



Full Length Article

Extraction induced by emulsion breaking: A model study on metal extraction from mineral oil



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ARTICLE INFO

Keywords:

Extraction induced by emulsion breaking
Metals
Mineral oil
Surfactants

ABSTRACT

This work reports, for the first time, a detailed investigation on the effect of experimental parameters that affect the extraction induced by emulsion breaking. In this study, we evaluated the influence of the type (Triton X-100, Triton X-114, Tween 20 and sodium dodecylsulfate) and concentration of the surfactant employed as emulsifying agent, as well as the type (HCl or HNO₃) and concentration of the mineral acid employed for the extraction of As, Cr, Cu, Mn, Pb and V of spiked mineral oil. The metals were added to the mineral oil in the form of organometallic compounds. In all cases, the emulsion breakdown was induced by heating at 90 °C in a thermostatic bath and the extracts were analyzed by graphite furnace atomic absorption spectrometry (GF AAS). The time required to achieve emulsion breakdown and the extraction efficiency were taken as responses for evaluation. The obtained results showed that the extraction of metals was more efficient when Triton X-100 or Triton X-114 were employed in the preparation of the emulsions. Both HCl and HNO₃ provided quantitative extraction of the analytes when combined with these surfactants, except in the case of As, in which the extraction efficiencies were in the range of 22–60%. However, the emulsions prepared with HCl needed longer times to be broken down. Samples of mineral oils (new and used) from vacuum pumps were analyzed and the results compared with those obtained with the model sample. Only As and V could not be determined in the real samples.

1. Introduction

The determination of trace metals in organic liquids remains as a challenging task for analytical chemists. Atomic spectrometric techniques are regularly used for this purpose despite the number of interferences that can be observed due to the high carbon content present in the samples and to their physical characteristics. In general, two strategies have been used to overcome these problems: (i) development of approaches that permit direct introduction of the samples into the atomic spectrometers [1–10] and (ii) development of sample preparation procedures that allow the elimination of the matrix or the transference of the analytes to a simpler medium [11–20].

Direct introduction of organic liquids is considered a good option for the fast and simple determination of metals by spectrometric techniques in this kind of sample. Nevertheless, to achieve satisfactory results, the samples must be diluted in a convenient solvent [1–3] or modified prior to their introduction into the instrument [4–10]. Although some advantages can be observed when using this approach, the high cost and inherent instability of the organometallic standards used in the calibration process and the necessity of manipulation of toxic

solvents remain as serious drawbacks associated with strategies based on the direct introduction of organic liquids into the spectrometers.

The problem gets worse when plasma-based techniques are employed, since the simple dilution or modification of the samples in another medium – in general also containing high carbon content – is not enough to avoid the problems resulting from the high carbon load. In these cases, the setup must be reconfigured with the use of an auxiliary oxygen flux [21,22], in order to avoid the appearance of carbon deposits on the inner parts of the spectrometer. Also, the use of ultrasonic nebulizers [23,24] or electrothermal vaporization systems [25,26] makes possible the elimination of the most part of the organic content of the samples prior to atomization. However, these apparatuses present high cost and are not available in the majority of analytical laboratories. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) does not suffer of a such problem. In this technique, the carbon initially present in the samples is, in general, eliminated in the pyrolysis step, thus reducing a number of interferences that can occur in the measurement step (atomization). Even so, samples with very refractory matrix, as the mineral oils, require the elaboration of complex temperature programs to ensure the elimination

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of organic substances.

As mentioned previously, the determination of metals in organic liquids can also be performed after a convenient sample preparation. Certainly, the most general approach used in the preparation of organic liquids for spectrometric analysis is their total mineralization with acid, which can be achieved using dry ashing [12,13] or acid digestion with different heating systems, such as hot plates [11,14] and closed [15–18] and open-vessel [19] microwave systems. More recently, the use of a microwave-induced combustion system was employed in the destruction of the organic matter contained in diesel oil samples prior to the determination of metals by ICP-MS [20].

Extraction procedures are a good alternative to total mineralization, since they employ less drastic conditions. Some works report the use of ultrasound energy to enhance the extraction of metals from oil samples prior to their determination by atomic spectrometric techniques [27–29]. In this context, in 2010, our research group proposed the extraction of induced by emulsion breaking (EIEB) for the extraction of metals from oil samples [30]. Since then, different types of oils, such as diesel oil [31,32], vegetable oils [33–37], used lubricant oil [38,39], crude oil [40,41], biodiesel [42,43], insulating oil [44] and jet fuel [45] have been successfully analyzed using this approach, which was also employed for the extraction of chloride from crude oil [46]. In an interesting work, Bakircioglu et al. [33] compared EIEB with total mineralization and ultrasound-assisted extraction approaches for the determination of metals in Turkish edible oils. The authors concluded that very satisfactory results were obtained using the EIEB procedure, which proved to be faster and simpler than the other methods tested.

EIEB is based on the formation of water-in-oil (w/o) or oil-in-water (o/w) emulsions by vigorous mixing of the oil samples with a solution containing an emulsifying agent (usually a non-ionic surfactant) and acid, which is responsible for the extraction of metals. The obtained emulsions are characterized by the very small size of the droplets dispersed through the continuous phase, which promotes an intense contact between the two phases (high contact area), enhancing the transfer of the metal from the organic to the acidic aqueous phase. Afterwards, the emulsion is broken down by heating or centrifugation, resulting in the separation of the two original phases (oil and water). The acidic aqueous phase containing the extracted analytes is collected for analysis. It is important to remark that the movement of the small droplets during the coalescence process that results in the emulsion breakdown also helps to increase the extraction efficiency. EIEB presents some advantages, such as its inherent simplicity and speed, since the emulsion breakdown takes no more than 15–20 min. Also, the final medium containing the analytes is very simple, making possible the use of standard aqueous solutions for calibration [30].

The use of Triton X-100 and Triton X-114 as emulsifying agents was unanimous in the application of EIEB, independently of the type of sample. Also, nitric acid has always been chosen for the extraction of metals. Therefore, the goal of the present work was to investigate, in detail, the actual effect of these conditions on the performance of EIEB. The study was carried out using controlled conditions (mineral oil spiked with metals – As, Cr, Cu, Mn, Pb and V – in the form of organometallic compounds) and varying both the type and concentration of the surfactants employed as emulsifying agents, and the acid.

2. Experimental

2.1. Apparatus and instruments

The quantification of As, Cr, Cu, Mn, Pb and V in the extracts was performed by graphite furnace atomic absorption spectrometry (GFAAS). For this purpose, we employed a Varian AA240Z (Mulgrave, Australia) spectrometer equipped with a Varian GTA 120 atomization unit and a Varian PSD 120 autosampler. The spectrometer was also equipped with a Zeeman-based background correction system, which was used with a constant magnetic field of 0.8 T. Individual hollow

Table 1

Operational conditions employed for the measurements of the elements of interest by GFAAS.

Element	Lamp current (mA)	Wavelength (nm)	Slit width (nm)
As	10.0	193.7	0.5
Cr	7.0	357.9	0.2
Cu	10.0	324.8	0.5
Mn	5.0	279.5	0.2
Pb	10.0	283.3	0.5
V	20.0	318.5	0.2

cathode lamps of the elements of interest were used as radiation sources and the atomization was performed using graphite tubes with L'vov platform of pyrolytic graphite, which were also supplied by Varian. The GFAAS measurements were performed using the operational conditions shown in Table 1. Integrated absorbance was employed as a quantitative variable and high-purity argon (99.99%), supplied by Linde Gases (Macaé, Brazil), was used as protective gas.

A thermostatic water bath model NT-247, supplied by Nova Técnica (São Paulo, Brazil), was employed to induce emulsion breaking. It was set at 90 °C in all experiments.

2.2. Reagents and solutions

The deionized water used in this work was obtained with a Direct-Q3 system, supplied by Millipore (Milford, MA, USA). It always had resistivity of at least 18.2 MΩ cm.

Oil-based stock standard solutions of the elements of interest (As, Cr, Cu, Mn, Pb and V) with 1000 µg g⁻¹ concentration were all supplied by Conostan (Bale, Canada). The elements of interest were in the form of organometallic compounds. The oil-based stock standard solutions were diluted with HPLC-grade hexane (Tedia, Fairfield, OH, USA) for spiking the mineral oil employed in this model study.

Aqueous stock standard solutions of the elements of interest (As, Cr, Cu, Mn, Pb and V) with 1000 µg mL⁻¹ concentration were supplied by SPEX (Metuchen, NJ, USA). The stock standard solutions were diluted with a 2% (v/v) HNO₃ solution for the preparation of the standard solutions employed in the construction of the analytical curves used in the quantification process.

Concentrated nitric and hydrochloric acids from Tedia (Fairfield, OH, USA) were used to prepare diluted solutions of these acids. Dilution was always performed in a volumetric flask with deionized water.

The surfactant solutions were prepared using reagents from different brands. Triton X-114 was supplied by Acros Organics (Geel, Belgium), Triton X-100 by Tedia (Fairfield, OH, USA), Tween 20 by Vetec (Rio de Janeiro, Brazil) and sodium dodecylsulfate (SDS) by Sigma-Aldrich (St. Louis, MO, USA). The solutions of the surfactants were prepared by dissolving a suitable mass of the reagent in deionized water.

The palladium modifier solution with a concentration of 1000 µg mL⁻¹ of Pd, used in the determination of Pb by GFAAS, was prepared by diluting the Pd stock solution (10000 mg L⁻¹) (Merck, Darmstadt, Germany) with deionized water.

The mineral oil employed in this model study was supplied by Sigma-Aldrich (St. Louis, MO, USA). It was of spectroscopic grade and presented a specific mass of 0.8103 g cm⁻³ (at 25 °C) and a viscosity of 16.7 cps (at 40 °C). The mineral oil was spiked with 50 µg L⁻¹ of each element of interest and the fortified oil was employed in all experiments.

2.3. General procedure – Extraction induced by emulsion breaking

In this work, the procedure of extraction induced by emulsion breaking was carried out through the formation and breaking of emulsions prepared by mixing of 10 mL of oil fortified with metals with

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