



# Method development for the determination of chromium and thallium in fertilizer samples using graphite furnace atomic absorption spectrometry and direct solid sample analysis



Aline R. Borges<sup>a</sup>, Luciane L. François<sup>a</sup>, Emilene M. Becker<sup>a</sup>, Maria Goreti R. Vale<sup>a,c,\*</sup>, Bernhard Welz<sup>b,c</sup>

<sup>a</sup> Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, RS, Brazil

<sup>b</sup> Departamento de Química Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

<sup>c</sup> Instituto Nacional de Ciência e Tecnologia do CNPq-INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil

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## ABSTRACT

A method has been developed for the determination of chromium and thallium in fertilizer samples using line source graphite furnace atomic absorption spectrometry (LS-GF AAS) with Zeeman-effect background correction and direct solid sample analysis. The results obtained with this equipment were compared with those obtained with high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) to verify the absence of spectral interferences. For chromium, it was necessary to employ magnesium as a chemical modifier, and the optimum pyrolysis and atomization temperatures were 1600 °C and 2500 °C, respectively. For thallium, these temperatures were 900 °C and 1700 °C, and the determinations were made without a modifier. For chromium, the limit of detection (LoD) for LS-GF AAS and HR-CS GF AAS were 150 ng g<sup>-1</sup> and 60 ng g<sup>-1</sup>, respectively. For thallium the LoD were 15 ng g<sup>-1</sup> for LS-GF AAS and 3 ng g<sup>-1</sup> using HR-CS GF AAS. The accuracy of the methods was verified using the certified reference materials NIST SRM 695 and NIST SRM 2704. The results obtained with the two spectrometers showed no significant difference at the 95% level of confidence. Using HR-CS GF AAS, it was possible to confirm the absence of spectral interferences in the determination of both elements in the investigated fertilizers.

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## 1. Introduction

Fertilizers are extensively used to improve the quality of agricultural areas and to increase productivity. However, the uncontrolled use of these products can cause serious environmental problems due to the presence of hazardous elements in their composition. Hence, fertilization might result in accumulation of metals in soil and plants, which might this way, enter the food chain [1].

Among these metals are chromium and thallium. The presence of the chromium in raw materials that are employed in the production of fertilizers could be a significant source of contamination with this element for soil, water, and consequently for food [2]. While Cr(III) is considered a beneficial nutrient in trace amounts for humans and animals, the hexavalent form, Cr(VI), is regarded as class A human carcinogen [3]. For plants, chromium is a non-essential trace element; its toxicity could be observed in various forms, such as decrease of leaf

and root growth, inhibition of enzymatic activities and mutagenesis [4].

Thallium is distributed over the earth, mainly in rock formations and soils containing potassium feldspars and micas [2,5]. It is seldom recovered from metal-based mining, ore processing or smelting, and it is, therefore, discarded as part of the tailings into the environment [6]. Since fertilizers in general are produced using mineral resources and must have high amount of potassium in their composition, these products can also contain thallium as contaminant [2,5]. This metal exhibits high toxicity for humans; acute poisoning by thallium is characterized by gastroenteritis, with nausea, vomiting, diarrhea, abdominal pain, paresthesia, mental confusion, convulsions, respiratory and circulatory problems, followed by death [2,5].

Fertilizer contaminants are regulated by the United States Environment Protection Agency—U.S.EPA [7]. In Brazil, the Ministry of Agriculture, Livestock and Food Supply is a government agency that controls contaminants in fertilizers and soil additives [8]. Arsenic, cadmium, lead, chromium, mercury, nickel and selenium are the contaminants that must be determined in fertilizers, limestone, soil conditioners and plant substrates. In addition, to determine these contaminants, the analytical methods indicated by EPA usually use wet digestion for sample preparation [9]. These procedures have to be consistent with the

\* Corresponding author at: Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, RS, Brazil. Tel.: +55 51 3308 6278; fax: +55 51 3308 7304.

E-mail address: [mgrvale@ufrgs.br](mailto:mgrvale@ufrgs.br) (M.G.R. Vale).

analytical techniques, and the techniques most frequently reported in the literature are ICP OES [10–12] and ICP-MS [13,14].

However, sample preparation using wet digestion is usually labor intensive and time consuming; it involves significant sample handling, which may cause contamination of the sample and/or losses of volatile elements. Furthermore, the digestion or dissolution procedures contribute to dilution of the analytes, making solution analysis not necessarily suitable for the determination of the lowest trace concentrations [15, 16].

Using graphite furnace atomic absorption spectrometry (GF AAS), there are two well-established procedures for the analysis of solid samples: slurry sampling and direct solid sample analysis. These procedures have a number of distinct advantages over procedures that involve extensive sample preparation [15]. In slurry sampling, a small portion of the finely ground solid sample is dispersed into a solvent, forming a suspension, which can be introduced directly into the graphite tube [17].

In the last few years, our research group investigated methods for the determination of metals in fertilizers without previous digestion. Initially, a method was developed for the determination of lead in fertilizers using slurry sampling and line source graphite furnace atomic absorption spectrometry (LS-GF AAS) with Zeeman-effect background correction [18]. Five fertilizers were investigated and the best results were obtained using the Pd/Mg modifier in solution. In two other studies high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) was used for the determination of cadmium [19], and for the investigation of spectral interferences in the determination of lead in fertilizer samples [20]. The results showed that the determination of cadmium is without spectral interferences. However, for lead determination the use of HR-CS GF AAS was essential because it was possible to observe, identify and correct spectral interferences using least-squares background correction (LSBC) [15] for some fertilizer samples that could not be evaluated using LS-GF AAS.

Slurry sampling requires some additional attention to obtain accurate results: homogeneity of the samples, particle size, and choice of adequate diluent composition for slurry stabilization play an important role. In addition, slurry preparation causes dilution of the analyte [16]. On the other hand, direct solid sample analysis (SS) brings further advantages, as sample handling is reduced to a minimum. Only grinding and homogenization are usually required, procedures that are equally necessary prior to a sample digestion. Moreover, direct analysis of solid samples is more sensitive, since the analyte is not diluted during sample preparation, and it is much less affected by the particle size [16,17].

The objective of this study is the development of methods for the determination of chromium and thallium in fertilizer samples by LS-GF AAS using direct solid sample analysis. In order to investigate possible spectral interferences, the method was compared using HR-CS GF AAS.

## 2. Experimental

### 2.1. Instrumentation

The methods for the determination of chromium and thallium were developed using a Model ZEE nit 650P line source atomic absorption spectrometer equipped with a transversely heated graphite tube furnace and Zeeman-effect background correction with a transverse magnetic field (Analytik Jena, Jena, Germany). Hollow cathode lamps (Analytik Jena, Jena, Germany) were used with a current of 3 mA. A secondary analytical line at 427.5 nm was used for chromium, and the primary line at 276.8 nm for thallium measurements.

A Model contrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena, Jena, Germany) was used for the comparison of the results. This instrument is equipped with a flame and a graphite furnace atomizer in two separate sample compartments and a xenon short-arc lamp with a nominal power of 300 W operating in a hot-spot mode, which emits a spectral continuum between

190 and 900 nm. The analytical lines used were at 427.480 nm and 276.786 nm for chromium and thallium, respectively. The high-resolution double monochromator with a linear charge coupled device (CCD) array detector with 588 pixels has a spectral resolution of about 1.5 pm per pixel at 200 nm. The integrated absorbance of three pixels, the center pixel (CP) and the two adjacent pixels, i.e.  $CP \pm 1$ , was summed and used for signal evaluation for both analytes.

Transversely heated and pyrolytically coated solid sampling graphite tubes (Analytik Jena Part Nos. 407-152.316 and 407-A81.303 for LS-GF AAS and HR-CS GF AAS, respectively) and SS graphite platforms (Analytik Jena. Part No. 407-152.023) were used for all measurements. The graphite furnace temperature program used for all measurements is shown in Table 1.

An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena, Jena, Germany), was used to transfer the platforms to the atomizer. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as purge and protective gas.

All statistical calculations were performed using GraphPad InStat software (GraphPad InStat Software Inc., Version 3.06, 2007). A 95% significance level was adopted for all comparisons.

### 2.2. Reagents

The nitric acid (Merck, Germany), used to prepare the aqueous calibration standards, 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 18.2 M $\Omega$  cm from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout. All containers and glassware were soaked in 1.4 mol L<sup>-1</sup> HNO<sub>3</sub> for at least 24 h and rinsed three times with DDW before use. The chromium and thallium stock standard solutions (1000 mg L<sup>-1</sup> in 0.014 mol L<sup>-1</sup> nitric acid) were prepared from Titrisol concentrates (Merck). The working standards were prepared by serial dilution of the stock solution with 0.014 mol L<sup>-1</sup> nitric acid.

The chemical modifier solution used for the determination for chromium was magnesium nitrate modifier stock solution (Merck) 10.0 ± 0.2 g L<sup>-1</sup> Mg(NO<sub>3</sub>)<sub>2</sub> in 15% (v/v) HNO<sub>3</sub>.

### 2.3. Samples and reference materials

The fertilizer samples used in this study were acquired at local agricultural stores in Rio Grande do Sul, Brazil. The samples used in this work were: limestone, N:P:K fertilizer in percentage by weight 04:14:08, 10:10:10, 00:18:00, 01:18:00; fertilizers with composition 23.1% K<sub>2</sub>O + 11.3% Mg + 22.5% S and 46% P<sub>2</sub>O<sub>5</sub> + 15% Ca. The certified reference materials used to check the accuracy of the methods were from the National Institute of Standards and Technology, Gaithersburg, MD, USA: NIST SRM 695 (Trace Elements in Multi-Nutrient Fertilizer) and NIST SRM 2704 (Buffalo River Sediment).

**Table 1**

Graphite furnace temperature program for the determination of Cr and Tl by GF AAS. For Cr determination, an argon gas flow-rate of 2 L min<sup>-1</sup> was maintained during all stages, whereas for Tl, the Ar flow was stopped during the atomization stage.

| Stage       | Cr<br>Temperature/ramp/hold<br>°C/°C s <sup>-1</sup> /s | Tl<br>Temperature/ramp/hold<br>°C/°C s <sup>-1</sup> /s |
|-------------|---------------------------------------------------------|---------------------------------------------------------|
| Drying      | 90/15/15                                                | –                                                       |
| Drying      | 120/10/10                                               | 100/15/15                                               |
| Drying      | 150/10/15                                               | 150/15/15                                               |
| Pyrolysis   | 1600/150/40                                             | 900/300/10                                              |
| Atomization | 2500/3000/6                                             | 2000/3000/8                                             |
| Cleaning    | 2600/1000/6                                             | 2400/1000/4                                             |

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