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Determination of Copper, Iron, Nickel, and Zinc in Ethanol Fuel by Flame Atomic Absorption Spectrometry Using On-Line Preconcentration System

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Abstract: In this work, an on-line system for preconcentration and determination of copper, iron, nickel, and zinc at $\mu g\,L^{-1}$ level by flame atomic absorption spectrometry (FAAS) has been developed. Amberlite XAD-4 functionalized with 3,4-dihydroxybenzoic acid packed in a minicolumn was used as metal sorbent. The retained metals can be quickly eluted from sorbent material, with the eluent stream consisting of hydrochloric acid solution, directly to the nebulizer burner system of the FAAS. Analytical parameters were evaluated and the results demonstrated that all studied metals can be determined, using borate buffer to adjust the sample pH at 8.0. The results showed that the proposed method is simple and rapid. The limits of detection were estimated as 2.3, 5.0, 7.8, and 0.1 $\mu g\,L^{-1}$ for copper, iron, nickel, and zinc, respectively, using a preconcentration time of 60 s and a sample flow rate of 5.5 $mL\,min^{-1}$. Enrichment factors of 22, 15, 12, and 54 and coefficients of variations of 3.5, 4.4, 4.4, and 3.2% were obtained in the determination of copper, iron, nickel, and zinc, respectively. The system presented an analytical throughput of 10 samples per hour and was successfully applied in the determination of metals in ethanol fuel.

Keywords: Flame atomic absorption spectrometry, ethanol fuel, on-line preconcentration, amberlite XAD-2

INTRODUCTION

Ethyl alcohol is of increasing interest as fuel substitutes for conventional hydrocarbon fuels. Private and government programs have been established in many countries in order to find viable alternative fuels to replace petroleum derivatives. Brazil is the country that has attempted the large-scale use of alcohol as an automobile fuel by the use of ethanol-gasoline blended fuel (gasohol, mixture of 75% gasoline and 25% anhydrous ethanol) or by the use of light duty cars exclusively driven using hydrated ethanol as fuel (1, 2). Owing to chemical differences between hydrocarbon fuels and alcohols, corrosion problems are intrinsically more severe with the alcohols. Alcohols dissolve both water and inorganic salts and the water content of alcohol fuel plays a significant role in metal corrosion. Furthermore, the physical and chemical properties of alcohols influence corrosion (3). So, metallic species can be introduced into the fuels by corrosion of equipments during fuel processing and storage (4).

The presence of metallic species in automotive fuels is generally not desirable because it is associated with corrosion, undesirable metal deposition in parts of the engine, and poor fuel performance due to oxidative decomposition reactions. It has been well established that trace quantities of certain metals promote autoxidation of organic compounds and initiate chemical processes that may lead to the formation of gums and sediments in aircraft fuel systems that are deleterious to optimal performance. In addition, fuel combustion may also contribute significantly to the emissions of metals of environmental concern (4–6). Brazilian legislation has stipulated concentration limits for some metals in ethanol fuel, and they vary according to the type of fuel (anhydrous or hydrated). For example, Cu limit is $0.07\,\mu g\,g^{-1}$ in anhydrous ethanol, while the maximum value for Fe in hydrated ethanol is $5\,\mu g\,g^{-1}$ (4, 7). Due to large production volume of ethanol fuel and the presence of metals as contaminant in this fuel, it is necessary sensitivity and accuracy in analytical methods for determination of these compounds in this kind of matrix (8–10).

Despite the selectivity and sensitivity of atomic absorption spectrometry technique, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples. Liquid–liquid extraction is a classical method for preconcentrating metal ions. Solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, specially using on-line preconcentration systems due to its flexibility, simplicity, high sampling rate, and versatility (11–17).

In this paper, an on-line preconcentration system for determination of copper, iron, nickel, and zinc in ethanol fuel using flame atomic absorption spectrometry (FAAS) was proposed. The procedure is based on solid-phase extraction of metals ions as 3,4-dihydroxybenzoic acid (DHB) complexes on Amberlite XAD-2 (DHB-XAD resin) (17). The purpose of this article is to evaluate FAAS coupled with on-line preconcentration as a sensitive and practical procedure to determine metal ions in automotive alcohol samples.

EXPERIMENTAL

Apparatus

A Varian Model SpectrAA 220 flame atomic absorption spectrometer (Mulgrave, Vic., Australia) was used for the analysis. All measurements were based on integrated absorbance. The metals hollow cathode lamps were run under the conditions suggested by the manufacturer. The flame composition was acetylene (flow rate: $2.0\,L\,min^{-1}$) and air (flow rate: $13.5\,L\,min^{-1}$). Nebulizer flow rate was $5.0\,mL\,min^{-1}$.

An Alitea C-6 XV (Stockholm, Sweden) peristaltic pump furnished with Tygon tubes was used to propel all solutions. A Rheodyne 5041 (Cotati, California, USA) model four-way manual valve was used to select preconcentration/elution steps. All connections were made using fittings, unions, and tees made of plastic and PEEK materials. The manifold was built up with PTFE tube of 0.5 mm bore.

A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used.

Reagents and Solutions

All reagents were of analytical-grade quality, and freshly distilled and deionized water was used. Ethanol absolute (Merck, min. 99.8%) was used to prepare the ethanolic solutions. Hydrochloric acid solution ($0.5\,\mathrm{mol\,L^{-1}}$) was prepared by direct dilution with water from the concentrated suprapur solution (Merck). Metals working solutions were prepared daily by diluting $1000\,\mu\mathrm{g\,mL^{-1}}$ copper, iron, nickel, or zinc solutions (atomic absorption Aldrich) with ethanol absolute. Acetate, TRIS (tris-(hydroxymethyl) aminomethane), borate and ammoniacal buffers conveniently prepared were used to adjust the sample pH range of 4.8–6.0, 7.0–10.0, 8.0–9.0, and 9.0–10.0, respectively. Amberlite XAD-2 (Sigma, 20–60 mesh), DHB (Sigma), nitric and sulphuric acids (Merck), and sodium nitrite (Reagen) were used for synthesis of the sorbent.

Samples

Six hydrated ethanol fuel samples were randomly collected from different gas stations in Salvador, Bahia State, Brazil (Texaco, Shell, Esso, CBPI, BR, Petrobahia). So, 95 mL portion of each sample was transferred to 100 mL volumetric flasks and the volume was filled with borate buffer solution (pH 8.0). At least one blank solution (deionized water and borate buffer) was run for each sample in order to evaluate metal contamination by the reagents used.

Column Preparation

Procedure described previously in literature was used to synthesis of DHB-XAD (17). A home-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm containing about 100 mg of DHB-XAD was used in the on-line preconcentration procedure. A syringe was used to put the sorbent inside the minicolumn. Plastic foams were placed at the inlet and outlet of the minicolumn to avoid removal of the resin by carrier stream. Afterward, the minicolumn was washed with ethanol 5% (v/v), nitric acid solution, and deionized water, respectively, at $2.50\,\mathrm{mL\,min^{-1}}$ flow rate. The DHB-XAD minicolumn was washed with nitric acid and ethanol to prevent any metal or organic contamination, respectively. All minicolumns prepared by this way show good reproducibility.

On-Line Preconcentration System

A diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was carried out using a peristaltic pump fitted with Tygon

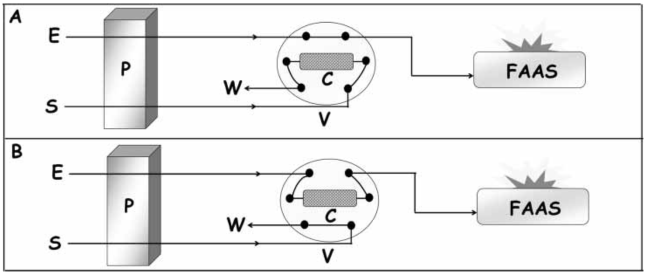

Figure 1. Schematic diagram of the flow system used for preconcentration and determination of copper, iron, nickel, and zinc by FAAS. S, sample; E, eluent; P, peristaltic pump; C, DHB-XAD minicolumn; V, Fourway valve; FAAS, flame atomic absorption spectrometer, and W, waste. (A) Fourway valve in the preconcentration step and (B) four-way valve in the elution position.

tubes, a four-way valve and a minicolumn packed with DHB-XAD resin coupled to a flame atomic absorption spectrometer. The length of the capillary PTFE tube between the end of minicolumn and the nebulizer was as short as possible (about 5 cm) to minimize the sample dispersion.

The flow system was operated in a time-based mode, in which a sample solution (S) pumped at 5.5 mL min^{-1} percolated through the minicolumn that contained the solid sorbent. Then metals ions were retained by chemical sorption as DHB complex and the remaining solution was discharged (W). By switching the valve, a stream of 1 mol L^{-1} hydrochloric acid (E) that flowed at 5.5 mL min^{-1}, displaced the metals complexes. This eluate was taken direct to the nebulizer-burner system of the flame atomic absorption spectrometer. Preconcentration time was 60 s. Signals were measured as peak area by using the instrument software. At the end of each cycle the minicolumn was reconditioned by percolation of the buffer solution for 10 s. This procedure was adopted for each metal determination (copper, iron, nickel or zinc). Achieved sampling rate was 10 samples per hour for preconcentration time of 60 s, elution time of 10 s and recondition time of 10 s.

RESULTS AND DISCUSSION

To determine the best chemical and hydrodynamic conditions for copper, iron, nickel, and zinc determination the continuous flow system was optimized. The system was optimized by using the univariate method in order to determine best chemical and flow conditions for the studied metals determination with good sensibility. A solution containing 30.0 μg L^{-1} of each ion was employed for these studies.

Chemical Variables

The effect of the sample pH on the metals ions retention and determination response was investigated within the range of 5.0–10.0. Appropriated buffer solutions were used to adjust the pH of a multielementar solution containing $30\,\mu g\,L^{-1}$ of each metal studied. No significant variation in the retention efficiency and signals was observed in the pH range of 7.0–8.5, for all studied metals. So, a borate buffer solution at pH 8.0 was selected to control the medium pH. The effect of the buffer concentration on the metals determination was studied and according to the results no effect in the retention and absorption signals were observed within borate final concentration raging from 5.0×10^{-4} to $2.0 \times 10^{-3}\,mol\,L^{-1}$. The final concentration of $1.0 \times 10^{-3}\,mol\,L^{-1}$ of borate was selected for hereafter work.

The metals elution from the minicolumn was studied by using hydrochloric acid solutions at different concentrations ($0.01–1.00\,mol\,L^{-1}$) as stripping agent using a flow rate at $5.6\,mL\,min^{-1}$. Total metals elution was reached in concentrations over $0.05\,mol\,L^{-1}$. So, $0.1\,mol\,L^{-1}$ hydrochloric acid solution was selected as eluent for further studies. The time of elution was also studied, because it determinates the quantity of acid that passes by minicolumn. It was found that for elution time superior than 10 s the absorbance signal was constant, using $0.1\,mol\,L^{-1}$ hydrochloric acid as eluent solution. So, an elution time of 10 s was chosen for posterior experiments in order to pass a minimum quantity of acid by the minicolumn and to increase the sample throughput.

It was observed that the DHB-XAD minicolumn was very stable in acidic and ethanolic solutions and under rough changes of pH conditions. This fact allowed its use for more than 100 measurements without affecting the retention of the studied metals.

Hydrodynamic Variables

The effect of the sample flow rate in the proposed system was studied. So a multielementar solution containing $30\,\mu g\,L^{-1}$ of each metal studied was pumped into the system at flow rates varying from 2.2 to $9.1\,mL\,min^{-1}$ for 60 s. For all metals studied it was observed that analytical signals decreased at high flow rates of upper $6.0\,mL\,min^{-1}$. Thus, a sample flow rate of $5.5\,mL\,min^{-1}$ was chosen for posterior experiments as a compromise between retention efficiency and sample throughput.

The preconcentration time was studied in the range from 30 to 240 s using a multielementar solution containing $30\,\mu g\,L^{-1}$ of each metal studied at a sample flow rate of $5.5\,mL\,min^{-1}$. It was observed that the analytical signal increased proportionally with the preconcentration time up to 150 s for all metals tested. So, a preconcentration time of 60 s was chosen as a compromise between sensitivity and efficiency. When more sensitive determinations are required, preconcentration time can be increased if not exceeding the limit of 150 s, using a sample flow rate of 5.5 mL min^{-1}.

The effect of the flow rate on the elution of the metals retained on DHB-XAD minicolumn was investigated using 0.1 mol L^{-1} hydrochloric acid as cleaning solution. It was observed that a change in flow rate from 4.0 to 6.0 mL min^{-1} did not affect the metals desorption when it was used 10 s of elution time. These results demonstrated that the metals desorption is fast and independent of the elution flow rate. So a flow rate of 5.5 mL min^{-1} was selected for further system application.

Features of the Method

Under the optimized conditions described, the experimental procedure was applied to obtain the features of the proposed method. The analytical curves were obtained using multielementar standard solutions (10.0–60.0 μg L^{-1}) prepared by diluting copper, iron, nickel, and zinc concentrated solutions with ethanol absolute. The pH was adjusted with borate buffer. Procedural blank solution, prepared in a similar way without any analyte, was analyzed along with the sample solutions. The coefficient of variation was calculated for 10 independent, and the detection limit was calculated as three times the standard deviation of the blank solution. The experimental preconcentration factor was calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, using 60 s of preconcentration time. These preconcentration factors indicate the increase in the FAAS signal, and it varies for each metal. The analytical characteristics of the proposed procedure are summarized in Table 1. The capacity of DHB-XAD for cations was determined by equilibrating 0.50 g of the resin with 100 mL of 5.0 mg L^{-1} Cu(II), Fe(III), Ni(II) or Zn(II) solutions at pH 8.0 (borate buffer) for 4 h. Metals were determined in each filtrate. The resin capacity for metals is found in Table 1. The limit of detection (LOD), defined as the absolute mass of metal that gives a response equivalent to three times the standard deviation (σ) of the blank ($n = 11$), was also calculated. Achieved sampling rate was 10 samples per hour considering a preconcentration time of 60 s, elution time of 10 s, and recondition time of 10 s between preconcentration and elution procedures.

Application

The proposed method has been applied to the determination of copper, iron, nickel, and zinc in hydrated ethanol fuel from different fuel distributors. Initially, the method validation was made through spike recovery tests with the addition of 20 μg L^{-1} of each metal in two different fuel samples. Each result was obtained as the average of three replicates of each fuel and results are showed in the Table 2. As can be seen, the method has good

Table 1. Analytical characteristics of the proposed procedure[a]

	Metal			
Analytical parameters	Copper	Iron	Nickel	Zinc
Wave length, nm	324,7	248,3	232,0	213,9
Analytical curve, A = absorbance and C = metal concentration ($\mu g\,L^{-1}$)	$A = 2.7 \times 10^{-3}\,C + 0.013$	$A = 7.0 \times 10^{-4}\,C + 0.0082$	$A = 1.1 \times 10^{-3}\,C + 0.0092$	$A = 6.3 \times 10^{-3}\,C + 0.016$
Correlation coefficient, n = 5	0.998	0.997	0.999	0.999
Limit of detection[b] (3σ), $\mu g\,L^{-1}$	2.3	5.0	7.8	0.1
Coefficient of variation (10.0 $\mu g\,L^{-1}$ of each metal), n = 10	3.5	4.0	4.4	3.2
Coefficient of variation (30.0 $\mu g\,L^{-1}$ of each metal), n = 10	1.8	2.5	2.8	1.2
Sorption capacity, mmol g^{-1}	2.4	1.9	1.5	3.2
Preconcentration factor	22	15	12	54

[a] 60 s of preconcentration time; n: number of determinations; σ: standard deviation.

[b] Calculated as three times the standard deviation of the blank solution (n = 30).

Table 2. Determination of copper, iron, nickel, and zinc ($\mu g\,L^{-1}$) in hydrated ethanol fuel (n = 3) through spike recovery tests with the addition of 20 $\mu g\,L^{-1}$ of each metal (n = 3, at 95% of confidence level)

	Sample 1	Sample 2
Sample with copper addition	36.9 ± 0.2	34.9 ± 0.4
Sample without copper addition	17.6 ± 2.1	15.1 ± 0.9
Copper recovery, %	96	99
Sample with iron addition	42.8 ± 1.0	40.6 ± 2.9
Sample without iron found	23.7 ± 1.2	21.6 ± 1.2
Iron recovery, %	96	95
Sample with nickel addition	38.4 ± 2.1	44.50 ± 1.6
Sample without nickel found	19.9 ± 2.8	26.3 ± 1.7
Nickel recovery, %	92	93
Sample with zinc addition	72.1 ± 0.3	68.9 ± 1.0
Sample without zinc addition	52.2 ± 1.7	48.2 ± 0.3
Zinc recovery, %	100	101

accuracy and the recovery was between 92 and 101%. Other metals can be present in minor concentration in the analyzed samples and can be retained in DHB-XAD resign. However, the presence of these metals did not interfere in the determination of the Cu, Fe, Ni, and Zn. It was confirmed by the recovery test results obtained. So the proposed method was applied to metals determination in four hydrated ethanol fuel samples collected from different gas stations. Results are shown in the Table 3.

CONCLUSION

The developed procedure provides a sensitive and simple approach for the determination of copper, iron, nickel, and zinc by metals retention onto minicolumn packed with DHB-XAD resin. The method is highly sensitive and an inexpensive

Table 3. Determination of copper, iron, nickel, and zinc ($\mu g\,L^{-1}$) in hydrated ethanol fuel (n = 3, at 95 % of confidence level)

	Metal			
Sample	Copper	Iron	Nickel	Zinc
Distributor 3	22.9 ± 2.3	14.3 ± 2.3	14.4 ± 8.7	44.0 ± 2.8
Distributor 4	21.4 ± 0.4	11.0 ± 2.9	15.2 ± 3.4	41.2 ± 1.0
Distributor 5	18.5 ± 3.8	12.0 ± 3.4	11.9 ± 1.2	38.4 ± 1.2
Distributor 6	16.1 ± 2.1	11.5 ± 2.6	7.8 ± 1.5	42.2 ± 1.0

alternative for metal determination in ethanol fuel with the concomitant benefits from the use of the FI-FAAS preconcentration (safety, cost, high separation yield, versatility). Besides, the method can be easily employed not necessarily for the analysis of all species but alternatively for the detection of either of them in the presence of the other. The on-line preconcentration system developed using flame atomic absorption spectrometry (FAAS) is rapid and robust and allowed metals determination in ethanol fuel without any sample pretreatment.

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