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Direct determination of copper in gasoline by flame atomic absorption spectrometry after sorption and preconcentration on *Moringa oleifera* husks ☆

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ABSTRACT

In this study a new method for the determination of copper in gasoline using *Moringa oleifera* husks as a biosorbent in an on-line preconcentration system coupled to flame atomic absorption spectrometry (F AAS) was developed. The flow and chemical variables of the proposed system were optimized through multivariate experimental designs. Initially the influence of sample pH and flow rate, adsorbent mass and eluent concentration were evaluated by a 2^3 factorial design. Adsorbent mass and sample flow rate were evaluated using the Doehlert Matrix. Employing the best conditions, the preconcentration factor was 14.0 and limit of detection for copper was 0.75 $\mu g\ L^{-1}$ and the precision was below 1.86% (50.0 $\mu g\ L^{-1}$, n = 9). The analytical curve was linear from 0.75 to 500 $\mu g\ L^{-1}$, with a correlation coefficient of 0.9951. The method developed was successfully applied for direct copper determination in spiked gasoline and the accuracy was assessed through recovery tests, with results ranging from 89.0 to 110%.

1. Introduction

Automotive gasoline is a complex mixture of olefinic, paraffinic, naphthenic and aromatic hydrocarbons, plus small amounts of sulfur, oxygen and, to a lesser degree, nitrogen compounds, with carbon content in the C_4–C_{12} range and boiling points between around 30 and 220 °C [1]. The combination of these hydrocarbons with the oxygenate compounds present determines the physicochemical properties of the fuel and has a great influence on engine performance.

In Brazil, the gasoline used as automotive fuel contains between 20 and 25% (v/v) of ethanol, being referred to as gasohol [2]. The National Agency of Petroleum, Natural Gas and Biofuels (ANP) establishes maximum concentrations for Cu, Fe and Na in alcohol fuel as 0.07, 5.0 and 2.0 mg kg^{-1}, respectively, because of their effect on the fuel performance. However, no such legislation is in place in relation to these elements in gasoline [3]. Lead in gasoline is the only metal that has a maximum allowed concentration, which is 5 $\mu g\ L^{-1}$, according to ANP, although this element is no longer employed as a gasoline additive [4].

The presence of some elements in fuels can damage the performance of the engine, due to the decomposition of the fuel, formation of precipitates and/or promotion of the corrosion of engine parts. Toxic elements in fuels represent an important source of pollution, mainly in megacities and in the proximity of roads, even in low concentrations. Some elements occur in unrefined petroleum and, consequently, in

the oil and gasoline derivatives. Others can be introduced through contact with refining and distilling equipment or during storage and/or transportation. In addition, some elements can be added, normally in organic form, to improve specific characteristics of the fuel. Since the combustion of fuels can release these elements into the atmosphere, it is very important to quantify their concentration, in order to control pollution levels [5].

Different procedures are found in the literature for the determination of metals in petroleum derivatives. Direct analysis of gasoline by most analytical techniques is hindered because of its volatility, low viscosity, corrosive nature and immiscibility with water. Additionally, metals are usually present only in very low concentrations in gasoline, requiring very sensitive techniques or preconcentration steps for their determination. Inductively coupled plasma (ICP) is a sensitive multi-element technique extensively used for the determination of metals, but the introduction of organic solvents into the plasma requires special care, as the organic load may destabilize or extinguish the plasma [6,7]. Atomic absorption spectrometry (AAS) can be used for the determination of metals in petroleum derivatives, but the direct introduction of the sample may cause the flame to become excessively fuel-rich and unstable [8]. Moreover, the high organic content of the sample may produce high noise levels, thus reducing the detectability by AAS. Chromogenic reagents are used for metal determination in gasoline samples by spectrophotometry, however, extraction and previous digestion procedures are necessary [9]. Generally, these methods are time consuming and a preliminary step is required, e.g., dry or wet ashing for the decomposition of organic material in order to obtain aqueous solutions [10,11].

Several methods have been developed for copper determination; however, most require a sample pre-treatment step. Saint' Pierre et al. used electrothermal vaporization inductively coupled plasma mass spectrometry with analyte addition and isotope dilution calibration techniques for the determination of copper in gasoline and the limits of detection were higher than 5 µg L^{-1} [12]. Campos et al. used electrothermal atomic absorption spectrometry with three-component solutions for the determination of copper, iron, nickel and lead in gasoline and the detection limits were 0.4, 3.0, 0.8 and 1.8 µg L^{-1}, respectively [13].

Many methods for the preconcentration of metal ions in solution have been described. Of particular interest are those which involve inorganic solid surfaces modified with chelating groups to increase the selectivity [14,15]. Preconcentration methods can also overcome some interference issues and improve the limits of detection [16–18].

Roldan et al. used F AAS after sorption and preconcentration on silica modified with 2-aminotiazole groups for the determination of copper, iron, nickel and zinc in gasoline and the detection limits of the method for copper, iron, nickel and zinc were reportedly 0.8, 3, 2 and 0.1 µg L^{-1}, respectively [18].

Among the existing preconcentration techniques, solid phase extraction has some advantages such as simplicity and high analytical frequency and enrichment factors, besides reducing the matrix effects [19–22].

Studies involving metal preconcentration have been reported, with the use of commercially available sorbents. However, other materials known as 'natural adsorbents' have recently been successfully employed in metal adsorption processes [23–25].

The use of natural adsorbents in procedures for solid phase extraction become more attractive when coupled on-line with the detection system and when using an adsorbent with high adsorptive capacity, such as the seeds of Moringa oleifera. Alves et al. developed a method for the determination of cadmium in alcohol fuel using M. oleifera seeds as a biosorbent in an on-line preconcentration system coupled to flame atomic absorption spectrometry [22]. The limit of detection for cadmium was 5.5 µg L^{-1} and the precision was below 2.3%. Although the method developed was successfully applied in the determination of cadmium, there are no reports in the literature on the use of moringa as a solid phase extraction substrate for copper adsorption.

Thus, due to the possible sources of contamination by metal ions, such as copper, during the production of gasoline, the objective of this study was to develop a methodology for an on-line preconcentration system, using M. oleifera husks as a biosorbent, coupled to flame atomic absorption spectrometry, for the determination of copper in gasoline.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 220 (Victoria, Australia) flame atomic absorption spectrometer, equipped with a copper hollow cathode lamp, and a deuterium lamp for background correction, was used for the detection of copper. The instrument was operated under the conditions recommended by the manufacturer: lamp current of 4 mA, wavelength of 324.7 nm, slit width of 0.1 nm, burner height of 14 mm, acetylene flow rate of 1.0 L min^{-1} and air flow rate of 10.0 L min^{-1}. A Mettler Toledo 320 pH meter was used to set the pH of the samples and working solutions. A Gilson Minipuls 3 peristaltic pump (Villiers Le Bel, France) equipped with eight channels was used in the copper preconcentration step. Tygon® tubes were used to pump the solutions through the mini-column (60 mm × 3.0 mm) containing the adsorbent.

2.2. Reagents and solutions

All working solutions were prepared with ultra-pure water obtained from Milli-Q (Millipore, Bedford, MA, USA). All reagents were of analytical grade.

All laboratory glassware was washed with a neutral detergent and then kept overnight in 10% acid aqueous solutions, followed by ultrasonification for 1 h and finally rinsing with deionized water.

Working solutions were prepared daily through dilution of a 1000 mg L^{-1} stock solution of copper in a solution containing 50% (v/v) of gasoline and 50% (v/v) of ethanol.

The nitric acid solution used as the eluent was prepared through dilution in water of concentrated nitric acid obtained from Merck (Darmstadt, Germany).

The gasoline samples were purchased in local shops. Initially, the samples were diluted with ethanol in a 50% (v/v) ratio, and the pH adjusted for 4.0.

2.3. Preparation of the column

The husks of moringa seeds used to construct the minicolumn were obtained from trees cultivated in the city of Ituiutaba (Minas Gerais, Brazil) and collected during January–July 2010. The husks were separated from the seeds, washed with deionized water and dried at 25 °C. After drying, the husks were crushed in a blender (Black & Decker, Sao Paulo, Brazil) and passed through 850 µm sieves.

The minicolumns were comprised of polyethylene tubes with an inner diameter of 3.0 mm and were sealed at both ends with glass wool. The minicolumn (60 mm × 3.0 mm) was filled with 96 mg of the husks and the performance was stable during all experiments.

2.4. On-line preconcentration system

The on-line flow system used for the development of the proposed method is shown in Fig. 1. The flow system consists of a peristaltic pump equipped with Tygon® tubes, four 3-way solenoid valves and a mini-column filled with biosorbent. The system was coupled to the AAS instrument. During the preconcentration step (Fig. 1A) valve 1 is ON and the other valves remain OFF, the samples or working solutions are pumped through the mini-column and the effluent is discharged. In the elution step (Fig. 1B), valve 1 is OFF and valves 2, 3 and 4 are ON. The water flow is stopped and the eluent percolates through the mini-column in the opposite direction to that of the sample undergoing the preconcentration step. The eluate is carried directly to the nebulization system of the AAS instrument.

2.5. Optimization system

The optimization of the parameters affecting the sorption of Cu by the M. oleifera husks was performed using a two-level full factorial experimental design involving four factors with final optimization based on the response surface. All experiments were carried out in duplicate, using 15.0 mL of a 10 µg L^{-1} Cu solution. The variables studied were sample pH, adsorbent mass, eluent concentration and sample flow rate.

3. Results and discussion

3.1. Optimization strategies

Preliminary studies showed that the relative standard deviation (RSD) of 10 measurements was 14% when pure gasoline samples were introduced into the preconcentration system. Thus, further preliminary tests were performed to investigate the best gasoline/ethanol ratio to be introduced into the preconcentration system. A mixture composed of 50% (v/v) gasoline/ethanol was found to be adequate due to higher reproducibility (RSD = 0.29%) and better analytical signal provided (Fig. 2).

Pure gasoline is almost immiscible in water whereas ethanol is completely miscible in gasoline and water in all concentrations. Ethanol added to gasoline acts by reducing the interfacial tension of the mixture.