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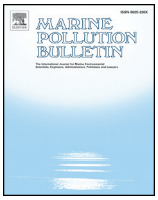

Optimization of a cloud point extraction procedure with response surface methodology for the quantification of dissolved iron in produced water from the petroleum industry using FAAS

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ABSTRACT

The characterization of inorganic elements in the produced water (PW) samples is a difficult task because of the complexity of the matrix. This work deals with a study of a methodology for dissolved Fe quantification in PW from oil industry by flame atomic absorption spectrometry (FAAS) after cloud point extraction (CPE). The procedure is based on the CPE using PAN as complexing agent and Triton X-114 as surfactant. The best conditions for Fe extraction parameters were studied using a Box-Behnken design. The proposed method presented a LOQ of 0.010 μg mL^{-1} and LOD of 0.003 μg mL^{-1}. The precision of the method was evaluated in terms of repeatability, obtaining a coefficient of variation of 2.54%. The accuracy of the method was assessed by recovery experiments of Fe spiked that presented recovery of 103.28%. The method was applied with satisfactory performance to determine Fe by FAAS in PW samples.

1. Introduction

Produced water (PW) is water which is produced along with crude oil obtained in petroleum extraction activities. It comprises the mixture of water naturally present in sedimentary formations and the water injected into the well to increase the pressure, in order to allow the extraction of the crude oil (Fakhru'l-Razi et al., 2009). The amount of water produced by a reservoir can reach five times the amount of oil, which can be, after the extraction process, reinjected into a well or discarded into the ocean (Cruz and Cassella, 2015). The problem of the last option is that PW can contain several toxic organic (benzene, toluene, xylenes, polycycling aromatic hydrocarbons (PAH), phenol, alkylated phenols and organic acids) and inorganic (As, Cd, Cr, Cu, Ni, Pb, V, among others besides radionuclides) substances that can contaminate surface and underground water and soil. In this way, the PW must be treated before it is discarded (Zheng et al., 2016). As well as environmental issues, the analysis of PW is important because its chemical composition can affect the efficiency of crude oil extraction. The presence of some substances, such as iron, can be undesirable because they can cause crusting in the production columns (Nacheva et al., 2008).

The major inputs of iron to the oceans are from the atmosphere, continental shelf sediments, hydrothermal vents, rivers and glacial melt in polar regions. In the deep ocean water, iron is present due to the dissolution of iron ores by carbonic gas, which is in the water. Although iron is not a toxic element, the iron found in PW can provoke crust formation in the ducts of the petroleum production and growth of iron-bacteria, the latter being a water biological contaminant. Therefore, it is essential to monitor the level of iron in PW (Achterberg et al., 2001; Worsfold et al., 2014; Yeung et al., 2011).

In order to quantify inorganic elements in PW samples and verify whether they conform with the legislation, inductively coupled plasma optical emission spectrometry (ICP OES) technique can be applied for the analysis of the majority of the elements. However, since PW is characterized by having a high salinity, even higher than seawater, transport, light scattering and ionic suppression interferences in spectrometric techniques can occur. The matrix effects caused by high salinity can be minimized with the dilution of samples of one hundred times or more. On the other hand, the dilution strategy can limit the quantification of the elements due to prejudice the limit of detection of the method, particularly dissolved iron, by ICP OES. Consequently, techniques with sensitivity in parts per billion, graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS), are preferred to quantify trace elements in PW samples (Bezerra et al., 2006b; Bezerra et al., 2007b). The disadvantages of these techniques are the high cost of analysis and the difficulty of operation. Moreover, they are rarely found in laboratories of routine analysis. The high concentration of dissolved salts can provoke clogging of the cones in the ICP-MS, even though the dilution of the PW samples is performed prior the analysis. In this way, separation methods to

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isolate the analytes from the matrix become necessary before ICP-MS analysis. Thus, the study of less expensive and simpler alternative methods to determine trace elements in PW is important.

Flame atomic absorption spectrometry (FAAS) presents sensitivity similar to ICP OES and the same susceptibility to interferences provoked by high salinity of PW samples. Therefore, the detection limit of FAAS would be not enough to quantify iron in PW after dilution of the sample. Preliminary preconcentration/separation step would be required. However, FAAS is less expensive, faster, easier to operate and more available compared with the techniques above mentioned.

Several techniques have been used for the separation/preconcentration of trace metals in PW, such as solid-phase extraction (SPE) (Oliveira et al., 2011), ionic liquid microextraction (Cruz and Cassella, 2015), Chelex® 100-resin (Freire and Santelli, 2012) and cloud point extraction (CPE) (Bezerra et al., 2004; Bezerra et al., 2006b; Bezerra et al., 2007a). CPE is characterized by its efficiency, simple experimental procedure and low cost. Moreover, it follows the principles of green chemistry, since CPE uses surfactants as an alternative to organic solvents, which are generally characterized by a high toxicity. The Tritons, surfactants most widely used for metal analysis, have low toxicity and are used in small amounts. The principle of CPE is based on the phenomenon in which an aqueous solution of a surfactant becomes turbid and separates into two isotropic phases if some condition, such as temperature or pressure, is changed or if an appropriate substance is added to the solution. The surfactant solution becomes turbid because it attains the cloud point. At this point, the original surfactant solution separates into a surfactant phase of small volume, which is rich in the surfactant and contain the analyte trapped by micellar structures; and a bulk diluted aqueous phase that can be discarded (Bezerra et al., 2007b; Mukherjee et al., 2011; Quina and Hinze, 1999; Samaddar and Sen, 2014).

Several parameters must be optimized to develop an efficient CPE procedure, such as concentration of complexing agent, pH and concentration of surfactant. Experimental design is a useful chemometric tool to optimize methods involving many variables, since a large number of factors can be varied simultaneously, with a reduced number of experiments. This strategy provides results that are more reliable than the traditional optimization technique in which only one variable is changed while all the others remain constant (Bezerra et al., 2008; Bezerra et al., 2006a; Tarley et al., 2009).

In this work, the CPE method to quantify dissolved iron in PW samples using FAAS was developed applying full factorial design and response surface methodology (RSM). The method proposed employed PAN as complexing agent and Triton X-114 as surfactant.

2. Experimental

2.1. Instrumentation

Flame Atomic Absorption Spectrometer (Varian AA24DFS) was used for dissolved iron determination. Fe hollow cathode lamp (Varian) operating at a lamp current of 7.0 mA was used and all measurements were carried out at 248.3 nm. A spectral slit-width of 0.2 nm and a D2 background correction was used. The flame composition was acetylene (flow rate 2.0 L min^{-1}) and air (flow rate 10.0 L min^{-1}). A 300 Analyser (São Paulo, Brazil) pH meter was used to measure pH.

A centrifuge Janetzki T 32C (Berlin, German) and a thermostatic bath Fanem (São Paulo, Brazil) were used in the CPE experiments.

2.2. Samples and reagents

Samples of produced water (PW) were acquired from the petroleum industry in Brazil and mixed together to compose a pool of the samples in order to ensure the volume necessary to conduct all experiments. Samples were filtered (Qualy, 17 μm), acidified with 65% w w^{-1} nitric acid (Merck, Darmstadt, Germany) and stored at 15 °C.

Solutions were prepared using ultrapure water (resistivity of 18.2 M Ω cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glassware and polypropylene flasks were immersed in 10% v v^{-1} nitric acid for 24 h and rinsed with ultrapure water prior to use.

The solution 4 mmol L^{-1} of 1-(2-pyridylazo)2-naphtol (PAN) (Merck, Darmstadt, Germany) was prepared by dissolution of 0.1 g of the compound in 100 mL of 68% w w^{-1} ethanol (Synth, São Paulo, Brazil). Acetate buffer was prepared by mixing 0.2 mol L^{-1} of sodium acetate trihydrate (Vetec, Rio de Janeiro, Brazil) and 0.2 mol L^{-1} of glacial acetic acid (Synth), the pH was adjusted using NaOH (Synth). Triton X-114 (Acros Organics) solution (10% w v^{-1}) was prepared by dilution. A 50% v v^{-1} ethanol solution was prepared in 1% v v^{-1} nitric acid to decrease the viscosity of the rich phase prior to analysis.

The calibration curve without preconcentration (1–7 μg mL^{-1} Fe) was prepared after successive dilutions from 1000 mg L^{-1} Fe stock solution in 1% v v^{-1} HNO_3. The calibration curve with preconcentration (0.02–0.40 μg mL^{-1} Fe) was prepared after successive dilutions from 1000 mg L^{-1} Fe stock solution in 0.17 mol L^{-1} sodium chloride solution. These solutions were submitted to the optimized CPE methodology. The CPE analytical blank was a sodium chloride solution 0.17 mol L^{-1} that was analogously subjected to CPE procedure.

2.3. Procedure for cloud point extraction

The procedure for cloud point extraction was implemented using 45 mL of a PW sample and 0.16 mol L^{-1} PAN in acetate buffer (0.2 mol L^{-1}, pH 4.5) medium. The mixture was mechanically shaken and after complete complexation reaction (20 min) between the analyte and PAN, Triton X-114 0.09% (w v^{-1}) was added to the sample solution and the final volume was adjusted to 50 mL with ultrapure water. The time for complete reaction between Fe and PAN was previously studied. The cloud point was reached by heating in a controlled temperature bath at 40 °C for 30 min. After this, the samples were spun in a centrifuge at 1500 rpm for 10 min. The mixture was cooled in an ice bath (5 min) in an effort to increase the viscosity of the surfactant-rich phase. Then, the surfactant-rich phase was diluted to 5 mL by adding ethanol acid solution prior to Fe determination by FAAS.

2.4. Experimental design

The optimization of the CPE of Fe procedure was performed using a full factorial design 2^k, where k refers to the number of variables. The variables studied were: pH, concentration of complexing PAN, concentration of surfactant Triton X-114 and centrifugation time. Table 1 shows the factorial design with the levels studied for each variable. The 2^4 factorial design was accomplished with 16 experiments in triplicate. The minimum and maximum levels for each variable were chosen according to their significant effects evaluated in prior tests.

After evaluation of the most significant variables, the optimization of the method was performed applying a response surface methodology, which was based on modeling by minimum squares using Box-Behnken experimental design with three independent variables. The variables studied were: the pH of complexation, the concentration of surfactant (Triton X-114) and the concentration of complexing agent (PAN). These factors were studied at different levels chosen based on the outcome of the full factorial design. The procedure used was the same as

Table 1
Variables and levels used in the factorial design for extraction of Fe.

Variables	High level (+)	Low level (−)
pH	8.5	3.5
PAN conc (mmol L^{-1})	0.3	0.03
Triton X-114 conc. (% m v^{-1})	0.2	0.05
Centrifuged time (min)	20	10

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