



## Development of methods for the determination of cadmium and thallium in oil shale by-products with graphite furnace atomic absorption spectrometry using direct analysis



Helen R. Oliveira<sup>a</sup>, Marcia F. Mesko<sup>a</sup>, Maria Goreti R. Vale<sup>b,c</sup>, Carlos Augusto P. Silveira<sup>d</sup>, Rochele S. Picoloto<sup>e</sup>, Emilene M. Becker<sup>b,\*</sup>

<sup>a</sup> Centro de Ciências Químicas Farmacêuticas e Alimentos, Universidade Federal de Pelotas, 96160-000 Capão do Leão, RS, Brazil

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

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

<sup>d</sup> Embrapa Clima Temperado, BR 116 Km 78 s/n°, 96010-971 Pelotas, RS, Brazil

<sup>e</sup> Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

### ARTICLE INFO

#### Article history:

Received 31 January 2014

Received in revised form 9 April 2014

Accepted 10 April 2014

Available online 21 April 2014

#### Keywords:

Oil shale by-products

Cadmium

Thallium

Direct analysis

GF AAS

ICP-MS

### ABSTRACT

The purpose of this work was the development of methods for the determination of cadmium (Cd) and thallium (Tl) in oil shale by-products by graphite furnace atomic absorption spectrometry with Zeeman-effect background correction (ZBC-GF AAS) using direct analysis. Direct solid sampling (SS) was compared to slurry sampling (SIS). The pyrolysis temperatures for Cd by SS and SIS determination were 500 and 800 °C, respectively, and the atomization temperature was 1700 °C, using a mixture Pd/Mg as the chemical modifier. The limits of detection (LOD) were 3.4 ng g<sup>-1</sup> for SS and 5.5 ng g<sup>-1</sup> for SIS. For Tl determination, temperatures of pyrolysis and atomization were 900 and 1800 °C, respectively, and a chemical modifier was not employed. The LOD obtained for solid and slurry sampling analysis were 11 and 36 ng g<sup>-1</sup>, respectively. The accuracy of methods was evaluated using standard reference materials BCSS1 and NIST SRM 2704. The results of the SS and SIS methods were in agreement with certified values for both elements (no significance difference with 95% of confidence level). In order to compare the results, ZBC-GF AAS and ICP-MS were employed to determine Cd and Tl after wet digestion procedures, in closed vessels assisted by microwave radiation and a conventional wet digestion in open vessels using a digester block. The results obtained by SS-GF AAS were in agreement with those obtained by ICP-MS after digestion by microwave-assisted digestion in closed vessels for all the samples investigated.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Oil shale is a fine-grained sedimentary rock that contains kerogen as organic material. Due to these attributes, it may represent an important alternative source of fossil fuels, since oil and gas can be extracted with conditions of high pressures and temperatures [1]. By-products from the oil shale industry, such as retortate oil shale and powdered oil shale, have high amounts of minerals and trace elements that may be used as soil additives in agriculture [2]. However, the use of different raw material as fertilizer additives, such as oil shale by-products and other rocks, must have careful quality control [3].

In addition to essential and beneficial substances in these by-products, compounds that offer high risk to human health, plants and

animals such as polycyclic aromatic hydrocarbons (PAHs) and toxic trace elements may be present [3,4]. Regarding trace elements, such as cadmium (Cd), thallium (Tl), arsenic and others, there is still concern about the leaching of these elements into groundwater thus causing a significant environmental impact [5]. The potential toxic trace elements have their content in fertilizers and soil additives in Brazil regulated by Brazilian Ministry of Agriculture [6].

Cadmium occurs naturally, and it is generally connected to sulfides. Besides having no biological function in the organisms, Cd is highly toxic to animals and human beings [7]. Ongoing exposure to low levels of this element may result in bio-accumulation and cause significant harm to human health. The toxic effects of Cd possibly occur as a result of it interfering in the biological functions of zinc-dependent enzymes due to the chemical similarity of zinc and Cd [7]. According to the Brazilian legislation, the maximum limit of Cd in fertilizers and soil additives is 8 µg g<sup>-1</sup> [6].

Thallium occurrence in the earth crust is associated mainly with bedrock and soil composition. This element exhibits an isomorphous

\* Corresponding author. Tel.: +55 51 3308 7209; fax: +55 51 3308 7304.  
E-mail address: [emilene.becker@ufrgs.br](mailto:emilene.becker@ufrgs.br) (E.M. Becker).

with potassium and can generally exchange it in natural environmental and biological systems. Although its full toxicity is unknown, there is evidence that Tl exhibits more acute toxic effects than lead, mercury and Cd [8,9]. Regarding the legislation control, Tl is not reported as a contaminant of soil additives in the Brazilian legislation.

To make characterization/determination of Cd and Tl suitable in complex samples such as oil shale by-products, sensitive analytical techniques are usually necessary. Among them, radiochemical neutron activation analysis (NAA), inductively coupled mass atomic emission spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS) techniques can be used for this purpose [8–19]. However, the effectiveness of methods available for trace analysis is dependent on the type and quantity of the sample to be analyzed and the analytes to be determined. On the other hand, usually to be compatible with most techniques, extensive and careful sample preparation procedures are required in order to obtain a solution and to avoid systematic errors.

Direct analysis has advantages over sample digestion procedures, such as the use of lower amounts of sample material and minimal handling [12,14,20]. Other advantages that are important to highlight are the reduced sample preparation time and hence a faster analysis; higher accuracy and sensitivity due to the absence of any dilution; and the absence of any corrosive or toxic waste [12]. X-ray fluorescence spectrometry (XRF) [21], laser ablation inductively coupled plasma mass spectrometry [22], electrothermal vaporization inductively coupled plasma mass spectrometry [23] and solid and slurry sampling associated to GF AAS [24–26] are the techniques that employ direct analysis. Among these techniques, direct analysis GF AAS is nowadays the most elect technique due to analytical performance, low limit of detection (LOD, usually below  $\mu\text{g g}^{-1}$ ), simplicity and relative low cost [13–20,24–27]. The associated problems concerning direct analysis GF AAS are the spectral interferences and adequate method of calibration. In general, in order to avoid spectral interferences, Zeeman-effect background correction (ZBC) may successfully be employed. The calibration using aqueous standard solution has advantages in analytical performance, and it has been used to analyze complex matrices [25,27].

Although direct analysis by GF AAS has already been used to determine Cd and Tl as well as other trace elements in a variety of geological and environmental samples, there is no information available in the literature with respect to the direct analysis of oil shale by-products using this technique. For this reason, new simple, reliable and rapid methods are necessary to characterize oil shale by-products, hence the method used to trace analysis characterization of oil shale samples is usually ICP-MS [21,28,29].

In this work, the development of methods for the determination of Cd and Tl in oil shale by-product samples was performed by means of ZBC-GF AAS using direct solid sampling (SS) and slurry sampling (SIS). These elements were chosen because their presence in by-products that have potential use as soil additives may cause high toxicity to the environment. Other rocks that can also be used as soil additives were also analyzed. In order to compare the results obtained by direct analysis, wet digestion in closed vessels assisted by microwave radiation and a conventional wet digestion in open vessel were also evaluated. Cd and Tl were determined in digests using ZBC-GF AAS and ICP-MS.

## 2. Experimental

### 2.1. Instrumentation

A ZEE nit 650 P line source atomic absorption spectrometer (Analytik Jena, Jena, Germany), equipped with a transversely heated graphite tube furnace and Zeeman-effect background correction with a transverse magnetic field (0.8 T) was used for Cd and Tl measurements. Hollow cathode lamps of Cd and Tl were used as the radiation sources

using lamp currents of 2.5 mA (slit 0.8 nm) and 4.0 mA (slit 0.5 nm) respectively.

SS-GF AAS measurements were carried out using pyrolytically coated solid sampling graphite tubes (Analytik Jena Part No 407-152.316) without a dosing hole and solid sampling (SS) graphite platforms (Analytik Jena Part No 407-152.023). An M2P micro-balance (Sartorius, Göttingen, Germany) was used for weighing the samples directly on the SS platform. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessories (Analytik Jena), was used to transfer the SS platforms to the atomizer.

For SIS-GF AAS measurements and analysis in solution, an MPE 60 furnace autosampler (Analytik Jena) was employed for the introduction of solutions in general. Pyrolytically coated graphite tubes with an integrated PIN platform (Analytik Jena Part No 407-A81.026) were used for Cd, while those without a platform (Analytik Jena Part No 407-152.315) were used for Tl.

The optimized graphite furnace temperature programs for both elements using SS – and SIS-GF AAS are given in Table 1. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used with a flow-rate of  $2 \text{ L min}^{-1}$  during all stages, except during atomization, where the flow was stopped. Integrated absorbance,  $A_{\text{int}}$ , was used for signal evaluation and quantification.

The wet digestion procedures were performed using a digester block model MA-4025 (Marconi, São Paulo, Brazil) and a microwave oven model Multiwave 3000 (Anton Paar, Graz, Austria) equipped with a rotor for eight high-pressure quartz vessels (capacity of 80 mL, maximum pressure and operation temperature of 80 bar and  $280 \text{ }^\circ\text{C}$ , respectively).

An inductively coupled plasma mass spectrometer (PerkinElmer-SCIEX, model Elan DRC II, Thornhill, Canada) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a quartz torch with a quartz injector tube (2 mm i.d.) was used for element determination. The operational parameters are present in Table 2.

### 2.2. Reagents, solutions and samples

Analytical grade reagents were used throughout the study. Water with a specific resistivity of  $18 \text{ M}\Omega \text{ cm}$  from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all standards and solutions. Concentrated nitric acid (Merck, Darmstadt, Germany) was purified by double sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). All containers and glassware were soaked in  $1.4 \text{ mol L}^{-1} \text{ HNO}_3$  for at least 24 h, and rinsed three times with distilled and deionized water before use. The standard working solutions were prepared by serial dilution of  $1000 \text{ mg L}^{-1}$  of Cd and Tl stock solutions (Merck, Darmstadt, Germany) with  $0.014 \text{ mol L}^{-1}$  nitric acid. A solution of 0.1% Pd (w/v) plus 0.06% Mg in the presence of 0.05% (v/v) Triton X-100 was prepared from  $10.0 \pm 0.2 \text{ g L}^{-1} \text{ Pd}(\text{NO}_3)_2$  and  $10.0 \pm 0.2 \text{ g L}^{-1} \text{ Mg}(\text{NO}_3)_2$

**Table 1**

Graphite furnace temperature programs for the determination of Cd, using  $10 \mu\text{g Pd} + 6 \mu\text{g}$  in 0.05% (v/v) Triton X-100 as the chemical modifier, and of Tl in oil shale by-products by means of GF AAS.

Stage	Temperature/ $^\circ\text{C}$	Ramp/ $^\circ\text{C s}^{-1}$	Hold time/s
Drying 1	90 <sup>b,d</sup>	15	20
Drying 2	120	5	10
Drying 3	150	5	30
Pyrolysis	500 <sup>a</sup> ; 800 <sup>b</sup> ; 900 <sup>c,d</sup>	300	30; 40 <sup>c</sup>
Atomization	1700 <sup>a,b</sup> ; 1800 <sup>c,d</sup>	3000	6
Cleaning	2300	1000	4

<sup>a</sup> Cd SS-GF AAS.

<sup>b</sup> Cd SIS-GF AAS.

<sup>c</sup> Tl SS-GF AAS.

<sup>d</sup> Tl SIS-GF AAS.

Download English Version:

<https://daneshyari.com/en/article/7642879>

Download Persian Version:

<https://daneshyari.com/article/7642879>

[Daneshyari.com](https://daneshyari.com)