



Analytical Note

Determination of copper and mercury in phosphate fertilizers employing direct solid sampling analysis and high resolution continuum source graphite furnace atomic absorption spectrometry



Sidnei de Oliveira Souza ^{a,b}, Luciane Luiza François ^c, Aline Rocha Borges ^c,
 Maria Goreti Rodrigues Vale ^{c,d}, Rennan Geovanny Oliveira Araujo ^{a,b,*}

^a Departamento de Química Analítica, Instituto de Química, Universidade Federal da Bahia (UFBA), Campus Universitário Ondina, 40.170-115 Salvador, BA, Brazil

^b Laboratório de Química Analítica Ambiental (LQA), Departamento de Química, Centro de Ciências Exatas e Tecnologia, Universidade Federal de Sergipe (UFS), 49.100-000 São Cristóvão, SE, Brazil

^c Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), 91.501-970 Porto Alegre, RS, Brazil

^d Instituto Nacional de Ciência e Tecnologia do CNPq-INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil

ARTICLE INFO

Article history:

Received 4 July 2015

Accepted 8 October 2015

Available online 19 October 2015

Keywords:

Phosphate fertilizer

Mercury

Copper

Solid sample analysis

HR-CS GF AAS

ABSTRACT

The present study proposes the determination of copper and mercury in phosphate fertilizers by direct solid sampling analysis (SS) employing high resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). For Cu determination, two analytical lines were used: 327.3960 nm and 249.2146 nm. Hg determination was carried out on the line 253.6521 nm and 100 $\mu\text{g KMnO}_4$ was used as chemical modifier. The optimal pyrolysis temperature for Cu determination was 1300 °C. Atomization temperatures for Cu and Hg were 2400 and 1100 °C, respectively. External calibration with aqueous standard solutions was adopted for both elements. The limits of quantification (LoQs) and characteristic mass (m_0) obtained for Cu determination were 0.4 $\mu\text{g g}^{-1}$ and 1.12 ng, respectively, on line 249.2146 nm, and 64 $\mu\text{g g}^{-1}$ and 25 pg on 327.3960 nm. For mercury, LoQ and m_0 were 4.8 ng g^{-1} and 39 pg, respectively. The accuracy of the proposed methods was confirmed by the analysis of standard reference material (SRM) of Trace Elements in Multi-Nutrient Fertilizer (SRM NIST 695). The precision expressed as relative standard deviation (RSD), was better than 8.2% for Hg and 7.7% for the Cu ($n = 5$), considered satisfactory for microanalysis in solid sample. Four fertilizer samples acquired in commercial establishments in the city of Salvador, Bahia, Brazil, were analyzed. The optimized analytical methods were simple, fast, accurate, precise and free of spectral interferences for the determination of Cu and Hg in phosphate fertilizer samples by SS–HR-CS GF AAS, avoiding the dissolution of the sample, the use of harmful reagents and the generation of residues.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The population growth observed in recent decades brought as consequence an increase in food demand. However, the cultivable areas grew at a slower rate and therefore it is necessary to intensify agricultural activities in the existing areas. Consequently, there was an increase in applications of agricultural inputs such as fertilizers, which are responsible for supplying the nutritional deficiencies of plants [1–3].

Among the types of fertilizers applied to agricultural supply are the phosphate ones, obtained from phosphate rocks extracted from nature. However, in addition to necessary nutrients to plants, as Cu, Se, Mo and Zn, these rocks may contain contaminants that can be introduced in the fertilizer and subsequently added to the soil. Excess of these toxic elements in soil may accumulate in plants and food chain, and because of

their harmful effects, become hazardous to both the environment and humans, as mercury can be introduced into the environment through emission from various sources, such as gold mining, chemical industries, metal smelting, coal combustion, natural resources and agricultural sources, among others [4–12].

Mercury released into the environment will remain for an indefinite period, in both organic and inorganic forms. The inorganic forms are the dimeric mercury ion, elemental Hg and mercuric ion. On the other hand the main organic forms found are methylmercury (CH_3Hg^+) and dimethylmercury [$(\text{CH}_3)_2\text{Hg}$] [13]. Organic and inorganic mercury can interchange with time, i. e., some percentage or even all concentration of organic mercury content can be slowly converted into inorganic mercury, or vice versa, due to the action of bacteria in the soil or water [10–13].

In order to regulate the maximum allowed values of potentially toxic elements in mineral fertilizers, the United States of America (USA), through the United States Environmental Protection Agency (USEPA) established limits for levels of As, Cd, Cr, Pb and Hg in zinc-based

* Corresponding author at: Departamento de Química Analítica, Instituto de Química, Universidade Federal da Bahia (UFBA), 40.170-115 Salvador, BA, Brazil.

E-mail addresses: rgeoa01@terra.com.br, rennan@ufba.br (R.G.O. Araujo).

fertilizers [14]. In Canada, there are no maximum limits for Hg in fertilizers, only the maximum levels for the elements As, Cd, Cu, Pb and Zn are established by the Federal Fertilizers Act [15]. In Brazil, the Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento – MAPA), through the Normative Instruction no 27 of June 5, 2006, establishes maximum allowable limits for As, Cd, Cr, Pb and Hg in mineral fertilizers [16].

Several studies report analytical methods for the determination of Cu by atomic spectrometry. Álvarez et al. determined Cu simultaneously with As, Cd, Cr, Ni Pb and Tl in sediment fraction samples by graphite furnace atomic absorption spectrometry (GF AAS) after total digestion of the samples [17]. Essential elements Cu, Se, Zn, Co and Mn, and potentially toxic elements Cd, Pb, Al, Ni, As and Hg in foodstuffs were determined by Nardi et al. [18]. Also Krawczyk determined the microelements as Cu, Cr, Fe, Mn and Se and the trace elements As, Cd and Pb in multivitamin supplements employing suspension analysis by high resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) [19].

Other studies mention analytical methods established for the determination of Hg in various matrices, and among them, the methods based on atomic spectrometry have been widely used. Bansal et al. determined the total Hg in bauxite and bauxite waste samples by cold vapor atomic absorption spectrometry (CV AAS) with flow injection [20]. Araujo et al. developed a method for Hg determination in airborne particulate matter samples in glass fiber using direct solid sampling analysis (SS) and detection by HR-CS GF AAS [13]. De Jesus et al. carried out the determination of Hg in phosphate fertilizers by (CV AAS) [21] whose main advantage was the application of slurry sampling as sample preparation.

As can be seen, analytical methods employing analytical atomic spectrometry have been highly recommended for the determination of mercury, in particular CV AAS, especially because of its sensitivity [11,20]. However, these methods required sample treatment and the use of reagents to generate the chemical vapor, having as consequence the generation residues.

Among various spectrometric techniques, the HR-CS GF AAS stands out because of its advantages such as viewing the spectral environment in high resolution, which allows the evaluation of spectral interferences. Furthermore the technique has a better signal-to-noise ratio due to the high intensity radiation source, resulting in better precision and limits of detection. The technique also allows the correction of structured background contribution using least-squares background correction (LSBC) [22,23].

Solid sample treatment procedure for determination of trace elements is conventionally a time consuming process, as well as a possible source of error, mainly due to the losses of analyte and/or contamination of the sample during the pre-treatment steps. Other important factors that should be taken into account are the safety of the analyst, the use of concentrated reactants and the chemical waste production [24]. Therefore, the direct solid sampling analysis (SS) is an attractive alternative to chemical analysis, due to the significant reduction in the risks of contamination and loss of analytes during sample preparation step; the increased sensitivity, since the samples are not diluted; the resulting economic and environmental benefits; and the faster analytical frequency because there is a reduction in the stage of sample preparation [25–27].

Studies for solid sampling analysis are reported in literature and one example is the work of Borges et al. reporting a comparison of a method for the determination of Cr and Tl in fertilizer samples using line source GF AAS (LS-GF AAS) and Zeeman-effect background correction with SS–HR-CS GF AAS to verify the absence of spectral interferences [4]. Another study to assess the capability of SS–HR-CS GF AAS for the determination of mercury in airborne particulate matter (APM) collected on glass fiber filters, avoiding the use of reagents, including fluoridric acid, was evaluated by Araujo et al. [13]. Cadmium and lead were determined in plastic material from electronic waste using SS–GF AAS and

calibration against aqueous standards. The method was sensitive, fast, and not requiring sample preparation [27].

In this context, this work proposes the optimization of analytical methods applicable to the routine laboratory for the determination of copper and mercury in phosphate fertilizers using direct solid sampling analysis and detection by HR-CS GF AAS, avoiding the dissolution of the sample, the use of harmful reagents and the generation of residues.

2. Experimental

2.1. Instrumentation

A high resolution continuum source atomic absorption spectrometer equipped with two atomizers: graphite furnace and flame, ContrAA 700 model (Analytik Jena, Jena, Germany) was used in all measurements and determinations. The equipment has a continuous source of radiation, a short-xenon arc lamp, operating in hot-spot mode at a nominal power of 300 W, and a double monochromator with high resolution linear array detector (charge-coupled device – CCD) with spectral resolution of 588 pixels and 1.2 pm per pixel [28]. For the determination of copper in the fertilizer samples the analytical line 327.3960 nm (45%) was used, however for the analysis of certified reference material the line 249.2146 nm (1.1%) was chosen. The determination of mercury was carried out using the line 253.6519 nm (100%). In order to evaluate the analytical signal, the integrated absorbance (A_{int}) at the center pixel (CP) was applied to the Cu. For mercury the peak volume selected absorbance (PVSA) [29], i.e. the sum of the absorbance measurement ($CP \pm 1$) around the core line ($A_{\Sigma 3, int}$) was used. More details of the equipment can be obtained from studies published in the group [27,30,31].

All experiments were performed in transversely-heated graphite tubes (Analytik Jena, Part No. 407-A81.303) specific for solid sampling (SS) (Analytik Jena, Part No. 407-152.023). The samples were directly weighed onto SS graphite platform using a micro-balance model M2P (Sartorius, Göttingen, Germany) accurate to 0.001 mg. The platforms were inserted into the graphite tubes using a pre-adjusted pair of tweezers, which is part of SSA6 model (Analytik Jena, Jena, Germany). Argon gas 99.996% purity (White Martins, São Paulo, Brazil) was used as purge and protection gas at all stages of the graphite furnace temperature program, except during the atomization stage, in which the gas flow was stopped. The graphite furnace temperature program used for determination of Cu and Hg are shown in Table 1.

2.2. Reagents and solutions

All reagents used were at least of analytical grade. Nitric acid 65% ($m\ m^{-1}$) suprapure quality (Merck, Germany), used to prepare standard solutions of external calibration curve, was purified using a sub-boiling distiller apparatus with quartz tube (Kürner Analysetechnik, Rosenheim, Germany). Deionized water used in the preparation of all solutions was obtained in a purification system Milli-Q (Millipore, Bedford, MA, USA) to a resistivity of 18.2 M Ω . Intermediate solutions

Table 1
Graphite furnace temperature program for the determination of Cu and Hg in phosphate fertilizer samples by SS–HR-CS GF AAS.

Stage	Temperature/°C	Ramp/°C s ⁻¹	Hold/s
Drying	80 ^a /90 ^b	10 ^a /15 ^b	5 ^{a,b}
Drying	200 ^a /130 ^b	20 ^a /10 ^b	15 ^a /5 ^b
Pyrolysis	1300 ^b	100 ^b	30 ^b
Auto zero	200 ^a /1300 ^b	20 ^a /0 ^b	15 ^{a,b}
Atomization	1100 ^a /2400 ^b	100 ^a /300 ^b	7 ^a /8 ^b
Cleaning	2000 ^a /2600 ^b	500 ^a /200 ^b	4 ^a /5 ^b

Purge gas (argon) flow rate 2 L min⁻¹ in all stages, except during atomization, where the gas flow was stopped.

^a Parameters of Hg determination.

^b Parameters of Cu determination.

Download English Version:

<https://daneshyari.com/en/article/1239776>

Download Persian Version:

<https://daneshyari.com/article/1239776>

[Daneshyari.com](https://daneshyari.com)