz. J. Anal. Chem.* **2020**, *7*, 31–39. [CrossRef]
20. Aly, A.A.; Górecki, T. Green approaches to sample preparation based on extraction techniques. *Molecules* **2020**, *25*, 1719. [CrossRef]
21. Kurowska-Susdorf, A.; Zwierżdżyński, M.; Bevanda, A.M.; Talić, S.; Ivanković, A.; Płotka-Wasylka, J. Green analytical chemistry: Social dimension and teaching. *TrAC Trends Anal. Chem.* **2019**, *111*, 185–196. [CrossRef]
22. Chemat, F.; Garrigues, S.; de la Guardia, M. Portability in analytical chemistry: A green and democratic way for sustainability. *Curr. Opin. Green Sustain. Chem.* **2019**, *19*, 94–98. [CrossRef]
23. Armenta, S.; Garrigues, S.; Esteve-Turrillas, F.A.; de la Guardia, M. Green extraction techniques in green analytical chemistry. *TrAC Trends Anal. Chem.* **2019**, *116*, 248–253. [CrossRef]
24. Bizzi, C.; Pedrotti, M.; Silva, J.; Barin, J.; Nóbrega, J.; Flores, E. Microwave-assisted digestion methods: Towards greener approaches for plasma-based analytical techniques. *J. Anal. At. Spectrom.* **2017**, *32*, 1448–1466. [CrossRef]
25. Gałuszka, A.; Migaszewski, Z.; Namieśnik, J. The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. *TrAC Trends Anal. Chem.* **2013**, *50*, 78–84. [CrossRef]
26. Guardia, M.; Garrigues, S. *Handbook of Green Analytical Chemistry*, 1st ed.; John Wiley & Sons: Hoboken, NJ, USA, 2012.
27. Tobiszewski, M.; Mechlińska, A.; Namieśnik, J. Green analytical chemistry—Theory and practice. *Chem. Soc. Rev.* **2010**, *39*, 2869–2878. [CrossRef] [PubMed]
28. Armenta, S.; de la Guardia, M. Green Spectroscopy: A Scientometric Picture. *Spectrosc. Lett.* **2009**, *42*, 277–283. [CrossRef]
29. Namieśnik, J. Green analytical chemistry—Some remarks. *J. Sep. Sci.* **2001**, *24*, 151–153. [CrossRef]
30. Shi, M.; Zheng, X.; Zhang, N.; Guo, Y.; Liu, M.; Yin, L. Overview of sixteen green analytical chemistry metrics for evaluation of the greenness of analytical methods. *TrAC Trends Anal. Chem.* **2023**, *166*, 117211. [CrossRef]
31. Diniz, P.H.G.D. Chemometrics-assisted color histogram-based analytical systems. *J. Chemom.* **2020**, *34*, e3242. [CrossRef]

32. Baumann, L.; Librelotto, M.; Pappis, C.; dos Santos, R.B.; Santos, R.O.; Helfer, G.A.; Lobo, E.A.; da Costa, A.B. Uso do aplicativo PhotoMetrix no monitoramento da concentração de flúor em sistemas alternativos de abastecimento de água. *Águas Subterrâneas* **2019**, *33*. [CrossRef]
33. McCracken, K.; Yoon, J.-Y. Recent approaches for optical smartphone sensing in resource-limited settings: A brief review. *Anal. Methods* **2016**, *8*, 6591–6601. [CrossRef]
34. Costa, A.B.; Helfer, G.A.; Barbosa, J.L.V.; Teixeira, I.D.; Santos, R.O.; Santos, R.B.; Voss, M.; Schlessner, S.K.; Barin, J.S. PhotoMetrix UVC: A new smartphone-based device for digital image colorimetric analysis using PLS regression. *J. Braz. Chem. Soc.* **2021**, *32*, 675–683. [CrossRef]
35. Moran, M.S.; Inoue, Y.; Barnes, E.M. Opportunities and limitations for image-based remote sensing in precision crop management. *Remote Sens. Environ.* **1997**, *61*, 319–346. [CrossRef]
36. Armenta, S.; Garrigues, S.; de la Guardia, M. Green Analytical Chemistry. *TrAC Trends Anal. Chem.* **2008**, *27*, 497–511. [CrossRef]
37. Holkem, A.P.; Voss, M.; Schlesner, S.K.; Helfer, G.A.; Costa, A.B.; Barin, J.S.; Müller, E.I.; Mello, P.A. A green and high throughput method for salt determination in crude oil using digital image-based colorimetry in a portable device. *Fuel* **2021**, *289*, 119941. [CrossRef]
38. Silva, J.S.; Diehl, L.O.; Picoloto, R.S.; Flores, E.M.M.; Mesko, M.F.; Barin, J.S.; Duarte, F.A. A solid sampling approach for direct determination of Cl and S in flour by an elemental analyzer. *Food Chem.* **2021**, *344*, 128671. [CrossRef] [PubMed]
39. Tobiszewski, M.; Tsakovski, S.; Simeonov, V.; Namieśnik, J.; Pena-Pereira, F. A solvent selection guide based on chemometrics and multicriteria decision analysis. *Green Chem.* **2015**, *17*, 4773–4785. [CrossRef]
40. Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C.R.; Abou-Shehada, S.; Dunn, P.J. CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.* **2015**, *18*, 288–296. [CrossRef]
41. Enders, M.S.P.; Gomes, A.O.; Oliveira, R.F.; Guimaraes, R.C.L.; Mesko, M.F.; Flores, E.M.M.; Müller, E.I. Determination of chlorine in crude oil by high-resolution continuum source graphite furnace molecular absorption spectrometry using AlCl, InCl, and SrCl molecules. *Energy Fuels* **2016**, *30*, 3637–3643. [CrossRef]
42. Oliveira, I.K.S.; Medeiros, R.L.S.; Silva, D.R.; Maranhão, T.A. Determination of chlorine in crude oil emulsified via the MgCl molecule by HR-CS MAS. *J. Braz. Chem. Soc.* **2018**, *29*, 571–578. [CrossRef]
43. Wojnowski, W.; Tobiszewski, M.; Pena-Pereira, F.; Psillakis, E. AGREEprep—Analytical greenness metric for sample preparation. *TrAC Trends Anal. Chem.* **2022**, *149*, 116553. [CrossRef]