

Microwave-Induced Combustion of Coal for Further Sulfur Determination by Inductively Coupled Plasma Optical Emission Spectrometry or Ion Chromatography

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In this work, a method using microwave-induced combustion (MIC) was optimized in order to obtain a fast, simple, efficient and greener sample preparation method for coal digestion and further determination of sulfur by inductively coupled plasma optical emission spectrometry (ICP OES). Accuracy was evaluated by comparison of the results with those obtained using elemental analysis by UV-fluorescence, microwave-assisted acid digestion with determination by ICP OES and by analysis of certified reference materials of coal. Some parameters that influence MIC method, such as the type and concentration of absorbing solution, the necessity of using a reflux step as well as the cooling time were carefully optimized. No statistical difference was observed for combustion without reflux followed by 5 min of cooling, in comparison to the reference values obtained by elemental analysis. Complete digestion was obtained with this fast and simple method (total digestion program required only 6 min) and using a diluted acid solution for quantitative recovery. The feasibility of digests for sulfur determination as sulfate by ion chromatography (IC) with conductivity detection was also demonstrated. The possibility of determining other elements, commonly monitored in coals, is another advantage of this high-efficiency digestion method (MIC) combined with the multielemental capacity of ICP OES or IC instruments.

Keywords: coal, sample preparation, sulfur, MIC, ICP OES

Introduction

Despite the environmental impact related to coal combustion it remains as one of the main energy sources used worldwide. One drawback for its use is that coal contains a variety of elements that are released to the atmosphere during coal processing.^{1,2} Among these elements, sulfur is a major component and its combustion process contributes to the sulfur emission (as SO₂ and SO₃). In the atmosphere, those molecules can react with water resulting in acid rain, with significant environmental impacts.³ Additionally, the sulfur content also impacts on the coal price, because it is directly related to the corrosion of equipment in processing power plants and defines the technology used for the desulfurization of coal.⁴

Due to the widespread use of coal and the importance of determining the content of sulfur, the development of a simple, fast and efficient method, in agreement with green chemistry recommendations is required. The American Society for Testing and Materials (ASTM) in ASTM D 4239-97⁵ method proposes the determination of sulfur in coal samples by titration. This method involves the sample burning in a furnace at 1350 °C for oxidation of sulfur to SO₂ and SO₃. Afterwards, determination can be carried out by acid-base or iodimetric titration, or by infrared absorption. In spite of some commercial instruments available for this purpose, the method requires calibration with certified reference materials (CRMs) and can be influenced by different species of sulfur or changes in matrix composition.

Some alternative methods have been proposed in the literature, but most of them showed the difficulties associated with coal digestion.⁶⁻⁸ Alternatively, direct analysis of

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coal was proposed by Baysal and Akman,⁹ using a high-resolution continuum source flame atomic absorption spectrophotometer by means of molecular absorption of CS formed in an air-acetylene flame. Baumbach and Einax¹⁰ used a direct solid sampling system coupled to high-resolution continuum source graphite furnace molecular absorption spectrometry (SS-HR-CS-GF MAS) for the determination of sulfur in coal by molecular absorption of SnS. Methods based on X-ray fluorescence have been also used, but are commonly affected by poor precision and, sometimes, by matrix interferences.¹¹ To overcome these problems, calibration with CRMs containing similar matrix or matrix matching are recommended to obtain accurate measurements. Alternatively, laser ablation inductively coupled plasma isotope dilution mass spectrometry (LA-ICP-IDMS),¹² electrothermal vaporization (ETV), inductively coupled plasma optical emission spectrometry (ICP OES) and ETV inductively coupled plasma mass spectrometry (ICP-MS)¹³ have been also used for the determination of sulfur, sulfur species and halogens.¹⁴

Additionally, the determination of sulfur can be performed using spectrometric (ICP OES or ICP-MS) or chromatographic (ion chromatography (IC) with conductivity detection) techniques. However, these techniques conventionally require bringing the analyte into an aqueous solution. Then, an efficient sample preparation method is needed and commonly is based on dry ashing, fusion or acid dissolution.¹⁵ Despite being one of the best options for organic matrices (e.g., coal), dry ashing is susceptible to analyte losses and thus can be considered not suitable for sulfur. Regarding the fusion method, the high salt content in digests can be a problem for measurements by ICP OES.^{15,16} Microwave-assisted wet digestion (MAWD) using concentrated acids (HNO₃, HCl and/or HF) for dissolution of organic and inorganic matrices is the most frequently method reported in literature.¹⁷⁻²¹ Nevertheless, high residual acidity and high carbon content in digests when digestion is not complete can interfere during elements determination by ICP OES.²² Especially for coal digestion, time consuming procedures and the use of high amounts of concentrated acids (HNO₃, HCl, HF and even HClO₄) have been commonly reported,⁸ despite other authors have proposed the use of H₂O₂.²³

Well-known as a high efficient method for digestion of organic matrices, combustion has been proposed for coal digestion and further determination of minor and major elements as well as for trace elements by spectrometric techniques. However, the possibility of losses of sulfur are mentioned due to the high temperature achieved inside the furnace.¹⁵ An alternative for digestion of coal is based on combustion in closed vessel, particularly suitable for

volatile analytes. Geng *et al.*²⁴ proposed the use of oxygen flask combustion (OFC) method for sample preparation of coal and further sulfur determination by ICP OES, using 6% H₂O₂ as absorbing solution demonstrating the potential of combustion methods for sample preparation of coals for sulfur determination.

Among the combustion methods, microwave-induced combustion (MIC) was demonstrated to be suitable for digestion of organic matrices, bringing the analytes into the absorbing solution. The advantages of MIC are the low residual carbon content (RCC) in digests, minimizing matrix interferences, the possibility of using absorbing solutions according to the analyte and detection technique (e.g., using alkaline solutions for halogens by IC or diluted acid solution for metals by ICP OES).²⁵ Antes *et al.*²⁶ showed the feasibility of MIC for digestion of 500 mg of coal. The absorbing solution was evaluated and diluted acid was employed. Flores *et al.*²⁷ used MIC for sample preparation of coal and further determination of halogens by IC, using 50 mmol L⁻¹ (NH₄)₂CO₃ as absorbing solution.

In this work, a MIC method was optimized for coal digestion for further sulfur determination by ICP OES. Parameters of MIC, such as absorbing solution and heating program were investigated. Results were compared with those obtained by elemental analysis (UV-fluorescence detection) and MAWD with determination by ICP OES. Certified reference materials of coal were also used for accuracy evaluation. Suitability of digests for sulfur determination by IC was evaluated and the feasibility of MIC for simultaneous sulfur and halogens determination in coal was demonstrated.

Experimental

Instrumentation

Coal was digested by MIC using a microwave oven (Multiwave 3000[®] microwave sample preparation system, Anton Paar, Graz, Austria, software version v1.27-Synt) running with a maximum pressure rate of 3 bar s⁻¹, which was modified from its original value (0.8 bar s⁻¹) to avoid interrupting microwaves during the combustion of samples. This system was equipped with up to eight high-pressure quartz vessels with 80 mL of internal volume and maximum operational temperature and pressure of 280 °C and 80 bar, respectively. Homemade quartz holders were used to introduce the samples inside the quartz vessels. Additionally, samples of coal were digested by MAWD using the same microwave system running with a maximum pressure rate of 0.8 bar s⁻¹. For MAWD, this system was equipped with up to sixteen polytetrafluoroethylene (PTFE)

vessels with 100 mL of internal volume and maximum operational temperature and pressure of 220 °C and 40 bar, respectively.

Sulfur and carbon determination was performed using an ICP OES with axial view configuration (Spectro Ciros CCD, Spectral Analytical Instruments, Kleve, Germany). Instrumental parameters are described in Table 1.

Table 1. Operational conditions for the determination of sulfur and carbon by ICP OES

Parameter	ICP OES
RF power / W	1400
Plasma gas flow rate / (L min ⁻¹)	12
Auxiliary gas flow rate / (L min ⁻¹)	1
Nebulizer gas flow rate / (L min ⁻¹)	1
Spray chamber	double pass Scott type
Nebulizer	cross-flow
Observation view	axial
Wavelength / nm	S (180.731) C (193.030)

An ion chromatograph (model 850 Professional IC, Metrohm, Herisau, Switzerland) equipped with an 858 Professional sample processor and conductivity detector was used for the determination of sulfur (as sulfate), as well as bromide, chloride and fluoride. An analytical column (Metrosep A Supp 5, Metrohm, 150 × 4 mm i.d., particle size 5 µm and polyvinyl alcohol with quaternary ammonium groups) was used. A guard column (Metrosep A Supp 5 Guard, Metrohm) with the same material was used. Additionally, a self-regeneration suppressor from Metrohm was used to reduce the conductivity of the mobile phase. The mobile phase was composed by a solution of 3.2 mmol L⁻¹ Na₂CO₃ and 1.0 mmol L⁻¹ NaHCO₃. The mobile phase flow rate was set at 0.7 mL min⁻¹ and a sample loop of 20 µL was used.

An analytical balance (AY 220, Shimadzu, Kyoto, Japan, 220 g, 0.0001 g of resolution) was used for weighing samples. A hydraulic press (Manual Hydraulic press 15 ton, Specac, Orpington, UK) was used for pressing samples as pellets, using 2 ton for 1 min. For results comparison, a total sulfur analyzer (Multi EA[®], Analytik Jena, Jena, Germany) was used for direct determination in coal samples by UV-fluorescence, based on ASTM D 5453-03.²⁸ Instrumental parameters are described in Table 2. In this case, samples were directly weighed in the platforms, which were inserted into the combustion tube by an automatic auto sampler.

All statistical calculations, including Student's *t*-test (confidence level of 95%, *p* > 0.05) and, in some cases,

Table 2. Operational conditions for sulfur determination by UV-fluorescence using an elemental analyzer

Parameter	Value
Combustion tube temperature / °C	1050
O ₂ flow rate (carrier) / (mL min ⁻¹)	100
time of combustion / s	90
O ₂ flow rate (combustion tube) / (mL min ⁻¹)	300
Ar flow rate (carrier) / (mL min ⁻¹)	100

one-way analysis of variance (ANOVA) were performed using GraphPad InStat (GraphPad InStat Software Inc, San Diego, CA, USA, version 3.00, 1997) software.

Reagents, samples and solutions

Water was purified using a Milli-Q system, (Millipore, Billerica, MA, USA, 18.2 MΩ cm) and it was used for preparation of standards and absorbing solutions. Concentrated HNO₃ (Merck, Darmstadt, Germany) was distilled in a sub-boiling system (DuoPur, Milestone, Sorisole, Italy) which was used for MAWD and as absorbing solution for MIC. Concentrated HF (40% v/v, Sigma-Aldrich, St. Louis, MO, USA) was used without previous purification for digestion by MAWD. Ammonium nitrate solution (6 mol L⁻¹) (Merck) and disks of filter paper (15 mm of diameter, about 15.3 ± 0.3 mg) with low ash content (Black Ribbon Ashless, Schleicher and Schuell, Dassel, Germany) were used as igniter aid for MIC. Ammonium carbonate (Merck), NH₄OH (28% v/v, Merck) and H₂O₂ (30% v/v, Merck) were used to prepare the absorbing solutions for MIC. Salts of Na₂CO₃ (Merck) and NaHCO₃ (Merck) were used to prepare the mobile phase, while H₂SO₄ (Merck) was used to prepare the solution used for suppression column regeneration.

Coal samples were obtained from coal industries from Rio Grande do Sul and Santa Catarina States, in Brazil and were named as A, B and C. The ash content in these samples ranged from 14 to 32%. Certified reference materials of coal were used: National Institute of Standards and Technology (NIST) 1632c, SARM 19 from Council for Mineral Technology, Republic of South Africa and BCR 181 (coking coal) from Institute for Reference Materials and Measurements (IRMM).

A sulfur standard solution (10 mg L⁻¹, Spex Certiprep, Metuchen, USA) was used to prepare the calibration solutions for sulfur determination by ICP OES (from 0.1 to 10 mg L⁻¹). For sulfur determination by UV-fluorescence using elemental analysis a white mineral oil containing 5000 µg g⁻¹ of sulfur (AccuStandard, New Haven, CT, USA) was used to prepare analytical standards from 10 to

250 $\mu\text{g g}^{-1}$ by sequential dilution in toluene (Tedia, Fairfield, OH, USA). A standard solution for anions (10 mg kg^{-1} , Fluka, Sigma-Aldrich, in water) was used to prepare standard solutions (from 10 to 1000 $\mu\text{g L}^{-1}$) for calibration of IC instrument. For RCC determination, a stock reference solution was prepared by dissolution of citric acid (Vetec, Rio de Janeiro, Brazil) in water and yttrium (Fluka, Sigma-Aldrich, 1000 mg L^{-1}) was added as internal standard (final concentration of 1 mg L^{-1}).

For plasma generation, nebulization and as auxiliary gas, as well as a supply for the elemental analyzer, argon with a purity of 99.996% (White Martins-Praxair Inc., São Paulo, Brazil) was used. Oxygen (99.6%, White Martins-Praxair Inc.) was used for MIC and to supply oxygen for the elemental analyzer.

Sample preparation

Microwave-induced combustion

Microwave-induced combustion was evaluated using 250 mg of sample which was pressed as a pellet. Pellet of sample was placed in a disk of filter paper on the quartz holder containing 50 μL of 6 mol L^{-1} NH_4NO_3 solution. The holder was placed inside the quartz vessel containing 6 mL of absorbing solution (2 mol L^{-1} HNO_3 , 14 mol L^{-1} HNO_3 , H_2O , 5% H_2O_2 , 50 mmol L^{-1} NH_4OH or 50 mmol L^{-1} $(\text{NH}_4)_2\text{CO}_3$). The vessels were pressurized with oxygen at 20 bar for 1 min. The microwave heating program was optimized to achieve a faster and effective digestion by MIC. Thus, the reflux step and the cooling time were evaluated from 60 s to 15 min and from 0 to 20 min, respectively. Maximum microwave power (1400 W) was used to allow ignition and to maintain the heating for reflux of absorbing solution. After heating, digests were diluted with ultrapure water up to 25 mL.

Microwave-assisted digestion

Coal samples (250 mg) were weighed and placed into the PTFE vessels with 7 mL of 14 mol L^{-1} HNO_3 and 1 mL of 40% HF. The heating program was: (i) 1400 W for 40 min (ramp of 10 min) and (ii) 0 W for 20 min (cooling step). After heating, the digests were diluted up to 25 mL and analyzed by ICP OES.

Results and Discussion

Optimization of MIC: sample mass, ignition and combustion time

The use of MIC as a method for digestion of organic samples has been demonstrated for many solid matrices such

as petroleum coke,²⁹ pitch,³⁰ carbon nanotubes,³¹ polymers,³² food and biological materials,³³⁻³⁵ among others. Even though MIC method can be considered simple and a general protocol can be proposed,³⁶ a careful optimization regarding sample mass and combustion behavior must be performed. Taking into account some differences in matrices and analytes, high pressure and incomplete combustion can be observed for some materials, providing a non-quantitative analytes recovery. In these cases, some additives³⁷ and/or changes are required in the conventional protocol.³⁸

Initial experiments were performed with sample masses from 100 to 500 mg and with oxygen pressure of 20 bar, in order to achieve safe conditions during coal combustion. The increase of sample mass is important for obtaining better limits of quantification (LOQs). These results are shown in Figure 1.

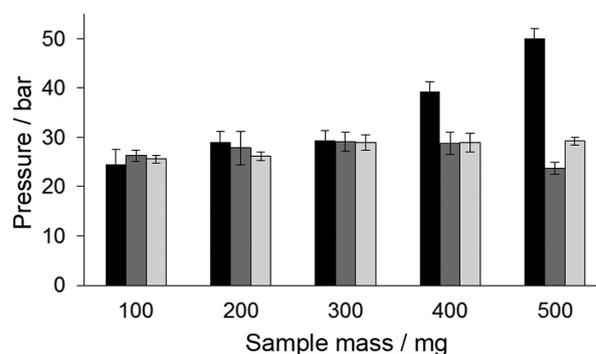


Figure 1. Maximum pressure reached during combustion of 100 to 500 mg of coal A (■), B (■) and C (□).

It is possible to see in Figure 1 that samples presented different behavior, mainly for higher sample mass (400 and 500 mg). This was probably a consequence of the organic content of samples (74, 53 and 30% of carbon content for samples A, B and C, respectively). Considering sample A, the combustion of 500 mg of sample exceeded about 50% of maximum pressure that quartz vessels support (80 bar). Thus, due to safety reasons, 500 mg was the maximum sample mass that was considered suitable for coal digestion using MIC. It is important to emphasize that when using coal with higher inorganic fraction (sample C), maximum pressure was only about 30 bar, allowing safe conditions. Considering the determination of sulfur in coal by ICP OES, sample mass selected for further experiments was 250 mg, since high concentration of this element is commonly found in fossil fuels. Nevertheless, this study was very important for knowing the associated risk of combustion of a given sample, and to investigate the possibility of increasing the sample mass for improving the LOQ for analytes at low concentration or for application of this method for low sulfur content coals.

Table 3. Ignition time, combustion time and maximum pressure for coal digestion using MIC (values represent the mean and standard deviation, $n = 3$)^a

Sample	Sample mass / mg	Ignition time / s	Combustion time / s	Maximum pressure / bar
A	247 ± 2	4	40 ± 9	29.4 ± 0.5
B	253 ± 6	5	53 ± 16	27.7 ± 0.1
C	248 ± 2	2	60 ± 10	26.7 ± 0.7

^aInitial O₂ pressure of 20 bar and 6 mL H₂O as absorbing solution.

In addition to the study of sample mass, the ignition time and combustion time were also investigated and results are shown in Table 3. The ignition time ranged from 2 to 4 s after microwave irradiation had been started and the combustion time ranged from 40 to 60 s. For samples with higher ash content, the complete combustion of organic fraction required longer time (about 60 s), which is an important aspect considering the temperature inside the vessel for analyte recovery and the time selected for reflux of absorbing solution.

Optimization of absorbing solution

It is well established in the literature that the absorbing solution used to retain the analytes in MIC procedure is an important parameter since it can affect the analytes recovery.²⁵ In general, to retain metals and metalloids and in order to obtain digests suitable for determination by plasma-based techniques (e.g., ICP OES and ICP-MS) the use of diluted nitric acid has been recommended.²⁶ On the other hand, for halogens absorption and further determination by ICP OES, ICP-MS or IC, alkaline diluted solutions have been reported as more suitable.^{27,34} Thus, a study to select the suitable absorbing solution for sulfur was performed. Sample C was selected for these experiments since it presents the higher ash content and remains longer time burning. Thus, 6 mL of 14 mol L⁻¹ HNO₃, 2 mol L⁻¹ HNO₃, H₂O, 5% H₂O₂, 50 mmol L⁻¹ NH₄OH and 50 mmol L⁻¹ (NH₄)₂CO₃ were evaluated. Results were compared with those obtained using elemental analyzer by UV-fluorescence, which were used as reference for all evaluations (Figure 2).

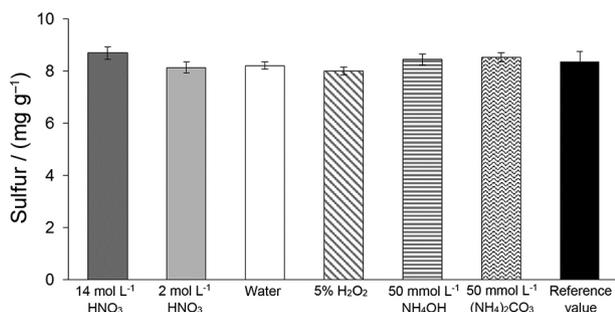


Figure 2. Evaluation of absorbing solution for sulfur recovery using MIC. Reference values (obtained using elemental analysis by UV-fluorescence) are shown for comparison (■). Determination by ICP OES, $n = 3$.

No statistical difference ($p > 0.05$) was observed comparing all solutions and reference value. Therefore, the solution can be chosen according to the instrument selected for analyte detection or if other analytes are of interest. For example, water or alkaline solutions are suitable for the determination by IC whereas diluted HNO₃ is suitable for determination by plasma-based techniques. Additionally, it is important to mention that diluted HNO₃, H₂O, H₂O₂ or alkaline solutions show some advantages such as low consumption of reagents and low residues generation, in agreement with greening sample preparation.³⁹

Optimization of heating program

Methods using MIC previously reported in the literature for many matrices recommend the use of at least 5 min of reflux for quantitative analytes recovery.^{27,33,34} The reflux step is commonly necessary for washing the holder and internal vessel walls, thus ensuring the recovery of analytes. This is an important advantage of MIC in comparison with OFC and combustion bomb methods.³⁶ Thus, the use of a reflux step was evaluated (5 and 15 min of reflux or only combustion without reflux). For these experiments, the heating program was: (i) MIC without reflux: 60 s of microwave irradiation (1400 W) for burning the sample, followed by 20 min of cooling; or (ii) MIC with reflux: 5 or 15 min of microwave irradiation (1400 W) for burning the sample and reflux of the absorbing solution, followed by 20 min of cooling. Results are shown in Figure 3a and are compared with the reference values (elemental analysis by UV-fluorescence).

From this study, no statistical difference was observed ($p > 0.05$) between the results obtained with reflux (5 or 15 min) and without reflux in comparison with the reference value. Thus, the heating program without reflux was chosen in order to propose a fast method. An important aspect regarding the use of a reflux step is that the relative standard deviation (RSD) was about 3% using the reflux step. In contrast, when no reflux was applied the RSD was slightly worse (about 7%), but still can be considered feasible for an analytical method. Thus, in order to propose a fast method, MIC without reflux was preferred and further experiments were carried out

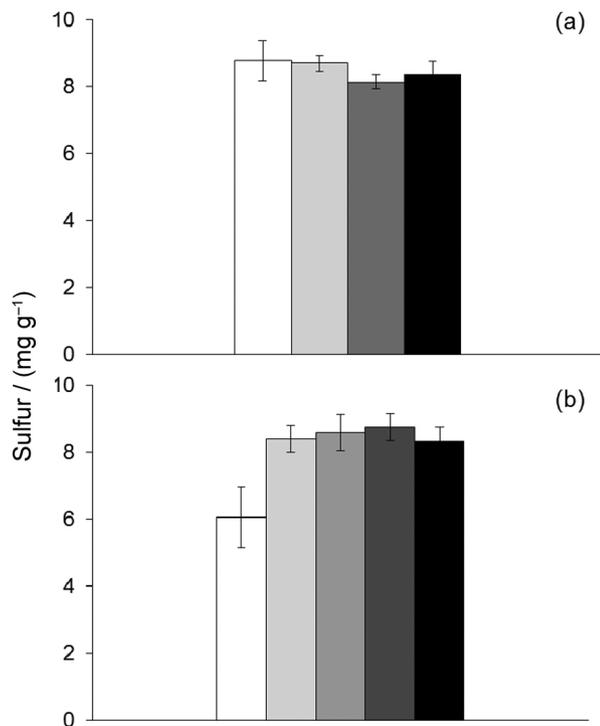


Figure 3. (a) Evaluation of reflux step after MIC: MIC without reflux step (□), MIC with reflux (5 min, ◻) and MIC with reflux (15 min, ◼); and (b) effect of cooling step: 0 min (□), 5 min (◻), 10 min (◼) and 20 min (◼) on sulfur recovery. Reference values (obtained using elemental analysis by UV-fluorescence) are shown for comparison (◼). Determination by ICP OES, $n = 3$.

to optimize the cooling step. For these experiments the heating program was set as MIC without reflux (60 s for burning the sample), followed by: (i) no cooling; (ii) 5 min of cooling; (iii) 10 min of cooling; or (iv) 20 min of cooling. Results are shown in Figure 3b.

Results obtained using no cooling time (just opening the vessels immediately after 60 s of combustion) were lower than the reference values (sulfur recovery about 70%). No statistical difference was observed ($p > 0.05$) between the results obtained using 5, 10 or 20 min of cooling step in comparison with the reference values. Thus, the heating

program can be performed without reflux step, using just 60 s for sample burning followed by 5 min of cooling step, performing 6 min for a complete digestion program. This time can be considered as a fast sample preparation method mainly taking into account the “difficult to digest” characteristic of coal.

Accuracy of MIC method and comparison with MAWD

In order to evaluate the accuracy of the proposed MIC method, a MAWD method using concentrated HNO₃ and HF was performed for results comparison. Additionally, CRMs of coal (NIST 1632c and SARM 19) were digested under optimized conditions: MIC without reflux (1400 W for 60 s) followed by 5 min of cooling using 2 mol L⁻¹ HNO₃ as absorbing solution. The results for samples A, B and C obtained by ICP OES after digestion by MIC and MAWD are shown in Table 4, as well as the results obtained using the elemental analysis by UV-fluorescence and results for CRMs.

It was possible to observe that no statistical difference was observed (ANOVA, $p > 0.05$) by comparison of all methods for samples A, B and C. In addition, agreement with certified values was also obtained, showing the accuracy of the proposed MIC method for coal digestion and further sulfur determination. In particular for sulfur determination by plasma-based techniques (e.g., ICP OES), the carbon content in digests is an important parameter since it can cause interferences and some problems to the equipment. So, the carbon content in digests was determined and RCC was calculated based on the original carbon content in coal samples. The RCC values by MIC were below 0.5%. On the other hand, by MAWD method the RCC values were about 30%. The low RCC obtained by MIC method can be attributed to the high temperature (about 1400 °C) achieved during the coal combustion, assuring complete digestion of organic matrix and avoiding interferences in ICP OES measurements.²⁷

Table 4. Results for sulfur determination in coals and CRMs of coal obtained by ICP OES after MIC, MAWD and elemental analysis (values represent the mean and standard deviation, $n = 3$)

Sample	Sulfur / (mg g ⁻¹)			
	MIC	MAWD	Elemental analysis ^a	Certified value
A	12.1 ± 0.3	12.2 ± 0.9	13.9 ± 1.9	–
B	16.1 ± 0.4	16.4 ± 1.4	14.3 ± 1.7	–
C	8.40 ± 0.20	8.57 ± 0.36	8.36 ± 0.39	–
NIST 1632c	13.8 ± 0.3	13.7 ± 1.2	ND	14.6 ± 0.5
SARM 19	14.8 ± 0.3	14.1 ± 0.3	12.9 ± 1.6	14.9 ^b

^aDetermination by UV-fluorescence; ^bconfidence level is 14.2–15.5 mg g⁻¹. MIC: microwave-induced combustion; MAWD: microwave-assisted wet digestion; ND: not determined.

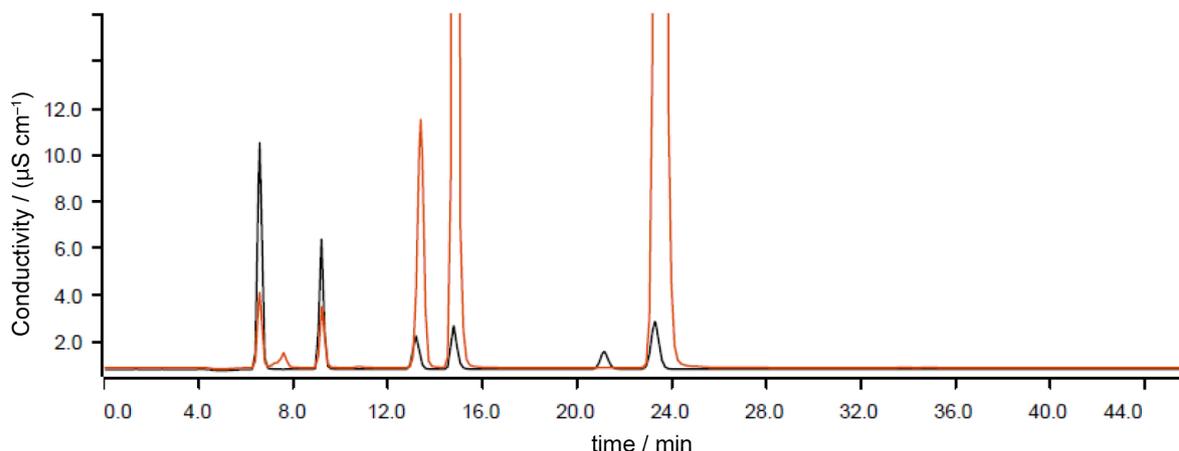


Figure 4. IC chromatograms for a $1000 \mu\text{g L}^{-1}$ standard solution of halogens and sulfate (—) and a MIC digest for coal A (—) diluted in water (10 times).

Another advantage of MIC in comparison with MAWD was the time required for digestion (6 min for MIC and 70 min for MAWD). In addition, the use of concentrated HNO_3 and HF was not necessary for MIC. Despite the simplicity of using the elemental analyzer, the digestion of coal by MIC for further determination by ICP OES allows the possibility of determining other analytes simultaneously. The limits of detection (LODs, 3σ) obtained by ICP OES were $2.5 \mu\text{g g}^{-1}$ using the proposed MIC method and $13 \mu\text{g g}^{-1}$ using MAWD.

Suitability of digests for IC and determination of sulfur and halogens

The possibility to determine sulfur using IC was also demonstrated taking into account that this is an instrument commonly available in many laboratories and also allows the simultaneous determination of sulfur and halogens. In this way, an alkaline solution (NH_4OH) was chosen to assure quantitative absorption of halogens according to a previous work.²⁷ A coal sample (A) and CRMs of coal (NIST 1632c, SARM 19 and BCR 181) were digested and analyzed by IC (250 mg of sample, 6 mL of 50 mmol L^{-1} NH_4OH as absorbing solution, heating program was 5 min of reflux and 20 min for cooling). The chromatograms of a $1000 \mu\text{g L}^{-1}$ standard solution and a digest of sample A (10 times diluted in water) are shown in Figure 4.

Results obtained for sulfur (as sulfate) by IC in coal samples (A, B and C) presented no statistical difference ($p > 0.05$) in comparison with the results obtained by ICP OES. In addition, it was possible to suppose that sulfate was the only species of sulfur present after MIC which is probably a consequence of the high oxygen pressure (20 bar) during combustion. In addition, results for CRMs were in agreement with the certified values for F in NIST 1632c ($70.3 \pm 3.9 \mu\text{g g}^{-1}$ was obtained by MIC and

certified value is $72.7 \pm 6.8 \mu\text{g g}^{-1}$), for Cl in NIST 1632c ($1114 \pm 52 \mu\text{g g}^{-1}$ was obtained by MIC and certified value is $1139 \pm 41 \mu\text{g g}^{-1}$) and also in BCR 181 ($1404 \pm 57 \mu\text{g g}^{-1}$ was obtained by MIC and certified value is $1380 \pm 50 \mu\text{g g}^{-1}$). For Br in SARM 19, the result obtained by MIC was lower than the LOD ($5.3 \mu\text{g g}^{-1}$) and the informed value is $2 \mu\text{g g}^{-1}$. Finally, results for sulfur (as sulfate) in CRMs obtained by IC after MIC were also in agreement with the certified values showing the feasibility of MIC for simultaneous determination of sulfur and halogens in coal.

Conclusions

The proposed MIC method was optimized for coal digestion and subsequent determination of sulfur by ICP OES. The proposed MIC method was performed without reflux followed by only 5 min of cooling step, allowing to propose a method that requires only 6 min for sample digestion. The results obtained by MIC for sulfur were in agreement with those obtained using MAWD and the reference values obtained using elemental analysis by UV-fluorescence. Agreement with certified values was also observed for the digestion of CRMs using MIC. Up to eight samples could be processed simultaneously in less time (only 6 min) by MIC in contrast to MAWD (70 min). This can be considered advantageous for routine analysis, comprising a fast and simple method and opening new possibilities for simultaneous determination of sulfur and other analytes in coal. The suitability of digests for IC was demonstrated by the simultaneous analysis of sulfur and halogens. Using the proposed MIC method it is possible to choose the absorbing solution according to the detection technique, providing digests with negligible carbon content, minimizing interferences and contributing to a greening sample preparation method.

Acknowledgments

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) for supporting this study.

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Submitted: November 18, 2015

Published online: February 1, 2016

FAPERGS/CAPES has sponsored the publication of this article.