Magnetic Solid Phase Microextraction using CoFe₂O₄ Nanoparticles for Determination of Cu, Cd, Pb and V in Sugar Cane Spirit Samples by Energy Dispersive X-Ray Fluorescence Spectrometry
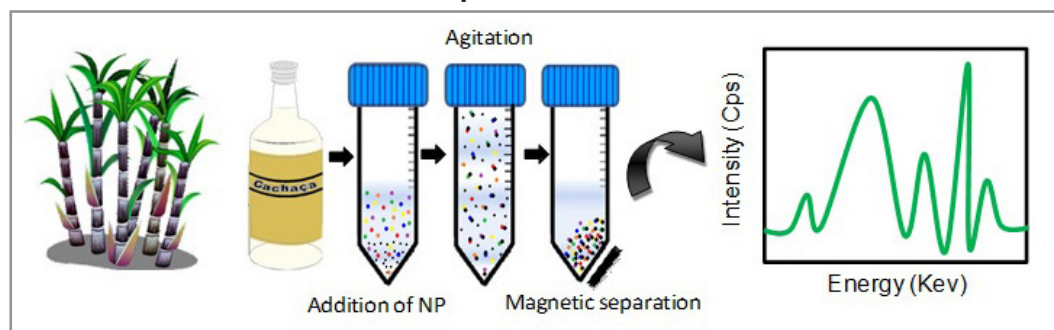
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Graphical Abstract

Determination of Cu, Cd, Pb and V in sugar cane spirit samples by EDXRF after preconcentration using CoFe₂O₄

A method for the determination of Cu, Cd, Pb and V in Brazilian sugarcane spirit (*"cachaça"* in Brazil) using CoFe₂O₄ nanoparticles impregnated with 1-(2-pyridylazo)-naphthol (PAN) for extraction of the metals with posterior determination by X-ray fluorescence spectrometry directly in the solid phase is described. The recommended conditions for extraction were: pH 6.0 (1.0 mol L⁻¹ hexamethylenetetramine (HMTA)/ nitric acid buffer solution); sample volume, 25 mL; and nanoparticle mass, 100 mg. The precisions for the determination of each element, expressed as relative standard deviations (RSD) of standard solutions containing 0.20 mg L⁻¹ of each analyte, were 1.5, 1.8, 1.2 and 2.9% (n = 10), respectively. Limits of detection of 0.032, 0.038, 0.016 and 0.028 mg L⁻¹ were obtained for Cu, Cd, Pb and V, respectively. Addition and recovery tests were performed, and the results ranged from 97 to 115% for Cu, 85 to 115% for Cd, 85 to 99% for Pb and 85 to 110% for V. The method was successfully applied in extraction and determination of Cd, Pb, Cu and V in sugar cane spirit samples from Brazil.

Keywords: sugar cane spirit; energy dispersive X-ray fluorescence spectrometry; multi-element determination; magnetic solid-phase microextraction.

INTRODUCTION

The sugar cane spirit (usually known as *"cachaça"* in Brazil) is the typical and exclusive denomination of cane brandy produced in Brazil, with an alcoholic content of 38-48% (v v⁻¹) and peculiar sensorial characteristics [1,2]. The *cachaça* is the third most consumed distilled beverage in the world, and in

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Brazil, occupies the first place [3].

Metals can be introduced in sugar cane spirit during the production process, transport and tankage due to the oxidation of parts of the metallic equipment's or with the use of raw material with inorganic contaminants [4]. The quantification of metallic specie is important for product quality control, observing the inorganic composition assurance and the presence of toxic elements to humans [5]. These determinations are routinely performed by flame atomic absorption spectrometry (F AAS), [6-9], inductively coupled plasma mass spectrometry (ICP-MS) [10], electrothermal atomic absorption spectrometry ET AAS [2,4,11,12,13] and UV-Vis spectrophotometry [14,15]. However, the energy dispersive X-ray fluorescence spectrometry (EDXRF) has not been explored for determination of inorganic species in sugar cane spirit.

Energy dispersive X-ray fluorescence spectrometry is a successful technique, since it allows multi-element determination with sufficient spectral resolution in metals determination. However, EDXRF has low sensitivity and it may be difficult to use liquid and volatile samples, such as sugar cane spirit. Thus, it is common to include a step for metal extraction and preconcentration prior the determinations using the EDXRF [16-21].

Extraction and pre-concentration of metals using magnetic nanoferrites have been explored in association with different analytical techniques of detection [22], including EDXRF [17]. In the latter case, the possibility of association of magnetic nanoparticles with EDXRF for ethanolic matrix analysis (specifically, fuel ethanol) was shown. The objective of this work was to verify the possibility of expanding the application of the extraction and determination of Cu, Cd, Pb and V in sugar cane spirit samples using magnetic solid phase dispersive microextraction with CoFe$_2$O$_4$ nanoparticles (NPs) as solid support for measurements by EDXRF.

MATERIALS AND METHODS

Instrumentation

An energy dispersive X-ray spectrometry S2 Ranger (Bruker, Billerica, MA, USA) was used for the measurements. The equipment has a palladium-targeted X-ray tube. The equipment calibration was performed using a copper disk (40 mm diameter).

After the extraction procedure, nanoferrites rich in metals of interest were placed in the center of a polyethylene cup spectrometer cell and the sample holder was sealed with a Mylar® film. The instrumental conditions were: irradiation time, 90 s; tube tension, 40 kV; tube current, 30 mA; and a helium atmosphere. The analytical lines used were: Cd, 23.1 keV (Kα); Pb, 10.6 keV (Lα); Cu, 8.04 keV (Kα) and V, 5.00 keV (Kα).

A model 827 digital pH meter (Metrohm Ltd., Switzerland) with a combined glass electrode was used in the pH adjustments of the solutions. An ultrasonic bath (model 75D from VWR International™, Cortland, New York) of 60 kHz and 2 L of power and internal capacity, respectively, was used to accelerate CoFe$_2$O$_4$ impregnation with PAN. An analytical balance (model TE214 S from Sartorius, Goettingen, Germany) with an accuracy of ± 0.1 mg was used for weighing of the masses of substances used. Centrifuge conical tubes with internal capacity of 50 mL were used in the experiments.

A Varian Vista (Mulgrave, Australia) simultaneous inductively coupled plasma optical emission spectrometer instrument with axial viewing, equipped with charge coupled device (CCD), and a V-Groove nebulizer, was used as a comparative method for determination of Cu, Cd, Pb e V. The metal determinations were carried in the following conditions: power (1.4 kW), plasma gas flow (15.0 L min^{-1}), nebulizer gas flow (0.7 L min^{-1}), and auxiliary gas flow (1.5 L min^{-1}). The emission lines used in the determination were: Cu (324.752 nm), Cd (214.439 nm), Pb (220.353 nm) and V (318.397 nm).

Reagents, solutions and samples

All reagents used were at least of analytical grade. Water with a resistivity of 18.2 MΩ cm was obtained from a Milli-Q system (Millipore, Bedford, MA, USA) and used in all solution preparation. Nitric

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acid was purified by double sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). All flasks were cleaned by soaking in a 1.4 mol L^{-1} HNO$_3$ solution for at least 24 h and rinsed abundantly with high-purity deionized water before use.

All solvents and reagents were of the highest commercially available purity grade. Mixed working standard solutions for Cd, Pb, Cu and V (0.20 mg L^{-1}) were prepared by dilution from 1000 mg L^{-1} stock solutions (Specsol Quimlab, Brazil). The solutions of each element were prepared by dilution in 1.0 mol L^{-1} hexamethylenetetramine (HMTA)/nitric acid buffer solution and ethyl alcohol PA.

Nanoferrites were synthesized from their metal precursors in the form of nitrate (Exodus Científica, Brazil) and impregnated with 1-(2-pyridylazo)-naphthol (PAN) (0.005 mol L^{-1}) (Merck, Darmstadt, Germany) as previously described [17,23,24].

Unaged sugar cane spirit (cachaça) samples were obtained from different industrial producers in Brazil. The samples were transparent and were produced for immediate consumption, without going through aging process in wooden barrels. They were purchased in supermarkets in the metropolitan region of Salvador, Bahia, Brazil, and stored in a refrigerator at 4 °C until analysis.

Synthesis and impregnation of CoFe$_2$O$_4$ nanoparticles

The CoFe$_2$O$_4$ nanoparticles were synthesized following a co-precipitation procedure as described in a previous work [17]. Briefly, iron nitrate and cobalt nitrate solutions were mixed in an stoichiometry ratio of 2:1 (Fe:Co) in the presence of a sucrose solution. Then, NaOH solution was added until precipitate formation. After filtration, the precipitate was washed, heated and calcined. Once synthesized, the nanoparticles were impregnated with the reagent 1-(2-pyridylazo)-naphthol (PAN). A mass of 2.0 g of CoFe$_2$O$_4$ was immersed in 20 mL of PAN solution (0.005 mol L^{-1}) and 10 mL of sodium dodecyl sulfate (SDS) solution (0.018 mol L^{-1}) in a glass vessel of 100 mL of internal capacity. The mixture was sonicated for 20 min. After impregnation, the nanoferrites were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The nanoparticles presented a particle size of (8.5 ± 2.8) nm. More detailed information of the synthesis and characterization of the nanoferrites used in this work are described in a previous work [17].

General procedure

A volume of 22.0 mL of each sugar cane spirit sample was added directly into a centrifuge tube. Subsequently, 3.0 mL of 0.1 mol L^{-1} HMTA /nitric acid buffer solution (pH 6.0) was added to the medium. Then, 100 mg of CoFe$_2$O$_4$ NPs was added to the medium and the mixture was stirred manually for 10 min. Then, the NPs were separated from the supernatant with the aid of a magnet. Subsequently, the solid phase was conducted to the drying stage at room temperature and then subjected to the determination of the metal ions contained in the solid support itself (nanoferrite) using EDXRF.

Calibration curves were prepared in alcoholic medium attending a concentration range of 0.107–1.000, 0.127–1.000, 0.053–1.000 and 0.093–1.000 mg L^{-1} for Cu, Cd, Pb and V respectively. The alcohol content of the reference solutions was adjusted to (40 ± 5)% (v v^{-1}), to simulate the matrix of the samples, using PA hydrated ethyl alcohol (Merck, 95.1%). The blank solutions were prepared through the same procedure using pure hydrated ethanol (95.1%, Merck, Germany) with the addition of the buffer solution giving solutions with final ethanol content of (40 ± 5)% (v v^{-1}). Blank solutions were analyzed by EDXRF and the analytical signals were low and comparable to background signals. All standard solutions, including blanks, were subjected to the extraction procedure for the purpose of constructing the calibration curve.

Comparative method

The comparative method for the determination of Cu, Cd, Pb and V in sugar cane samples was performed using the inductively coupled plasma optical emission spectrometry (ICP OES) technique. The external calibration in acid medium (HNO$_3$ 0.01 mol L^{-1}) was used for all the elements. Samples of

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sugar cane spirit were pretreated prior to determination of the metals by evaporation to near dryness at constant temperature, thereafter they were adjusted to known volumes using dilute nitric acid. In this way, it was possible to obtain sufficient conditions to allow the analysis by ICP OES.

RESULTS AND DISCUSSION

The instrumental conditions of the equipment operation were established previously when ethanol fuel analysis by EDXRF was proposed: irradiation time, 90 s; tube voltage, 40 kV; current, 30 mA and atmosphere helium condition [17].

In solid phase microextraction, the pH value plays a critical role in the extraction of metals. The surface charge density of CoFe$_2$O$_4$/NPs is a major factor affecting the extraction of the analytes and their amount varies strongly with the pH values [24]. In this way, the extraction capacity of the metals at pH 1-12 was evaluated. Practically, no extraction for the metals investigated was observed for pH values between 1-3. Low pH values make the surface of the nanoparticle positive, leading to low metal retention [25-27]. The analytical signals for all metals increase significantly from pH 5 and highest extractions were obtained in the pH range of 5-7. For pH above 8, a decrease in analytical signals was observed, possibly due to the formation of metal hydroxides, which compromises the extraction of the ions. Thus, the pH of the samples was adjusted to 6.0 for extraction of all metals in accordance with the previous work when ethanol fuel was analyzed [17].

The total sample volume was evaluated in the range 3-100 mL. Firstly, the test was performed keeping the analyte mass constant in order to verify if an increase of sample volume affects the extraction efficiency. In addition, the formation of particle agglomerates can occur, varying the contact surface of the nanoparticles and sample [28]. The results indicated that there was no significant difference in the analytical signals when sample volumes in the range 3-100 mL were employed. However, when different volumes with constant concentrations are used the analyte signal increases linearly up to the volume of 25 mL. Thus, to guarantee the sensitivity of the developed method, 25 mL of sample were used. Using a 25 mL volume, the contact time between sample and nanoparticles was evaluated for 5-20 min, and it was noted that there was no significant variation in the results for contact times greater than 10 min.

The ethanol content is another important variable to be investigated, because, depending on the alcoholic content of the medium, there may be release of the PAN from the nanoparticle to the solution. Previous works report the stability of the nanoferrite in the presence of organic solvents, such as ethanol [17,29]. However, a release of PAN was visually observed for ethanol content above 70% (v v^{-1}) [17]. Considering that the concentration of alcohol in sugar cane spirit is typically 38-48% (v v^{-1}), the concentration of ethanol was adjusted in this range in the standard solutions for calibration purpose

For use of CoFe$_2$O$_4$ nanoparticles in the pre-concentration of metals and direct determination on the solid support by X-ray fluorescence spectrometry, it is necessary to establish the mass of the NPs suitable for the procedure. A small mass is insufficient to retain a significant amount of metals. In addition, there is a difficulty in working with EDXRF using low amounts of solid support, because affects the accuracy of the measurements. High mass of CoFe$_2$O$_4$ nanoparticle can generate physical interference [27]. In this way, the nanoparticle mass was evaluated from 100-800 mg and through the results obtained 100 mg was choose (Figure 1).
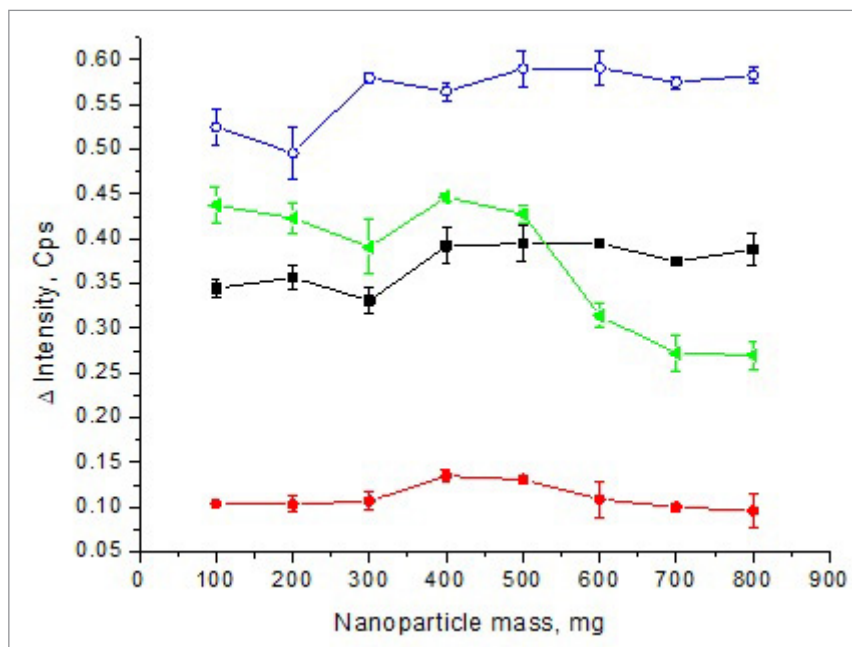
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Figure 1. Effect of the mass of the magnetic nanoferrite on the analytical signal for determination of Cu (■), Cd (●), Pb (◄) and V(○)in sugar cane spirit samples. Conditions: concentration of all metals, 0.20 mg L^{-1}; pH 6.0; buffer solution HMTA/nitric acid, 1.0 mol L^{-1}; contact time, 10 min; sample volume, 25 mL; ethanol content, 35% (v v^{-1}).

Analytical features and application

Using the general procedure, a series of experiments was performed to obtain the calibration graph, linear range, precision, limit of detection and limit of quantification for determination of the analytes. The relative standard deviation (RSD) was obtained for the repetitive determinations of 0.2 mg L^{-1} of all metals (n = 10). The limit of detection (LOD) and quantification (LOQ) were calculated using the criterion 3xSb/m and 10xSb/m, where Sb is the standard deviation of the blank measurements and m is the calibration slope. The analytical characteristics of the proposed method are shown in Table I.

The sugar cane spirit samples were analyzed using spike recovery tests. These results were obtained as the averages of three replicates of each sample. As shown in Table II, the recoveries varied from 97 to 115% for Cu, 85 to 115% for Cd, 85 to 99% for Pb and 85 to 110% for V. Good agreement was found between the results obtained using the proposed method and the comparative method for the results of concentrations of the analytes.

Table I. Analytical characteristics of the proposed method for the determination of Cu, Cd, Pb and V in sugar cane spirit samples

Parameters	Cu	Cd	Pb	V
Calibration curve	I = 0.491x + 1.085	I = 0.376x + 0.123	I= 1.525x + 2.073	I= 1.402x + 0.956
Coefficient of correlation	0.994	0.996	0.993	0.996
Linear range, mg L^{-1}	0.107-1.000	0.127-1.000	0.053-1.000	0.093-1.000
LOD, mg L^{-1}	0.032	0.038	0.016	0.028
LOQ, mg L^{-1}	0.107	0.127	0.053	0.093
RSD, % (0.2 mg L^{-1}; n = 10)	1.5	1.8	1.2	2.9

LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation; I: intensity of fluorescence, cps; x: concentration of the respective analyte, mg L^{-1}.

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Table II. Determination of Pb, Cd, Cu and V in sugar cane spirit samples by EDXRF after magnetic solid-phase microextraction procedure and by the comparative method (n= 3)

	Concentration (mg L^{-1})			
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**
Sample without lead addition	<LQ	<LQ	0.075 ± 0.002	0.081 ± 0.002
Sample with lead addition*	0.17 ± 0.05	0.18 ± 0.02	0.25 ± 0.02	0.28 ± 0.02
Recovery (%)	85	90	88	99
Comparative method[a]	<LQ	<LQ	0.102 ± 0.025	0.08 ± 0.02
Sample without cadmium addition	<LQ	0.17 ± 0.02	<LQ	<LQ
Sample with cadmium addition*	0.202 ± 0.005	0.39 ± 0.05	0.17 ± 0.02	0.23 ± 0.04
Recovery (%)	101	110	85	115
Comparative method[a]	<LQ	0.17 ± 0.01	<LQ	<LQ
Sample without copper addition	0.25 ± 0.05	0.21 ± 0.05	0.86 ± 0.04	<LQ
Sample with copper addition*	0.444 ± 0.001	0.44 ± 0.01	1.08 ± 0.02	0.21 ± 0.06
Recovery (%)	97	115	110	105
Comparative method[a]	0.32 ± 0.05	0.23 ± 0.03	0.76 ± 0.12	<LQ
Sample without vanadium addition	<LQ	<LQ	<LQ	0.11 ± 0.01
Sample with vanadium addition*	0.17 ± 0.02	0.17 ± 0.05	0.18 ± 0.02	0.33 ± 0.02
Recovery (%)	85	85	90	110
Comparative method[a]	<LQ	<LQ	<LQ	0.10 ± 0.02

[a]Determination by ICP OES; *Recovery tests: 0.2 mg L^{-1} of each metal.

CONCLUSION

The proposed method provides a highly sensitive and simple approach for the determination of copper, cadmium, lead and vanadium in sugar cane spirit samples by EDXRF after the application of a magnetic solid-phase dispersive microextraction procedure. The method is simple and does not require a drastic pretreatment with the use of concentrated acids or long time for analysis.

Acknowledgments

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