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Determination of copper in airborne particulate matter using slurry sampling and chemical vapor generation atomic absorption spectrometry



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ABSTRACT

The present paper describes the development of a method for the determination of copper in airborne particulate matter using slurry sampling and chemical vapor generation atomic absorption spectrometry (CVG AAS). Chemometric tools were employed to characterize the influence of several factors on the generation of volatile copper species. First, a two-level full factorial design was performed that included the following chemical variables: hydrochloric acid concentration, tetrahydroborate concentration, sulfanilamide concentration and tetrahydroborate volume, using absorbance as the response. Under the established experimental conditions, the hydrochloric acid concentration had the greatest influence on the generation of volatile copper species. Subsequently, a Box–Behnken design was performed to determine the optimum conditions for these parameters. A second chemometric study employing a two-level full factorial design was performed to evaluate the following physical factors: tetrahydroborate flow rate, flame composition, alcohol volume and sample volume. The results of this study demonstrated that the tetrahydroborate flow rate was critical for the process. The chemometric experiments determined the following experimental conditions for the method: hydrochloric acid concentration, 0.208 M; tetrahydroborate concentration, 4.59%; sulfanilamide concentration, 0.79%; tetrahydroborate volume, 2.50 mL; tetrahydroborate flow rate, 6.50 mL min⁻¹; alcohol volume, 200 μL; and sample volume, 7.0 mL. Thus, this method, using a slurry volume of 500 μL and a final dilution of 7 mL, allowed for the determination of copper with limits of detection and quantification of 0.30 and 0.99 μg L⁻¹, respectively. Precisions, expressed as RSD%, of 4.6 and 2.8% were obtained using copper solutions at concentrations of 5.0 and 50.0 μg L⁻¹, respectively. The accuracy was evaluated by the analysis of a certified reference material of urban particulate matter. The copper concentration obtained was 570 ± 63 mg kg⁻¹, and the certified value was 610 ± 70 mg kg⁻¹. This method was applied for the determination of copper in airborne particulate matter samples collected in two Brazilian regions of Bahia State, Brazil. The copper contents found varied from 14.46 to 164.31 ng m⁻³.

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1. Introduction

Chemical vapor generation (CVG) coupled with spectroanalytical methods is a commonly used technique for the determination of metalloids and some metals (such as Hg, Pb and Cd) [1–4]. However, reactions involved in the chemical vapor generation of other metals remain an area of active investigation and have been the subject of several studies and review papers [5–8].

The reaction between Cu(II) ions and tetrahydroborate ions generates volatile species that have been used in analytical methods for the determination of copper by several authors [8–12]. However, this chemical reaction is not well known, and further studies need to be conducted to understand this reaction and to characterize the volatile species of copper that are formed. The first application of the chemical vapor generation technique (CVG) for the determination of copper was developed for use in environmental samples employing inductively coupled plasma optical emission spectrometry (ICP OES) [9]. Fang et al. determined the copper in human hair and rice standard reference materials using a flow system. In this system, sample solutions in the presence of o-phenanthroline and nitric acid

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reacted with a sodium tetrahydroborate solution to produce volatile species of copper. After a separation step, the copper was determined using FI-CVG-AAS [10]. De Campos developed a procedure for the determination of Cu, Cd and Zn using an electrothermal atomization atomic absorption spectrometry (ET-AAS). This method is based on the generation of volatile species at room temperature by the addition of sodium tetrahydroborate to an acidified solution of analytes. Subsequently, the vapor phase species are rapidly transported to a pre-heated graphite tube that has been previously treated with iridium as a permanent chemical modifier [11]. He et al. developed an online system for chemical vapor generation during the determination of copper in biological samples using atomic fluorescence spectrometry (AFS). Volatile copper species were formed by the addition of a potassium tetrahydroborate solution to the sample solutions in the presence of nitric acid and 1,10-phenanthroline [12]. Zheng et al. established a method for the determination of copper employing ET-AAS, in which a flow injection system for the generation of volatile species was utilized. This system was coupled to a graphite furnace for in situ collection of the analyte and subsequent detection. The chemical generation was established in 1% formic acid media [13].

Slurry sampling is a technique that allows chemical analysis under experimental conditions in which the sample is not completely solubilized. This technique has served as an alternative for the analysis of complex matrices and also for the determination of volatile elements [14–16].

Chemometric techniques have often been employed in the optimization of analytical methods. The advantages of these techniques include a reduction in the number of experiments required, which results in lower reagent consumption and less laboratory work. In addition, these techniques allow for the development of mathematical models that permit an assessment of the statistical significance of the factor effects studied as well as an evaluation of the interaction effects between these factors [17–19].

In this study, chemometric tools were utilized to evaluate the experimental parameters in the chemical generation of volatile species resulting from the reaction of Cu(II) ions with tetrahydroborate ions. Two-level full factorial designs were performed to better understand effects of the chemical and physical factors, and Box–Behnken designs were used to determine the optimal experimental conditions for the proposed analytical method. A complete validation study was performed, and the proposed method was applied to the determination of copper in airborne particulate matter samples collected from two regions of Bahia State, Brazil.

2. Experimental

2.1. Instrumentation for the determination of copper by CVG-QT-AAS

A CONTRAA 700 spectrometer from Analytik Jena (GLE, Berlin, Germany) was used to measure the copper concentrations in all of experiments. This instrument consisted of a high-intensity xenon short-arc lamp operating in the hot-spot mode, a high-resolution double monochromator and a CCD array detector. The instrument was set to operate at a wavelength of 324.7540 nm, and the copper concentration was determined by analyzing the peak height. The flame composition included acetylene (70 L h^{-1}) and air (440 L h^{-1}), resulting in a ratio (fuel/oxidant) of 0.159. The delay and reading time for the analytical measurements were 23 s and 25 s, respectively.

An HS50 hydride generator module from Analytik Jena (GLE, Berlin, Germany) was coupled to the CONTRAA 700 spectrometer, and it was operated in batch mode. The module utilized the principle of pneumatic transport for transporting the reducer to the reaction cell. The quartz T tube cell was heated using an

Table 1
Specification of the main functional modules of the HS50.

Unit reaction	Batch module: PTFE beaker with tapered bottom	
Dispensing bottle	300 mL	
Cell holder	Fitted to 50 mm single slot burner	
Quartz cell	Length: 140 mm, waisted in the middle section ID 16/8 mm with detachable quartz windows.	
Inert gas: Argon		
Inert gas	Purity	At least 99,999 Vol%
	Inlet pressure	3–6 bar
	Operating pressure	0.5 bar
	Gas flows	F1 = 15 L/h (transport gas) F2 = 12 L/h (purge gas)

air-acetylene flame. The specifications of this system are shown in Table 1.

The slurries were prepared using a UNIQUE USC-1850 ultrasonic bath (Indaiatuba, SP, Brazil) with a frequency of 25 kHz and a power of 154 W.

2.2. Reagents

Analytical grade reagents were used in this study, and all solutions were prepared using high-purity water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) obtained from a Milli-Q Plus water purification system from Millipore (Bedford, MA, USA). Copper standard solutions over a concentration range of $0.99\text{--}100 \mu\text{g L}^{-1}$ were prepared by dilution of a stock solution (1000 mg L^{-1}) from Merck (Germany). A 6 mol L^{-1} HCl solution was prepared from concentrated HCl (37% v/v, Merck). The 2.0% (w/v) sulfanilamide solution was prepared by dilution of the reagent with high-purity water. Reducer reagent solutions of 4.6% (w/v) sodium tetrahydroborate were prepared daily by dissolving solid NaBH_4 (Merck) in a 0.5% (w/v) NaOH solution. The accuracy evaluation was performed using the certified reference material SRM 1648a Urban Particulate Matter, which was provided by the National Institute of Standards and Technology (Gaithersburg, MD, USA). The sulfanilamide was previously tested as a chelating reagent in the method proposed for the determination of cadmium in soil samples using CVG-AFS [20].

2.3. Samples of airborne particulate matter

The airborne particulate matter samples were collected from two different regions in Bahia State, Brazil. Two samples were collected in *Bananeira Island*, and two samples were collected in *Aratu Harbor*. *Bananeira Village* is situated on the *Todos os Santos Bay* (Bahia, Brazil), approximately 300 m away from *Aratu Port*, in a north–northwest direction. This small village has a population of approximately 1000 inhabitants, whose principal activities include handcraft work and fishery. The *Aratu Harbor* is the main port for *Bahia State*, Brazil. It is located on the *Aratu Bay*, and it provides support to the industrial center of *Aratu* (CIA) as well as to the petrochemical complex of *Camaçari*.

Particulate matter samples were collected using a Hi-Vol sampler under an average flow rate of $1.14 \text{ m}^3 \text{ min}^{-1}$ over a 24 h sampling period on quartz filters with a 403.06 cm^2 collection area ($22.8 \times 17.7 \text{ cm}^2$, Energética, RJ, Brazil). Sample masses were determined by weighing filters before and after sampling using an analytical balance (Sartorius Analytic, Goettingen, Germany). The filters were folded and packed in vegetal paper, placed inside sealed plastic bags and transported to the laboratory. In the lab, filters were cut into disks with a 4.8 cm diameter (18.09 cm^2 area) before being folded, packed in vegetal paper and stored in a refrigerator until analysis.

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