



Fast ultrasound-assisted treatment of inorganic fertilizers for mercury determination by atomic absorption spectrometry and microwave-induced plasma spectrometry with the aid of the cold-vapor technique



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ABSTRACT

This work reports a fast and efficient ultrasound-assisted extraction of mercury in inorganic fertilizers for its determination by cold vapor atomic absorption spectrometry (CV AAS) and microwave-induced plasma optical emission spectrometry (MIP OES), using a 10% (w/v) SnCl₂ as reductant agent. A multi-mode sample introduction system (MSIS) was coupled to the MIP OES equipment to make possible the generation of mercury vapor in the nebulizer chamber. The optimized protocol involved the treatment of 150 mg of fertilizer with 4 mL of 30% (v/v) HCl inside glass tubes using a conventional ultrasonic bath for 5 min. Comparable analytical results were obtained for mercury determined by both CV AAS and MIP OES, with better detection limits for the latter technique. The proposed extraction procedure is simple and versatile, and contributes to minimal generation of waste (low volume of diluted HCl) in comparison to the official method.

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1. Introduction

Inorganic fertilizers constitute an important source of nutrients for plants, including a number of metals. Notwithstanding, a special attention is given to the toxic metals (contaminants) such as cadmium, lead, mercury, among others, mainly due to their high toxicity, which is being deposited in soils due to the general use of such a class of fertilizers [1,2]. According to the Ministry of Agriculture, Livestock and Supply (Ministério da Agricultura, Pecuária e Abastecimento – MAPA), the elements which are considered as contaminants and remain present in fertilizers are cadmium, lead, chromium, nickel, arsenic, selenium and mercury [3].

Such contaminants can be absorbed by plants in agricultural areas or transported in sediments or dissolved in water, compromising the health of the aquatic ecosystem. The most severe effect of pollution by such contaminants in aquatic environments occurs due to the gradual increase of concentration of those metals dissolved in water [4]. Agricultural inputs like lime and phosphatic fertilizers might contain not only essential nutrients to plants but also present in its composition undesirable elements such as cadmium, lead and mercury [5]. These metals might accumulate in the soil and according to their bioavailability may be absorbed by plants and consequently, may be inserted in the food

chain to animals and human beings, considering the biogeochemical cycle as a whole [6].

A study revealed concentrations of up to 800 mg kg⁻¹ of mercury in soils collected in the region of Rio Grande, Brazil, which receives emissions from industries of phosphatic fertilizers [11]. Another study evaluating 196 samples of fertilizers from 12 European countries pointed out that phosphate rocks and the fertilizers derived from them presented in their constitution significant concentration of arsenic, mercury, chromium, cadmium and lead [7]. Hence, the quality control of fertilizers is of primordial importance to avoid environmental pollution by toxic metals. The method proposed by MAPA to determine mercury in inorganic fertilizers involves a sample preparation step before the determination by atomic absorption spectrometry coupled with cold vapor generation of mercury [3].

The generation of cold vapor of mercury coupled to instrumental techniques such as atomic absorption spectrometry (CV AAS), atomic fluorescence spectrometry (CV AFS), inductively coupled plasma optical emission spectrometry (CV ICP OES) and inductively coupled plasma mass spectrometry (CV ICP-MS) is usually employed [8,9]. The microwave-induced plasma optical emission spectrometry (MIP OES) exhibits satisfactory results for the determination of metals in samples of both environmental and agricultural interest [10].

While developing an analytical method, the sample preparation step is fundamental to obtain accurate analytical results. Traditional procedures of digestion are slow, subject to external contamination and to loss of volatiles [11]. The use of microwave ovens is being successfully

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employed on the preparation of samples avoiding the problems of traditional procedures [12–15]. However, their high cost prevents their acquisition by a considerable number of laboratories. On the other hand, methods employing ultrasonic energy have been presented for metal extraction from several environmental and biological samples, especially using ultrasonic baths for the development of faster procedures and in less drastic conditions (room temperature, atmospheric pressure and reduced volume of concentrated acids and sample) [16–24]. The combination of an ultrasonic probe with an ultrasonic bath was applied for Hg extraction in seafood samples [25]. The use of a cup-horn sonoreactor (associated to high power ultrasonic probe) with the possibility of treating eight samples simultaneously has been described for the extraction of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in organic fertilizers prior FAAS sequential determinations [26]. CV AAS determination of mercury in phosphate fertilizers was accomplished after the metal extraction using an ultrasonic bath for 20 min in the presence of lanthanum chloride, HCl and thiourea to liberate mercury ions for further cold vapor generation using sodium tetrahydroborate [27].

Microwave-induced plasma optical emission spectrometry (MIP OES) using helium gas for supporting the plasma source has been applied for the determination of hydride forming elements and mercury in biological (animal tissues) and environmental (marine sediment) samples after sonication treatment for 90 s using an ultrasonic probe [28]. The use of MIP OES has been recently reported for the determination of copper, iron, manganese and zinc in fertilizers after hot plate and microwave digestion procedures with better results in comparison with AAS or ICP OES [10]. This work has performed the new commercially available MIP OES instrument (4100 MP-AES) that uses a nitrogen plasma generated at atmospheric pressure and a conventional pneumatic nebulizer [10]. The same instrument was applied for the analysis of gasoline and ethanol fuel [29] and herbal medicines after microwave digestion [30].

The present work describes the fast US-assisted extraction of mercury in inorganic fertilizers for its determination by CV AAS and MIP OES.

2. Experimental

2.1. Instrumentation

A Hsl-600 CTA Ultrasonic Systems ultrasonic bath operating at 40 kHz and 200 W was applied for the mercury extractions from the samples of mineral fertilizers. A Fanem (model 211) centrifuge with capacity for 4 tubes of 15 mL was used for centrifugation of the extracts. Mercury determination in the extracts was performed by two analytical methods using a Varian atomic absorption spectrometer (model SpectrAA 220 FS) coupled to a Varian hydride generator (model VGA 77), and an Agilent (4100 MP-AES) microwave-induced plasma atomic emission spectrometer integrated to a 3-channel peristaltic pump. This equipment offers versions with a 5-channel peristaltic pump for determinations of Hg, As, and Se that requires a cold vapor or hydride

generator. In this work, the cold vapor generator for MIP OES determination is illustrated in Fig. 1. In the first channel, a 10% (w/v) SnCl₂ was suctioned entering through the top of multi-mode sample introduction system (MSIS). The second channel was linked to a connection with two inputs and one output (T-type) before and after the peristaltic pump, to suction the sample and a 10 mol L⁻¹ HCl solution. A flow control (restrictor of catheter) was inserted in the HCl solution channel. The mixture of sample and HCl solution is introduced through the bottom of MSIS, at which occurs the reaction with 10% (w v⁻¹) SnCl₂ solution to generate mercury vapor that is carried to the torch formed by nitrogen. The third channel was used to discharge the residual solutions from the MSIS. Tables 1 and 2 present the operating conditions for each equipment. The instruments were operated under the conditions recommended by the respective manufacturers. The MSIS spray chamber was pre-conditioned for 15 s (stabilization time in Table 2) using the acid and reducing agent solutions (washing step) before the next sample introduction. The analytical frequency was around 80 samples per hour.

Ultra-pure water used in the analytical stages, as well as the water employed during the cleaning of material and used to prepare solutions, was obtained by a Gehaka-Master-System deionization equipment model OS 20LX, presenting resistivity higher than 18 M Ω-cm.

2.2. Reagents, samples and materials

A stock reference solution of 1000 mg L⁻¹ Hg in 0.3 mol L⁻¹ HNO₃ Titrisol® (Merck, Darmstadt, Germany) was used to obtain analytical curves. Analytical grade reagents employed in the preparation of extracting solutions were 37 wt.% HCl, 69 wt.% HNO₃ and 70 wt.% HClO₄ (Vetec, Rio de Janeiro, Brazil). The extractions were performed in 15-mL closed glass tubes.

Two commercial samples of inorganic fertilizers and three secondary reference samples identified as MRR01 (year 2010), 05A (year 2012) and 05B (year 2013) provided by the inter-laboratory program of National Association for the Promotion of Fertilizers (Associação Nacional para Difusão de Adubos, ANDA, Brazil) were analyzed. The two commercial samples are NPK-based fertilizers (containing N, P, and K in the proportion of 10/10/10 wt.% and 5/25/20 wt.%, respectively, in which N and P are originated from monoammonium phosphate and K from KCl) mixed with some metallic ores (Cu, Zn, Fe, Mn, Co and Mo). The other three inorganic fertilizers (reference samples) are a mixture of cuprite (Cu₂O), pirolusite (MnO₂) and calamine (ZnO).

2.3. Ultrasound-assisted extraction

The reference sample MRR N° 01 (year 2010) was employed in the study to determine the best conditions for the accelerated and simplified extraction of mercury in the samples. The best compositions and concentrations for extracting solutions employing nitric, hydrochloridric and perchloric acids were evaluated. Univariate analysis was performed

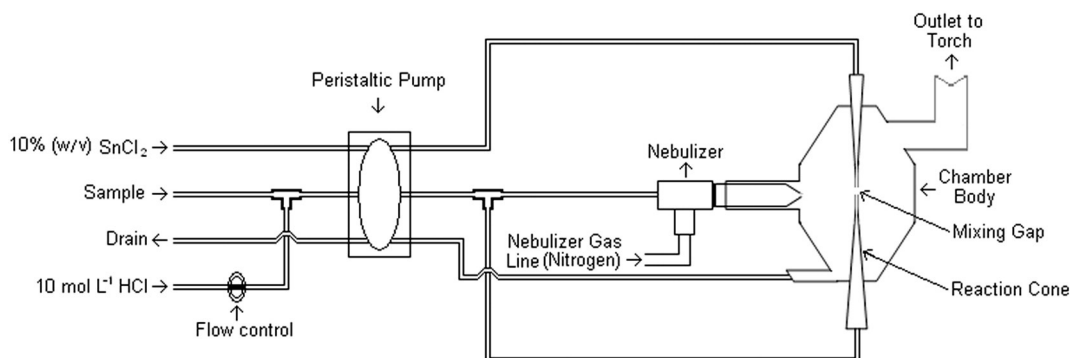


Fig. 1. Component diagram of the MIP OES system.

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