Determination of chloride in brazilian crude oils by ion chromatography after extraction induced by emulsion breaking

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ABSTRACT

The present paper reports on the development of a novel extraction induced by emulsion breaking (EIEB) method for the determination of chloride in crude oils. The proposed method was based on the formation and breaking of oil-in-water emulsions with the samples and the consequential transference of the highly water-soluble chloride to the aqueous phase during emulsion breaking, which was achieved by centrifugation. The determination of chloride in the extracts was performed by ion chromatography (IC) with conductivity detection. Several parameters (oil phase:aqueous phase ratio, crude oil:mineral oil ratio, shaking time and type and concentration of surfactant) that could affect the performance of the method were evaluated. Total extraction of chloride from samples could be achieved when 1.0 g of oil phase (0.5 g of sample + 0.5 g of mineral oil) was emulsified in 5 mL of a 2.5% (m/v) solution of Triton X-114. The obtained emulsion was shaken for 60 min and broken by centrifugation for 5 min at 5000 rpm. The separated aqueous phase was collected, filtered and diluted before analysis by IC. Under these conditions, the limit of detection was 0.5 $\mu g\,g^{-1}$ NaCl and the limit of quantification was 1.6 $\mu g\,g^{-1}$ NaCl. We applied the method to the determination of chloride in six Brazilian crude oils and the results did not differ statistically from those obtained by the ASTM D6470 method when the paired Student-t-test, at 95% confidence level, was applied.

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1. Introduction

Petroleum is a complex mixture of hydrocarbons containing variable concentrations of organometallic and heteroatomic organic compounds, and inorganic substances. Liquid petroleum is usually called of crude oil, which is associated with water in the form of an emulsion; thus it contains dissolved inorganic salts. The association of petroleum with water primarily results from contact with the saline water naturally present in the geological formation of the reservoir where the oil is stored. Also, it is important to consider that seawater is used in the prospection operations carried out offshore. Therefore, chloride is considered one of the main contaminants of crude oil because it interferes with the refining process and is transferred to the final derived products [1,2]. The presence of chloride can lead to the formation of HCl during refining, which enhances corrosion of metallic parts of the processing unities. Additionally, chloride ions deactivate metallic catalysts (Ni, Cu or Pd-based) usually employed in the catalytic cracking process [3].

The determination of chloride in crude oils (expressed in terms of NaCl concentration) is commonly performed by the Mohr method ($AgNO_3$ titration) or by a potentiometric titration. These methods are limited by their poor sensitivity and can be affected by the presence of other halides in the samples [4]. Some official methods can also be cited. Perhaps, the most important official method employed for chloride determination in crude is the ASTM (American Society for Testing and Materials) D6470 [5]. In this method, the samples are submitted to solvent extraction with a mixture of acetone, water and ethyl alcohol. The extracted chloride is titrated either with $AgNO_3$ or potentiometrically. The main drawbacks of this method are the potential interference of other halide ions that are extracted along with chloride, and the large volume of solvent required to complete the procedure. The ASTM D3230 method [6] is recommended for the determination of crude oil salinity. However, in this method, no extraction is required and the samples are simply diluted with a mixture of xylene, ethyl alcohol and water. The conductivity of the final mixture is measured and related to the oil salinity.

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Alternative methods have been proposed to determine chloride in crude oils. Souza et al. [7] proposed an interesting way to estimate the chloride concentration in crude oil samples through determination of selected counter ions (Na(I), Ca(II), Ba(II), Sr(II) and Fe(III)) after their extraction with hot water. Hajian et al. [8] developed an apparatus for liquid-liquid extraction of chloride from crude oils. A mixture of solvents (toluene, ethanol and acetone) was used to extract chloride from the samples. The final extracts were analyzed using the Volhard method. Moraes et al. [9] developed a method for microwave-assisted extraction of chloride from heavy crude oils. The method required 60 min of microwave irradiation at 800 W to achieve total extraction of chloride from samples and 20 min for the cooling of the flasks. Chloride was determined in the aqueous phase by ICP OES.

In 2010, our research group proposed a novel method for the extraction of metal cations from organic liquids, named extraction induced by emulsion breaking (EIEB). It is based on the formation and breaking of water-in-oil emulsions with the consequential transference of the metal cations to the acidic aqueous phase. This approach has been successfully employed for the determination of metals in different types of oil samples (vegetable oils [10–12], used lubricating oil [13,14], diesel oil [15–17], biodiesel [18,19] and mineral oil [20]). Since the chloride ion is highly soluble in water, we are now proposing to employ the extraction induced by emulsion breaking technique to chloride ion extraction from crude oil. It is important to note that, in the present work, no acid was added to the emulsions in order to avoid the introduction of very high concentrations of anions (typically nitrate, since nitric acid has been commonly used in EIEB) and, contrary to other EIEB systems, we decided to work with oil-in-water emulsions instead of typical water-in-oil emulsions in order to enhance the efficiency of the extraction process.

2. Experimental

2.1. Solutions and reagents

The ultrapure water employed in this work was obtained with a Direct-Q 3 system from Millipore (Milford, MA, USA). The ultrapure water always presented resistivity of 18.2 MΩ cm or higher.

Working standard solutions of chloride ions were prepared daily by diluting the 1000 mg L^{-1} chloride stock standard solution supplied by Fluka (Buchs, Switzerland) with ultrapure water. The stock standard solution supplied by Fluka was prepared with NaCl.

The 25% m/v Triton X-100 (Sigma-Aldrich, St. Louis, MO, USA) and Triton X-114 (Sigma-Aldrich) stock solutions were prepared by dissolving, separately, 12.5 g of each surfactant in approximately 40 mL of ultrapure water. After the surfactant was dissolved and the foam decreased, the obtained solution was transferred to a 50 mL volumetric flask. Then, the volume was completed to the mark with ultrapure water. The solutions employed in the emulsification of the samples were prepared, daily, by suitable dilution of the Triton X-100 and Triton X-114 stock solutions with ultrapure water.

A spectroscopy-grade mineral oil (viscosity = 16.7 cps at 40 °C, d = 0.838 g mL^{-1} at 25 °C), supplied by Sigma-Aldrich, was employed in the dilution of the crude oil samples.

2.2. Apparatus and instruments

The ion chromatography system employed in this work was a Dionex ICS 2100 system (Sunnyvale, CA, USA), equipped with an integrated eluent (potassium hydroxide) generator, model RFIC-EG (EGC III KOH cartridge) and an AERS 500 2 mm membrane conductivity suppressor. Conductivity signals were measured with a DS6 heated conductivity cell and the chromatograms were acquired using Chromeleon software, version 7.2, also supplied by Dionex. The separation of chloride ions was obtained with an Ion-Pac AS15 analytical column (2 × 250 mm, 7.5 μm particle size and 56.25 μeq column^{-1} capacity) and an IonPac AG15 guard column (2 × 50 mm) was used to protect the analytical column. A sample volume of 20 μL was injected in all experiments.

Emulsions were prepared using a Fisatom magnetic stirrer (São Paulo, Brazil), model 754A. They were broken with the aid of a centrifuge, model 5804, furnished by Eppendorf (Hamburg, Germany).

2.3. General procedure for extraction induced by emulsion breaking of chloride

The proposed procedure is based on the formation and breaking of oil-in-water emulsions in order to extract chloride from crude oil. The emulsions were formed by vigorously stirring a 0.5 g sample of crude oil with 0.5 g of mineral oil and 5 mL of the emulsifying solution (2.5% m/v Triton X-114) for 90 min. Afterwards, the emulsion was broken by centrifugation at 5000 rpm for 20 min (Fig. 1). Then, exactly 2 mL of the aqueous phase containing the extracted chloride was taken and diluted to 10 mL with ultrapure water in a volumetric flask. The final obtained solution was filtered through a cellulose acetate membrane with 0.20 μm pore diameter and injected into the chromatographic system.

2.4. Chromatographic conditions

The chromatographic run for separation of chloride was divided into three steps. In the first step (0–6 min), a KOH concentration of 38 mM was employed. The chloride peak appeared at 5.6 ± 0.1 min. In the second step (6–15 min), the KOH concentration was increased to 50 mM in order to provide a convenient cleaning of the column. Finally, in the third step (15–20 min), the KOH concentration was returned to 38 mM to prepare the column for a new separation cycle. The current in the suppressor system was set to 41 mA, the mobile phase flow-rate was 0.33 mL min^{-1} during the entire chromatographic run and the injection volume was always 20 μL. Typical chromatograms of the chloride standard solution (0.1 μg mL^{-1}) and for an actual sample of crude oil treated by the proposed method are presented in Fig. 2.

2.5. Samples

Crude oil samples analyzed in this work were kindly supplied by Petrobras (Rio de Janeiro, Brazil). They were stored in sealed, dark, glass flasks, at ambient laboratory temperature. Sample S$_2$ was employed in the optimization experiments.

3. Results and discussion

The development of the proposed extraction methodology was performed in two steps: (i) evaluation/optimization of the extraction conditions and (ii) application to real samples of crude oil, including a comparison of the obtained results with those obtained using the ASTM D6470 standard method. The methodology was optimized by studying the effect of the following variables: (i) type and concentration of surfactant, (ii) the ratio of oil (crude oil + mineral oil):aqueous phases, (iii) the amount of mineral oil added to the crude oil before emulsification and (iv) emulsion shaking time.

3.1. Effect of oil phase:aqueous phase ratio

One of the most important parameters to be studied in the proposed extraction method was the ratio of oil phase/aqueous phase. This parameter controlled the amount of sample employed in the