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Direct determination of Cu and Fe in jet fuel by electrothermal atomic absorption spectrometry with injection of sample as detergent emulsions

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ABSTRACT

This paper reports the development of a method for the determination of copper and iron in jet fuels employing the electrothermal atomic absorption spectrometry (ETAAS). In order to allow the direct determination of the analytes, the samples were injected into the graphite furnace as detergent emulsions in order to avoid their volatilization during analysis. The results obtained in this work indicated that a stable emulsion can be formed by mixing 1 mL of a 7% m/v Triton X-100 solution containing 10% v/v HNO_3 with 4 mL of jet fuel. The injection of emulsions provided integrated absorbance signals with suitable sensitivity and precision for 300 min at least. The addition of chemical modifier was not necessary because background values were always very low, allowing the use of pyrolysis temperature around 1000 °C for both analytes. Both Triton X-100 and HNO_3 concentrations in the solution used to form the emulsion had remarkable influence on the sensitivity as well as the heating rate employed in the drying step. Under the best conditions established in the present work, limits of detection of 0.50 and 0.46 $\mu g\ L^{-1}$ were observed for copper when oil-based and aqueous standards were added to the emulsions for calibration, respectively. For iron, the limits of detection were 0.88 and 0.90 $\mu g\ L^{-1}$ for oil-based and aqueous standards, respectively. The method was applied in the determination of Cu and Fe in five samples of jet fuels and a recovery test was performed, producing recovery percentages between 95% and 105%.

1. Introduction

Nowadays it is well known that the presence of metallic species in petroleum-derived products, even in trace quantities, can result in a number of distinct problems. In the first place, the stability of these products can be strongly reduced due to the presence of trace metals, since they catalyze oxidative reactions of certain heteroatomic compounds containing N, O or S and hydrocarbons like alkenes, indenes and cyclic hydrocarbons, resulting in the formation of solid deposits [1], which are commonly called gum. The accumulation of gum on the internal metallic surfaces of the engines affects negatively their efficiency, performance and durability [2,3]. Also, the presence of metals in liquid fuels is associated with corrosion, metal deposition on engine parts and poor fuel performance [4,5]. In this sense it is clear that liquid fuels containing high metals concentration have their stability compromised and that the development of suitable analytical methods for the determination of low level concentrations of metals in fuel samples is required as an important tool for quality control.

Electrothermal atomic absorption spectrometry (ETAAS) has been employed by our research group for the determination of metallic elements in various petroleum industry-related samples [6–11]. ETAAS technique is very selective and sensitive and, for that reason, it is especially useful when the analytes are found in very low concentrations in the samples. However, although the advantages observed in the use of ETAAS, the analysis of volatile fuels is still a challenge because of the intrinsic instability of the samples. In order to overcome this drawback, the employment of stabilizing methods of samples has grown up in the last few years as alternative to keep them unchanged during the whole analysis. Undoubtedly, the injection of samples in the form of emulsions [11–16] or microemulsions [17,18] are excellent alternatives for this purpose, in spite of the problems derived from these procedures like the increase of the blank values and excessive handling of samples.

Although microemulsions are more stable than emulsions [19], in general, they require higher dilution of the samples to be formed. This fact leads to the development of procedures with poorer detection and quantification limits in relation to the formation of emulsions for the stabilization of samples. The injection of emulsions is still not a procedure widely employed in the determination of metals in liquid fuel samples by ETAAS (or even by other

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analytical technique). Only few works can be found in the literature regarding this subject [11–16] and, to our knowledge, none of them are related to the analysis of jet fuels.

Cassella et al. emulsified the samples with Triton X-100 as stabilization strategy for the determination of As and Sb in petrochemical naphtha by ETAAS [11]. Aucelio et al. [12–14] also used Triton X-100 for the emulsification of lubricating oils, gasoline, and kerosene in the determination of Sb, Sn, Ag, As, and Se by ETAAS. Meeravali and Kumar [15] determined Ni and V in naphtha samples by ETAAS with Ir–W permanent modifier. In this study, the very low stability of the naphtha was pointed out, thereby confirming that the formation of emulsion is an excellent alternative to solve the problem related to the high instability of the signals. Recently, the emulsification was also explored for the determination of metals (Ni, V and Co) in non-volatile oil samples by ETAAS. In this work, the calibration could be carried out with aqueous standards, which facilitated the whole procedure [16].

The main objective of the present work was to develop a methodology to determine Cu and Fe in jet fuel by ETAAS. The samples were injected in the form of detergent emulsions in order to keep them stable during the analysis. According to Teixeira et al. [20], which studied the effect of various metals on the gum formation in automotive gasolines, Cu and Fe are the most critical metallic elements, inducing the gum formation only after 7 days of storage.

2. Experimental

2.1. Apparatus

All experiments were performed on a Varian (Mulgrave, Australia) polarized Zeeman-effect electrothermal atomic absorption spectrometer, model AA240Z, equipped with a Varian GTA 120 graphite furnace unit and coupled to a Varian PSD 120 auto sampler. Hollow cathode lamps for copper and iron, also furnished by Varian, were employed in all experiments. Integrated absorbance measurements were made by using three types of pyrolytical coated graphite tubes also supplied by Varian: with (Part No. 63-100026-00) and without (Part No. 63-100011-00) L'vov platform and partitioned one (Part No. 63-100012-00). Operational conditions used for the measurements of both Cu and Fe are shown in Table 1.

2.2. Reagents and solutions

All solutions were prepared with purified water obtained in a Direct-Q 3 System (Millipore, Milford, MA, USA). Trace metal grade nitric acid and analytical grade Triton X-100, supplied by Tedia (São Paulo, Brazil), were used in the experiments.

Aqueous stock copper solution of 1000 μg mL^{-1} was supplied by SPEX (Metuchen, NJ, USA). All standard solutions used in this work were prepared daily by dilution of the stock solution. Copper oil-based standard with 1000 μg g^{-1} was furnished by Conostan (Houston, TX, USA).

Aqueous stock iron solution of 1000 μg mL^{-1} was also supplied by SPEX (Metuchen, NJ, USA). As for copper, standard solutions were prepared daily from this stock solution just before use. The iron oil-based standard with 1000 μg g^{-1} was also supplied by Conostan.

Table 1
Operational conditions employed in the determination of copper and iron in jet fuel by ETAAS with emulsified sample introduction.

Parameter	Copper	Iron
Wavelength	324.8 nm	248.3 nm
Slit width	0.5 nm	0.2 nm
Lamp current	4 mA	5 mA
Purge gas	Ar	Ar
Background correction	Transverse Zeeman-effect	Transverse Zeeman-effect

Diluted Cu and Fe organic standards were prepared by diluting oil-based standard solutions in HPLC grade hexane supplied by Tedia (São Paulo, Brazil).

The 7% w/v Triton X-100 solution was prepared by dissolving 7 g of Triton X-100 in 10% v/v HNO_3 solution enough to complete 100 mL.

Jet fuel free of metals was supplied by PETROBRAS and was employed during the optimization of the methodology in the preparation of standard emulsions.

2.3. Emulsion preparation

The emulsions were prepared by mixing 4 mL of jet fuel sample (or standard) with 1 mL of 7% w/v Triton X-100 solution prepared in a 10% v/v HNO_3 medium in a plastic capped tube with 6 mL capacity. The obtained mixture was vigorously shaken, manually, until the formation of the emulsion. After that, the obtained emulsion was transferred to the auto sampler cup and injected into the graphite tube. Both Cu and Fe were measured using this same emulsion.

For the quantification of Cu and Fe in the samples, calibration was performed with jet fuel standard emulsions prepared in the same way that the samples were prepared, but employing jet fuel free of metals and oil-based standard solutions of the analytes.

2.4. General procedure for the determination of copper and iron by ETAAS

For both Cu and Fe, a volume of 20 μL of sample or standard emulsions was injected into a partitioned (pyrolytic coated) graphite tube and the temperature program was run. Measurements were carried out by integrated atomic absorbance mode under the conditions shown in Table 1. The temperature programs used for copper and iron are listed in Table 2.

3. Results and discussion

The optimization of the present methodology was carried out taking into consideration two premises: (i) establishment of better conditions for emulsion formation, considering, mainly, its stability; and (ii) the achievement of the highest sensitivity as possible for each analyte. These objectives were reached through the optimization of distinct parameters associated to the preparation of the emulsion and to the temperature program used in the ETAAS measurements.

3.1. Study of the emulsion formation and stability

The main problem in the direct measurement of trace elements in jet fuel by ETAAS is related to the high volatility of the samples,

Table 2
Temperature programs employed in the determination of copper and iron by ETAAS with emulsion sample introduction.

Step	T (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying	50	5	0	300
	250[a]	100[a]	10	300
Pyrolysis	1000[a] (Cu) 1000[a] (Fe)	1	5	300
Atomization	2300[a] (Cu) 2400[a] (Fe)	1	2	0
Cleaning	2400 (Cu) 2500 (Fe)	1	2	300

[a] Values obtained after optimization of the methodology.