

Combination of sonication and heating for metal extraction from inorganic fertilizers prior to microwave-induced plasma spectrometry determinations



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ABSTRACT

This work reports a fast and efficient method for metal extraction in inorganic fertilizers by combining heating and sonication using an ultrasonic bath. Microwave-induced plasma optical emission spectrometry (MIP OES) was applied for the determination of Cd, Cu, Cr, Mn, Pb, and Zn in the extracts. Higher efficiency of metal extraction (~100% for all metals except to Cd) was obtained for the treatment of 150 mg of fertilizer with 4 mL of 50% (v/v) HCl sonicated for 10 min and heating at 85 °C. Extractions applying only heating did not provide satisfactory results. The proposed procedure is simple and contributes to reduced production of waste in comparison to the official method.

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1. Introduction

The increasing search for food production has pushed the use of organic and inorganic fertilizers to increase agriculture efficiency. However, inorganic fertilizers are a major source of metals, which can be absorbed by plant in agricultural lands and also can reach natural waters. The addition of fertilizers into agricultural lands to supply phosphate and essential metals, such as Cu, Mn and Zn, to soils can also contribute to the contamination of agricultural lands by Cd, Cr and Pb, which are nonessential metals that can be found in fertilizers [1,2]. Fertilizers containing metal concentrations (Pb and Cd) higher than the values established by regulatory agencies have been reported [3,4].

According to the Brazilian Ministry of Agriculture, Livestock and Supply (*Ministério da Agricultura, Pecuária e Abastecimento*, MAPA), which controls and establishes upper limits of contaminants in fertilizers, the elements which are considered as contaminants are Cd, Pb, Cr, Ni, As, Se and Hg [5]. Agricultural inputs like lime and phosphatic fertilizers may contain not only essential nutrients to plants but also present in its composition undesirable elements [6]. These metals can accumulate in the soil and according to their bioavailability could be absorbed by plants and consequently, may be inserted in the food chain to animals and humans [7]. These toxic metals can compromise the whole ecosystem balance that is

directly connected to the environment in which these classes of fertilizers are applied. The most deleterious effects of metal pollution in the aquatic environment are caused by the presence of dissolved metal species in water [1,8].

Therefore, the quality control of fertilizers is indispensable to prevent environmental pollution by metals. The Brazilian Ministry of Agriculture MAPA proposes an analytical method in which the sample preparation consists of wet digestion with concentrated hydrochloric (10 mL) and nitric (2.5 mL) acids in hot plate for 40 min to release the metals from fertilizers [5]. Thus this protocol is time-consuming and large volumes of acids and sample are required, which contributes to the generation of a considerable amount of chemical waste in routine laboratories.

Sample preparation is of capital importance in the development of an analytical method and this step typically brings the most significant error source. Microwave-assisted methods for sample preparation have been preferred over traditional digestion procedures due to decrease in time of analysis, reduced contamination from external sources and losses of volatile elements [9–13]. An elegant alternative to microwave-assisted methods is based on the use of ultrasound energy for sample preparation mainly using ultrasonic baths, which are operated at room-temperature and atmospheric-pressure, employ lower amount of concentrated acids and large sample amounts, and are typically faster [14–18]. The use of sonication for metal extraction from fertilizers have been reported recently in the literature using either ultrasonic baths [8,19,20] or high-power ultrasonic probes [21]. To our knowledge,

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the combination of sonication with heating has not been evaluated for metal extraction from fertilizers.

The application of microwave-induced plasma optical emission spectrometry (MIP OES), using the commercially available 4100 MP-AES (Agilent), presented similar results in comparison to atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP OES) for the determination of Cu, Fe, Mn and Zn in fertilizers after hot plate and microwave digestion procedures; the nitrogen plasma of MIP OES provided economy in the overall analytical method [22]. A similar spectrometer, which employs nitrogen plasma generated at atmospheric pressure and a conventional pneumatic nebulizer, was applied for mercury determination in fertilizer samples after US-assisted extraction [19], analysis of gasoline and ethanol fuel [23] and herbal medicines after microwave digestion [24].

In this work, a fast and efficient method for metal extraction in inorganic fertilizers by combining heating and sonication using an ultrasonic bath is presented. MIP OES was applied for the determination of Cd, Cu, Cr, Mn, Pb, and Zn in the extracts. The principal aim of this study was to establish an analytical condition to extract Cu, Zn, Mn, Pb, Cd and Cr from fertilizer samples simultaneously, employing a single step of pretreatment. For this, variables such as temperature, acid solution extraction and sonication time were tested. Sample mass and volume and concentration of acid solutions were fixed according to previous studies [8,19].

2. Experimental

2.1. Instrumentation

A T50220 Unique ultrasonic bath operating at 40 kHz and 200 W was applied for metal extractions from mineral fertilizer samples. A MarqLabor thermostatic bath with recycling water was applied to control the heating temperature of the water inside the ultrasonic bath according to Fig. 1. A FTR (24BT – SIMPLEX II) centrifuge with capacity for 24 tubes of 15 mL was used for centrifugation of the extracts. Metal determinations in the extracts were performed using an Agilent (4100 MP-AES) microwave-induced plasma atomic emission spectrometer integrated to a 3-channel peristaltic pump. Table 1 presents the operating conditions of the spectrometer.

2.2. Reagents, samples and materials

Stock reference solutions of 1000 mg L⁻¹ of Cd, Cr, Cu, Mn, Pb and Zn in 0.3 mol L⁻¹ HNO₃ Titrisol® (Merck, Darmstadt, Germany) was used to obtain the analytical curves. Analytical grade reagents employed in the metal extractions were 37 wt.% HCl and 69 wt.% HNO₃ (Vetec, Rio de Janeiro, Brazil). The extractions were performed in 15-mL closed glass tubes.

Table 1
Operating instrumental conditions for metal determinations by MIP OES.

Parameters	Cu	Pb	Mn	Zn	Cr	Cd
Wavelength (nm)	324.75	405.78	403.08	213.86	425.43	228.80
Nebulizer pressure (kPa)	200	200	220	120	240	140
Viewing position (mm)	-10	0	-10	10	-10	10
Analytical curve (mg L ⁻¹)	2.0–10.0		2.0–20.0		1.0–10.0	0.1–0.5
Nebulizer						Inert OneNeb
Spray chamber						Cyclonic single-pass
Speed peristaltic pump (rpm)						15
Read time (s)						5
Number of replicates						3
Stabilization time (s)						7
Uptake sample time (s)						7
Nitrogen (L min ⁻¹)						22.5
Sample flow rate (mL min ⁻¹)						6.0

A reference sample of fertilizer, with inorganic matrix classified as mix micro (containing Cu, Mn, Zn, Co, Mo, Pb, Cd, Cr and Hg) identified as 38b (year 2013), provided by the inter-laboratory program of National Association for the Promotion of Fertilizers (*Associação Nacional para Difusão de Adubos*, ANDA, Brazil) was used in this study.

Ultra-pure water used in all analytical stages as well as employed during the cleaning of material was obtained by a Gehaka–Master-System deionization equipment model OS 20LX with resistivity higher than 18 MΩ cm.

2.3. Ultrasound-assisted extraction

The parameters evaluated for the simultaneous extraction of Cd, Cr, Cu, Mn, Pb, Cd and Zn in the reference sample of fertilizer 38b (year 2013) were heating at 25, 50 and 85 °C, sonication time of 5, 10 and 30 min, and extracting solutions (HNO₃ and HCl both at 50% v v⁻¹). The sample mass was fixed in 150 mg based on a previous work [6].

The US-assisted extraction procedure consisted of adding 4.0 mL of 50% (v v⁻¹) hydrochloric acid or nitric acid to treat 150 mg of samples in glass tubes with capacity of 15 mL. The tubes were placed in the region of higher cavitation intensity, previously mapped according to the literature [18,25]. After US-assisted extractions, extracts were centrifuged to separate aliquots free of particulates and diluted to 10.0 mL with deionized water. The final extracts were analyzed by MIP OES before appropriate dilution.

The limits of detection (LOD) and of quantification (LOQ) were calculated according to IUPAC (LOD = 3s_B/S and LOQ = 10s_B/S, in which s_B is the standard deviation of 10 consecutive measurements of a blank solution and S is the slope of the respective curves). The respective LOD values obtained employing MIP OES for Cu, Zn, Mn,

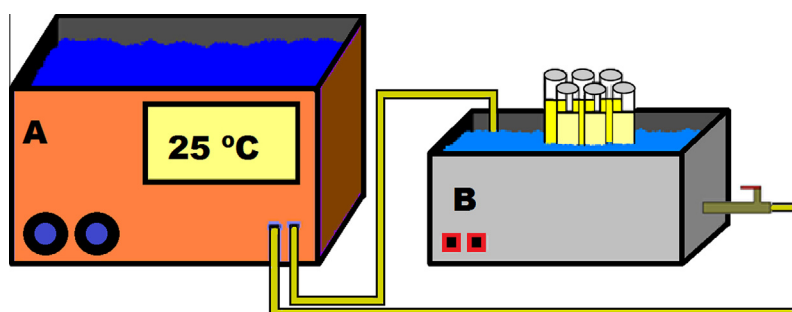


Fig. 1. Thermostatic bath (A) coupled with the ultrasonic bath (B).

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