Ultrasound-assisted Extraction of Cr, K, Na, Pb, and Zn in NPK Fertilizers and Determination by FAAS and FAES

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ABSTRACT

The use of ultrasound radiation for the extraction of Cr, K, Na, Pb, and Zn in NPK fertilizer samples was investigated, and their determination by flame atomic absorption (FAAS) and emission spectrometry (FAES). Extraction was performed using 0.05 g of sample, 5.0 mL of HNO_3+HCl (50% v/v), and six steps of sonication (20 minutes) in an ultrasound bath, followed by homogenization with a vortex mixer (1 minute). The LOD and LOQ values ranged from 0.6 and 1.8 mg kg^{-1} and from 3.1 to 6.1 mg kg^{-1}, respectively. The method showed adequate precision (RSD < 5%) and accuracy (recoveries between 90 and 103%). The proposed method requires only small amounts of sample and reagents. All sample pretreatment is carried out in one single flask which avoids sample contamination and analyte loss. The analyte concentrations in the samples were found to be below the maximum limits as established by Brazilian legislation.

INTRODUCTION

The deficiency of micronutrients in agricultural soils is of growing concern and this problem may be accentuated in the future. Cultivation in low fertility soils associated with liming and high productivity are factors that are causing micronutrient deficiency (1). To minimize this problem, use of fertilizers has become a common practice to supply enough nutrients to the vegetables (2). In Brazil, fertilizers are classified in two categories: organic fertilizers, derived from animal and industrial waste, and inorganic fertilizers whose main components are nitrogen, phosphorus, and potassium (NPK) (3,4). In humans and animals, potassium (K) acts as a co-factor of many enzymes and is necessary for the secretion of insulin, phosphorylation of creatinine, and for the metabolism of carbohydrates and proteins (5). Nitrogen (N) is essential for increasing agricultural productivity because it is a component of proteins and chlorophyll, while phosphorus (P) is responsible for the life processes of plants such as for storage and use of energy, root growth, improvement of grain quality, and acceleration of fruit ripening (4).

The raw materials used in fertilizer production are usually obtained from the oil industry (N) or mineral extraction activities (P and K), followed by extraction procedures made with mineral acids (3). However, the presence of toxic trace elements in the composition of fertilizers is undesirable and was investigated in this work. Among such trace elements, chromium (Cr) and lead (Pb) must be highlighted. Both can come from different sources, but the post furnaces (used for zinc enrichment) are an important example (6-8). Although non-essential trace elements usually occur in rocks and minerals, the impact of metal content in soil is governed by the amount and the chemical form of these metals, which can be mobilized if associated with organic or inorganic compounds in the soil (9). In fact, toxic metallic species may affect the morphology, growth, and metabolism of microorganisms, reducing the amount and activity of the microbial biomass in the soil (6).

The determination of essential (Na and K) and trace elements (Cr, Pb, and Zn) in fertilizer samples can be performed by different analytical techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) (8-11). AAS is a well-established technique, widely used in laboratory routines, and possesses the ability to determine metallic and semi-metallic elements in various matrices (12-14).

The flame emission spectrometry (FAES) and flame atomic absorption spectrometry (FAAS) techniques are widely used for the determination of metals and semimetals in different matrices. Among the advantages of these techniques are low cost, simplicity of operation, and satisfactory analytical performance (10, 15-17).

For sample preparation, use of an appropriate method is crucial to obtain adequate results with most analytical techniques (18, 19). Due to their ease of use, wet digestion and dry ashing performed in open vessels, for example, are often used for fertilizer samples. However, these methods present limitations such as long processing time, analyte loss by volatilization, and risk of sample contamination (19-23). Recent research has shown that ultrasonic extraction (US-EX) is an alternative step for faster sample

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preparation. When ultrasonic waves are applied to liquids, powerful chemical and physical reactions occur (23, 24). In the sonication process, the rupture of particles, which leads to an increase in the surface area, is caused by the collapse of gas microbubbles in the interstices of the solid and by violent collision between the particles (20). Additionally, ultrasonic extraction often requires the use of dilute reagents, is low cost, and supports green chemistry by resulting in small amounts of residue (11, 25).

The objective of this work was to evaluate and apply ultrasonic radiation for the sample preparation of NPK fertilizers. The analyses were performed by FAAS (for Cr, Pb, and Zn) and FAES (for K and Na). The commercial samples were analyzed and the analyte concentrations compared to the maximum limits established by Brazilian legislation.

EXPERIMENTAL

Instrumentation

Cr, Pb, and Zn determination was performed using a Solar M5 flame atomic absorption spectrometer (Thermo Scientific, P.R. China), and the instrumental operating parameters are listed in Table I. For sample preparation, a vortex mixer (Ciencor Scientific Genie 2, USA), a hot plate (Biomixer DB-IVAC plate, São Paulo, Brazil), and an ultrasound bath (UNIQUE Ultrasonic Cleaner, 150 W, São Paulo, Brazil) were employed.

The flame atomic emission spectrometry measurements of K and Na were performed by using a flame photometer (Digimed DM 61, São Paulo, Brazil), equipped with a mist chamber for introduction of the fuel (LPG -Liquefied Petroleum Gas, Ultragaz, Juiz de Fora, Brazil), and compressed air as an oxidant. The gas flow rate was 2.7 mL min^{-1}. Lithium (Li) was used as an internal standard, and all measurements were performed in triplicate.

Reagents and Solutions

Nitric acid 69.5% (v/v) (Vetec, São Paulo, Brazil), hydrochloric acid 37.5% (v/v) (Vetec, São Paulo, Brazil), and hydrogen peroxide 30% (m/v) (ISOFAR, Duque de Caxias, Brazil) were used for digestion of the samples. Calibrations of the standard solutions were prepared from metal stock solutions (1000 mg L^{-1}) of Cr (Vetec, São Paulo, Brazil), Pb (Spec Sun, São Paulo, Brazil) and Zn (PerkinElmer, Inc., São Paulo, Brazil).

For FAES analysis, the standards were prepared from the salts of NaCl, KCl, and LiCl (Vetec, São Paulo, Brazil). Milli-Q® deionized water (Direct-Q UV, Millipore Corporation, Bedford, MA, USA, 18.3 MΩ-cm) was used to prepare all solutions.

One of the samples used to develop the extraction method was donated by a fertilizer company, located in the Zona da Mata of Minas Gerais. The other four samples used for this study were obtained from a local market.

Procedure

Two methods for the extraction of essential and trace elements in fertilizer samples were compared: (a) the EPA 3050B method (which requires abot 0.5 g of sample) and (b) the method developed in this work, which was based on simillar works (26, 27) using a small sample amount (ca. 0.05 g) and *aqua regia* [a mixture of HCl and HNO_3 (3:1) v/v)] associated with ultrasonic radiation (US-EX).

Digestion of Fertilizer Samples – EPA 3050B Method

Since the Brazilian Ministry of Agriculture, Livestock and Supply (in Portuguese: Ministério da Agricultura Pecuária e Abastecimento, MAPA) established use of the EPA 3050B method for the analysis of inorganic fertilizers, it was used as the reference method for this study. However, the sample mass of the method was 0.5 ± 0.0001 g. The total time needed to perform this method was approximately five hours.

Ultrasound Extraction (US-EX) Method Employing aqua regia

About 0.0500 g of fertilizer sample was treated with 5.00 mL of *aqua regia* (50% v/v) in graduated plastic tubes. The samples were placed in an ultrasound bath at 60 ºC for 20 minutes. Then the samples were stirred for one minute using a vortex mixer. The sonication and mixer steps were repeated six times. After that, the extract was transferred to another tube and filled to 14.0 mL volume with deionized water. The total extraction time was approximately three hours.

Precision and Accuracy Study of US-EX Method

In order to investigate possible matrix effects, the standard addition method was used for all of the analytes after sample preparation

TABLE I
Instrumental Operating Parameters for the FAAS Determination of Cr, Pb, and Zn

Analyte	Wavelength (nm)	Gas Flow (L min^{-1})	Gas	Working Range (mg L^{-1})
Cr	357.8	4.0	N_2O/C_2H_2	0.1 – 3.0
Pb	217.0	1.1	Air/C_2H_2	0.1 – 3.0
Zn	213.8	1.0	Air/C_2H_2	0.2 – 2.0

according to the developed method. In the absence of a standard reference material (SRM), the method's accuracy was evaluated using spike tests, which were performed with a randomly selected fertilizer sample, employing two levels of concentration: for the trace elements Cr, Pb, and Zn, the levels used were 0.1 and 1.5 mg L^{-1} (as the sample solution final concentration); for Na and K, the levels were 10.0 and 50.0 mg L^{-1} (as the sample solution final concentration). The spiked amounts of each analyte were added immediately after weighing of the samples, and then all extraction stages were carried out (28). The method's precision was evaluated using the standard deviation (SD) and the relative standard deviation (RSD) of the samples was prepared in authentic triplicates.

Figures of Merit

The limits of detection (LOD) and the limits of quantification (LOQ) were calculated according to IUPAC recommendations where LOD = 3sB/S and LOQ = 10sB/S, in which sB is the standard deviation of 10 consecutive measurements of the blank and S is the slope of the respective analytical curve (18). Characteristic concentration (c_0) was used to evaluate the sensitivity of the FAAS method (for each analyte) and was calculated by dividing the value of 0.0044 by the slope of the analytical curves (29, 30).

RESULTS AND DISCUSSION

US-EX Method Employing aqua regia

The US-EX results were compared with those obtained with the 3050B EPA method at a confidence level of 95%, and no significant differences were observed. The results obtained for both the digestion and the extraction preparations for the selected sample are listed in Table II.

It can be seen that the two methods present similar results, proving the efficiency of the developed method when compared to the reference method.

Precision and Accuracy Study of US-EX Method

For the spike tests, the recovery values were 100, 93, 102, 103, and 90% at the low level and 100, 99, 96, 101, and 95% at the high level for Cr, K, Na, Pb, and Zn, respectively. The high recovery values obtained indicates good accuracy of the method (28, 30, 31). The relative standard deviation (RSD) of the samples analyzed was below 5% for all studied analytes, showing that the method also provides good precision (28).

Figures of Merit

The LOD, LOQ, and characteristic concentration values were also evaluated and the results are listed in Table III. The LOD and LOQ for the method ranged from 0.6 to 1.8 mg kg^{-1} and from 3.1 to 5.9 mg kg^{-1}, respectively. The Brazilian legislation (MAPA, 2006) determines the maximum values allowed only for Pb. For Cr there is no maximum permitted value, just a base which takes into account the levels of P_2O_5 in the fertilizer. These values were compared with the maximum allowed in other countries, such as Canada, Australia, and China, and the LOD and the LOQ values of this study were lower than the maximum allowed values (32). This shows that the proposed method has adequate detectability for regu-

TABLE II
Metal Concentrations Obtained by FAAS in NPK Fertilizer Sample After Extraction Using 3050B EPA and US-EX Method

Analytes	3050B EPA[a]	US-EX[b]	
	AC	SA	AC
Cr[c]	22.9 ± 1.5	23.6 ± 0.5	23.2 ± 2.1
K[d]	35.7 ± 1.6	35.8 ± 0.9	35.7 ± 1.4
Na[d]	6.1 ± 0.2	6.20 ± 0.03	6.20 ± 0.04
Pb[c]	41.4 ± 3.3	48.3 ± 0.7	47.6 ± 0.5
Zn[c]	278 ± 11	315 ± 8	311 ± 10

[a] Reference method.
[b] Developed method (ultrasound extraction).
[c] = Concentration (mg kg^{-1}) ± confidence interval, n = 3;
[d] = Concentration (g kg^{-1}) ± confidence interval, n = 3;
AC = analytical curve;
SA = standard addition.

TABLE III
Limits of Detection (LOD) and Quantification (LOQ) (n = 10), Characteristic Concentration (c_0), and Maximum Values Allowed in NPK Fertilizers by Brazilian Legislation (MAPA)

Analyte	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	c_0 (mg L^{-1})	MAPA (mg kg^{-1})
K	0.9	3.1	-	-
Na	0.6	6.9	-	-
Cr	1.8	5.9	0.08	200 – 560
Pb	1.2	3.9	0.008	1,000
Zn	1.8	5.9	0.009	-

latory purposes and can be used not only in Brazil. The characteristic concentration was also assessed and the results were in good agreement with those reported in the literature (Cr 0.040, Pb 0.080, and Zn 0.010) (30).

A comparison of the 3050B EPA method, which is often used for extraction of metals in fertilizer samples, with the developed method shows several advantages such as requiring a lower amount of reagents, only one single flask (which reduces the risk of contamination), lower extraction time (which favors the analytical throughput), and diluted reagents.

Application of the Developed Method

The US-EX method was applied for the analysis of four different samples of NPK fertilizer and the results are listed in Table IV. The concentrations of the analytes in the samples varied from 41.4 to 162 mg kg^{-1} for Cr; 24.8 to 35.2 g kg^{-1} for K; 5.9 to 6.5 g kg^{-1} for Na; 13.2 to 47.6 mg kg^{-1} for Pb, and 38.7 to 310 mg kg^{-1} for Zn. In this context, it is important to emphasize that the metal concentrations in fertilizers normally vary from one sample to another which is probably due to the different raw materials used in fertilizer preparation. In relation to the Brazilian legislation, the obtained results for Cr and Pb were found to be lower than the allowed values.

CONCLUSION

Ultrasound extraction (US-EX) of samples using diluted *aqua regia* as the extraction solution demonstrated good efficiency for the extraction of Cr, K, Na, Pb, and Zn from NPK fertilizers. The analytes Cr, Pb, and Zn were determined by FAAS and K and Na by FAES using traditional analytical curves (external calibration). The developed method showed good precision (RSD < 5%) and accuracy (recoveries between 90 and 103%) and was faster than the reference method (EPA 3050B), with a total extraction time of approximately three and five hours, respectively. The LOD and LOQ values ranged from 0.6 and 1.8 mg kg^{-1} and from 3.1 to 6.1 mg kg^{-1}, respectively and are consistent with the techniques used, and the values of the elements studied were lower than allowed by the Brazilian legislation and the legislations of other countries. This indicates that the proposed method is a good alternative to monitoring metals in fertilizers. However, the limits proposed by the Brazilian legislation can be considered relatively high when compared to the allowable limits by other countries. Thus, these types of fertilizers must be used with caution in order to prevent damage to both humans and the environment.

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TABLE IV
Results Obtained for Samples of Commercial Fertilizers Using US-EX Procedure With aqua regia Dilution 50% (v/v)

Samples	Cr[a]	K[b]	Na[b]	Pb[a]	Zn[a]
1	41 ± 3	24.8 ± 0.07	6.3 ± 0.07	44 ± 3.5	238 ± 3
2	91 ± 2	35.1 ± 0.04	6.4 ± 0.02	43 ± 3.9	289 ± 4
3	72 ± 3	30.0 ± 0.04	6.5 ± 0.03	13 ± 1.2	138 ± 5
4	162 ± 4	34.1 ± 0.05	5.8 ± 0.04	48 ± 2.2	310 ± 11

[a] Concentration (mg kg^{-1}) ± confidence interval, n = 3.
[b] Concentration (g kg^{-1}) ± confidence interval, n = 3.

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