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

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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].

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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.

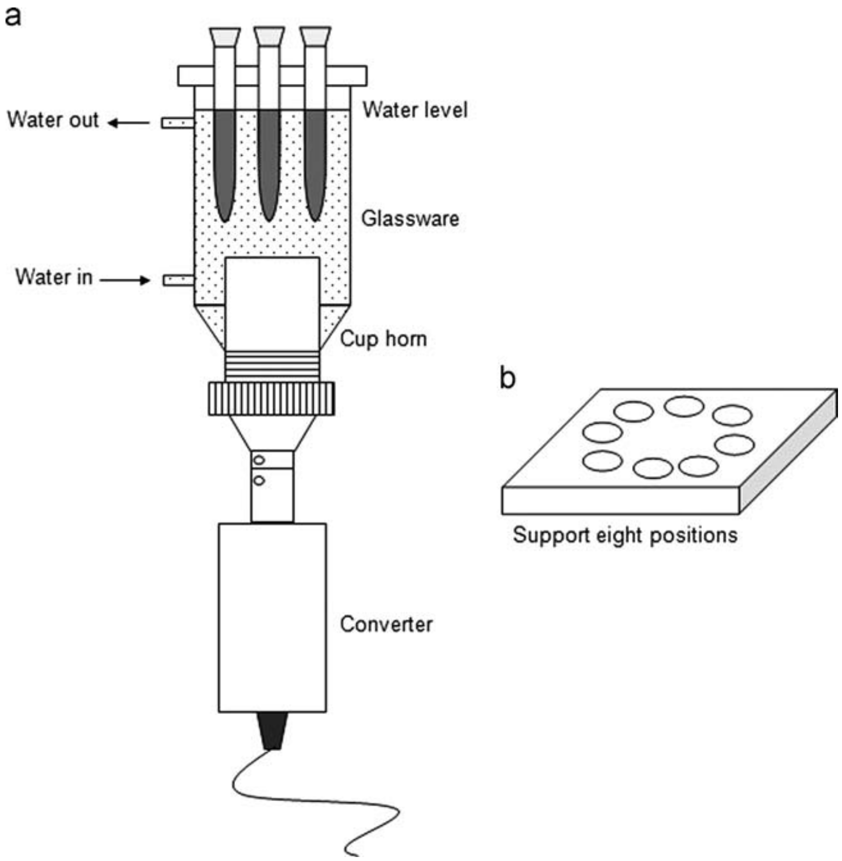

**Fig. 1.** Scheme of the cup-horn sonoreactor system (a) with support eight positions (b) employed in the proposed method.

**Table 2**
Matrix of the $2^{5-2}$ fractional factorial design used to evaluate the extraction conditions.

| Experiment | Extractor | Vol. HF (μL) | Vol. extractor (mL) | Time (min) | Amplitude (%) | Overall response | |
|---|---|---|---|---|---|---|---|
| | | | | | | $OR_1$[a] | $OR_2$[a] |
| 1 | $HNO_3$ | 0 | 1.00 | 10 | 60 | 3.64 | 3.59 |
| 2 | $HNO_3+HCl$[b] | 0 | 1.00 | 20 | 40 | 4.26 | 4.12 |
| 3 | $HNO_3$ | 100 | 1.00 | 20 | 40 | 5.03 | 5.05 |
| 4 | $HNO_3+HCl$[b] | 100 | 1.00 | 10 | 60 | 5.25 | 4.73 |
| 5 | $HNO_3$ | 0 | 1.50 | 20 | 60 | 3.21 | 3.18 |
| 6 | $HNO_3+HCl$[b] | 0 | 1.50 | 10 | 40 | 3.60 | 3.78 |
| 7 | $HNO_3$ | 100 | 1.50 | 10 | 40 | 4.61 | 4.42 |
| 8 | $HNO_3+HCl$[b] | 100 | 1.50 | 20 | 60 | 4.91 | 5.12 |

[a] Replicates.
[b] Acid mixture: $HNO_3+HCl$ (1:1, v/v).

microwave-assisted decomposition (reference method) for comparison. All of the samples were homogenized by grinding in an analytical mill, sieved through a steel sieve ($<300$ μm mesh size) and stored in prewashed and dried polyethylene vessels. The values of pH, amount of organic matter (OM), organic carbon (C-Total), total nitrogen (N-Total), C/N values and electrical conductivity of the samples were determined according to manual of official analytical methods for minerals, organic fertilizers and correctives of the Ministry of Agriculture, Livestock and Supplies [30].

### 2.3. Optimization of ultrasound-assisted extraction

The ultrasound-assisted extraction was conducted using the cup-horn sonoreactor described above. The extraction was assessed using multivariate strategy.

To determine the conditions that simultaneously achieve the quantitative extraction of all of the elements, the overall response [31] (OR) was adopted $OR=C(M_1)/HC(M_1)+\cdots+C(M_n)/HC(M_n)$, *where* $C(M)$ is the concentration of a particular element in a particular experiment, and $HC(M)$ is the highest concentration in the set of experiments for that element.

Initially, the factors composition extractor, volume extractor, HF addition, amplitude of ultrasound and sonication time were studied by $2^{5-2}$ fractional factorial design in duplicate (Table 2).

The proportions of concentrated $HNO_3$, HCl and HF were optimized using a $2^3$ central composite design with central point in quadruplicate, totaling 18 experiments (Table 3). In all the procedures, the concentrated acids remained in contact with the sample mass (approximately 120 mg) for about 20 min. Deionized water was subsequently added to provide the final volume of the extractor.

### *2.4. General procedure for ultrasound-assisted extraction*

The sample mass was directly measured in polypropylene tubes (5.0 mL capacity). Subsequently, 0.5 mL of the mixed concentrated acid solution ($HNO_3$/HCl/HF, 5:3:3, v/v/v) was added. After 20 min of contact, 0.5 mL of deionized water was added. The tubes were subjected to sonication for 10 min with an amplitude of 50%. To prevent the heating of the system during sonication, a flow of water at room temperature was circulated through the glassware. Following sonication, the samples were transferred to graduated tubes with a capacity of 15.0 mL, 1.5 mL of $H_3BO_3$ 4% ($m\,v^{-1}$) was added and the final volume was adjusted to 10.0 mL using ultrapure water. Lastly, the sample was centrifuged prior to the subsequent determination of the metal content in the supernatant by FS FAAS.

### *2.5. Microwave-assisted acid digestion*

Microwave-assisted acid digestion was used as a reference method for comparison with the optimized ultrasound-assisted extraction. A mass of 200 mg of sample was weighed into PTFE-vessels. Volumes of 4.5 mL of $HNO_3$, 1.5 mL of HCl and 2.0 mL of $H_2O_2$ were added separately to each of the vessels, which were then submitted to a heating program in the microwave oven: first step – 10 min to 200 °C, second step – 15 min at 200 °C and third step – 30 min ventilation. The digests were diluted to 20.0 mL for the subsequent determination of metals by FS FAAS.

**Table 3**
Matrix of the $2^3$ composite central used for the optimization of the proportions of concentrated $HNO_3$, HCl and HF.

| Experiment | Volume (μL) | | | Overall response |
|---|---|---|---|---|
| | $HNO_3$ | HCl | HF | |
| 1 | 140 | 140 | 70 | 5.13 |
| 2 | 260 | 140 | 70 | 5.10 |
| 3 | 140 | 260 | 70 | 5.09 |
| 4 | 260 | 260 | 70 | 5.32 |
| 5 | 140 | 140 | 130 | 5.29 |
| 6 | 260 | 140 | 130 | 5.79 |
| 7 | 140 | 260 | 130 | 5.56 |
| 8 | 260 | 260 | 130 | 5.60 |
| 9 | 100 | 200 | 100 | 5.41 |
| 10 | 300 | 200 | 100 | 5.37 |
| 11 | 200 | 100 | 100 | 5.31 |
| 12 | 200 | 300 | 100 | 5.44 |
| 13 | 200 | 200 | 50 | 5.12 |
| 14 | 200 | 200 | 150 | 5.73 |
| $CP_1$[a] | 200 | 200 | 100 | 5.25 |
| $CP_2$[a] | 200 | 200 | 100 | 5.33 |
| $CP_3$[a] | 200 | 200 | 100 | 5.26 |
| $CP_4$[a] | 200 | 200 | 100 | 5.18 |

[a] Central point (intermediaries experimental conditions).

## 3. Results and discussion

### *3.1. Characterization of samples*

Some important characteristics were determined in organic fertilizers and organic wastes studied (Table 4). According to the Brazilian legislation, the solid organic fertilizers must display the values of pH, C-Total (%) and N-Total (%) greater than 6.0, 15.0 and 0.5, respectively, and C/N value to be lower than 20. Thus, earthworm humus and vegetable earth sample are not within the required standards of quality, since the first sample had pH of 4.75 and the second shows the C/N value of 49.9, far exceeding the maximum allowed.

### *3.2. Optimization of ultrasound-assisted extraction*

Urban waste compost was chosen for use in the optimization step. Through preliminary experiments, we observed higher percentages of extraction when the concentrated acids were left in contact with the sample for 20 min. Moreover, the contact of the samples with the acid mixture prior to the sonication process prevented the formation of foam in some of the samples; the sonication process can enhance the formation of foam, leading to sample loss.

In all of the experiments, the sample mass was fixed at 120 mg. It was found that masses lower than 120 mg were often not representative of the sample, as evidenced by relative standard deviations (RSD) greater than 10%. However, when masses greater than 120 mg were evaluated, a decrease in the percentage of metal extraction was observed.

#### *3.2.1. $2^{5-2}$ Fractional factorial design*

The results obtained from the $2^{5-2}$ fractional factorial design indicated that the factors HF, extractor composition and extractor volume exerted significant effects (Fig. 2). However, at the levels studied, the sonication time and amplitude did not significantly affect the extraction process.

Among the factors studied, HF exhibited the highest effect on the extraction of metals (Fig. 2). The addition of HF was responsible for an average increase of 20% in the recovery of the analytes (Fig. 3). The role of HF in the extraction procedure can be exemplified in the analysis of urban waste compost, a complex sample; mild conditions, temperatures and dilute acids would be insufficient for extracting this type of sample because it contains

**Table 4**
Characteristics of commercial fertilizers and organic wastes studied.

| Sample | pH[a] | EC[b] ($dS\,m^{-1}$) | C-Total (%) | OM[c] (%) | N-Total (%) | C/N |
|---|---|---|---|---|---|---|
| Sewage sludge (CRM 029)[d] | 7.13 ± 0.03 | 25.8 ± 0.5 | 30.0 ± 0.5 | 51.8 ± 0.8 | 4.48 ± 0.10 | 6.70 |
| Urban waste compost[e] | 6.32 ± 0.02 | 9.20 ± 0.15 | 18.2 ± 0.3 | 31.4 ± 0.5 | 1.38 ± 0.12 | 13.3 |
| Mixed: urban waste compost + castor bean meal[e] | 7.40 ± 0.06 | 10.8 ± 0.1 | 22.5 ± 1.0 | 38.8 ± 1.7 | 3.35 ± 0.21 | 6.73 |
| Vegetable earth[e] | 7.04 ± 0.06 | 1.56 ± 0.03 | 4.49 ± 0.59 | 7.74 ± 1.02 | 0.090 ± 0.005 | 49.9 |
| Humus earthworm[e] | 4.97 ± 0.07 | 9.00 ± 0.16 | 21.0 ± 0.6 | 36.1 ± 1.1 | 1.14 ± 0.18 | 18.5 |
| Sewage sludge 1[f] | 6.32 ± 0.06 | 11.4 ± 0.1 | 26.7 ± 0.3 | 46.1 ± 0.4 | 2.98 ± 0.01 | 8.98 |
| Sewage sludge 2[f] | 4.75 ± 0.03 | 21.7 ± 0.5 | 28.9 ± 0.4 | 49.8 ± 0.3 | 3.65 ± 0.06 | 7.92 |
| Urban waste compost[f] | 6.99 ± 0.06 | 15.7 ± 0.3 | 20.1 ± 0.4 | 34.6 ± 0.6 | 1.92 ± 0.14 | 10.5 |

[a] $CaCl_2$ 0.01 mol $L^{-1}$ (1.0 g: 5.0 mL).
[b] Electrical conductivity in deionized water (1.0 g: 10.0 mL).
[c] OM = C-Total*1.724.
[d] Certified reference material.
[e] Commercial fertilizer.
[f] Organic waste.

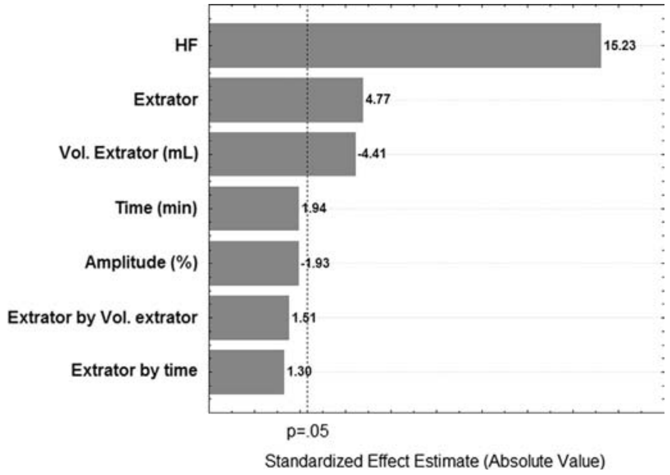

**Fig. 2.** Pareto chart of the standardized effects obtained in the $2^{5-2}$ fractional factorial design using the overall responses.

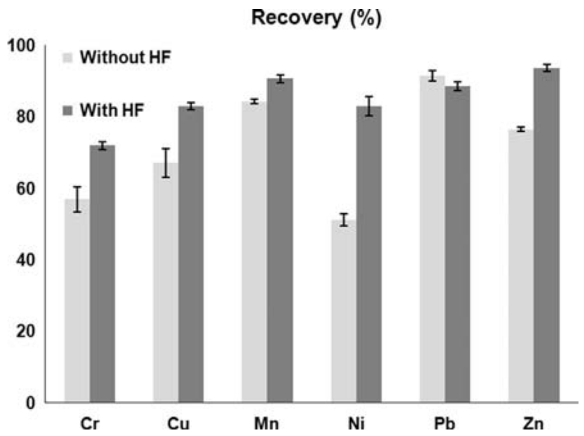

**Fig. 3.** Recovery of metals with and without the addition of 100.0 μL of 40% HF. Organic fertilizer: urban waste compost. Fixed conditions: 0.5 mL of acid (HCl/$HNO_3$, 1:1, v/v), 0.5 mL of deionized water, and 10 min of sonication and 50% amplitude. Cd and Co < LOQ.

both organic and inorganic fractions, including silicon oxides. However, because HF is able to solubilize oxides of silicon, it destabilizes the aggregates, favoring fragmentation of the solid particles and thus resulting in improved extraction. Furthermore, fluoride ions can complex with the metal elements, favoring the solubilization of the inorganic fraction [32].

The extractor composition exerted a positive effect (4.77) on the extraction percentage, indicating that the presence of HCl in the extractor is important (Fig. 2). This effect could be due to the complexation of chloride ions with the metal ions, favoring the solubilization of minerals, and due to the formation nitrous chloride (NOCl), highly oxidizing species [6].

The volume of the extractor was significant and negative (−4.41, Fig. 2). This result may have been caused by two factors: higher final volumes resulted in lower HF concentrations, given that the volume of added HF (40%,w $w^{-1}$) was kept constant at 100 μL; in addition, it was observed that the solids in the tubes containing greater final volumes were stirred with lower turbulence. This reduced turbulence can result in less fragmentation of the particles, leading to smaller surface areas and hence lower extraction efficiencies.

### 3.2.2. $2^3$ Central composite design

Based on the results obtained using fractional factorial design, the amplitude, extractor volume and sonication time were fixed at 50%, 1.0 mL and 10 min, respectively. Although the fractional factorial design results indicated the use of smaller volumes (negative significant effect), the volume of the extractor was set to 1.0 mL. This choice was justified by practical issues: the mixture (sample and extractor) produced by sonication formed a paste when extractor volumes less than 1.0 mL were evaluated, complicating the quantitative transfer of the samples to the centrifuge tubes.

The acid proportions were optimized using a $2^3$ central composite design with central point (CP) in quadruplicate (Table 3). The mathematical models produced as response surfaces displayed inadequate fits to the experimental data ($R_{Adj.}=0.66$). By the fact that the recovery percentages for the majority of the experiments were higher than 85%, we selected the acid proportion that resulted in the highest extraction efficiency for the most elements.

Fig. 4 displays the metal recoveries for different acid proportions. Only the extraction of Cr was significantly influenced by the extractor composition within the range evaluated. The highest recoveries were observed in experiments 6 and 14 (Table 3). The conditions in experiment 6 (260, 140 and 130 μL of $HNO_3$, HCl and HF, respectively) were considered to be optimal for metal extraction from organic fertilizers because they employed a larger amount of $HNO_3$, which is responsible for the partial oxidation of organic matter, and used less HF, requiring smaller amounts of $H_3BO_3$ to neutralize the excess fluoride ions [32].

The optimal conditions for the ultrasound-assisted extraction of metals in organic fertilizer, obtained from preliminary experiments and multivariate optimization, are summarized in Table 5.

From these conditions, it appears that the method developed is an interesting alternative for the analysis of organic fertilizers

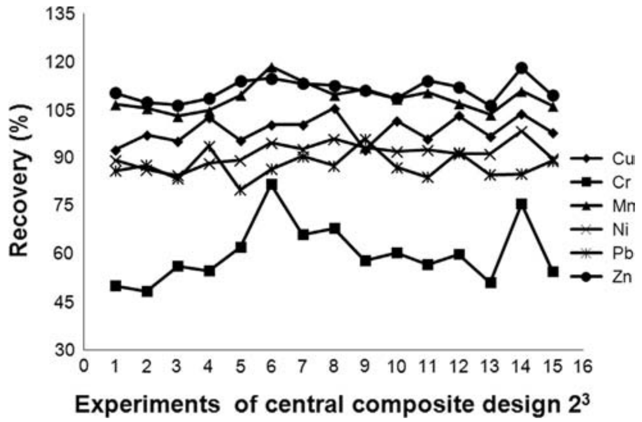

**Fig. 4.** Recoveries obtained with the central composite design experiments. Fixed conditions: mass (120 mg), extractor volume (1.0 mL), final volume (10.0 mL), sonication time (10 min) and amplitude (50%). Repetition of the center point, experiment 15, ($n=4$), RSD < 5% for all metals.

**Table 5**
Optimized conditions for the ultrasound-assisted extraction for inorganic constituents in organic fertilizers.

| Factor | Value |
|---|---|
| Mass (mg) | 120 |
| Volume of acid mixture – $HNO_3$/HCl/HF, 5:3:3 – (μL) | 500 |
| Contact time with the acidic mixture (min) | 20 |
| Volume of deionized water (μL) | 500 |
| Amplitude (%) | 50 |
| Pulse (s) | 2 on, 1 off |
| Sonication time (min) | 10 |
| Temperature (°C) | 25 |

**Table 6**
Linear range, regression, correlation coefficient (*R*), LOD and LOQ of the proposed method.

| Element | Linear range (mg $L^{-1}$) | Regression | Correlation coefficient (*R*) | LOD (mg $kg^{-1}$) | LOQ (mg $kg^{-1}$) | Limit of legislation[a] (mg $kg^{-1}$) |
|---|---|---|---|---|---|---|
| Cd | 0–0.6 | $Y=0.1686X+0.0010$ | 0.9997 | 0.237 | 0.789 | $<3$ |
| Co | 0–2.5 | $Y=0.0620X+0.0023$ | 0.9994 | 2.84 | 9.47 | $>50$ |
| Cr | | $Y=0.0369X+0.0004$ | 0.9998 | 2.17 | 7.24 | $<200$ |
| Cu | | $Y=0.1047X+0.0025$ | 0.9998 | 0.604 | 2.01 | $>500$ |
| Mn | | $Y=0.1608X+0.0049$ | 0.9995 | 0.623 | 2.08 | $>500$ |
| Ni | | $Y=0.0364X+0.0004$ | 0.9995 | 3.78 | 12.6 | $>50$[b], $<70$[c] |
| Pb | | $Y=0.0369X+0.0006$ | 0.9999 | 2.39 | 7.98 | $<150$ |
| Zn | 0–0.6 | $Y=0.5213X+0.0027$ | 0.9997 | 1.15 | 3.84 | $>1000$ |

[a] Brazilian legislation [34,35].
[b] Micronutrient.
[c] Contaminant.

**Table 7**
Certified and determined values of metals in CRM sewage sludge (mean ± standard deviation, $n=5$) and the recoveries and precision of the proposed method.

| Element | Certified value ($x \pm s$) (mg $kg^{-1}$) | Found value ($x \pm s$) (mg $kg^{-1}$) | Recovery ($x \pm s$) (%) | Precision (%) |
|---|---|---|---|---|
| Cd | 487 ± 18 | 487 ± 5 | 100 ± 1 | 0.930 |
| Co | 5.70 ± 0.24 | < LOQ | – | – |
| Cr | 345 ± 15 | 377 ± 14 | 109 ± 4 | 3.74 |
| Cu | 1100 ± 24 | 1058 ± 6 | 96.1 ± 0.6 | 0.58 |
| Mn | 399 ± 14 | 367 ± 3 | 92.0 ± 0.7 | 0.787 |
| Ni | 172 ± 8 | 173 ± 4 | 101 ± 2 | 2.43 |
| Pb | 300 ± 12 | 311 ± 9 | 104 ± 3 | 2.83 |
| Zn | 1400 ± 34 | 1427 ± 80 | 102 ± 6 | 5.61 |

compared to conventional methods based on acid decomposition, both in a microwave oven and as block digesters.

The proposed method requires less reagents and sample, enabling cost and waste reductions. Significantly, in addition to generating smaller volumes of waste, the concentration of the acid wastes is as low as 2% (v $v^{-1}$). The entire extraction procedure is conducted at atmospheric pressure and ambient temperature, ensuring the safety of the operator and reducing sample losses due to volatilization. The analytical throughput is also remarkable, allowing the extraction of up to 32 samples/h. In addition, FS AAS allows the determination of several analytes in a shorter time.

### 3.3. *Method validation*

The performance of the analytical method was evaluated based on its detection limit (LOD), quantification limit (LOQ), linearity, precision and accuracy. This evaluation was conducted via experimental tests using standard solutions, blanks and certified reference materials, in accordance with the recommendations of the European Commission [33].

The analytical characteristics of the proposed method were obtained for the eight elements studied under the optimized conditions. Table 6 presents the linear ranges used for calibration, the coefficients of determination (*R*) used to assess the linearity ($R > 0.99$), and the limits of detection (LOD) and quantification (LOQ), defined as $3^{*}s/m$ and $10^{*}s/m$, respectively, where *s* is the standard deviation corresponding to 10 analytical blanks and *m* is the slope of the calibration curve.

The Brazilian legislation establishes maximum levels for contaminants and minimum levels for micronutrients in organic fertilizers [34,35] (Table 6). Therefore, the limits of quantification exhibited by our method are suitable for the determination of these elements in organic fertilizers.

The precision of the method, expressed as the relative standard deviation (RSD) of five independent replicate measurements of sludge sewage (CRM), ranged from 0.58% to 5.6% for the various metals (Table 7). The low RSD values reflect the simplicity of the proposed procedure. The accuracy, assessed by analyses of CRM (sewage sludge) and expressed in terms of the percentage recovery of the analytes, ranged from 92% to 109% (Table 7). Thus, the proposed method exhibits performance parameters suitable for the determination of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in organic fertilizers.

### 3.4. *Organic fertilizers analyses*

The optimized ultrasound-assisted extraction was used to analyze commercial organic fertilizers and possible raw materials, such as sewage sludge and waste compost. The results obtained using the proposed method were compared with those obtained by microwave-assisted decomposition. Table 8 displays the concentrations determined using the two methods and the recoveries achieved using the extraction procedure.

The recoveries ranged from (80 ± 2)% to (117 ± 2)%, which is in agreement with the European Commission [33] standard stating that recoveries from 80% to 120% are acceptable. However, in most cases, the recovery values obtained were greater than 90%, indicating that the extraction procedure achieved quantitative extraction of the analytes under mild conditions. In spite of the samples presenting different characteristics such as electrical conductivity, organic matter content and C/N (Table 4), the proposed method showed good performance in general, demonstrating that the extraction efficiency was not affected by these features.

None of the studied samples exhibited levels of Cd above the LOQ of the method, indicating that for this element, the samples comply with the Brazilian legislation [34,35] that establishes the maximum allowed concentration as 3 mg $kg^{-1}$.

Among the evaluated samples, only one sewage sludge and the urban waste compost were not in accordance with the Brazilian legislation regarding the acceptable levels of contaminants. The sample “sewage sludge 2” exhibited high concentrations of Cr and Ni, and the urban waste compost exhibited high concentrations of Ni. These samples, therefore, should not be used as fertilizer, unless they are mixed with other organic wastes to ensure that the content of Cr and Ni fall below the maximum allowed levels.

With respect to micronutrient content, although the evaluated fertilizers did not meet the minimum concentrations established by the Brazilian legislation, they can still be marketed as long as the concentration of the elements is specified on the product label.

## 4. Conclusions

The method developed in this study provides an interesting alternative for the determination of Co, Cd, Cr, Cu, Mn, Ni, Pb and

**Table 8**
Concentrations determined using the reference method (microwave-assisted digestion) and proposed method (ultrasound-assisted extraction).

| Element | Reference method | Found value | |
|---|---|---|---|
| | MW<br>$(x \pm s)$ (mg kg$^{-1}$) | US<br>$(x \pm s)$ (mg kg$^{-1}$) | Recovery<br>$(x \pm s)$ (%) |
| Urban waste compost[a] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 121 ± 3 | 100 ± 4 | 82.6 ± 3.3 |
| Cu | 59.9 ± 0.7 | 52.9 ± 0.6 | 88.4 ± 0.9 |
| Mn | 528 ± 20 | 480 ± 13 | 90.8 ± 2.5 |
| Ni | 37.9 ± 0.8 | 33.3 ± 0.9 | 88.0 ± 2.5 |
| Pb | 61.8 ± 0.6 | 57.1 ± 1.8 | 92.4 ± 2.9 |
| Zn | 483 ± 1 | 478 ± 9 | 100 ± 1 |
| Mixed: urban waste compost + castor bean meal[a] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 50.5 ± 2.6 | 40.6 ± 1.1 | 80.4 ± 2.1 |
| Cu | 16.9 ± 0.5 | 15.2 ± 0.7 | 90.3 ± 4.2 |
| Mn | 333 ± 17 | 328 ± 9 | 98.5 ± 2.7 |
| Ni | 8.13 ± 0.97 | 8.95 ± 0.74 | 110 ± 9 |
| Pb | < LOQ | < LOQ | – |
| Zn | 61.2 ± 3.9 | 61.5 ± 0.8 | 100 ± 1 |
| Humus earthworm[a] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 126 ± 4 | 118 ± 2 | 93.8 ± 2.0 |
| Cu | 161 ± 3 | 142 ± 2 | 88.4 ± 1.5 |
| Mn | 274 ± 4 | 258 ± 6 | 94.1 ± 2.0 |
| Ni | 21.7 ± 4.0 | 25.3 ± 0.5 | 117 ± 2 |
| Pb | 66.8 ± 3.9 | 57.0 ± 0.4 | 85.3 ± 0.6 |
| Zn | 67.8 ± 1.8 | 68.1 ± 0.9 | 101 ± 1 |
| Vegetable earth[a] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 83.0 ± 5.0 | 71.5 ± 3.8 | 86.2 ± 4.6 |
| Cu | 11.6 ± 0.5 | 10.1 ± 0.3 | 87.9 ± 2.5 |
| Mn | 241 ± 7 | 200 ± 4 | 83.2 ± 1.9 |
| Ni | 19.6 ± 1.8 | 19.0 ± 0.7 | 96.6 ± 3.5 |
| Pb | < LOQ | < LOQ | – |
| Zn | 25.8 ± 0.2 | 21.2 ± 0.3 | 82.3 ± 1.0 |
| Sewage sludge 1[b] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 177 ± 2 | 163 ± 3 | 92.1 ± 1.9 |
| Cu | 227 ± 5 | 224 ± 5 | 98.6 ± 2.2 |
| Mn | 224 ± 5 | 212 ± 6 | 94.8 ± 2.9 |
| Ni | 53.0 ± 1.8 | 44.5 ± 0.6 | 83.8 ± 1.1 |
| Pb | 50.1 ± 1.9 | 54.0 ± 0.4 | 109 ± 1 |
| Zn | 1368 ± 31 | 1442 ± 33 | 105 ± 2 |
| Sewage sludge 2[b] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | 34.0 ± 1.2 | 34.2 ± 2.2 | 101 ± 6 |
| Cr | 464 ± 3 | 546 ± 11 | 117 ± 2 |
| Cu | 491 ± 13 | 447 ± 7 | 91.1 ± 1.5 |
| Mn | 251 ± 7 | 236 ± 5 | 94.2 ± 1.9 |
| Ni | 151 ± 7 | 138 ± 1 | 91.5 ± 0.5 |
| Pb | 90.8 ± 1.7 | 89.7 ± 6.4 | 98.8 ± 7.1 |
| Zn | 6936 ± 276 | 7282 ± 371 | 105 ± 5 |
| Urban waste compost[b] | | | |
| Cd | < LOQ | < LOQ | – |
| Co | < LOQ | < LOQ | – |
| Cr | 211 ± 9 | 188 ± 1 | 89.1 ± 0.6 |
| Cu | 120 ± 5 | 99.4 ± 1.4 | 82.8 ± 1.1 |
| Mn | 2015 ± 67 | 1917 ± 45 | 95.1 ± 2.2 |
| Ni | 52.1 ± 1 | 47.3 ± 0.2 | 90.9 ± 0.4 |
| Pb | 31.0 ± 0.5 | 27.7 ± 1.6 | 92.2 ± 5.3 |
| Zn | 378 ± 14 | 365 ± 19 | 96.5 ± 5.0 |

[a] Commercial fertilizer.
[b] Organic waste.

Zn in organic fertilizers because it is simple, fast, consumes less reagents and takes place at room temperature, preventing analyte losses due to volatilization. Furthermore, the determination by FS FAAS allows the quantification of eight elements in less time, increasing the analytical throughput compared to the equipment using FAAS in a single-element mode.

The analysis of the organic fertilizers and organic wastes demonstrated the importance of the monitoring required by the legislation, with Cr and Ni exceeding the allowed levels in two samples. Therefore, the proposed method provides important contributions to the field of green analytical chemistry by enabling a simple and economically viable method for the quality control of organic fertilizers.

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