

Solid Phase Extraction Using SiO₂/Al₂O₃/TiO₂ Ternary Oxide for Cu²⁺ Preconcentration

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The present work aims at studying the preconcentration of Cu²⁺ ions by solid phase extraction using SiO₂/Al₂O₃/TiO₂ ternary oxide as adsorbent material. This methodology consists of the affinity of the analyte for the adsorbent material and its subsequent elution with the least amount of solvent. Subsequently, the aqueous phase containing the extracted analyte was collected and analyzed by square wave anodic stripping voltammetry (SW-ASV). For the applied solid phase extraction (SPE) methodology, a complete factorial design was carried out with 3 variables at 2 levels (pH, elution flow rate and analyte concentration) to optimize the extraction conditions. The results showed that at pH 9, the SiO₂/Al₂O₃/TiO₂ oxide presents excellent Cu²⁺ adsorption capacity with recovery values between 81.0 and 104% for this pH range. The limit of detection (LOD) and limit of quantification (LOQ) values were determined to be 1.71 and 5.64 µg L⁻¹, respectively. The study of recovery for SPE method revealed results of 102 and 103%.

Keywords: solid phase extraction, ternary oxide, preconcentration, copper ions, cachaça, square wave anodic stripping voltammetry

Introduction

Copper is a micronutrient present in the human body and is essential for human health at trace levels. However, the high consumption of copper through alcoholic beverages has caused harmful effects by interfering with the normal catalytic activities of some enzymes.¹

In recent years, the consumption of cachaça has been extremely high; the maximum copper content allowed by Brazilian legislation is 5 mg L⁻¹, according to Federal Decree No. 2314 and normative No. 13.² In other countries, such as the United States, legislation does not tolerate more than 2 mg L⁻¹ of copper in alcoholic distillates.³ In the European Union, legislation is even more stringent with regards to copper content; its content cannot be higher than 1 mg L⁻¹.⁴

Artisanal cachaça has a sharper flavor and is therefore the most highly sought by consumers, which is concerning

since its production requires copper distillers. The oxidation of copper causes an accumulation of azinhavre on the walls of the distillers, which is solubilized into the brandy and therefore contaminates the cachaça.⁵

Excess copper in the body can cause a number of complications, most commonly Wilson's disease, which is considered a recessive disorder characterized by copper buildup in the liver, brain, kidneys and corneas. The excess of metal in the brain leads to tissue damage, causing progressive mental deterioration and, when not treated effectively, leads to death.^{6,7}

Küchler and Silva¹ described a method for the determination of copper in brandy using a spectrophotometric technique with diethyldithiocarbamate in amyl alcohol, and this methodology is an accepted standard in Brazil. Other methods are described in the literature for the determination of copper in cachaça using square wave anodic stripping voltammetry (SW-ASV) and correlated methods, atomic absorption spectrometry (AAS), and molecular spectrophotometry in UV-Vis, among others.^{1,8}

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Some techniques as molecular spectrophotometry in UV-Vis still have limitations regarding detection limits. Thus, the determination of these elements at trace levels requires preconcentration of the analyte, which aims to improve the detectability of the techniques.⁹ Solid phase extraction (SPE) has advantages over liquid-liquid extraction, including simplicity, high concentration factor, speed, lack of emulsion, availability of numerous adsorbent materials, relatively low cost, ease of automation, and easy adaptation in systems by flow analysis, among others.¹⁰

The development of alternative technologies for the quantification of copper has generated an increased interest in the search for new adsorbent materials. In this scenario, the sol-gel process stands out due to the high dispersion of organic and inorganic components, as well as the control during all stages of synthesis, from choosing precursors to the product in the oxide form.¹¹

Silica plays an important role in these new adsorbent materials since the modification of its surface increases its potential for the extraction of trace elements due the presence of the Brønsted and Lewis acid sites on its surface.¹² Some examples presented in the literature include silica modified with zirconium(IV) oxide,¹³ titanium(IV) oxide,¹⁴ and niobium(V) oxide,¹⁵ among others.

The surface modification of silica with metal oxides is carried out through the sol-gel process, where metal oxides are formed through the synthesis of silica. The new materials obtained by the sol-gel process have several advantages including an increased surface area and porosity; high uniformity in the distribution of the metal oxides on the surface of the silica matrix; and use in a large pH range due to the amphoteric mixed oxides. Additionally, these materials combine the mechanical properties of the silica matrix with the chemical properties of metal oxides.^{10,12}

Costa *et al.*¹⁰ used the $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$ mixed oxide for the preconcentration of Cd^{2+} in cigarette and water samples, and Tarley *et al.*¹⁶ used the mixed oxide for the preconcentration of Zn^{2+} in water. Diniz *et al.*¹⁷ and Tarley *et al.*¹⁸ used $\text{SiO}_2/\text{Nb}_2\text{O}_5/\text{ZnO}$ and $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2$ ternary oxides and silica gel functionalized with 3-(2-aminoethylamino) propyl ($\text{SiO}_2/\text{AAP-TMS}$) in on-line preconcentration systems of Co^{II} and speciation of Cr^{III} and Cr^{IV} , respectively, through flow injection analysis (FIA) coupled to spectrometric techniques such as flame atomic absorption spectrometry (FAAS).

These examples cited above show the importance of the development of new materials obtained by the sol-gel process and their application in new analytical methodologies for the determination of toxic metals.

Furthermore, there are no studies in the literature employing square wave anodic stripping voltammetry (SW-ASV) coupled to Cu^{2+} preconcentration using mixed oxides as the adsorbent material.

Although the literature presents some works using SW-ASV to direct copper determination,¹⁹⁻²¹ this work aimed to study a method for Cu^{2+} preconcentration/separation using $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2$ ternary mixed oxides synthesized via sol-gel. The detection method chosen was SW-ASV.

Experimental

Adsorbent material and samples

The $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2$ (designated SiAlTi) ternary oxide applied as an adsorbent material was obtained by the sol-gel process, and its synthesis is described in the literature.^{18,22} The SiAlTi material has a specific surface area (S_{BET}) of $437 \text{ m}^2 \text{ g}^{-1}$, mean pore size of 18.3 \AA (making it microporous), and mean pore volume of $0.0395 \text{ cm}^3 \text{ g}^{-1}$. X-ray fluorescence determined a mass percentage of 9.8% for Al_2O_3 and 30.3% for TiO_2 in the material.

The samples of cachaça are of artisanal origin and were acquired in the states of São Paulo and Espírito Santo (Brazil).

Reagents and solutions

All solutions were prepared with ultrapure water (resistivity $>18 \text{ M}\Omega \text{ cm}$, $25 \text{ }^\circ\text{C}$; Millipore Milli-Q purification system, Belford, MA, USA). To avoid contamination of the solutions, all glassware was cleaned in a 10% (v/v) HNO_3 (Vetec Química, Rio de Janeiro, RJ, Brazil, 99.7%) bath for 24 h and then washed with ultrapure water. Hydrochloric acid (99.7%), acetic acid (99.7%) and ammonium hydroxide (28-30%) were obtained from Vetec (Rio de Janeiro, RJ, Brazil). Acetate, phosphate and ammoniacal buffer solutions consisted of ammonium chloride (Grupo Química, Rio de Janeiro, RJ, Brazil, 100%), anhydrous monobasic potassium phosphate (Labsynth, Diadema, SP, Brazil, 99.0%) and sodium phosphate bibasic (Controltec, Rio de Janeiro, RJ, Brazil, 99.0%). The copper sulfate (98-102%) used to prepare the stock solution was purchased from Controltec, Rio de Janeiro, RJ, Brazil. The sulfuric acid used to clean the electrode was purchased from Merck (Darmstadt, Germany, 99.7%).

Experimental design

A complete 2^3 factorial design was performed to optimize the solid phase extraction procedure. The variables

studied were the flow rate of the eluent, the pH of the sample (adjusted with adequate buffer solution), and the concentration of copper adsorbed to determine if cartridge saturation occurred. Copper recovery was analyzed by square wave anodic stripping voltammetry.

Elution was performed with 2 mL of 1 mol L⁻¹ nitric acid, and the mass of the adsorbent material (SiAlTi) was 200 mg. The appropriate ranges for variables were determined by previous studies. The experimental data were analyzed in Microsoft Excel, allowing significance calculations for each variable.

Solid phase extraction

Microcolumn preparation

Microcolumns were packed by first sealing a 1 mL syringe with one piece of cotton and then transferring 200 mg of SiAlTi material into the syringe. This syringe was chosen to increase the chromatographic path by the number of theoretical plates. The maximum capacity of this syringe is 200 mg of the adsorbent material.

Uniform deposition of the adsorbent material was carried out using a manifold (Visiprep, model 12 ports, Darmstadt, Germany) coupled to a vacuum pump (Primatec, model 121, Itu, SP, Brazil) and the addition of the ammonia buffer solution.

Solid phase extraction procedure

The SPE was carried out in a manifold (Supelco, Visiprep, model 12 ports, Darmstadt, Germany) connected to a vacuum pump of Primatec (Model 121, Itu, SP, Brazil). The solid phase extraction procedure (Figure S1, Supplementary Information (SI) section) first consisted of conditioning the cartridge with 10 mL of the 0.14 mol L⁻¹ ammoniacal buffer solution. Then, 5 mL of the samples containing Cu²⁺ was diluted in the ammoniacal buffer and percolated in the cartridge. Copper ions were eluted by adding 2 mL of 1 mol L⁻¹ nitric acid. The flow rate used to percolate the samples and solvents through the solid phase was 1 mL min⁻¹.

Square wave anodic stripping voltammetry (SW-ASV)

Electrochemical cell

The electrochemical system consisted of a platinum wire as the auxiliary electrode, Ag/AgCl/Cl⁻ (3 mol L⁻¹) as the reference electrode, and a glassy carbon (GC) electrode with an area equivalent to 11.3 mm² as the working electrode.

The parameters and conditions used for SW-ASV were based on data described in the literature^{23,24} and are shown in Table S1 (SI section).

Determination of Cu²⁺ in cachaça samples

Quantification of preconcentrated samples (samples 1 and 2) involved adding 600 µL of the samples into 0.1 mol L⁻¹ HCl solution, with a final volume of 5 mL in the electrochemical cell. The samples were diluted in the ammoniacal buffer prior to preconcentration, and analytical curves were generated to correlate the voltammetric wave area with [Cu²⁺].

Graphite furnace atomic absorption spectrometry (GFAAS)

The samples were analyzed before and after preconcentration on the oxide by graphite furnace atomic absorption spectrometry since this method is well-established for trace metal analysis. The samples were quantified using an analytical curve constructed from standards with the following concentrations: 1, 5, 10, 15, 20 and 30 µg L⁻¹. Table S2 (SI section) shows the temperature program used in the analyses.

Partial validation of the proposed method

The purpose of method validation is to verify that the results obtained are reliable for the purpose, that is, it meets the requirements and standards for the specific proposed use. The parameters studied (SI section) were linearity, limit of detection (LOD), limit of quantification (LOQ) and precision (repeatability and intermediate precision).²⁵⁻²⁷

Results and Discussion

Experimental design for the optimization of solid phase extraction

The data obtained with the experimental design are shown in Table 1, and the coefficients obtained for the model are shown in Table 2. The confidence intervals corresponding to the coefficients in the model show that the adsorption pH is the only significant coefficient since the value suggests that an increase in pH from 5 to 9 raises the response approximately 25-fold.

Although they are not significant variables, the eluent flow rate and Cu²⁺ concentration interact with the adsorption pH, and these interactions are significant. We consider significant all the effects and interactions that have a nonzero value for the confidence interval.²⁸ This can be confirmed by observing the recoveries in Table 1; when the eluent flow rate and the Cu²⁺ concentration are maintained at a fixed level, the increase in adsorption pH causes a considerable increase in recovery of the analyte.

Table 1. Factors, levels, coded matrix and responses for 2³ factorial design with central points in triplicate for the SPE

Issue	X ₁	X ₂	X ₃	Recovery / %
1	-1	-1	-1	64.9
2	+1	-1	-1	57.0
3	-1	+1	-1	95.4
4	+1	+1	-1	104
5	-1	-1	+1	79.0
6	+1	-1	+1	74.7
7	-1	+1	+1	81.0
8	+1	+1	+1	98.5
9	0	0	0	78.9
10	0	0	0	71.0
11	0	0	0	71.3

X₁ (flow rate in mL min⁻¹) (-1): 0.5, (0): 0.75, (+1): 1; X₂ (adsorption pH) (-1): 5, (0): 7, (+1): 9; X₃ ([Cu²⁺] in µg L⁻¹) (-1): 100, (0): 150, (+1): 200.

Table 2. Statistical results for 2³ factorial designs with central points in triplicate

Factor	Coefficient
b ₀	81.8 ± 7.4
b ₁	3.38 ± 7.4
b ₂	25.7 ± 7.4
b ₃	3.10 ± 7.4
b ₁₂	9.51 ± 7.4
b ₁₃	3.25 ± 7.4
b ₂₃	-12.8 ± 7.4
b ₁₂₃	1.39 ± 7.4
S	4.50 ± 7.4

s: experimental standard deviation.

The same does not occur when the adsorption pH is fixed and when one of the variables is changed.

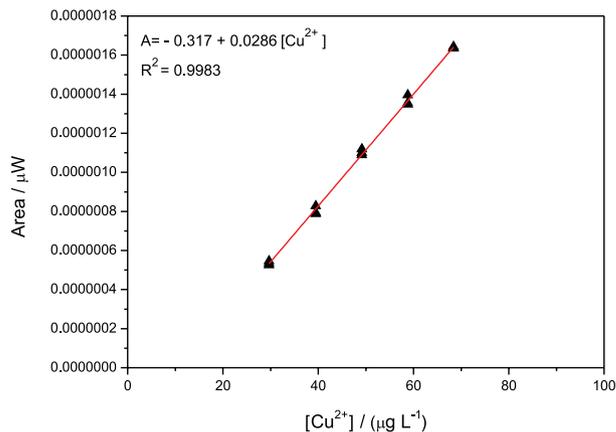
The best recoveries were obtained when the eluent flow rate and the adsorption pH were maintained at the (+1) level. Thus, the extraction conditions used in this work were an eluent flow rate of 1 mL min⁻¹ and analyte adsorption pH on the column equal to 9. This study also showed that concentrations less than or equal to 200 µg L⁻¹ do not saturate the adsorbent material.

Partial validation of the proposed method

Linearity

The analytical curve used for the linearity study was obtained with copper standards ranging from 29.7 to 68.4 µg L⁻¹, as shown in Figure 1. To guarantee the homogeneity of variances, the Cochran test was applied

to the curve (Figure 1), taking into account the number of replicates (n = 3) and the number of concentrations (k = 5). The calculated C value (0.426) was lower than the tabulated C value (0.683), revealing homogeneous variances as the concentration increased. This result was effective for all the curves, indicating homoscedastic behavior.

**Figure 1.** Analytical curve obtained for copper standards using SW-ASV with GC as the working electrode in a 0.1 mol L⁻¹ HCl solution.

The analytical curve indicated good linearity in the established working range (29.7 to 68.4 µg L⁻¹) with a coefficient of determination ($R^2 = 0.9983$) higher than the acceptance criterion (0.99).

Limit of detection and limit of quantification

The LOD and LOQ determined by the slope criterion were 1.71 and 5.64 µg L⁻¹, respectively. These values are lower than the limit required by national regulatory agencies (5 mg L⁻¹).

Precision (repeatability and intermediate precision)

Figure 2 shows two analytical curves for the proposed method with concentrations ranging from 29.7 to 68.4 µg L⁻¹, obtained by the same operator on different days. The standard deviations for low, medium and high concentrations within the analytical curves are shown in Table 3.

The relative standard deviations were all lower than 5%, demonstrating the repeatability of the method.

Comparing variances for analytical curves obtained by the same operator and analysis conditions on different days (Figure 2) gave an F_{cal} of 0.22, which was lower than the F_{crit} (9.28) with a confidence interval of 95%, indicating that the variances are equal and that the hypothesis is acceptable. The slopes for the analytical curves were also compared, and the calculated *t*-value (0.11) was lower than the critical *t*-value (2.45) at a 95% confidence level. This indicates that the slopes for these two curves are equal; thus, both curves have the same sensitivity.

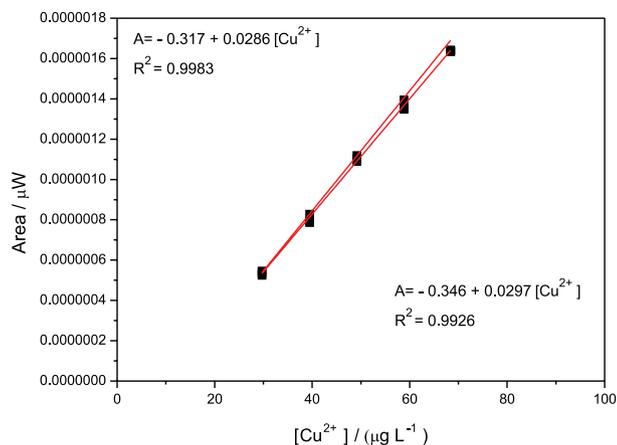


Figure 2. Analytical curves obtained for Cu²⁺ standards from 29.7 to 68.4 μg L⁻¹ in 0.1 mol L⁻¹ HCl solution.

Table 3. Precision (repeatability) obtained by the proposed method

Concentration / (μg L ⁻¹)	RSD / %
Low (29.7), n = 1	2.0
Medium (49.2), n = 2	1.3
High (68.4), n = 3	0.3

RSD: relative standard deviation.

Determination of Cu²⁺ in cachaça samples using preconcentration coupled to SW-ASV

The efficiency of the extraction process was studied with two samples of cachaça, which were analyzed before and after preconcentration on the oxide. Quantification of copper was performed by SW-ASV using the analytical curve shown in Figure 3. Table 4 shows the copper ion concentration before and after preconcentration and the recovery obtained by the proposed method.

Sample 1 was also analyzed by graphite furnace atomic absorption spectrometry (GFAAS) before and after preconcentration to evaluate the efficiency of the solid phase extraction using the mixed oxide. By comparing the copper content obtained before and after the solid phase extraction, the recovery of the proposed method was 95.5%. This value is satisfactory since accepted recoveries are within the range of 70-120%.²⁷

Compared to other methods presented in the literature, the developed method improved Cu²⁺ quantification (Table 5) presenting a LOD of 1.71 μg L⁻¹. Oliveira *et al.*²¹ and Costa *et al.*²⁹ quantified Cu²⁺ by differential pulse anodic stripping voltammetry, whereas in this work it was performed by square wave anodic stripping voltammetry. Though in the work of Tavares *et al.*²⁰ the technique was the same, the electrode was different as well as the experimental parameters.

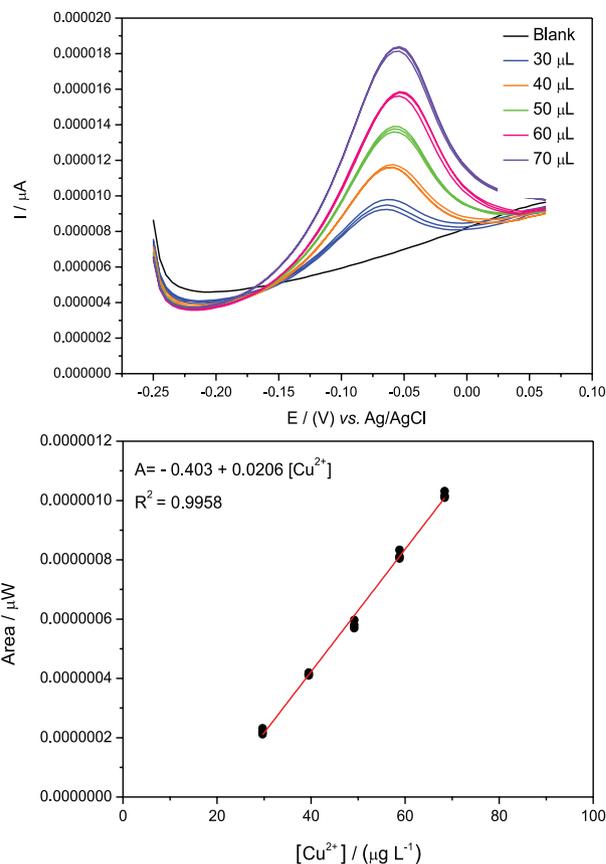


Figure 3. Voltammograms using SW-ASV with GC as the working electrode in a 0.1 mol L⁻¹ HCl solution, and the respective analytical curve for copper quantification in preconcentrated samples of cachaça.

Table 4. Copper ion concentration before and after preconcentration and the recovery obtained by the solid phase extraction method

Sample	[Cu ²⁺] before preconcentration / (mg L ⁻¹)	[Cu ²⁺] after preconcentration / (mg L ⁻¹)	Recovery / %
1	1.28 ± 0.02	1.31 ± 0.04	102
2	1.49 ± 0.01	1.53 ± 0.02	103

Conclusions

Our results showed that the solid phase extraction using SiO₂/Al₂O₃/TiO₂ ternary oxide as adsorbent material coupled square wave anodic stripping voltammetry is efficient for Cu²⁺ quantification.

Applying the complete 2³ factorial design to the solid phase extraction method made it possible to optimize working conditions for the extraction of Cu²⁺ ions with the proposed oxide.

The developed detection method using GCE and SW-ASV was linear in the range of 29.7-68.4 μg L⁻¹ with LOD and LOQ equal to 1.71 and 5.64 μg L⁻¹, respectively. In

Table 5. Comparison of analytical parameters for the proposed method with other literature methods for Cu²⁺ determination

Reference	Technique	Electrode	LOD / (µg L ⁻¹)	LOQ / (µg L ⁻¹)
20	SW-ASV	CPE-AaCNT	23.9	78.87
21	DP-AdSV	CPE-B	24.4	–
29	DP-ASV	SPCPE-SiAt	110	330
Our work	SW-ASV	GCE	1.71	5.64

LOD: limit of detection; LOQ: limit of quantification; SW-ASV: square wave anodic stripping voltammetry; DP-AdSV: differential pulse adsorptive stripping voltammetry; DP-ASV: differential pulse anodic stripping voltammetry; CPE-AaCNT: carbon paste electrode modified with ascorbic acid and carbon nanotubes; CPE-B: carbon paste electrode modified with Biochar; SPCPE-SiAt: solid paraffin-based carbon paste electrode modified with 2-aminothiazole-silica-gel; GCE: glassy carbon electrode.

this scenario, after SPE, it was possible to quantify Cu²⁺ in samples of cachaça with recoveries of 102-103%, showing that our extraction method is adequate.

For a comparative study, one of the cachaça samples was analyzed for copper content by GFAAS since it is the current standard methodology in Brazil. Our extraction method exhibited 95.5% recovery by comparing the copper content before and after the SPE.

The results indicated that the developed method using SW-ASV coupled to SPE with SiAlTi was accurate and adequate for the determination of Cu²⁺ in cachaça samples. Therefore, the proposed method proved to be an alternative procedure for copper ion analysis.

Supplementary Information

Supplementary information is available free of charge at <http://jbcbs.sbq.org.br> as PDF file.

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