



Determination of toxic elements in coal by ICP-MS after digestion using microwave-induced combustion

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ABSTRACT

A microwave-induced combustion (MIC) procedure was applied for coal digestion for subsequent determination of As, Cd and Pb by inductively coupled plasma mass spectrometry (ICP-MS) and Hg using cold vapor (CV) generation coupled to ICP-MS. Pellets of coal (500 mg) were combusted using 20 bar of oxygen and ammonium nitrate as aid for ignition. The use of nitric acid as absorbing solution (1.7, 3.5, 5.0, 7.0 and 14 mol L⁻¹) was evaluated. For coal samples with higher ash content, better results were found using 7.0 mol L⁻¹ HNO₃ and an additional reflux step of 5 min after combustion step. For coal samples with ash content lower than 8%, 5.0 mol L⁻¹ nitric acid was suitable to the absorption of all analytes. Accuracy was evaluated using certified reference material (CRM) of coal and spikes. Agreement with certified values and recoveries was better than 95 and 97%, respectively, for all the analytes. For comparison of results, a procedure recommended by the American Society of Testing and Materials (ASTM) was used. Additionally, a conventional microwave-assisted digestion (MAD) in pressurized vessels was also performed. Using ASTM procedure, analyte losses were observed and a relatively long time was necessary for digestion (>6 h). By comparison with MAD procedure, higher sample mass can be digested using MIC allowing better limits of detection. Additionally, the use of concentrated acids was not necessary that is an important aspect in order to obtain low blank levels and lower limits of detection, respectively. The residual carbon content in digests obtained by MAD and MIC was about 15% and <1%, respectively, showing the better digestion efficiency of MIC procedure. Using MIC it was possible to digest completely and simultaneously up to eight samples in only 25 min with relatively lower generation of laboratory effluents.

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1. Introduction

The use of coal as energy source may cause serious environmental impacts due to pollutants emission resulting contamination of soil, water and air [1]. In this concern, several toxic elements, especially As, Cd, Hg and Pb, are responsible for many environmental risks associated to the use of coal, even if they are present in low levels. These elements are mostly concentrated in the inorganic fraction of coal and can be transferred to environment during coal combustion [2,3]. Thereby, the accurate determination of toxic elements at low levels in coal is very important in order to evaluate the potential of environment impact.

Analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) [4] and inductively coupled plasma optical emission spectrometry (ICP OES) [5,6] have been used for toxic elements determination. In the case of mercury determination it has been currently determined by cold vapor (CV) coupled to atomic absorption spectrometry (AAS) [7–9], ICP-MS or ICP OES techniques. However, trace elements determination in coal is still a challenging task because coal is particularly difficult to bring into solution and complex and time-consuming sample preparation procedures are generally required. Solid sampling methods using graphite furnace atomic absorption spectrometry (ET AAS) [10], ICP-MS with electrothermal vaporization or laser ablation have been used for coal analysis [4,11,12]. However, matrix effects can increase the limits of detection (LOD) and problems related to sample homogeneity can affect the accuracy of these methods. On the other hand, neutron activation analysis could be also used but the unavailability of this technique for most

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of laboratories practically prevents its use for routine analysis [13].

Coal must be previously digested for conventional analysis using ICP-MS, ICP OES and AAS. Usually, procedures for coal digestion involve dry ashing [14], microwave assisted wet digestion (MAD) in closed vessels [15], pyrohydrolysis [16,17] and combustion techniques [18–20]. Acid extraction procedures have been also used [21]. Different methods proposed by the American Society for Testing and Materials (ASTM) recommend a dry ashing step following by ash digestion with a mixture of aqua regia and further dissolution in nitric acid or hydrofluoric acid or, in some cases, sample fusion and dissolution with nitric acid or dissolution with a mixture of hydrochloric–hydrofluoric acid and boric acid [22–24]. For these recommended procedures by ASTM the determination of elements should be performed by ICP-MS [22], ICP OES [23], ET AAS [22] or flame atomic absorption spectrometry (F AAS) [24].

Microwave-assisted wet digestion in closed vessels has been extensively used for sample digestion probably in view of its high digestion efficiency for most of samples, relatively low reagent consumption and reduced risks of losses and contamination in comparison to conventional digestion procedures [25]. However, even using concentrated acids and high temperature and pressure, incomplete coal digestion has been reported [26]. On the other hand, maximum sample mass is usually lower than 0.2 g that makes difficult to obtain low limits of detection [14,26].

As an alternative, combustion techniques have been considered suitable for coal digestion due to the relatively low reagent consumption and high digestion efficiency [27]. However, the sample mass is generally restricted to about 0.15 g when using oxygen flask combustion systems [18]. Techniques based on combustion reactions present the advantage to convert organic materials to the respective combustion products using only oxygen, which minimizes the risk of contamination [27,28]. Recently, Geng et al. [18] have used oxygen flask combustion method for coal digestion and further sulfur and mercury determination by ICP OES. A solution of KMnO_4 was used for mercury absorption and despite a good agreement with certified values has been found, maximum sample mass of 0.11 g could only be decomposed. Dias and Satté [29] used combustion bomb to digest coal and other environmental samples for subsequent analysis by ET AAS. Although samples masses up to 1.5 g could be digested with good efficiency the proposed procedure was time consuming considering that only a single digestion could be performed each time.

The feasibility of microwave-induced combustion (MIC) and its advantages over conventional combustion methods has been recently demonstrated for complete digestion of organic samples in closed vessels [30,31]. This method combines the features of classical combustion techniques with those of MAD systems. The MIC technique involves the combustion of samples in closed quartz vessels pressurized with oxygen and ignition by microwave radiation. An optional reflux step enables additional dissolution of the remaining inorganic compounds and allows quantitative analyte recoveries [32–38]. The use of concentrated acids is avoided and diluted acids could be used for most of analytes. This procedure could be considered safe as it is performed in a dedicated microwave oven and, in addition, it allows a relatively high sample throughput. Furthermore, the residual carbon content (RCC) is extremely low, avoiding interferences on measuring methods. This procedure was already used for coal digestion for further halogens determination, using ammonium carbonate as absorbing solution with good results [19] but no application for further metals and metalloids determination was demonstrated up to now.

In this work, a MIC procedure is proposed for coal digestion for subsequent determination of As, Cd, Hg and Pb. The operational parameters of MIC such as the kind of absorbing solution and the use of additional reflux step were investigated. Accuracy was eval-

uated using certified reference materials (CRMs) and by analyte recovery tests. The proposed procedure was applied for digestion of coal samples with different ash contents. Arsenic, Cd and Pb were determined by ICP-MS and Hg by CV-ICP-MS. For comparison of results, measurements were also performed by ICP OES and the same CV system used in ICP-MS determinations was coupled to ICP OES for Hg determination.

2. Experimental

2.1. Instrumentation

For the proposed MIC procedure, conventional high pressure wet digestion and extraction procedures a microwave sample preparation system Multiwave 3000 (Anton Paar, Graz, Austria) equipped with up to eight high-pressure quartz vessels was used. The conditions for MIC were performed according to previous works [19]. Using this system it was possible the operation at maximum pressure and temperature of 80 bar and 280 °C, respectively. The software version was v1.27-Synt and the microwave program was previously changed to run with a maximum pressure rate of 3 bar s^{-1} . In this work, each run was always performed with a minimum of four vessels.

An inductively coupled plasma mass spectrometer (Perkin Elmer 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 As, Cd and Pb determination. Mercury was determined using a CV continuous flow (CF) system, built according to previous work [39] but coupled to ICP-MS instead of AAS and using a CF instead of flow injection. Briefly, it consists of a CV system, composed by a peristaltic pump (Gilson, Miniplus, France), a manual injector and a U-type gas–liquid separator. Tygon® pump tubings with 1.14 mm i.d. were used to transport 0.1% (w/v) NaBH_4 and sample solutions and 1.69 mm i.d. tubings were used for 1.0 mol L^{-1} HCl transfer. Water was used as sample carrier and samples were on line mixed with 1.0 mol L^{-1} HCl using a T-type connector (0.8 mm i.d.) and carried to another T-type connector (0.8 mm i.d.). After, the NaBH_4 solution was also on line mixed. The mixture was pumped to the gas–liquid separator and Hg was measured by ICP-MS. The CF-CV system is shown in Fig. 1.

A spectrometer Optima 4300 DV (Perkin Elmer, Shelton, USA) with axial view configuration was used for the determination of As, Cd, Hg and Pb by ICP OES. For the determination of As, Cd and Pb, a concentric nebulizer coupled to a cyclonic nebulization spray chamber was used. Mercury determination was performed by CF-CV-ICP OES, using the same system described in Fig. 1. For RCC determination, an ICP OES (Model Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany) with axial view configuration was used. This spectrometer was equipped with a cross flow nebulizer coupled to a Scott type double pass nebulization spray chamber. Residual carbon content measurements were performed according to the conditions previously described [40].

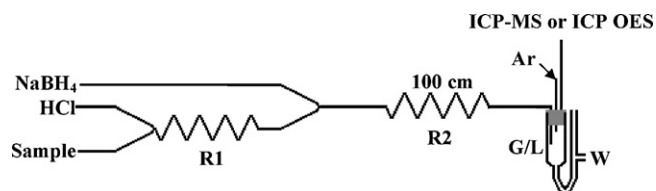


Fig. 1. Continuous flow system for CV. R1: 50 cm; R2: 50 cm; G/L: gas/liquid separator; Ar: argon; W: waste.

Table 1
Instrumental parameters for As, Cd, Hg and Pb determination by ICP-MS and ICP-OES.

Parameter	As, Cd, Hg and Pb determination	
	ICP-MS	ICP-OES
RF power (W)	1300	1300
Plasma gas flow rate (L min ⁻¹)	15	15
Auxiliary gas flow rate (L min ⁻¹)	1.2	0.2
Nebulizer gas flow rate (L min ⁻¹)	1.15	0.65
Isotope (m/z)	⁷⁵ As ¹¹¹ Cd ²⁰² Hg ²⁰⁸ Pb	– – – –
Wavelength (nm)	–	As 193.696 Cd 228.802 Pb 220.351 Hg 253.652 C 193.091
NaBH ₄ concentration (%)	0.1	Hg (CF-CV-ICP-MS and CF-CV-ICP OES)
HCl concentration (mol L ⁻¹)	1.0	

However, instead of heating at 120 °C, digests were sonicated using an ultrasonic probe (Model VCX 130 PB, 130 W, 20 kHz, Sonics and Materials Inc., Newton, USA) for 2 min to remove the volatile carbon compounds before RCC measurements [19]. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used. Instrumental parameters for measurements of As, Cd, Pb (ICP-MS and ICP OES) and Hg (CF-CV-ICP-MS and CF-CV-ICP OES) are shown in Table 1.

For coal digestion by MIC, pellets of samples were prepared using a hydraulic press set at 5 ton during 3 min (Specac, Orpington, UK). A small disc of filter paper (10 mm of diameter, 10 mg) with low ash content (Black Ribbon Ashless, Schleicher and Schuell GmbH, Dassel, Germany) was used as auxiliary for the combustion process. Filter papers were previously washed with a 1.4 mol L⁻¹ HNO₃ solution for 20 min in an ultrasonic bath and dried in an oven for 2 h at 60 °C before the use.

The temperature during coal combustion was determined using an optical pyrometer (Ultimax Infrared Thermometer, Ircon, Niles, IL) equipped with a close-up VX-CL1 lens.

2.2. Reagents

Distilled and deionized water was further purified using a Milli-Q system (Millipore Corp., Bedford, USA). Concentrated HNO₃ and HCl (Merck, Darmstadt, Germany) were purified using a sub-boiling system (Milestone, Model Duopur, Bergamo, Italy). Hydrofluoric acid (40%, w/w) was purchased from Merck. Hydrogen peroxide (30%, w/w) was purchased from Synth (Diadema, Brazil). Sodium tetrahydroborate (Vetec, Duque de Caxias, Brazil) solution (0.1%, w/v) was prepared daily by dissolving the solid reagent in 0.1% (w/v) NaOH solution (Merck). Ammonium nitrate (Merck) was dissolved (6 mol L⁻¹) in water, and this solution was used as igniter for the combustion process.

2.3. Standards

Multielement stock standard solution containing 10 mg L⁻¹ of As, Cd and Pb (SCP33MS, SCP Science, Quebec, Canada) was used to prepare analytical standards by sequential dilution in 5% (v/v) HNO₃, in the range of 0.025–10 µg L⁻¹ for ICP-MS and 5–100 µg L⁻¹ for ICP OES. Mercury standard solutions in the range

of 0.025–1 µg L⁻¹ for CV-ICP-MS and 5–50 µg L⁻¹ for CV-ICP OES were prepared by serial dilution of a 1000 mg L⁻¹ stock standard solution (Merck).

2.4. Samples

Three coal samples (Brazilian coal A, B and C) were obtained from coal mines of south of Brazil. For the accuracy evaluation, four certified reference materials (CRM) of coals were used: SARM 19 (coal), SARM 20 (coal), NIST 1632c (bituminous coal) and BCR 40 (coal). The ash content in Brazilian coal samples was 21.5, 30.0 and 6.8% for coal A, B and C, respectively, while the ash content in CRMs SARM 19, SARM 20 and BCR 40 (based on the sum of SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO content) was 24.7, 30.1 and 7.8%. The ash content in NIST 1632c (reference value) was 7.2%. The particle size of all certified and no certified samples was lower than 100 µm, with exception of CRM NIST 1632c that presented particle size lower than 250 µm. All samples were dried at 60 °C by 24 h before use.

2.5. Sample preparation procedures

For the proposed MIC procedure, sample pellets of 500 mg were weighed and transferred together the filter paper to the quartz holder of MIC system. The holder containing the sample was placed into a quartz vessel. Quartz vessels were previously charged with 6 mL of absorbing solution (1.7, 3.5, 5.0, 7.0 and 14 mol L⁻¹ HNO₃). Ammonium nitrate solution (50 µL of 6 mol L⁻¹) was immediately added on the paper. After closing the vessels and capping the rotor, vessels were pressurized with oxygen at 20 bar for 1 min as previously described [19]. The rotor with eight quartz vessels was placed inside the microwave cavity. The microwave irradiation program used for the MIC procedure was 1400 W for 1 min or 1400 W for 5 min (optional reflux step) and 0 W for 20 min (cooling). The resultant solutions were diluted up to 30 mL in polypropylene vessels. After each run, holders were soaked with concentrated HNO₃ for 10 min followed by rinsing with water. After dilution, As, Cd and Pb were determined by ICP-MS and ICP OES and Hg was determined by CF-CV-ICP-MS or CF-CV-ICP OES.

Sample decomposition was also performed by conventional MAD in high-pressure closed vessels. In this case, about 250 mg of coal were weighted inside quartz vessels and 6 mL of concentrated nitric acid and 2 mL of 30% (w/w) H₂O₂ were added. The operational conditions and the heating program used were carried out according to recommendations of the manufacturer [41] as follows: 1400 W (10 min of ramp), 1400 W for 40 min and 0 W for 20 min (cooling). After cooling, digests were diluted with water to 30 mL in polypropylene vessels for further analysis.

The recommended ASTM procedure was applied for sample digestion and further analytes determination [22]. In this case, coal samples and CRMs were previously ashed in a muffle furnace up to 500 °C during 2 h. Ashes were transferred to a PTFE vessel and dissolved with 20 mL of aqua regia and 20 mL of concentrated hydrofluoric acid by heating at 150 °C. After dryness, 1 mL of nitric acid and 20 mL of water were added and the mixture was heated for 1 h. The solution was then diluted to 50 mL in polypropylene vessels and analysed by ICP-MS and ICP OES.

All statistical calculations were performed using GraphPad InStat (GraphPad InStat Software Inc, Version 3.00, 1997) software. A significance level of $P < 0.05$ was adopted for all the statistical evaluation.

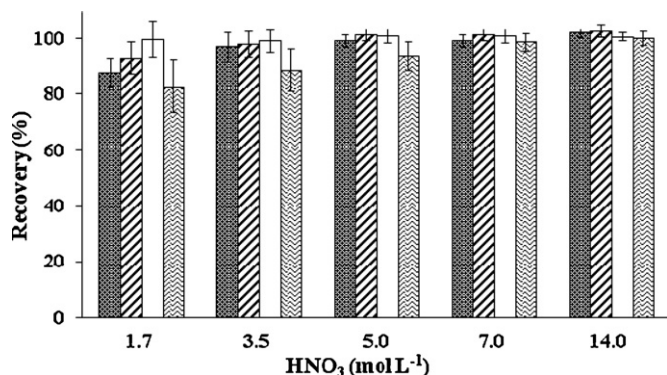


Fig. 2. Influence of absorbing solution on As (▨), Cd (▩), Hg (□) and Pb (▧) recoveries in coal using the proposed MIC procedure with 5 min of reflux. Determination of As, Cd and Pb by ICP-MS and Hg determination by CF-CV-ICP-MS (error bars represents the standard deviation, $n = 3$).

3. Results and discussion

3.1. Operational conditions for coal digestion by microwave-induced combustion

Conditions used in this work were based on those previously used in a previous work [19]. Initial studies were performed for the evaluation of the safety aspects of the coal combustion process. The maximum pressure achieved during the combustion of 500 mg of coal samples using 20 bar as initial oxygen pressure was below 40 bar. The maximum pressure was 50% of the maximum working pressure recommended by the manufacturer (80 bar). Therefore, as the procedure was considered safe for digestion up to 500 mg of coal and also to allow obtaining suitable LOD for all analytes, this mass was chosen for the MIC procedure. The temperature achieved during combustion of 500 mg of coal was about 1430 °C, assuring a complete oxidation of coal samples.

3.2. Influence of absorbing solution on As, Cd, Hg and Pb recoveries using MIC

The absorbing solution has an important role because the type and concentration could not be the same for different analytes as well as the time for absorption. In MIC procedure, if microwave radiation is applied after the combustion step, the absorbing solution can quickly reflux making possible to obtain an effective washing of the sample holder and internal parts of vessels improving quantitative analyte recovery [19,32]. In this way, a systematic study was carried out by evaluating the concentration of HNO₃ as absorbing solution in order to select a suitable medium for all analytes.

Spike recoveries in a noncertified coal sample (Brazilian coal A) were evaluated for each absorbing solution (1.7, 3.5, 5.0, 7.0 and 14 mol L⁻¹ HNO₃) as well as the effect of using an additional reflux step. Results obtained using different absorbing solutions are shown in Fig. 2. For these tests As, Cd and Pb determination was carried out by ICP-MS and Hg determination was performed by CF-CV-ICP-MS. Maximum recoveries, about 80%, were obtained for As using 1.7 mol L⁻¹ nitric acid and without a reflux step. Recoveries obtained for this element using 3.5, 5.0 and 7.0 mol L⁻¹ HNO₃ and without a reflux step were very similar than those obtained using 1.7 mol L⁻¹ nitric acid (results not shown in Fig. 2). However, using an additional reflux step of 5 min after combustion, recoveries were better than 97% using 3.5–14 mol L⁻¹ HNO₃ as absorbing solution (Fig. 2). The RSD for 3.5 mol L⁻¹ HNO₃ was lower than 6% and using 5.0, 7.0 and 14 mol L⁻¹ HNO₃ it was lower than 3% showing the

improvement of analyte recovery when using an additional reflux step.

Results obtained for Cd were similar with those obtained for As. Without a reflux step after combustion, recoveries lower than 90% were obtained using diluted acids solutions. With the use of 14 mol L⁻¹ HNO₃ recoveries were between 90 and 93% and the RSD was lower than 10%. On the other hand, with an additional reflux step cadmium recoveries were practically the same (98–103%) using absorbing solution with concentration higher than 3.5 mol L⁻¹ HNO₃. In this case, RSD values were lower than 4% (Fig. 2).

For Hg, recoveries from 90 to 101% were obtained without the reflux step for all absorbing solutions (RSD lower than 6%). Moreover, using a reflux step after combustion better recoveries (from 99 to 102%) for Hg were obtained for all absorbing solutions (RSD < 5%, Fig. 2). Therefore, for this element any of the absorbing solutions evaluated could be used assuring quantitative recoveries.

For lead different results were obtained when compared with other analytes. For this element, using 1.7, 3.5 and 5.0 mol L⁻¹ HNO₃ recoveries were not higher than 80, 85 and 94%, respectively, and the RSD was not better than 10% (tests performed without a reflux step). However, using 7.0 mol L⁻¹ HNO₃ as absorbing solution and an additional reflux step, recoveries were better than 98% and the RSD was lower than 4%.

Experiments were also performed with the same absorbing solutions but using a reflux step of 10 min instead of 5 min. However, the results obtained for all elements were very similar to those obtained using 5 min of reflux step, showing that 5 min of reflux was enough to ensure maximum analyte absorption. It is important to emphasize that lower values of RSD were obtained when the reflux step was applied and this effect could be explained due to more efficient leaching of internal vessel wall when compared to other processes such as, e.g., manual shaking.

Due to the different ash content of certified and Brazilian coal samples, experiments were performed using 1.7–14 mol L⁻¹ HNO₃ absorbing solutions for NIST 1632c, BCR 40, SARM 19 and SARM 20, which have ash content of 7.2, 7.8, 24.8 and 30.1%, respectively. It was observed that for CRMs with lower ash content (NIST 1632c and BCR 40), the accuracy with certified values was higher than 97% for all elements using 5.0 mol L⁻¹ HNO₃. However, for SARM 19 and SARM 20, accuracy better than 97% for all elements was obtained only using at least 7.0 mol L⁻¹ HNO₃ solution. Therefore, it is possible to conclude that for coals with ash content below about 8%, a 5.0 mol L⁻¹ HNO₃ could be used as absorbing solution for further As, Cd, Hg and Pb determination. For coals with higher ash content, a 7.0 mol L⁻¹ HNO₃ solution must be used.

It is important to point out that for routine analysis the possibility of using a single solution for simultaneous absorption of As, Cd, Hg and Pb in coal is an important aspect. This study showed that MIC procedure using only 5.0 mol L⁻¹ HNO₃ (or 7.0 mol L⁻¹ HNO₃ for samples with higher ash content) and 5 min of reflux was suitable for further determination of As, Cd and Pb by ICP-MS or ICP OES and Hg by CF-CV-ICP OES or CF-CV-ICP-MS. In addition, using the selected absorbing solutions, recoveries higher than 97% with RSD lower than 4% for all analytes were obtained.

3.3. Determination of As, Cd, Hg and Pb in coal and CRM samples after MIC procedure

In order to evaluate the applicability of MIC for coal digestion for further As, Cd, Hg and Pb determination, the proposed procedure was applied for CRMs and coal samples with different SiO₂ content taking into account the similar matrix composition. A 5.0 mol L⁻¹ HNO₃ solution was used as absorbing solution for MIC with 5 min of reflux. Digests were analysed by ICP-MS and ICP OES and the results are shown in Table 2. For all the analytes no statistical difference

Table 2
Results for As, Cd, Hg and Pb in Brazilian coals and CRMs using MIC digestion procedure and determination by ICP-MS and ICP OES (values represent the mean and standard deviation for $n=3$).

Element	Sample	Concentration ($\mu\text{g g}^{-1}$)		
		ICP OES	ICP-MS	Certified value
As	NIST 1632c	6.38 ± 0.25	6.49 ± 0.23	6.18 ± 0.27
	SARM 19	6.97 ± 0.26	7.04 ± 0.25	7 (6–8) ^b
	SARM 20	4.45 ± 0.15	4.40 ± 0.14	4.7 (4.6–6.0) ^b
	BCR 40	12.9 ± 0.50	13.1 ± 0.49	13.2 ± 1.1
	Brazilian coal A	6.20 ± 0.24	6.25 ± 0.20	–
	Brazilian coal B	7.32 ± 0.28	7.45 ± 0.27	–
	Brazilian coal C	5.35 ± 0.20	5.44 ± 0.20	–
	Cd	NIST 1632c	<0.12	0.069 ± 0.002
SARM 19		<0.12	0.11 ± 0.01	–
SARM 20		<0.12	0.078 ± 0.010	–
BCR 40		<0.12	0.12 ± 0.01	0.11 ± 0.02
Brazilian coal A		0.16 ± 0.01	0.15 ± 0.01	–
Brazilian coal B		<0.12	0.055 ± 0.002	–
Brazilian coal C		<0.12	0.052 ± 0.002	–
Hg ^a		NIST 1632c	<0.25	0.099 ± 0.003
	SARM 19	<0.25	0.20 ± 0.01	0.2 ^c
	SARM 20	<0.25	0.24 ± 0.01	0.25 (0.18–0.27) ^b
	BCR 40	0.37 ± 0.01	0.38 ± 0.01	0.35 ± 0.06
	Brazilian coal A	<0.25	0.23 ± 0.01	–
	Brazilian coal B	<0.25	0.066 ± 0.002	–
	Brazilian coal C	<0.25	0.095 ± 0.003	–
	Pb	NIST 1632c	3.65 ± 0.14	3.62 ± 0.12
SARM 19		20.5 ± 0.8	20.2 ± 0.8	20 (17–23) ^b
SARM 20		23.4 ± 0.9	24.8 ± 0.9	26 (20–29) ^b
BCR 40		23.8 ± 0.8	23.9 ± 1.0	24.2 ± 1.7
Brazilian coal A		7.90 ± 0.29	7.90 ± 0.28	–
Brazilian coal B		3.30 ± 0.11	3.36 ± 0.11	–
Brazilian coal C		4.58 ± 0.16	4.62 ± 0.15	–

^a Determination by CF-CV-ICP OES or CF-CV-ICP-MS.

^b Values represents the mean and the confidence level.

^c Informed value.

(t test, $P < 0.05$) was observed between results obtained by both determination techniques. Additionally, the agreement of results obtained with certified values was better than 95% for all analytes.

The concentrations of As, Cd, Hg and Pb in Brazilian coal samples were in the range of 5.3–7.5, 0.05–0.15, 0.06–0.23 and 3.3–7.9 $\mu\text{g g}^{-1}$, respectively (determination by ICP-MS). The limit of quantification (LOQ, 10σ , $n = 10$) by ICP-MS determination was 0.009, 0.0018 and 0.0032 $\mu\text{g g}^{-1}$, respectively for As, Cd, and Pb and 0.0027 $\mu\text{g g}^{-1}$ for Hg determination by CV-ICP-MS. For ICP OES determination, the LOQ for As, Cd, and Pb was 1.8, 0.12 and 0.16 $\mu\text{g g}^{-1}$, respectively and 0.25 $\mu\text{g g}^{-1}$ for Hg determination by CV-ICP OES.

In a general way, MIC was suitable for As, Cd, Hg and Pb determination in different coal samples with variable content of each analyte. In addition, the MIC procedure avoided the use of concentrated acids or excessive volume of reagents, reducing blank values and the generation of laboratory effluents.

3.4. Comparison of the proposed procedure with MAD and ASTM procedures

Microwave-assisted digestion in high-pressure closed vessels and ASTM procedures were carried out for comparison of results with those by using the proposed method by MIC. Results are shown in Table 3. Although similar results in comparison to MIC have been obtained using MAD procedure (t test, $P < 0.05$), using MAD more acid residues were generated and higher blank values were obtained. For ASTM recommended procedure, the results for Hg obtained were lower than those obtained using the proposed MIC procedure. It could be supposed that analyte losses have occurred in view of the high temperature using ASTM procedure (about 500 °C) and the sample preparation to

be carried out in an open vessel. In addition, only the results for Pb using ASTM procedure were similar (t test, $P < 0.05$) to MIC.

Therefore, MAD and ASTM procedures were not suitable for the subsequent determination of As, Cd, Hg and Pb in coal samples using a single solution. In addition, these procedures were more time consuming than the proposed procedure. Using MIC with a reflux step, it was possible to determine As, Cd, Hg and Pb by ICP-MS and ICP OES in coal and the total required time was only 25 min, for up to eight samples simultaneously processed.

Table 3

Comparison of results obtained for As, Cd, Pb (ICP-MS) and Hg (CF-CV-ICP-MS) after sample digestion by MIC, MAD and ASTM procedures (values represent the mean and standard deviation for $n = 3$).

Element	Concentration ($\mu\text{g g}^{-1}$)			
	Sample	MIC	MAD	ASTM
As	Brazilian coal A	6.25 ± 0.20	6.03 ± 0.73	nd ^a
	Brazilian coal B	7.45 ± 0.27	nd ^a	3.31 ± 0.52
	NIST 1632c ^b	6.49 ± 0.23	nd ^a	2.79 ± 0.31
Cd	Brazilian coal A	0.15 ± 0.01	0.137 ± 0.05	nd ^a
	Brazilian coal B	0.055 ± 0.002	nd ^a	0.16 ± 0.13
	NIST 1632c ^b	0.069 ± 0.002	nd ^a	0.22 ± 0.04
Hg	Brazilian coal A	0.23 ± 0.01	0.21 ± 0.31	nd ^a
	Brazilian coal B	0.066 ± 0.002	nd ^a	<0.003
	NIST 1632c ^b	0.099 ± 0.003	nd ^a	<0.003
Pb	Brazilian coal A	7.90 ± 0.28	8.1 ± 0.6	nd ^a
	Brazilian coal B	3.36 ± 0.11	nd ^a	3.60 ± 0.38
	NIST 1632c ^b	3.62 ± 0.12	nd ^a	3.43 ± 0.28

^a nd = not determined.

^b NIST 1632c certified values ($\mu\text{g g}^{-1}$): As: 6.18 ± 0.27; Cd: 0.072 ± 0.007; Hg: 0.0938 ± 0.0037; Pb: 3.79 ± 0.07.

3.5. Residual carbon content in digests

The RCC has been currently used to evaluate the efficiency of digestion procedures [18,39]. In this work, RCC was determined in samples digested by MIC and by microwave-assisted digestion, following the procedure reported in previous work [19]. Using MAD the RCC was about 15% whereas the RCC in MIC digests was always below 1% which is in the same level of results commonly mentioned for dry ashing or combustion techniques. The low RCC obtained with the proposed procedure could be explained by the high temperature (about 1400 °C) during combustion. Under this condition practically all the organic matrix is oxidized, which prevents interferences on ICP-MS determinations.

4. Conclusions

The proposed MIC procedure was suitable for coal digestion for subsequent determination of As, Cd and Pb by ICP OES and ICP-MS, determination by CF-CV-ICP OES or CF-CV-ICP-MS. It was possible to digest up to eight samples simultaneously using sample masses up to 500 mg. It is important to point out that in addition to the necessity of environmental control to minimize contamination the ASTM procedure was not suitable in view of the analyte losses. Contrarily of the other combustion techniques, MIC allowed a reflux step that minimizes potential losses due to analyte adsorption. In general, the proposed procedure showed good performance for coal digestion due to complete oxidation of the organic matrix, safety, and relatively high throughput, which is important for routine analysis. Moreover, as only diluted nitric acid was necessary, lower volume of effluents generation can be expected when compared with conventional procedures of digestion. This aspect is important in view of green chemistry recommendations.

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