



Analytical note

Simultaneous determination of macronutrients, micronutrients and trace elements in mineral fertilizers by inductively coupled plasma optical emission spectrometry



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ABSTRACT

An analytical method for simultaneous determination of macronutrients (Ca, Mg, Na and P), micronutrients (Cu, Fe, Mn and Zn) and trace elements (Al, As, Cd, Pb and V) in mineral fertilizers was optimized. Two-level full factorial design was applied to evaluate the optimal proportions of reagents used in the sample digestion on hot plate. A Doehlert design for two variables was used to evaluate the operating conditions of the inductively coupled plasma optical emission spectrometer in order to accomplish the simultaneous determination of the analyte concentrations. The limits of quantification (LOQs) ranged from 2.0 mg kg⁻¹ for Mn to 77.3 mg kg⁻¹ for P. The accuracy and precision of the proposed method were evaluated by analysis of standard reference materials (SRMs) of Western phosphate rock (NIST 694), Florida phosphate rock (NIST 120C) and Trace elements in multi-nutrient fertilizer (NIST 695), considered to be adequate for simultaneous determination. Twenty-one samples of mineral fertilizers collected in Sergipe State, Brazil, were analyzed. For all samples, the As, Ca, Cd and Pb concentrations were below the LOQ values of the analytical method. For As, Cd and Pb the obtained LOQ values were below the maximum limit allowed by the Brazilian Ministry of Agriculture, Livestock and Food Supply (Ministério da Agricultura, Pecuária e Abastecimento – MAPA). The optimized method presented good accuracy and was effectively applied to quantitative simultaneous determination of the analytes in mineral fertilizers by inductively coupled plasma optical emission spectrometry (ICP OES).

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1. Introduction

The analysis of mineral fertilizer using a multielement technique is of great importance since the agricultural productivity is directly linked to the use of agricultural input magnifiers, containing many elements, and some of them can be toxic, contaminate soils and ultimately reach food products. These inputs are defined as any substance, mineral or organic, natural or synthetic, which supplies one or more plant nutrients [1].

Concern regarding food security has gained prominence mostly due to the indiscriminate use of agricultural inputs and the consequent contamination of the soil, resulting in the accumulation of chemicals by foodstuffs [2–4]. On the other hand, the control of these inputs results in improvement of the agricultural production, i.e., it requires a more

efficient quality control of the fertilizers used in agricultural production [5]. The fertilizers can be a source of contamination from the raw material or unreliable sources, used as intermediates in the manufacturing process, whose composition may contain, in addition to the essential elements, hazardous substances, namely, contaminants [6–9].

In Brazil, the Ministry of Agriculture, Livestock and Food Supply (Ministério da Agricultura, Pecuária e Abastecimento – MAPA) establishes, through the Normative no. 27 (June 5, 2006), the maximum permitted limits for contaminants, such as As, Cd, Cr, Hg and Pb in mineral fertilizers. In the United States, each American state has its own regulations and one federal law regulates fertilizers and only regarding zinc as a contaminant, as published in July 24, 2002 by the United State Environmental Protection Agency (USEPA). Canada, through the Federal Fertilizers Act, regulates contaminants' content in mineral fertilizers [10–12].

Since the determination of the mineral composition in fertilizers is of great importance, many techniques have been used with this purpose [3,4,13]. Studies using different techniques, such as graphite furnace atomic absorption spectrometry (GF AAS) [3] and cold vapor atomic

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absorption spectrometry (CV AAS) [13], have been reported. Even radioactive elements such as uranium, radium and thorium were determined in fertilizers [15,16]. The inductively coupled plasma optical emission spectrometry (ICP OES), which makes it possible simultaneous determinations and allows rapid analysis, is also reported [4,14]. The use of microwave digestion and ICP OES to determine As, Cd, Co, Cr, Pb, Mo, Ni and Se in fertilizers [4] is described by Kane and Hall.

ICP OES is recognized as a powerful analytical technique for the determination of chemical elements because its high sensitivity and detection power are relatively free of interference, allow simultaneous or sequential multi-element determination and have wide applicability, among other advantages [17–19]. However, quantitative analysis by ICP OES requires the complete digestion of the samples, otherwise the results can be affected by many factors leading to errors on the analysis [20].

The design of experiments is an important approach and has been successfully employed in sample preparation procedures to identify the optimum conditions and select the proportions between the reactants, allowing a faster acquiring of results, minimizing costs and time involved [21–23]. The use of diluted reagents in decomposition or extraction procedures, which leads to media with reduced acidity and also decreases the amount of corrosive substances, is an example of the experimental design application [24–26]. Chemometric tools were used to establish the appropriate experimental conditions for determination of mercury by CV AAS [27], arsenic (III) and total arsenic by hydride generation atomic absorption spectrometer (HG AAS) in phosphate fertilizer [28] and determination of Se and As in estuarine sediments by ICP OES using a concomitant metal analyzer as a hydride generator [29].

Thus, this paper purpose is a multivariate optimization of an analytical method to determine the mineral composition of mineral fertilizers employing ICP OES.

2. Experimental

2.1. Material and reagents

All reagents used were analytical grade, and solutions were prepared with deionized water obtained from a reverse osmosis water purification system (OS 20 LX, GEHAKA, SP–Brazil). The nitric acid and hydrogen peroxide used were of suprapure quality (Merck, USA). External calibration was prepared from multielement stock solution (Ag, Al, B, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, P, Pb, Si, Sn, Sr, Ti, V and Zn) of 100 mg L⁻¹ (Specsol®). Also, 1000 mg L⁻¹ stock solutions (Specsol®) of Al, Ca, Fe, Mg, P and S, were diluted according to the working range required. The calibration curves were prepared in a range of concentrations from 0.1 to 5.0 mg L⁻¹ for Al, As, Cd, Cu, Fe, Mn, Pb, V and Zn, and from 5.0 to 200.0 mg L⁻¹ for Al, Ca, Fe, Mg, Na and P. The glassware used in the experiments was previously decontaminated with a nitric acid solution (10% v v⁻¹) for 24 h [29,30], subsequently washed with ultra-pure water and dried at room temperature.

2.2. Quality control and mineral fertilizer samples

To assess the quality of the data obtained applying the proposed analytical methods, standard reference materials (SRMs) for Trace elements in multi-nutrient fertilizer (NIST 695), Western phosphate rock (NIST 694) and Florida phosphate rock (NIST 120C) [4,27,28] were employed. These materials present similar composition to the fertilizer samples and are adequate as reference material [6]. In addition twenty-one samples of mineral fertilizers sold in Sergipe State, Brazil were analyzed. The samples underwent a preparation in which they were dried in an oven with air circulation for 48 h at a temperature of 40 °C [31,32]. After that, the samples were cooled in a desiccator to room temperature, then weighed and kept inside the desiccator.

2.3. Preparation of mineral fertilizer samples

A mass of approximately 0.20 g (dry weight) of the samples was placed in Teflon pumps, suitable for block digestion. Into these containers, 1.4 mL of concentrated HNO₃ (65% w v⁻¹), 1.0 mL of H₂O₂ (30% w v⁻¹) and 7.6 mL of deionized water were added to a final volume of 10.0 mL. The system was closed and the samples were heated and kept at 180 °C for 2 h. After digestion the samples were transferred to 50.0 mL polyethylene tubes (falcon), and completed to a final volume of 25.0 mL with deionized water. All procedures were performed in triplicate, including the blank solutions and SRMs [27,33]. In this procedure, the reactant ratio was optimized through a two-level full factorial design, in order to minimize the use of concentrated reagents. The use of diluted reagents presents a great attractiveness in the decomposition of solid samples and also is in agreement with the principles of green chemistry, minimizing the generation of acid wastes [34].

2.4. Instrumentation

For the analysis of the fertilizer samples an inductively coupled plasma optical emission spectrometer with axial view (ICP OES, Vista Pro, Varian, Mulgrave, Australia) was used, and the operating conditions are detailed in Table 1.

2.5. Optimization strategy and analysis of the data

The sample preparation procedure, using a digestion block, was optimized using a full two-level factorial design. The factors were the concentrations of the three diluted reagents: hydrochloric acid, hydrogen peroxide and nitric acid. The concentrations of Fe, Cr and Mn and Mg were used as the multiple response of the factorial design. The Doehlert design was employed to optimize the ICP OES operational conditions. The response was the ratio between the intensities of the magnesium emission lines, Mg II 280.265 nm/Mg I 285.208 nm. Triplicates of the central point were performed to evaluate experimental error. The analysis of the data obtained from the experimental designs was performed using Statistica® 8.0 software (StatSoft, USA). The measurements were performed in triplicate and the data are expressed as mean ± 95% confidence interval (CI).

3. Results and discussion

3.1. Multivariate optimization

3.1.1. Evaluation of sample digestion conditions using a two-level full factorial design

The application of diluted reagents for digestion of the fertilizers is justified because they are salts easily dissolvable. Moreover, the sample preparation method proposed is environmentally friendly, compared to the standard procedure of USEPA 3050B and the method proposed by Nziguheba and Smolders, which use large amounts of reagents in the process, generating more acidic wastes [34–36].

The matrix of the 2³ factorial design with triplicate of the central point was used to evaluate the different reactant ratios, using as variables the concentration of diluted reagents: nitric acid, hydrochloric acid and hydrogen peroxide in order to minimize the amounts of reagents required for sample preparation in digestion block as shown in Table 2. The experiments were performed in random order. The triplicate of the central point was used to estimate the experimental error in the factorial design. Approximately 0.20 g portions of commercial mineral fertilizer were used in these experiments. After applying the factorial design in the study, the concentration of the elements Fe, Cr, Mn and Mg in the solutions obtained in each experiment was used to calculate the responses for the mineral fertilizer sample. To optimize the analytical procedure, in order to achieve an efficient and simultaneous digestion of all elements of interest, a multiple response (MR) desirability

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