Talanta 119 (2014) 232–239

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Fast determination of trace elements in organic fertilizers using a cup-horn reactor for ultrasound-assisted extraction and fast sequential flame atomic absorption spectrometry

Leonel Silva Teixeira [a], Heulla Pereira Vieira [b], Cláudia Carvalhinho Windmöller [a], Clésia Cristina Nascentes [a,*]

[a] Instituto de Ciências Exatas, Departamento de Química, Universidade Federal de Minas Gerais, Avenida Presidente Antônio Carlos, 6627, Pampulha, PO Box 702, CEP 31270-901, Belo Horizonte, Minas Gerais, Brazil
[b] Laboratório de Química Agropecuária, Instituto Mineiro de Agropecuária (IMA), BR 040, Km 527, CEP 32145-900, Contagem, Minas Gerais, Brazil

ARTICLE INFO

*Article history:*
Received 19 August 2013
Received in revised form
6 November 2013
Accepted 6 November 2013
Available online 11 November 2013

*Keywords:*
Organic fertilizers
Metals
Ultrasonic extraction
FS FAAS
Fast determination
Low cost

ABSTRACT

A fast and accurate method based on ultrasound-assisted extraction in a cup-horn sonoreactor was developed to determine the total content of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in organic fertilizers by fast sequential flame atomic absorption spectrometry (FS FAAS). Multivariate optimization was used to establish the optimal conditions for the extraction procedure. An aliquot containing approximately 120 mg of the sample was added to a 500 μL volume of an acid mixture ($HNO_3$/HCl/HF, 5:3:3, v/v/v). After a few minutes, 500 μL of deionized water was added and eight samples were simultaneously sonicated for 10 min at 50% amplitude, allowing a sample throughput of 32 extractions per hour. The performance of the method was evaluated with a certified reference material of sewage sludge (CRM 029). The precision, expressed as the relative standard deviation, ranged from 0.58% to 5.6%. The recoveries of analytes were found to 100%, 109%, 96%, 92%, 101%, 104% and 102% for Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively. The linearity, limit of detection and limit of quantification were calculated and the values obtained were adequate for the quality control of organic fertilizers. The method was applied to the analysis of several commercial organic fertilizers and organic wastes used as fertilizers, and the results were compared with those obtained using the microwave digestion procedure. A good agreement was found between the results obtained by microwave and ultrasound procedures with recoveries ranging from 80.4% to 117%. Two organic waste samples were not in accordance with the Brazilian legislation regarding the acceptable levels of contaminants.

## 1. Introduction

The production of fertilizers from agricultural, municipal and industrial organic wastes provides an important means of recovering nutrients. The high content of organic matter present in these wastes contributes to the conditioning of the physico-chemical properties of soils, resulting in increased agricultural productivity. In addition, the recycling of wastes into fertilizers provides an economically viable method of final disposal [1–3]. However, it is necessary to strictly monitor the quality of these fertilizers because some residues may exhibit nutrient contents below the required minimum and/or concentrations of toxic metals above the legally allowed maximum. The presence of toxic metals in fertilizers can exert adverse effects on animal and human health through the contamination of soil, groundwater and plants [4]. Thus, accurate and precise analytical methods for the determination of nutrients and toxic metals in fertilizers are needed for the routine monitoring, risk assessment and regulation of the environment.

The techniques commonly employed for the measurement of nutrients and inorganic contaminants, such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), require the analyte to be available in a solution compatible with the measurement conditions [5].

The organic fertilizers consist of complex matrices containing both organic and inorganic fractions. In these cases, it is often necessary to perform a sample preparation step consisting of an acid digestion procedure, which involves high temperatures, large quantities of oxidizing reactants and long analysis time. These procedures increase the probability of contamination and analyte loss through volatilization [6,7]. Although the procedures for microwave-assisted digestion in closed vessels exhibit lower losses due to volatilization, most models of microwave oven cavity commonly available in laboratories require some milliliters of concentrated acid, and the dynamic range for the sample mass is limited by the high pressures generated during the process, especially for matrices with a high content of organic matter [8].

---

* Corresponding author. Tel.: +55 31 3409 5759; fax: +55 31 3409 5700.
*E-mail addresses:* clesia@qui.ufmg.br, clesianascentes@yahoo.com.br (C.C. Nascentes).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.11.018

In addition, these procedures are typically characterized by long processing time and low throughput. For these reasons, ultrasound-assisted extraction has been proposed as an alternative to acid digestion procedures [9]. Ultrasonic energy facilitates the sample processing by making the analyte available to dilute acid solutions under mild conditions (near room temperature and under atmospheric pressure) due to the acoustic cavitation phenomenon [9,10]. The formation and implosion of cavitation microbubbles occur during sonication, causing local increases in temperature and pressure. These conditions increase the solubility and diffusion of the analyte. Furthermore, the constant generation of new sample surfaces as a result of the fragmentation of the sample particles allows increased contact with the extractor. The formation of oxidizing species such as $H_2O_2$ and $OH^{\bullet}$ can also occur, assisting in the oxidation of organic matter [11–15]. Thus, the ultrasound-assisted extraction procedure results in minimal contamination and losses due to volatilization, low reagent consumption and the diminished generation of residue, reducing the analysis time and cost [9,11].

Ultrasound-assisted extraction procedures can be performed with an ultrasonic bath, an ultrasonic probe or a cup-horn sonoreactor. The sonoreactor cup-horn offers an interesting alternative to other analytical methods because it allows the sonication of up to eight samples simultaneously with homogeneous ultrasound distribution, which is not possible using an ultrasonic bath [12]. Moreover, the risk of contamination is lower compared with procedures employing an ultrasonic probe because acidic solutions, especially HF solutions, can lead to probe corrosion [12].

Several studies involving the ultrasound-assisted extraction of metals in biological and environmental samples [12,16–24], cigarettes [25], tablets [26], fuel [27] and inorganic fertilizer [28] have been reported in the literature, confirming the efficiency of ultrasound-based methods.

In this study, a fast and economic ultrasound-assisted extraction procedure employing a cup-horn sonoreactor was developed to determine the Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn contents in organic fertilizer. Importantly, this method was developed following the principles of green analytical chemistry [11,29], including reducing the amount of waste and the consumption of reagents and energy. Thus, our method presents an excellent alternative to acid decomposition procedures.

## 2. Experimental

### 2.1. Instrumentation

A Varian Spectra 220 (Mulgrave, Australia) flame atomic absorption spectrometer in sequential mode equipped with a deuterium background corrector was used for the determination of Cd, Co, Cu, Cr, Mn, Ni, Pb and Zn. Hollow cathode lamps of Cd and Pb and a hollow cathode multielemental lamp of Cr, Cu, Mn and Ni (Varian Inc., Mulgrave, Australia) were employed. The FS FAAS operating conditions were set according to the values recommended by the manufacturer (Table 1). A Milestone Ethos 1 – Advanced Microwave Digestion System microwave oven (Sorisole, Italy) was used for the sample digestion procedure.

A Sonics VCX 505 ultrasonic processor cup-horn system (Newtown, CT, USA), operating at 500 W and 20 kHz, was employed for the ultrasound-assisted extraction procedure. The system consists of cup-horn coupled to a reversed ultrasonic converter (Fig. 1a). The glassware possesses input and output ports for cooling water circulation. A support for polypropylene tubes with a capacity of 5.0 mL allows the processing of up to eight samples simultaneously (Fig. 1b). All of the procedures were performed in an acoustic insulation box.

A Tecnal TE394/1 oven with air circulation (São Paulo, Brazil) and a Quimis analytical mill (São Paulo, Brazil) were used for the pretreatment of the fertilizer samples. Other equipments used included a FANEM 206-BL Excelsa® centrifuge (São Paulo, Brazil) and a Shimadzu AX 200 analytical balance (São Paulo, Brazil).

A Marte® MB-10 pH meter (São Paulo, Brazil), a Químis Q405M conductivimeter (São Paulo, Brazil) and a Perkin-Elmer CHN 2400 elemental analyzer (Shelton, US) were used for characterizing the fertilizer and organic waste samples.

### 2.2. Reagents, solutions and samples

All reagents used were of analytical grade, and all of the solutions were prepared using ultrapure water (resistivity higher than18.2 MΩ cm) obtained by a Direct-Q system (Millipore, Billerica, MA, USA). Prior to use, the laboratory glassware, plastic bottles and microwave vessels were kept overnight in a 10% (v/v) nitric acid aqueous solution, rinsed with ultrapure water, and dried in a dust-free environment.

Nitric acid (65% m/m), hydrochloric acid (37% m/m), hydrofluoric acid (40% m/m) and hydrogen peroxide (30% v/v) (Merck, Darmstadt, Germany) were used for the sample preparation procedures. Boric acid (Panreac, Barcelona, Spain) was used for complexing any excess fluoride ions. The reference solutions for Cd, Co, Cr, Cu, Mn, Ni Pb and Zn were prepared by the dilution of certified standard solutions (1000 mg $L^{-1}$; Merck, Darmstadt, Germany) of the corresponding metal ions.

A sample of urban organic waste, sold as organic fertilizer, was used in the optimization of the ultrasound-assisted extraction procedure. A certified reference material, sewage sludge CRM029-50G (FLUKA, USA), was used to verify the accuracy of the developed method. Samples of organic fertilizers obtained from various raw materials (earthworm humus, vegetable earth, sewage sludge, urban organic waste, vegetable waste and castor beans) were analyzed employing both ultrasound-assisted extraction and

**Table 1**
Instrumental conditions employed for the determination of analytes in organic fertilizers by FS FAAS.

| Element | λ (nm) | Slit width (nm) | Current (mA) | Flame:air/acetylene (L $min^{-1}$) | | Reading time (s) | Delay time (s) |
|---|---|---|---|---|---|---|---|
| | | | | Air | Acetylene | | |
| Cd | 228.8 | 0.5 | 6.0 | 12.0 | 2.00 | 1.50 | 2.00 |
| Co | 240.7 | 0.2 | 10 | 12.0 | 2.00 | | |
| Cr | 357.9 | 0.2 | 10 | 11.0[a] | 6.63 | | |
| Cu | 324.8 | 0.5 | 10 | 12.0 | 2.00 | | |
| Mn | 279.5 | 0.2 | 10 | 12.0 | 2.00 | | |
| Ni | 232.0 | 0.2 | 10 | 12.0 | 2.00 | | |
| Pb | 217.0 | 1.0 | 10 | 12.0 | 2.00 | | |
| Zn | 213.9 | 1.0 | 10 | 12.0 | 2.00 | | |

[a] Nitrous oxide.