Analytical Note

Investigation of chemical modifiers for the determination of lead in fertilizers and limestone using graphite furnace atomic absorption spectrometry with Zeeman-effect background correction and slurry sampling

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ABSTRACT

In this work, chemical modifiers in solution (Pd/Mg, $NH_4H_2PO_4$ and NH_4NO_3/Pd) were compared with permanent modifiers (Ir and Ru) for the determination of lead in fertilizer and limestone samples using slurry sampling and graphite furnace atomic absorption spectrometry with Zeeman-effect background correction. The analytical line at 283.3 nm was used due to some spectral interference observed at 217.0 nm. The $NH_4H_2PO_4$ was abandoned due to severe spectral interference even at the 283.3-nm line. For Pd/Mg and NH_4NO_3/Pd the optimum pyrolysis and atomization temperatures were 900 °C and 1900 °C, respectively. For Ru and Ir, the integrated absorbance signal was stable up to pyrolysis temperatures of 700 °C and 900 °C, respectively, and up to atomization temperature of 1700 °C. The limit of detection (LOD) was 17 ng g^{-1} using Pd/Mg and 29 ng g^{-1} using NH_4NO_3/Pd. Among the permanent modifiers investigated, the LOD was 22 ng g^{-1} Pb for Ir and 10 ng g^{-1} Pb for Ru. The accuracy of the method was evaluated using the certified reference material NIST SRM 695. Although Ru provided lower LOD, which can be attributed to a lower blank signal, only the modifiers in solution showed concordant values of Pb concentration for the NIST SRM 695 and the most of analyzed samples. Moreover, the Pd/Mg modifier provided the highest sensitivity and for this reason it is more suitable for the determination of Pb in fertilizers samples in slurry; besides this it presented a better signal-to-noise ratio than NH_4NO_3/Pd.

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1. Introduction

The use of fertilizers is an integral part of agriculture nowadays; however, the extensive use of fertilizers might cause contamination of soils due to the presence of toxic metals, which could result in negative impact, such as loss of ecosystems, decrease of agricultural productivity, economic damage and health problems for humans and animals. Moreover, other soil amendments, such as limestone, required to maintain soil fertility and development of plants, might be naturally rich in trace elements, or be contaminated [1–3].

Once in the soil, these elements can accumulate in less soluble forms and enter into the food chain, from soil and biota to human beings, or they can move to rivers and lakes through leaching and erosion processes. Because mineral fertilizers might contain high levels of toxic elements, such as lead and cadmium, their long-term application can cause significant increase in the total metal concentration in the soil and consequently in the food chain [4,5].

Lead is toxic already at low concentration; data indicate that lead can substitute zinc in several proteins that work as transcriptional regulators. It further reduces the binding of these proteins to recognition elements in genomic DNA, which suggests an epigenetic involvement of lead in altered gene expression [6]. Lead exposure might increase the blood pressure and cause anemia and tumors. High levels of exposure severely damage the brain and kidneys in adults and children and might ultimately cause death [6,7].

Different analytical techniques have been used for the determination of heavy metals in fertilizers, such as inductively coupled plasma mass spectrometry (ICP-MS) [8–10], or inductively coupled plasma optical emission spectrometry (ICP OES) [11,12]. However, using these techniques the procedures usually include extensive sample preparation and/or extraction procedures prior to instrumental analysis. The standard method specified by the United States Environmental Protection Agency (EPA) for the determination of trace elements in fertilizers indicates the use of wet digestion for sample dissolution [13]. The conventional wet digestion procedures require large quantities of high-purity reagents, which generate a considerable amount of hazardous waste. They also might include intensive manipulation, besides being time-consuming and potentially introducing systematic errors due to

incomplete analyte extraction [14]. Modern microwave-assisted acid digestion techniques have been reported to minimize these risks and disadvantages; however, they require specialized equipment, are not suited for large-scale routine analyses, and are still producing a significant amount of hazardous waste [15].

The direct analysis using solid or slurry sampling graphite furnace atomic absorption spectrometry (GF AAS) was successfully used as an alternative for the determination of trace elements in various complex matrices. These techniques for direct sample introduction reduce sample handling and minimize errors inherent to any sample preparation stage [4,15–18].

Choosing the appropriate chemical modifier appears to be one of the most important tasks of GF AAS for the determination of volatile elements. The use of palladium and magnesium (Pd/Mg) as a 'universal' chemical modifier was reported for the determination of Pb in several different matrices such as sea water [19] and coal samples [20]. The mixture of ammonium nitrate and palladium with Triton X-100 (NH_4NO_3/Pd) was employed for food samples [21] and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) for biological samples [22]. Vale et al. [23] used for the first time a permanent chemical modifier for the direct analysis of solid samples; they covered the surface of the graphite platform with a layer of 400 μg Ru for the determination of Cd and Pb in mineral coal. Borges et al. [24] also used Ru as a permanent modifier for the determination of Pb in biological samples with direct solid sample analysis. Permanent modifiers have several advantages, such as simplifying the procedure of measurement, increasing the lifetime of the graphite tube and platform and reducing the blank value, as they are purified in the deposition process [25]. This kind of modifier was also investigated and successfully applied for the determination of Pb in sediment and soils [26] and botanical and biological samples [27].

However, there are also reports in the literature that permanent chemical modifiers might not be as efficient in slurry analysis, as they are in the direct analysis of solid samples. Using 400 μg Ir as a permanent modifier, da Silva et al. [28] successfully determined Cd in coal using direct solid sample analysis and a pyrolysis temperature of 700 °C, which allowed to remove the bulk of the matrix. Bianchin et al. [29], in contrast, investigated the same samples and a variety of permanent modifiers, including Ir, but using slurry sampling, permanent modifiers could stabilize Cd only to about 500–600 °C, which was not sufficient to remove the matrix efficiently; hence several problems and interferences were encountered. The high nitric acid concentration used for slurry preparation was suspected to impair the performance of the permanent modifiers.

The purpose of the present work is to investigate different modifiers in order to develop a method for the determination of Pb in fertilizer and limestone samples with slurry sampling using line source graphite furnace atomic absorption spectrometry. The chemical modifiers studied were Pd/Mg, $NH_4H_2PO_4$ and NH_4NO_3/Pd, all added in solution, and Ir and Ru, as permanent modifiers.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a Model ZEEnit 650 P (Analytik Jena, Jena, Germany) line source atomic absorption spectrometer, equipped with a transversely heated graphite tube furnace and Zeeman-effect background correction (ZBC) with a transverse magnetic field. A lead hollow cathode lamp (Analytik Jena) was used, operated with a current of 3 mA; the analytical line at 283.3 nm was used for all measurements, and integrated absorbance, A_{int}, was used exclusively for signal evaluation. Pyrolytically coated graphite tubes with an integrated PIN platform (Analytik Jena Part No 407-152.314) were used throughout.

An MPE 60 furnace autosampler (Analytik Jena) was used for the introduction of the slurry samples, standard and modifier solutions. Argon

with a purity of 99.996% (White Martins, São Paulo, Brazil), with a flow-rate of 2 L min^{-1}, was used as the purge and protective gas during all stages, except during atomization, where the flow was stopped. The optimized graphite furnace temperature program used for all the determinations is shown in Table 1. An M2P micro-balance (Sartorius, Göttingen, Germany) was used for weighing the samples.

2.2. Reagents

The nitric acid (Merck, Darmstadt, Germany), used for the preparation of the slurry samples and standard solutions, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). Distilled (in a quartz apparatus) and deionized water (DDW) with a specific resistivity of 18 MΩ cm, from a Milli-Q water purification system (Millipore, Bedford, MA) was used throughout. All containers and glassware were soaked in 1.4 mol L^{-1} HNO_3 for at least 24 h, and rinsed three times with DDW before use. The lead stock standard solution (1000 mg L^{-1} Pb in 0.014 mol L^{-1} HNO_3) was prepared from a Titrisol concentrate (Merck). The working standards were prepared by serial dilution of the stock solution with 0.014 mol L^{-1} nitric acid.

The following chemical modifier solutions were used (all solutions and reagents from Merck): Pd modifier stock solution, 10.0 ± 0.2 g L^{-1} Pd in 15% (v/v) HNO_3, Mg modifier stock solution, 10.0 ± 0.2 g L^{-1} $Mg(NO_3)_2$ in 15% (v/v) HNO_3; NH_4NO_3 extra pure; Ru 1000 mg L^{-1}; Ir 1000 mg L^{-1} and $NH_4H_2PO_4$ 100 ± 2 g L^{-1} in H_2O.

In order to cover the furnace platform with Ir or Ru as permanent modifier, nine and twelve aliquots, respectively, of 40 μL each of 1000 mg L^{-1} solution were injected onto the platform and the graphite tube was submitted to the first five stages of the temperature program [23]. After the last aliquot, the full temperature program was executed completing a deposit of 400 μg Ir or 520 μg Ru. An argon flow rate of 2 L min^{-1} was employed during all program stages.

2.3. Samples and slurry preparation

The samples investigated in this work were N:P:K fertilizers with a percentage by weight of 4:14:8 and 10:10:10, limestone, fertilizers with a composition of 23.1% K_2O + 11.3% Mg + 22.5% S and 46% P_2O_5 + 15% Ca. All samples were acquired at local agricultural stores in Rio Grande do Sul, Brazil. The certified reference material NIST SRM 695, Trace Elements in Multi-Nutrient Fertilizer (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to evaluate the trueness of the results.

The sample pre-treatment consisted of grinding the samples in a ball mill (Fritsch, Idar-Oberstein, Germany) in three cycles of 20 min each, maximum time of use recommended by the manufacturer. The particle size was controlled using a 45 μm polyester sieve. However, the amount of sample with a particle size <45 μm was very little. Hence, the larger particles were ground further manually in an agate mortar until a sufficient fraction of the sample had a particle size <45 μm. The samples

Table 1
Graphite furnace temperature program for the determination of lead by GF AAS using different modifiers.

Stage	Temperature/°C	Ramp/°C s^{-1}	Hold time/s
Drying	90	5	20
Drying	120	5	10
Drying	150	5	20
Pyrolysis	900[a],700[b]	500	30
Atomization	1900[c]; 1700[d]	3000	4
Cleaning	2200	1000	4

[a] Pd/Mg, NH_4NO_3/Pd and Ir.
[b] Ru.
[c] Pd/Mg and NH_4NO_3/Pd.
[d] Ru and Ir.