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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}.

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

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)

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 MΩ 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– 100 μg 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 m^3 min^{-1} over a 24 h sampling period on quartz filters with a 403.06 cm^2 collection area (22.8 × 17.7 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.

2.4. *Preparation of the sample slurries*

During the analysis, filters (with the real samples) were cut into pieces smaller than 1 cm in length using stainless steel scissors.

The slurries were prepared by placing the mass corresponding to half of the filter disk (approximately 60.0 mg) and 2.0 mL of a 6.0 mol L^{-1} hydrochloric acid solution into 25-mL volumetric flasks. These mixtures were then sonicated at room temperature for 30 min and subsequently diluted to a final volume using ultrapure water. Aqueous standard solutions were used to generate standard calibration curves. The same procedure was applied to the Urban Particulate Matter SRM 1648a, using a mass of 100.0 mg.

2.5. *Optimization strategy – chemometric tools*

Studies of the experimental parameters that affect the copper hydride generation using tetrahydroborate and the determination of the optimal conditions were conducted using a two-level full factorial design and a Box–Behnken design. The chemometric response evaluated was the peak height of the absorbance (Abs). All the chemometric data were processed using the Statistica 6.0 computer program. Experimental error was estimated using triplicates of the central point.

2.6. *General procedure*

Initially, 245 μL of 6 mol L^{-1} hydrochloric acid and 2.8 mL of 2% sulfanilamide were added to a 50-mL reaction cell. Then, 500-μL aliquots of the slurry sample or the standard solution and ultrapure water were added to the reactor to achieve a final volume of 7 mL. Next, 200 μL of isoamyl alcohol was added to the reaction cell, which was then connected to the hydride generator module (HS50). Finally, 2.5 mL of 4.6% (w/v) sodium tetrahydroborate was injected into the closed system at a flow rate of 6.58 mL min^{-1}. Copper hydride was generated and then transported to the quartz cell via an argon carrier gas with a purity of 99.996% (White Martins, São Paulo, Brazil).

3. Results and discussion

3.1. *Optimization of the chemical factors in the reaction of copper(II) ions with tetrahydroborate*

First, a two-level full factorial design was performed that included the following factors: hydrochloric acid concentration [HCl], sulfanilamide concentration [Sulfa], tetrahydroborate volume [Volume] and tetrahydroborate concentration [BH_4]. The experimental dominions of these factors (as coded and real values) and the chemometric responses (absorbance) are shown in Table 2.

The data obtained from the factorial design were evaluated, and effects of factors and interactions were calculated [16] as follows:

$\text{Effect}_{[\text{HCl}]}=(-0.0131 \pm 0.0007)$
$\text{Effect}_{[\text{HCl}] \times [\text{BH4}]}=(-0.0115 \pm 0.0007)$
$\text{Effect}_{[\text{BH4}]}=(0.0110 \pm 0.0007)$
$\text{Effect}_{[\text{Volume}] \times [\text{BH4}]}=(0.0031 \pm 0.0007)$
$\text{Effect}_{[\text{HCl}] \times [\text{Volume}]}=(-0.0029 \pm 0.0007)$
$\text{Effect}_{[\text{HCl}] \times [\text{Sulfa}]}=(-0.0019 \pm 0.0007)$
$\text{Effect}_{[\text{Sulfa}] \times [\text{BH4}]}=(0.0016 \pm 0.0007)$
$\text{Effect}_{[\text{Sulfa}]}=(0.0014 \pm 0.0007)$
$\text{Effect}_{[\text{Volume}]}=(0.0008 \pm 0.0007)$
$\text{Effect}_{[\text{Sulfa}] \times [\text{Volume}]}=(0.00003 \pm 0.00071)$

Table 2
Factorial design for chemical parameters involved in VG of copper species.

Experiment	**[HCl]**	**[Sulfa] (%)**	$NaBH_4$ **Volume** (mL)	**[$NaBH_4$] (%)**	**Absorbance**
1	−1 (0.5)	−1 (0)	−1 (1)	−1 (0.5)	0.00635
2	1 (2.5)	−1 (0)	−1 (1 mL)	−1 (0.5)	0.00660
3	−1 (0.5)	1 (0.4)	−1 (1)	−1 (0.5)	0.00753
4	1 (2.5)	1 (0.4)	−1 (1)	−1 (0.5)	0.00570
5	−1 (0.5)	−1 (0)	1 (4)	−1 (0.5)	0.00590
6	1 (2.5)	−1 (0)	1 (4)	−1 (0.5)	0.00324
7	−1 (0.5)	1 (0.4)	1 (4)	−1 (0.5)	0.00515
8	1 (2.5)	1 (0.4)	1 (4)	−1 (0.5)	0.00280
9	−1 (0.5)	−1 (0)	−1 (1)	1 (3.5)	0.02158
10	1 (2.5)	−1 (0)	−1 (1)	1 (3.5)	0.00487
11	−1 (0.5)	1 (0.4)	−1 (1)	1 (3.5)	0.02698
12	1 (2.5)	1 (0.4)	−1 (1)	1 (3.5)	0.00453
13	−1 (0.5)	−1 (0)	1 (4)	1 (3.5)	0.02951
14	1 (2.5)	−1 (0)	1 (4)	1 (3.5)	0.00386
15	−1 (0.5)	1 (0.4)	1 (4)	1 (3.5)	0.03451
16	1 (2.5)	1 (0.4)	1 (4)	1 (3.5)	0.00336
CP	0 (1.5)	0 (0.2)	0 (2.5)	0 (2.0)	0.00420
CP	0 (1.5)	0 (0.2)	0 (2.5)	0 (2.0)	0.00388
CP	0 (1.5)	0 (0.2)	0 (2.5)	0 (2.0)	0.00454

CP – central point; [HCl]=hydrochloric acid concentration; [Sulfa]=sulfanilamide concentration; Volume $NaBH_4$=tetrahydroborate volume; [$NaBH_4$]=tetrahydroborate concentration.

An evaluation of these results, considering the experimental dominions established, revealed that the hydrochloric acid concentration exerted the greatest influence on the generation of copper volatile species. The negative effect demonstrates statistically that the chemometric response (absorbance) increased with decreasing hydrochloric acid concentration. The interaction [HCl] × [BH_4] also had a great influence on the vapor generation process of the copper species. This interaction had a negative effect, which means that the chemometric response (absorbance) increased with decreasing hydrochloric acid concentration but increasing tetrahydroborate concentration. The positive effect for the tetrahydroborate concentration revealed that the absorbance increased with increasing concentration of the reductant. The other effects and interactions had less influence on the vapor generation of copper species. The interaction [Sulfa] × [Volume] did not have a significant effect on the chemical generation of volatile species of copper.

Considering all of these results, a Box–Behnken design was also performed that included the followings factors: hydrochloric acid concentration, tetrahydroborate concentration and sulfanilamide concentration. The tetrahydroborate volume factor had a low effect on the chemical vapor generation and was thus fixed at 2.50 mL. The coded and real values established in the Box–Behnken design are shown in Table 3.

The data obtained in this experiment generated a quadratic model, which exhibited a response surface with a maximal absorbance at the following experimental conditions: 0.208 M hydrochloric acid, 4.593% tetrahydroborate and 0.786% sulfanilamide.

Considering these results, the optimal experimental conditions established for the proposed method are as follows: hydrochloric acid concentration, 0.21 M; tetrahydroborate concentration, 4.60%; and sulfanilamide concentration, 0.80%.

3.2. *Optimization of the physical parameters in the determination of copper using CVG-QT-AAS*

In this step, factors studied were the flame composition employed in the spectrometer, the flow rate for the addition of the tetrahydroborate solution, the isoamyl alcohol volume and the volume of the initial liquid phase. Isoamyl alcohol is used to decrease the formation of bubbles (and consequently foam) that occurs during the addition of tetrahydroborate solution into the reaction cell. The initial liquid phase is the solution volume in the reaction cell before the addition of the tetrahydroborate solution.

Table 3
Box–Behnken design for chemical parameters involved in VG of copper species.

Experiment	[HCl] (M)	[NaBH$_4$] (%)	[Sulfa] (%)	Absorbance
1	−1 (0.04)	−1 (4)	0 (0.6)	0.0367
2	1 (0.40)	−1 (4)	0 (0.6)	0.0316
3	−1 (0.04)	1 (6)	0 (0.6)	0.0193
4	1 (0.40)	1 (6)	0 (0.6)	0.0149
5	−1 (0.04)	0 (5)	−1 (0.4)	0.0167
6	1 (0.40)	0 (5)	−1 (0.4)	0.0249
7	−1 (0.04)	0 (5)	1 (0.8)	0.0351
8	1 (0.40)	0 (5)	1 (0.8)	0.0297
9	0 (0.22)	−1 (4)	−1 (0.4)	0.0459
10	0 (0.22)	1 (6)	−1 (0.4)	0.0546
11	0 (0.22)	−1 (4)	1 (0.8)	0.0534
12	0 (0.22)	1 (6)	1 (0.8)	0.0597
13	0 (0.22)	0 (5)	0 (0.6)	0.0572
14	0 (0.22)	0 (5)	0 (0.6)	0.0625
15	0 (0.22)	0 (5)	0 (0.6)	0.0594

[HCl] = hydrochloric acid concentration; [NaBH$_4$] = tetrahydroborate concentration; [Sulfa] = sulfanilamide concentration.

Table 4
Factorial design for physical parameters involved in CVG of copper species.

Experiment	Flame composition[a]	NABH4 flow rate (mL min^{-1})	Alcohol volume (μL)	Sample volume (mL)	Absorbance
1	−1 (0.136)	−(6.50)	−1 (100)	−1 (2)	0.02015
2	+1 (0.182)	−(6.50)	−1 (100)	−1 (2)	0.02077
3	−1 (0.136)	+(16.50)	−1 (100)	−1 (2)	0.00803
4	+1 (0.182)	+(16.50)	−1 (100)	−1 (2)	0.01664
5	−1 (0.136)	−(6.50)	+1 (300)	−1 (2)	0.01517
6	+1 (0.182)	−(6.50)	+1 (300)	−1 (2)	0.02770
7	−1 (0.136)	+(16.50)	+1 (300)	−1 (2)	0.00950
8	+1 (0.182)	+(16.50)	+1 (300)	−1 (2)	0.01223
9	−1 (0.136)	−(6.50)	−1 (100)	+1 (6)	0.04242
10	+1 (0.182)	−(6.50)	−1 (100)	+1 (6)	0.01673
11	−1 (0.136)	+(16.50)	−1 (100)	+1 (6)	0.00350
12	+1 (0.182)	+(16.50)	−1 (100)	+1 (6)	0.00350
13	−1 (0.136)	−(6.50)	+1 (300)	+1 (6)	0.07330
14	+1 (0.182)	−(6.50)	+1 (300)	+1 (6)	0.07198
15	−1 (0.136)	+(16.50)	+1 (300)	+1 (6)	0.01529
16	+1 (0.182)	+(16.50)	+1 (300)	+1 (6)	0.01741
CP	0 (0.159)	0 (11.50)	0 (200)	0 (4)	0.03820
CP	0 (0.159)	0 (11.50)	0 (200)	0 (4)	0.03141
CP	0 (0.159)	0 (11.50)	0 (200)	0 (4)	0.03588

CP – central point.

[a] -(acetylene/air).

The experimental dominions (as coded and real values) and absorbances obtained in experiments are shown in Table 4.

The data obtained in this factorial design were evaluated, from which effects of factors and of interactions were calculated [16]. The effects of the principal factors and the significant interactions in the chemical generation of volatile species of copper are as follows:

$$\text{Effect}_{\text{Flow rate}} = (-0.0253 \pm 0.0074)$$
$$\text{Effect}_{(\text{Flow rate}) \times (\text{volume of the liquid phase})} = (-0.0159 \pm 0.0074)$$
$$\text{Effect}_{(\text{volume of the liquid phase})} = (0.0142 \pm 0.0074)$$
$$\text{Effect}_{(\text{alcohol volume}) \times (\text{volume of the liquid phase})} = (0.0141 \pm 0.0074)$$
$$\text{Effect}_{(\text{Alcohol volume})} = (0.0139 \pm 0.0074)$$
$$\text{Effect}_{(\text{Flow rate}) \times (\text{alcohol volume})} = (-0.0082 \pm 0.0074)$$

Among the four factors studied, the flow rate of the tetrahydroborate solution exerted the greatest influence on the reaction for forming volatile copper species. This factor had a negative effect, which means that absorbances (chemometric response) increased as the flow rate of the tetrahydroborate solution decreased. An analysis of the data in Table 4 showed that the highest analytical signals (absorbances) were obtained in experiments 13 and 14. The interaction (flow rate of the tetrahydroborate solution) × (volume of the initial liquid phase) was also statistically significant and had a negative effect, indicating that the chemometric response (absorbance) increased as the initial volume of the liquid phase increased and the flow rate of the tetrahydroborate solution decreased. The factor for the initial volume of the liquid phase had a positive and statistically significant effect. Thus, the increase in this factor allowed for an increased chemometric response (absorbance). The factor for alcohol volume also had a positive and statistically significant effect. This result indicates that the increased alcohol volume prevented the formation of bubbles/foam and clearly increased the detected copper signals (absorbance). The flame composition (Effect = -0.0001 ± 0.0074) and all of its interactions were not found to be statistically significant from the measured absorbances obtained during the chemical generation of volatile copper species.

Considering results obtained from the factorial design, experimental conditions were established for the following factors: flow rate of the tetrahydroborate solution, flame composition and initial volume of the liquid phase. The flow rate of the tetrahydroborate solution was fixed at 6.50 mL min^{-1}, which was the lower limit of the experimental dominion of the factorial design. For instrumental reasons, the tetrahydroborate flow rate cannot be less than this lower limit. The factorial design demonstrated that the flame composition and its interactions are not significant. This study was performed with flames with acetylene/air compositions ranging from 0.136 to 0.182. The initial volume of the liquid phase was established as 7.0 mL because the superior limit of the factorial design was 6.0 mL and because this factor had a positive effect on the process. Considering that the interaction (alcohol volume) × (volume of the liquid phase) was statistically significant and that the volume of the liquid phase was fixed at 7.0 mL, the alcohol volume established for the method was determined using a univariate optimization methodology. The experimental data obtained demonstrated that the analytical signals were constant for alcohol volumes in the range from 190 to 200 μL. Thus, the isoamyl alcohol volume established for the method was 200 μL. This alcohol volume completely prevented the formation of bubbles during the chemical vapor generation process.

3.3. *Analytical characteristics of the method*

Validation parameters were determined from the experimental conditions established in the optimization step. The limits of detection (LOD) and limits of quantification (LOQ) were determined by the IUPAC recommendations, LOD = $3\sigma/s$ and LOQ = $10\sigma/s$, where σ is the standard deviation of the measure of blank solutions and s is the slope of the calibration curve. The LOD and LOQ were found to be 0.30 and 0.99 μg L^{-1} for a slurry volume of 500 μL with a final dilution of 7 mL. These parameters were determined using a calibration curve with the following equation: Abs = $0.0025C_{Cu} + 0.0002$ and $R^2 = 0.9996$. The analytical curve was linear from 0.99 to 100.00 μg L^{-1}. Obviously, a higher sample volume could be used and thus limits of detection and quantification can be improved. The precision was estimated using seven replicates for two copper solutions with concentrations between 5.0 and 50.0 μg L^{-1}. The results, expressed as relative standard deviation (% RSD), were 4.6 and 2.8%, respectively. The accuracy was confirmed using a certified reference material of Urban Particulate Matter (SRM 1648a) furnished by the National Institute of Standards and Technology (NIST). The certified value was 610 ± 70 mg kg^{-1}, and the copper

Table 5
Spike test using an airborne particulate matter sample ($n=3$).

	Copper added ($\mu g\ L^{-1}$)	Copper found[a] ($\mu g\ L^{-1}$)	Recovery
Sample	0.00	63.30 ± 2.25	–
Sample + copper added	60.00	121.58 ± 1.23	97.13%

Sample collected from *Bananeira Village.*

[a] -Copper concentration in a slurry volume of 25 mL.

Table 6
Evaluation of the sample pre-treatment on the determination of copper using CVG-QT-AAS.

Extractor solvent	Conditions for copper determination	Copper found (mg Kg^{-1})	Copper recovery (%)
HCl 6.0 M	Slurry sampling	570 ± 63	93.44
HCl 6.0 M	Solution[a]	574 ± 66	94.10
HCl 0.50 M	Slurry sampling	79.7 ± 31.1	13.07
HCl 0.50 M	Solution[a]	61.6 ± 6.50	10.10
Water	Slurry sampling	56.6 ± 13.0	9.28
Water	Solution[a]	47.4 ± 7.80	7.77

[a] Determination of copper in solution after centrifugation and decantation.

content obtained was 570 ± 63 mg kg^{-1}. This result was expressed at the 95% confidence interval for three replicates.

In addition, an addition/recovery test was also performed using an atmospheric particulate matter sample from *Bananeira* Village, for which an average recovery of 97.13% was found. The complete results of this test are shown in Table 5. The obtained results demonstrated that the matrix sample does not interfere during the determination of copper using CVG-QT-AAS.

The sample pretreatment process was extensively studied. Experiments were performed using the general procedure for determination of copper in the certified reference material of Urban Particulate Matter (SRM 1648a) having an extractor solvent hydrochloric acid solutions with concentrations between 0.50 and 6.0 M and also water. The quantification was performed in the presence of suspended particles and also in solutions after centrifugation and decantation. The results demonstrated that 6 M hydrochloric acid solution extracts complete copper of the certified reference material. However, the extraction with 0.50 M hydrochloric acid solution and water is very low. All results are shown in Table 6.

3.4. Determination of copper in atmospheric particulate matter

Several studies have reported the great relevance of copper and iron in atmospheric reactions. These works have demonstrated that copper and iron are the most important transition metals in the chemical generation of reactive oxygen species, such as hydroxyl radical (OH^-), hydrogen peroxide (HOOH) and superoxide (O_2^-). These species can react with carbohydrates, lipids, proteins and nucleic acids, resulting in cell death and disease, and they play an important role in atmospheric chemistry [21–24],.

The method proposed herein was applied to the determination of copper in atmospheric particulate matter samples collected in *Bananeira* Village and in *Aratu* Port. The copper contents found, expressed at the 95% confidence interval, were 29.21 ± 3.64 and 14.46 ± 2.31 ng m^{-3} for the samples collected in *Bananeira* village and 130.22 ± 14.84 and 164.31 ± 10.87 ng m^{-3} for the samples from *Aratu* Port. These values are in agreement with those previously reported by Pereira et al. [25], which varied from 0.49 to 8.57 and from 5.19 to 257 ng m^{-3} for *Bananeira* and *Aratu* Harbor, respectively.

The copper contents found in *Aratu* Harbor were greater than those found in *Bananeira* Village. This result is likely because the *Aratu* Harbor is the location of discharges of copper concentrates, which are raw materials of a company that manufactures electrolytic copper in Dias Dávila City, Bahia State, Brazil. The values found in *Bananeira* were low because, on this island, there is no industrial activity or vehicular traffic, although copper emissions may appear depending on the wind direction in the *Aratú* Harbor. The access to *Bananeira* is only by small boats. Recently, Araujo et al. determined copper in atmospheric particulate matter samples collected from *Aracaju* City, Sergipe State, Brazil. Six samples were analyzed, and the copper contents varied from 32.4 to 237 ng m^3 [26].

4. Conclusions

The chemometric study presented herein demonstrated that copper can be determined by CVG-QT-AAS with the use of tetrahydroborate solution in high concentrations (with slow addition), hydrochloric acid solution in low concentrations and the addition of isoamyl alcohol to prevent the formation of foam.

This study established an analytical procedure that allows for the determination of trace amounts of copper in atmospheric particulate matter samples by employing CVG-QT-AAS with sensitivity, precision and accuracy.

This method using slurry sampling and CVG–AAS is advantageous over the ET-AAS and ICP OES techniques using complete digestion, because it does not require heating and use of concentrated oxidizing acids for sample digestion, it allows the direct determination of the analyte, reducing the time required for analysis and also minimizing the risks of contamination. In addition, the analytical measurement using CVG–AAS can be performed without a prior step of aspirating the slurry. The particle size of the slurry is a critical factor during the use of ET-AAS and ICP OES in slurry sampling.

The values determined for copper contents in samples analyzed herein are in agreement with results found by other authors in the same regions.

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