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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 [a], Marcia F. Mesko [a], Maria Goreti R. Vale [b,c], Carlos Augusto P. Silveira [d], Rochele S. Picoloto [e], Emilene M. Becker [b,*]

[a] Centro de Ciências Químicas Farmacêuticas e Alimentos, Universidade Federal de Pelotas, 96160-000 Capão do Leão, RS, Brazil
[b] Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, RS, Brazil
[c] Instituto Nacional de Ciência e Tecnologia do CNPq-INCT de Energia e Ambiente, UFBA, Salvador, BA, Brazil
[d] Embrapa Clima Temperado, BR 116 Km 78 s/n°, 96010-971 Pelotas, RS, Brazil
[e] Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

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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 (SlS). The pyrolysis temperatures for Cd by SS and SlS determination were 500 and 800 ºC, respectively, and the atomization temperature was 1700 ºC, using a mixture Pd/Mg as the chemical modifier. The limits of detection (LOD) were 3.4 ng g^{-1} for SS and 5.5 ng g^{-1} for SlS. For Tl determination, temperatures of pyrolysis and atomization were 900 and 1800 ºC, respectively, and a chemical modifier was not employed. The LOD obtained for solid and slurry sampling analysis were 11 and 36 ng g^{-1}, respectively. The accuracy of methods was evaluated using standard reference materials BCSS1 and NIST SRM 2704. The results of the SS and SlS 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.

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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^{-1} [6].

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

* Corresponding author. Tel.: +55 51 3308 7209; fax: +55 51 3308 7304.
E-mail address: 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 $\mu g \ g^{-1}$), 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 ZEEnit 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 L min^{-1} during all stages, except during atomization, where the flow was stopped. Integrated absorbance, A_{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 °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 MΩ 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 mol L^{-1} 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 mg L^{-1} of Cd and Tl stock solutions (Merck, Darmstadt, Germany) with 0.014 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 ± 0.2 g L^{-1} $Pd(NO_3)_2$ and 10.0 ± 0.2 g L^{-1} $Mg(NO_3)_2$

Table 1
Graphite furnace temperature programs for the determination of Cd, using 10 μg Pd + 6 μg 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/°C	Ramp/°C s^{-1}	Hold time/s
Drying 1	90[b,d]	15	20
Drying 2	120	5	10
Drying 3	150	5	30
Pyrolysis	500[a]; 800[b]; 900[c,d]	300	30; 40[c]
Atomization	1700[a,b]; 1800[c,d]	3000	6
Cleaning	2300	1000	4

[a] Cd SS-GF AAS.
[b] Cd SIS-GF AAS.
[c] Tl SS-GF AAS.
[d] Tl SIS-GF AAS.

Table 2
Operational parameters for Cd and Tl determination by ICP-MS.

Parameter	Condition
RF power	1300 W
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.20 L min^{-1}
Nebulizer gas flow rate	1.07 L min^{-1}
Sampler and skimmer cones	Pt
Isotopes (m/z)	^{111}Cd, ^{205}Tl
Linear range	0.1–5.0 μg L^{-1}

(Merck), and it was used as the chemical modifier for the determination of Cd by GF AAS.

The certified reference materials – SRM 2704, Buffalo River Sediment (National Institute of Standards and Technology, Gaithersburg, MD, USA) and BCSS1, Marine and Estuarine Sediment (National Research Council, Canada) – were employed to optimize and evaluate the accuracy of Tl and Cd direct analysis methods respectively.

The oil shale by-products, retorted oil shale and powdered oil shale and other rocks that can be used as soil additives such as zeolite and phosphorite were the samples investigated in this work. These samples were obtained from *Xisto Agrícola* Project developed at Embrapa Clima Temperado (Pelotas, RS, Brazil).

2.3. Direct analysis procedures

All samples were ground manually in an agate mortar until a sufficient fraction of the sample had a particle size between <50 μm and <90 μm. The samples were dried in an oven at 50 °C until they reach a constant weight. After attaining room temperature, the samples were passed through a polypropylene sieve (<50 μm) and kept stored in plastic vials in a desiccator until they were analyzed for SS- and SlS-GF AAS.

For SS-GF AAS, each sample was weighed on the SS platform and put into a GF AAS. The sample mass ranged from 0.03 to 1.6 mg for Cd, and from 0.3 to 2.0 mg for Tl determination. In order to compare the measurements from different sample masses, integrated absorbance, A_{int}, was normalized for an appropriate sample mass. The measurements were taken by using six replicates.

For the determination of Cd for SlS-GF AAS, the slurries were prepared according to literature data [27], using 5% (v/v) HNO$_3$ + 10% (v/v) ethanol + 0.05% (v/v) Triton X-100 as the diluent composition. Approximately 5 mg of the investigated samples was directly weighed in glass cups. For Tl, 40 mg of samples mass was used. A volume of 1.5 mL of diluent solution was added to the samples and the mixture was further sonicated for 30 min at room temperature. The same procedure was performed for certified reference materials, which were Buffalo River Sediment SRM 2704 and Marine and Estuarine Sediment BCSS1, using 25 and 15 mg of sample mass respectively. A drop of isopropanol reagent was used as anti-foaming agent (Merck). Subsequently, both analytes were determined by GF AAS using volumes of slurry between 5 and 20 μL. The slurries were prepared in triplicate and six aliquots of each one were analyzed.

2.4. Sample digestion

In order to evaluate the trueness of direct analysis methods, two sample digestion procedures were evaluated. The first one was by using a conventional open system based on EPA Method 3050B [30], established by the United States Environmental Protection Agency and recommended as a reference method by the Brazilian Ministry of Agriculture for soil additives. In this method, 5.0 mL of 50% (v/v) HNO$_3$ was added to 500 mg of the oil shale by-products that had previously been quantitatively transferred to glass digester tubes. The mixture was covered with a watch glass and heated to 95 ± 5 °C for 15 min. Aliquots of 5.0 mL concentrated nitric acid were added and heated again until no brown fumes were observed. After reaching

room temperature, aliquots of 1 mL 30% H$_2$O$_2$ were also added. The residual solution was transferred to volumetric flasks, and after adding ultrapure water the final volume was 25 mL. This procedure was performed in triplicate.

For the comparison of results, the microwave-assisted wet digestion in closed vessels was carried out. For this procedure, approximately 100 mg of oil shale by-products was directly weighed in quartz vessels and 6 mL of concentrated nitric acid was added. The digestion program was carried out as follows: 200 W for 2 min, 500 W for 5 min, 800 W for 5 min and 0 W for 20 min (cooling). After the cooling system, the digested samples were carefully transferred to volumetric flasks to which ultrapure water was added until the final volume up to 25 mL. This procedure was also performed in triplicate. Before each run, the vessels were soaked in concentrated HNO$_3$ for 10 min and rinsed with ultrapure water.

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.

3. Results and discussion

3.1. Method development for the determination of Cd

The establishment of the instrumental parameters for the determination of Cd was carried out by first employing SS-GF AAS, using 25 pg Cd aqueous solution, retorted oil shale, and the certified reference material (CRM) BCSS1. The main aspects considered for this evaluation were the atomic absorption profiles, sensitivity, and background signal intensity. The measurements were initially evaluated without a chemical modifier since some samples may successfully stabilize the analytical signal [26,27]. The universal Pd/Mg mixture as chemical modifier was also investigated. Fig. 1 shows the peak profile for the retorted oil shale and CRM at pyrolysis temperature of 500 °C. As the peak shape obtained using chemical modifier was more symmetric for the sample and CRM, the studies for Cd determination were performed using only Pd/Mg. The adequate mass of Pd/Mg to stabilize Cd was optimized using increased volumes (0 to 15 μL) of the solution 1.0 g L^{-1} Pd + 0.6 g L^{-1} Mg in 0.05% (v/v) Triton X-100. The solution was added directly to the standards and to the previously weighed samples on SS platform. The increase of sensitivity and proper symmetric peak shape were obtained using 10 μg Pd + 6 μg Mg + 0.05% (v/v) Triton X-100. It is important to highlight that the precision of measurements was improved by using two stages of drying in the heating program and by having Triton X-100 in the chemical modifier solution.

The results of pyrolysis and atomization curves using SS-GF AAS, which were established for aqueous calibration solution, retorted oil shale and CRM BCSS1, are shown in Fig. 2. The A_{int} value was normalized for 0.1 mg mass of both sample and CRM. The corresponding pyrolysis curves were obtained using 1700 °C as atomization temperature. As it is known, the aqueous Cd solution exhibits thermal stability until 900 °C. Nevertheless, retorted oil shale samples show an improvement of sensitivity with a temperature increase of up to 600 °C. Furthermore, as a significant increase of sensitivity was found by using 500 °C for the CRM BCSS1, this temperature was adopted for SS. According to the atomization temperature curves, the same thermal stability behavior was found for the standard solution, solid samples and CRM BCSS1, indicating that 1700 °C is an adequate temperature for all measurements.

Considering the SS-GF AAS results, even without a high background signal, masses of retorted oil shale larger than 0.16 mg could not be used due to linearity losses obtained from the correlation between A_{int} and sample mass (r = 0.98; slope = 3.95). This fact is consistent with expectations, since this result of A_{int} is out of the linear range against aqueous calibration.

In order to check the similarity of SlS and SS conditions and to determine Cd by GF AAS, brief studies were carried out using SIS. The thermal conditions were evaluated by using a standard solution and powdered
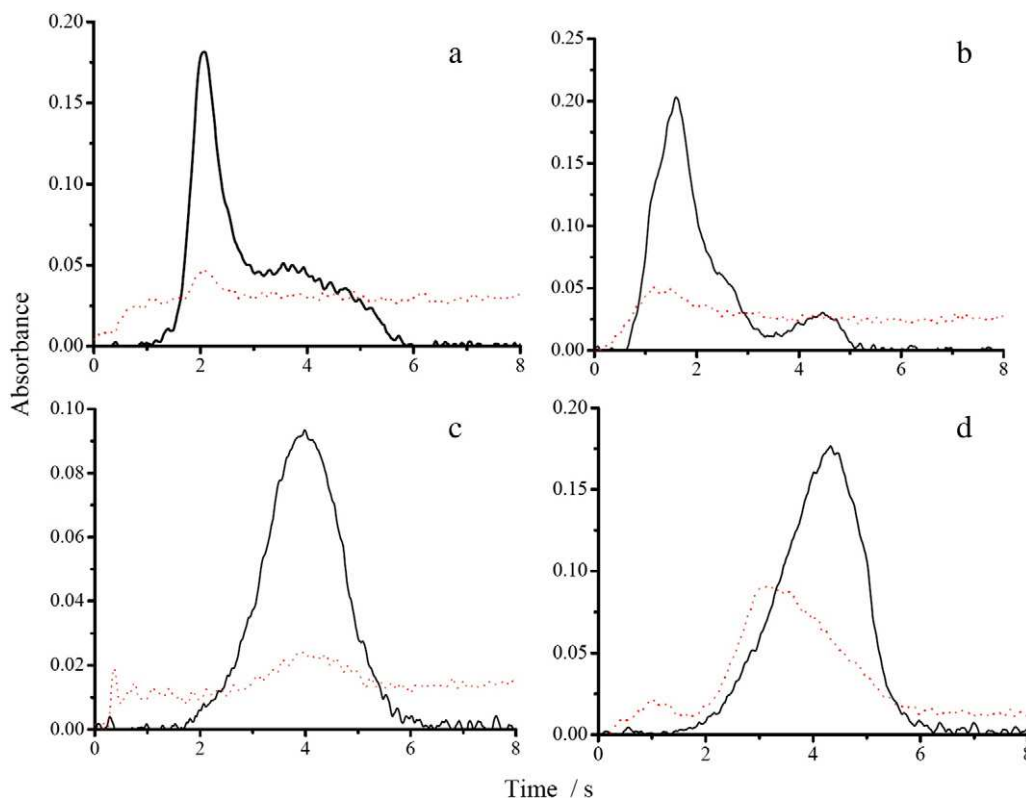
Fig. 1. Absorbance signals using DS–GF AAS for Cd (—) and background BG (—) of: (a) 0.109 mg retorted oil shale and (b) 0.149 mg CRM BCSS1 without modifier; (c) 0.048 mg retorted oil shale and (d) 0.095 mg CRM BCSS1 with 10 μg Pd + 6 μg Mg + 0.05% (v/v) Triton X-100 as chemical modifier. T_p: 500 °C; T_a: 1700 °C.

oil shale and using Pd/Mg as chemical modifier. This sample was investigated because, in slurry, its particles settle more easily than those of the retorted oil shale sample. The slurries were prepared in the concentration of 0.33% (w/v). The homogeneity of the slurries was maintained with manual shaking for 5 s just before pipetting the slurry. Regarding the diluent composition, the choice was made because the medium was more suitable to determine Cd in fertilizers and to result in higher sensitivity for Pb determination as reported in literature [27,31,32]. In this study, to determine Cd by means of SlS–GF AAS, the same SS atomization temperature condition was found, but the optimal pyrolysis temperature was 800 °C. Considering the use of an ultrasound step for slurry preparation, a study was performed in order to investigate the amount of Cd that was extracted to a liquid phase. For this purpose, the slurries were analyzed immediately after removal from the ultrasound bath without mixing before pipetting. Results showed

total extraction of Cd for CRM BCSS1; however, only 27% was extracted to the solution from retorted oil shale and no extraction was observed from powdered oil shale.

3.2. Method development for the determination of Tl

The method development for the determination of Tl using SS was performed without a chemical modifier. Fig. 3 exhibits the thermal behavior of 1.0 ng Tl aqueous standard solution in 0.014 mol L^{-1} HNO$_3$, retorted oil shale sample, and certified reference material SRM 2704. Pyrolysis curves were established using Ta 1800 °C. Retorted oil shale presented a slight decrease in sensitivity when the pyrolysis temperature increased from 700 to 900 °C, decreasing significantly only after 1000 °C, while the analytical signal of aqueous standard solution dropped after 900 °C. For the SRM 2704, the normalized
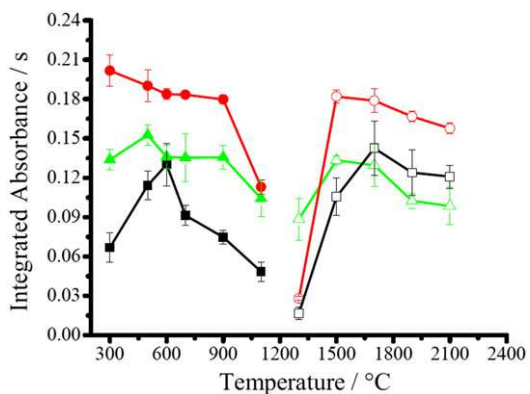

Fig. 2. Pyrolysis (full symbols) and atomization (open symbols) curves of (■) 25 pg Cd; (●) retorted oil shale and (◆) CRM BCSS1, integrated absorbance normalized for 0.1 mg with 10 μg Pd + 6 μg Mg + 0.05% (v/v) de Triton X-100 as chemical modifier by using SS–GF AAS; T_p: 500 °C; T_a: 1700 °C.
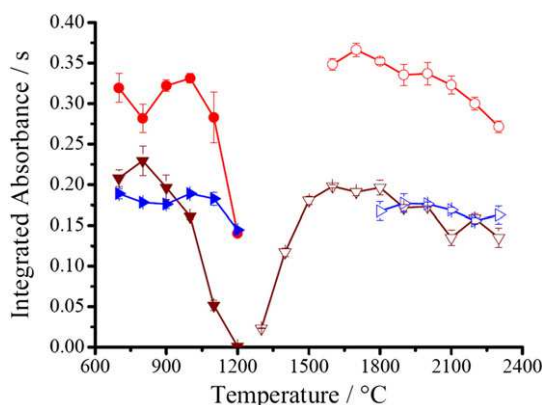

Fig. 3. Pyrolysis (full symbols) and atomization (open symbols) curves Tl-SS–GF AAS without chemical modifier of (▶) 1.0 ng Tl; (●) retorted oil shale and (▼) SRM 2704, integrated absorbance normalized for 1 mg T_p: 900 °C. T_a: 1800 °C.
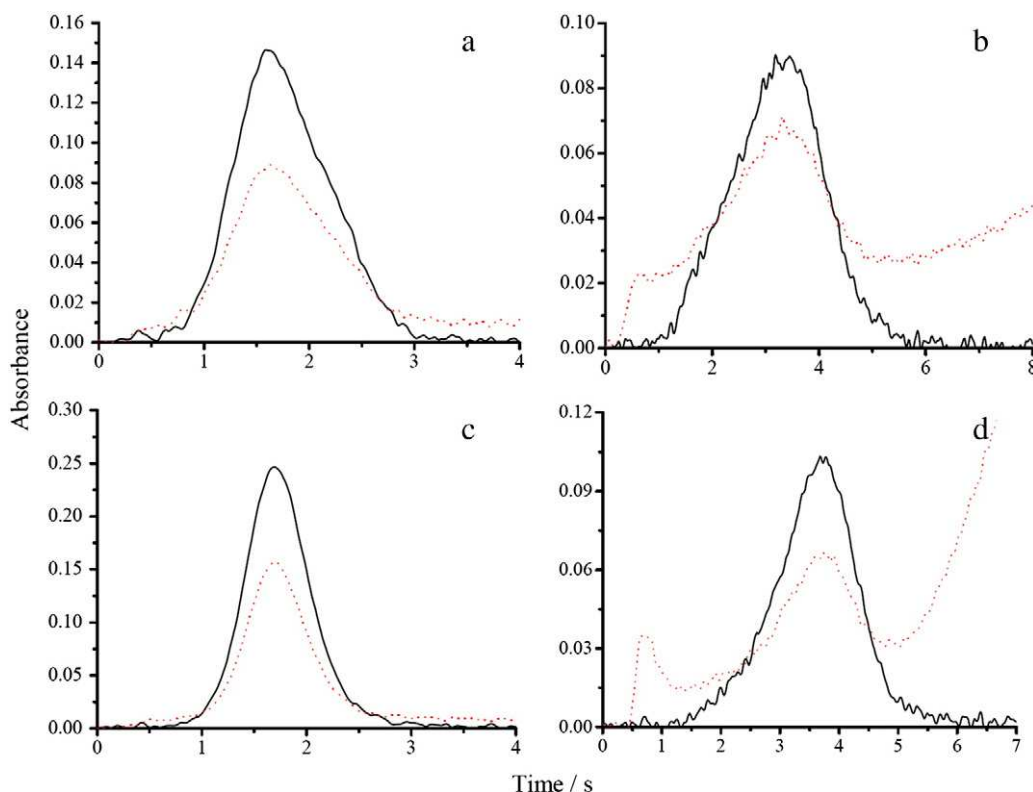
Fig. 4. Absorbance signals using SS-GF AAS (—) and background BG (—) of: (a) 1.0 ng Tl and (b) 0.557 mg retorted oil shale, T_a: 1700 °C; and of (c) 1.0 ng Tl and (d) 0.503 mg retorted oil shale, Ta: 1800 °C without chemical modifier, T_p: 900 °C.

A_{int} remained stable among all pyrolysis temperatures investigated. Concerning the evaluation of atomization curves, aqueous solution and SRM 2704 showed similar thermal behavior, with a plateau from 1700 until 2000 °C. For the retorted oil shale sample, however, there was a significant loss of sensitivity after 1800 °C. Although the sensitivity is slightly higher at 1700 °C, a symmetric profile was obtained at 1800 °C. Based on these results, 900 °C was used as the pyrolysis temperature, and 1800 °C as the atomization temperature for all further measurements. Under previously optimized SS conditions, retorted oil shale sample mass up to 2 mg had no negative influence on A_{int} analytical signal. (See Fig. 4.)

The evaluation of pyrolysis and atomization temperatures for SlS–GF AAS was performed using powdered oil shale slurry (1.0%, w/v) and Tl aqueous standard solution. Results showed the identical thermal conditions of SS.

3.3. Analytical characteristics and figures of merit

The figures of merit for the determination of Cd and Tl using SS- and SlS-GF AAS are summarized in Table 3. Calibration curves were established using a blank and seven calibration solutions in a concentration range from 0.5 to 12.5 µg L^{-1} of Cd (5.0 pg to 125 pg Cd) for SS. For SlS, the proper linear range was obtained up to 100 pg of Cd. The limits of detection (LOD) and quantification (LOQ) in both methods were calculated as three times and ten times the standard deviation of 10 measurements of a blank, respectively, divided by the slope of the calibration curves. In order to calculate the LOD and LOQ in ng g^{-1}, the maximum sample mass placed in the furnace was taken into account. For SS, blank measurements were carried out according to the "zero mass response" principle [26] by inserting an SS platform containing the modifier mixture in the graphite furnace and running the entire temperature program shown in Table 1. In this study, the sensitivity of methods was compared considering slopes, the characteristic mass, and LOD values. Even when a gain of sensitivity was obtained using SS for Cd, around 30% higher than SlS, the least desirable LOD was found. This difference may be attributed to the superior SNR that was obtained using SS. However, this result is not in accordance with that reported for Cd determination in wheat flour samples by using SlS and deuterium as background correction [32]. Considering direct analysis of solid and slurry sampling, the results of figure of merits in this work are in agreement with the values reported in the literature for Cd [17,18,33].

Regarding Tl determination by SS, the linear range was obtained by using 20 to 160 µg L^{-1} Tl (0.2 to 1.6 ng Tl). Unlike Cd results, the SS method presented higher sensitivity observed by slopes and m_0. The SlS linear range was broader as much as 2.0 ng Tl in this case. Although

Table 3
Figures of merit for the determination of Cd and Tl in oil shale by-products samples using SS- and SlS-GF AAS.

Analyte	Method	Regression equation	Correlation coefficient, r	LOD, ng g^{-1}	LOQ, ng g^{-1}	m_0, pg
Cd	SS[a]	$A_{int/s} = 0.0053 + 0.0035\ Cd_{(pg)}$	0.9965	3.4	11.2	1.1
	SlS[b]	$A_{int/s} = 0.0137 + 0.0049\ Cd_{(pg)}$	0.9954	5.5	18.3	0.8
Tl	SS[c]	$A_{int/s} = 0.0040 + 0.154\ Tl_{(ng)}$	0.9928	11	36	27
	SlS[d]	$A_{int/s} = 0.0020 + 0.118\ Tl_{(ng)}$	0.9940	36	119	37

LOD and LOQ were calculated for: [a] 0.30 mg of sample; [b] 0.15 mg of sample; [c] 2.00 mg of sample; [d] 0.50 mg of sample.

Table 4
Determination of the Cd and Tl in certified reference material (CRM) using SS-GF AAS (n = 6) and SlS-GF AAS using calibration against aqueous standards. Results are presented in µg g^{-1} ± sd, (n = 3).

Certified reference material	Cd		Tl	
	SS	SlS	SS	SlS
BCSS1	0.27 ± 0.02	0.21 ± 0.01	–	–
SRM 2704	–	–	1.3 ± 0.04	1.2 ± 0.001

BCSS1 Cd 0.25 ± 0.04 µg g^{-1}; SRM 2704 Tl 1.2 ± 0.2 µg g^{-1}.

the results of LOD obtained by SlS were 3 times higher than SS, it was suitable to determine Tl in most of the investigated samples. The figures of merit obtained in this study for both SS and SlS are in agreement with what has been reported in the literature [16,33]. However, it must be emphasized that until now, there has been no report of Cd and Tl in oil shale by-products using direct sampling.

3.4. Accuracy of methods and analytical application

In order to evaluate the accuracy of the proposed methods, certified reference materials were analyzed in two CRMs using calibration against aqueous standards. Results are shown in Table 4. The determination of Cd and Tl was performed by the measurement of six replicates of solid sample, and by measuring six samples for three independently prepared slurries. Results are not significantly different from the certified values, based on a Student t-test on a 95% confidence level, suggesting that the results obtained with the proposed methods be accurate. Furthermore, these results indicate that the calibration against aqueous standards can be used.

The SS–GF AAS and SlS-GF AAS proposed methods were applied in the determination of Cd and Tl in oil shale by-products and other rocks with potential use as soil additives. Results are presented in Table 5, and the relative standard deviation (RSD) is expressed in percentages. The results of each analyte were compared by using both methods, sample by sample, based on a Student t-test on a 95% confidence level.

For the determination of Cd, the concentration in the investigated samples ranged from 0.85 to 1.83 µg g^{-1}. The results between SS and SlS were in agreement for powdered oil shale ($t_{crit} = 2.36$; $t_{cal} = 0.14$) and phosphorite ($t_{crit} = 2.36$; $t_{cal} = 1.05$) samples, while a significant difference was found for the retorted oil shale sample ($t_{cal} = 2.98$).

Concerning Tl determination, the concentration values of samples were found to be between 0.73 and 2.60 µg g^{-1}. By comparing SS and SlS, retorted oil shale ($t_{cal} = 0.75$) and phosphorite ($t_{cal} = 0.30$), samples showed concordant results. However, the results of powdered oil shale were significantly different ($t_{cal} = 10.2$).

The precision of the SS–GF AAS measurements to Cd determination, evaluated by relative standard deviation (RSD) in general was lower than SlS-GF AAS, while for Tl determination, it was quite similar. The precision of the results is in accordance with what is expected for direct analysis.

Results of direct analysis were compared to two digestion procedures, based on the EPA 3050B and 3051 methods, which were adopted by the Ministry of Agriculture [30]. The determination of Cd and Tl was evaluated by means of GF AAS, and by ICP-MS. Results are summarized in Table 6. The sample preparation method performed in a conventional open system (3050B) showed significantly lower Cd and Tl concentration values when compared to those obtained with microwave-assisted digestion in closed vessels and those using direct analysis. Hence, the conventional system is not suitable as a sample decomposition method for oil shale by-products and other rocks. These results were consistent with ICP-MS measurements, since the Cd and Tl concentrations exhibited lower values using the 3050B method.

The measurements obtained by GF AAS and ICP-MS in the samples that were previously digested by microwave assisted digestion procedure were compared sample by sample, based on Student t-test on a 95% confidence level. For Cd and Tl, only powdered oil shale samples showed results in agreement with both techniques.

The comparison between ICP-MS measurements and direct analysis methods was evaluated by means of analysis of variance (ANOVA, Tukey–Kramer multiple comparisons test), considering a confidence interval of 95%. For Cd determination, the results obtained by using the SS–GF AAS method were in agreement with ICP-MS results for all samples. For powdered oil shale, however, the results of SlS–GF AAS were significantly different from those found by ICP-MS. Concerning Tl determination, retorted oil shale results were in agreement between SS and SlS methods as well as ICP-MS results. Nevertheless, the results for powdered oil shale sample were different for all investigated methods.

4. Conclusions

The developed devices using direct analysis have provided accurate results for the determination of Cd and Tl in samples of by-products

Table 5
Analytical results in µg g^{-1} (expressed as mean ± standard deviation) for Cd and Tl determinations in oil shale by-products and rocks used as agriculture additives determined by SS–GF AAS (n = 6) and SlS-GF AAS (n = 3).

Sample	Cd				Tl			
	SS		SlS		SS		SlS	
	Found value	RSD %	Found value	RSD %	Found value	RSD%	Found value	RSD%
Retorted oil shale	0.97 ± 0.06	6.2	0.85 ± 0.06	7.1	1.84 ± 0.06	3.3	1.89 ± 0.15	7.9
Powdered oil shale	0.91 ± 0.12	13	0.90 ± 0.01	1.1	2.00 ± 0.06	3.0	2.60 ± 0.12	4.6
Phosphorite	1.83 ± 0.20	11	1.70 ± 0.07	4.1	0.75 ± 0.11	15	0.73 ± 0.02	2.7
Zeolite	<3.4 ng g^{-1}	–	<5.5 ng g^{-1}	–	<11.0 ng g^{-1}	–	<36.0 ng g^{-1}	–

Table 6
Analytical results in µg g^{-1} (expressed as mean ± standard deviation) for Cd and Tl determinations in oil shale by-products after wet decomposition by using GF AAS and ICP-MS (n = 3).

Analyte	Samples	GF AAS		ICP-MS	
		Microwave oven	Conventional open system	Microwave oven	Conventional open system
Cd	Retorted oil shale	0.84 ± 0.04	0.55 ± 0.02	0.94 ± 0.02	0.65 ± 0.02
	Powdered oil shale	0.86 ± 0.06	0.65 ± 0.01	0.86 ± 0.02	0.79 ± 0.04
Tl	Retorted oil shale	1.58 ± 0.09	0.66 ± 0.04	1.86 ± 0.03	1.19 ± 0.02
	Powdered oil shale	1.59 ± 0.08	1,09 ± 0.01	1.71 ± 0.09	1.46 ± 0.04

of shale and other rocks by GF AAS. The use of aqueous solutions for calibration promoted the simplification of the steps of chemical analysis. Additionally, the methods were simple and sensitive, since LOD and LOQ for Cd were far below the maximum limits allowed by Brazilian legislation (8 μg g^{-1}). It is worth pointing out that in general SS is suitable for determining Cd content in oil shale by-products because the results obtained were in agreement with the ICP-MS reference technique. Concerning Tl determination methods using direct analysis, further investigations should be necessary since the methods were developed without chemical modifier and some oil shale by-product samples showed widely varying results.

Considering the great volume of residues produced by industrialization of oil shale, and the growing concern about the management of these by-products, suitable quality control must be carried out. New methods that are simple, fast and reliable for adequately determining traces of potentially toxic elements must be developed to meet the demand and be in compliance with legislation.

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