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Determination of Halogens in Coal after Digestion Using the Microwave-Induced Combustion Technique

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The microwave-induced combustion (MIC) technique was applied for coal digestion and further determination of bromide, chloride, fluoride, and iodide by ion chromatography (IC). Samples (up to 500 mg) were combusted at 2 MPa of oxygen. Combustion was complete in less than 50 s, and analytes were absorbed in water or $(NH_4)_2CO_3$ solution. A reflux step was applied to improve analyte absorption. Accuracy was evaluated for Br, Cl, and F using certified reference coal and spiked samples for I. For Br, Cl, and F, the agreement was between 96 and 103% using 50 mmol L^{-1} $(NH_4)_2CO_3$ as the absorbing solution and 5 min of reflux. With the use of the same conditions, the recoveries for I were better than 97%. Br, Cl, and I were also determined in MIC digests by inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, and F was determined by an ion-selective electrode with agreement better than 95% to the values obtained using IC. Temperature during combustion was higher than 1350 °C, and the residual carbon content was lower than 1%. With the use of the MIC technique, up to eight samples could be processed simultaneously, and a single absorbing solution was suitable for all analytes and determination techniques (limit of detection by IC was better than 3 $\mu g\ g^{-1}$ for all halogens).

The content of trace elements in coal is relevant to evaluate the environmental impact during mining, processing, and usage.[1,2] On this aspect, the emission of air pollutants arising from the combustion process, coal gasification, or liquefaction plants are of great concern. Particularly to halogens their determination in coal is very important to evaluate the risks of environmental impact, mainly those caused by power plants based on coal combustion.[3,4]

Renewed interest in the use of coal as a raw material in the industrial processes has created an additional need for the development of rapid and accurate methods for coal analysis, especially those related to the content of halogens. In this direction, analytical techniques such as inductively coupled plasma mass spectrometry (ICPMS),[5,6] ion-selective electrode (ISE),[7,8] and ion chromatography (IC)[5,8,9] have been currently used for halogen determination after a suitable sample pretreatment. Inductively coupled plasma optical emission spectrometry (ICP OES) has also been used in spite of the few reports described in the literature for simultaneous halogen determination.[10] Unfortunately, coal samples are particularly difficult to bring into solution and generally require complex and time-consuming sample preparation procedures.[9,11] The most used procedures involve the digestion of coal using dry ashing,[9] fusion,[12] microwave-assisted wet digestion in closed vessels,[13,14] pyrohydrolysis,[15−17] and combustion techniques.[7,18−20]

Combustion in closed vessels using combustion bombs or oxygen flasks have been currently used for coal digestion due to the low residual carbon content (RCC) of the digests and the suitability for determination by electroanalytical or chromato-

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(1) Vassilev, S. V.; Eskenazy, G. M.; Vassileva, C. G. *Fuel* **2000**, *79*, 903−921.
(2) Boylan, H. M.; Cain, R. D.; Kingston, H. M. *J. Air Waste Manage. Assoc.* **2003**, *53*, 1318−1325.
(3) Julien, S.; Brereton, C. M. H.; Lim, C. J.; Grace, J. R.; Anthony, E. J. *Fuel* **1996**, *75*, 1655−1663.
(4) Domazetis, G.; Raoarun, M.; Liesegang, J.; Pigram, P. J.; Brack, N.; Glaisher, R. *Energy Fuels* **2006**, *20*, 1556−1564.
(5) Bettinelli, M.; Spezia, S.; Minoia, C.; Ronchi, A. *At. Spectrosc.* **2002**, *23*, 105−110.
(6) Rodushkin, I.; Axelsson, M. D.; Burman, E. *Talanta* **2000**, *51*, 743−759.
(7) Geng, W.; Nakajima, T.; Takanashi, H.; Ohki, A. *Fuel* **2007**, *86*, 715−721.
(8) Álvarez-Ayuso, E.; Querol, X.; Tomás, A. *Chemosphere* **2006**, *65*, 2009−2017.
(9) Nadkarni, R. A. *Anal. Chem.* **1980**, *52*, 929−935.
(10) Naozuka, J.; Veiga, M. A. M. S.; Oliveira, P. V.; Oliveira, E. *J. Anal. At. Spectrom.* **2003**, *18*, 917−921.
(11) Sulcek, Z.; Povondra, P. *Methods of Decomposition in Inorganic Analysis*; CRC Press: Boca Raton, Florida, 1989; p 62, 68, 138, 161.
(12) Wood, R. A., Dale, L. S.; Riley, K. W. *Fuel* **2003**, *82*, 1587−1590.
(13) Knapp, G.; Panholzer, F.; Schalk, A.; Kettisch, P. In *Microwave-Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications*; Kingston, H. M. (Skip), Haswell, S. J., Eds.; American Chemical Society: Washington, DC, 1997; pp 423−451.
(14) Wang, J.; Nakazato, T.; Sakanishi, K.; Yamada, O.; Tao, H.; Saito, I. *Anal. Chim. Acta* **2004**, *514*, 115−120.
(15) Dressler, V. L.; Pozebon, D.; Flores, E. L. M.; Paniz, J. N. G.; Flores, E. M. M. *J. Braz. Chem. Soc.* **2003**, *14*, 334−338.
(16) Doolan, K. J. *Anal. Chim. Acta* **1987**, *202*, 61−73.
(17) Godbeer, W. G.; Swaine, D. J.; Goodarzi, F. *Fuel* **1994**, *73*, 1291−1294.
(18) Thomas, J., Jr.; Gluskoter, H. J. *Anal. Chem.* **1974**, *46*, 1321−1323.
(19) Martinez-Tarazona, R.; Cardin, J. M. *Fuel* **1986**, *65*, 1705−1708.
(20) Nadkarni, R. A.; Pond, D. M. *Anal. Chim. Acta* **1983**, *146*, 261−266.

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graphic techniques.[7,18,20] The official methods proposed by the American Society for Testing and Materials (ASTM) recommend combustion bombs as the digestion technique for the subsequent determination of chloride and fluoride in coal.[21,22] However, despite their importance up to now, there are no methods recommended by ASTM for bromide and iodide determination in coal.

In general, combustion techniques represent a very effective way for coal digestion in view of the possibility to reach almost complete matrix destruction due to the high temperature achieved during combustion, in general higher than 1000 °C.[23−28] Oxygen flask and combustion bombs show some advantages such as the relatively short time for coal digestion, low risks of contamination, and the possibility to use more convenient absorbing solutions for the subsequent determination step. On the other hand, these techniques present some drawbacks such as (i) only one sample can be processed each time causing low throughput, (ii) depending on the analyte, the cleaning step of the vessel walls (and analyte dissolution) is not effective and it must be performed manually, and (iii) for the oxygen flask, the sample mass can be limited to only 50 mg.[29−31] In spite of these drawbacks, there are many applications of the oxygen flask and combustion bombs for coal digestion and further nonmetals determination.[18,20,24,32−34] However, for halogens some studies showed that, especially for combustion bombs, it is necessary to wait 1 h after combustion for analyte absorption in the solution. Moreover, the analyte remaining in the gaseous phase can be lost when the combustion device is opened.[34,35] These problems should be minimized if a reflux step could be applied after the combustion. However, this step is not possible for the conventional oxygen flask and combustion bomb techniques.

In order to minimize the drawbacks currently found for combustion systems, a technique based on microwave-induced combustion (MIC) was recently proposed.[36] This technique involves the combustion of organic samples in closed quartz vessels pressurized with oxygen, and ignition is performed by microwave radiation. The equipment is the same conventionally used for microwave-assisted wet digestion with minimal changes. This technique allows the combination of the advantages of classical combustion techniques with those using conventional closed systems heated by microwave radiation.[36] In this system, a small quartz holder is placed inside a quartz vessel containing a suitable absorbing solution. The ignition is performed by microwave radiation, avoiding additional devices as electrodes that could cause contamination by metals. In addition, up to eight samples can be simultaneously burnt, increasing the throughput. Different from the oxygen flask and combustion bombs, the MIC technique allows a reflux step that effectively improves the washing of the vessel walls and quartz holder.[23,37,38] This aspect is particularly important for halogens in view of problems related to effective absorption in solution. However, despite this advantage, the MIC technique has been not applied to coal digestion for the determination of halogens.

In this work, the first application of the MIC technique for coal decomposition for further simultaneous determination of Br, Cl, F, and I by IC is described. In order to evaluate the suitability of the proposed digestion technique for other determination techniques, digests were also analyzed by ICPMS and ICP OES for Br, Cl and I and ISE for F. Validation of the procedure was evaluated using certified reference coals (for Br, Cl, and F) or spikes (for I). Different absorbing solutions (ammonium carbonate or water), the necessity of the reflux step, and the RCC in digests were also evaluated.

EXPERIMENTAL SECTION

Instrumentation. In this study, a microwave oven originally designed for closed vessels wet digestion (Multiwave 3000 microwave sample preparation system, Anton Paar, Graz, Austria) equipped with eight high-pressure quartz vessels was used for the proposed combustion procedure. The volume of the vessels was 80 mL, and the maximum operational temperature and pressure was set at 280 °C and 8 MPa, respectively. The software version was v1.27-Synt, and the microwave system was previously modified to run with a maximum pressure rate of 0.3 MPa s^{-1} (and not 0.08 MPa s^{-1} as in the original software). This change was necessary to prevent eventual interruption of the microwave radiation before ignition of all samples. Pressure was monitored in each vessel for all the runs. The quartz holder was designed in order to reduce the cool surfaces that might cause carbon deposits during the combustion. In addition there is a quartz disc mounted at the top of the holder to shield the polytetrafluorethylene lid of the quartz vessel from the flame of the burning sample.[37]

Bromide, chloride, fluoride, and iodide were determined using a modular IC chromatographic system (Metrohm Ion Analysis, Herisau, Switzerland), with an anion-exchange column (Metrosep A Supp 5, polyvinylalcohol with quaternary ammonium groups, 150 mm × 4 mm i.d.), a guard column (Metrosep A Supp 4/5 Guard), a chemical suppressor module, and a conductivity detector. A sample loop of 100 μL was used. The mobile phase

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(21) *Annual Book of ASTM Standards*; Standard test method for chlorine in coal, D 2361-02, 2002.

(22) *Annual Book of ASTM Standards*; Standard test method for total fluorine in coal by the oxygen bombcombustion/ion selective electrode method, D 3761-96, reapproved 2002.

(23) Barin, J. S.; Flores, E. M. M.; Knapp, G. In *Trends in Sample Preparation*; Arruda, M. A. Z. Nova Science Publishers: Hauppauge, NY, 2006; pp 73−114.

(24) MacDonald, A.M.G. *The oxygen flask method, Advances in Analytical Chemistry and Instrumentation*; John Willey and Sons: New York, 1965; pp 75−116.

(25) Truscott, E. D. *Anal. Chem.* **1970**, *42*, 1657−1657.

(26) Selig, W. *Fresenius Z. Anal. Chem.* **1968**, *234*, 261−269.

(27) Fujiwara, S.; Narasaki, H. *Anal. Chem.* **1968**, *40*, 2031−2032.

(28) Iyengar, G. V.; Subramanian, K. S.; Woittiez, J. R. W. *Element Analysis of Biological Samples: Principles and Practice*; CRC Press: Boca Raton, FL, 1997; pp 116−117.

(29) Mester, Z.; Sturgeon, R. *Sample Preparation for Trace Element Analysis*; Vol. XLI, Elsevier: Amsterdam, The Netherlands, 2003; pp 683−719.

(30) Stoeppler, M. *Sampling and Sample Preparation*; Springer-Verlag: Berlin, Germany, 1997; p 192.

(31) Sulcek, Z.; Povondra, P. *Methods of Decomposition in Inorganic Analysis*; CRC Press: Boca Raton, Florida, 1989; p 282.

(32) Flores, E. M. M.; Barin, J. S.; Mesko, M. F.; Knapp, G. *Spectrochim. Acta, Part B* **2007**, *62*, 1051−1064.

(33) Awad, W. I.; Gawargious, Y. A.; Hassan, S. S. M.; Milad, N. E. *Anal. Chim. Acta* **1966**, *36*, 339−345.

(34) Moszynski, Z. K. A. J. *Appl. Chem.* **1955**, *5*, 467−470.

(35) Ricks, J. E.; Fleenor, J. E.; Smith, H. R. *Anal. Chim. Acta* **1974**, *68*, 480−483.

(36) Flores, E. M. M.; Barin, J. S.; Paniz, J. N. G.; Medeiros, J. A.; Knapp, G. *Anal. Chem.* **2004**, *76*, 3525−3529.

(37) Mesko, M. F.; Moraes, D. P.; Barin, J. S.; Dressler, V. L.; Knapp, G.; Flores, E. M. M. *Microchem. J.* **2006**, *82*, 183−188.

(38) Moraes, D. P.; Mesko, M. F.; Mello, P. A.; Paniz, J. N. G.; Dressler, V. L.; Knapp, G.; Flores, E. M. M. *Spectrochim. Acta, Part B* **2007**, *62*, 1065−1071.

Table 1. Operational Parameters for Br, C, Cl, and I Determinations by ICP OES and ICPMS

parameter	ICP OES	ICPMS
rf power (W)	1650	1400
plasma gas flow rate (L min^{-1})	14.0	15.0
auxiliary gas flow rate (L min^{-1})	1.0	1.2
nebulizer gas flow rate (L min^{-1})	0.7	1.15
spray chamber	double pass, Scott type	cyclonic
nebulizer	crossflow	concentric
view	axial	
sampler and skimmer cones		Pt
ion lens (V)		7.2
dwell time (ms)		50
isotope (m/z)		^{79}Br ^{35}Cl ^{127}I
wavelength (nm)	Br 154.065 Cl 134.724 I 178.276 C[a] 193.091	

[a] RCC measurements were performed according to ref 41.

was 3.2 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$ at a flow rate of 0.7 mL min^{-1}.

Bromide, chloride, and iodide were also determined in digests after combustion using an inductively coupled plasma mass spectrometer (Perkin-Elmer-SCIEX, model Elan DRC II, Thornhill, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, CO), a cyclonic spray chamber (Glass Expansion, Inc., West Merbourne, Australia), and a quartz torch with a quartz injector tube (2 mm i.d.). Instrumental performance optimization, including nebulizer gas flow rate, ion lens voltage, and torch alignment, was carried out following the instructions of the manufacturer.[39] The operational conditions are shown in Table 1.

An inductively coupled plasma optical emission spectrometer (Spectro Ciros CCD, Spectro Analytical Instruments, Kleve, Germany) was used for Br, Cl, and I determinations with an axial view configuration. Nebulization was performed through a crossflow nebulizer coupled to a Scott double pass type nebulization chamber. Plasma operating conditions and selected wavelengths used for Br, Cl, and I determinations are listed in Table 1, and they were used as recommended by the instrument manufacturer.[40] This equipment was also used for the measurement of the residual carbon content, and the respective conditions were described elsewhere.[41] However, instead of heating at 120 °C, digests were sonicated with an ultrasonic probe (VCX 130 PB, 130 W, 20 kHz, Sonics and Materials Inc., Newton, CT) for 2 min to remove the volatile carbon compounds before RCC measurements. For ICPMS and ICP OES determinations, argon 99.996% (White Martins-Praxair, São Paulo, Brazil) was used for plasma generation, for nebulization, and as the auxiliary gas.

Fluoride was determined in digests using a potentiometer (model 781 pH/Ion Meter, Metrohm, Herisau, Switzerland) equipped with a fluoride ISE (model 6.0502.150, Metrohm). Analytical conditions were described elsewhere.[15]

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.

Samples, Reagents, and Standards. Initial studies were carried out using a Brazilian coal sample obtained from Santa Catarina State mine containing 27% of ash. This sample was ground using a cryogenic mill (Spex Certi Prep, model 6750, Metuchen, NJ) to obtain particle diameter below 102 μm. The following certified reference materials (CRM) were used in this work: IRMM BCR 40 (trace elements in coal), IRMM BCR 181 (coking coal), NIST SRM 1632b (trace elements in coal), NIST SRM 1632c (trace elements in coal), and SARM 19 (coal, O. F. S.). All the samples were pressed as pellets (diameter of 13 mm) using a hydraulic press set at 8 ton by 1 min (Specac, Orpington, U.K.).

Milli-Q water (18.2 MΩ cm) and analytical-grade reagents (Merck, Darmstadt, Germany) were used. Working analytical solutions for IC analysis were prepared before use by serial dilution of stock reference solutions containing 100 mg L^{-1} of fluoride, chloride, and bromide (multielement solution, Fluka, Buchs, Switzerland) in water. The iodide stock reference solution was prepared by dissolution of potassium iodide salt (Merck, Darmstadt, Germany) in water. For the determination by ICPMS and ICP OES, analytical solutions were prepared in 10 mmol L^{-1} $(NH_4)_2CO_3$.

Water and ammonium carbonate solutions were used as absorbing media for the halogens. Ammonium carbonate was dissolved in water in concentrations ranging from 10 to 200 mmol L^{-1}. An ammonium nitrate solution (6 mol L^{-1}) was used as an ignition aid. A small disc of filter paper (15 mm in diameter, 12 mg) with low ash content (Black Ribbon Ashless, Schleicher & Schuell GmbH, Dassel, Germany) was used as an aid for the combustion process. The filter paper was previously cleaned with absolute ethanol for 20 min in an ultrasonic bath and rinsed with water and dried in an oven for 2 h at 60 °C before use. Glass or quartz materials were soaked in 1.4 mol L^{-1} HNO_3 for 24 h and thoroughly washed with water before use.

Microwave-Induced Combustion Procedure. For the proposed MIC procedure, pellets of coal samples from 50 to 500 mg were weighed and placed together with the filter paper on the quartz holder. Quartz vessels were previously charged with 6 mL of absorbing solution (water or ammonium carbonate), and 50 μL of the 6 mol L^{-1} NH_4NO_3 solution was added to the filter paper. Then, the holder was introduced into the quartz vessel. After closure and capping of the rotor, the vessels were pressurized with 2 MPa of oxygen by means of the valve originally designed for pressure release after conventional acid sample digestion. Then the rotor was placed inside the oven, and the selected microwave heating program was started: (i) 1400 W for 60 s (sample ignition), (ii) 1400 W for 5 min (optional reflux step), and (iii) 0 W for 20 min (cooling step, if step ii was applied). During steps i and ii, the cooling fan of the microwave oven was selected at level 1 (level 3 was applied only for step iii). Vessels were opened 30 min after the combustion if only step "i" was used. The time for the optional reflux step after the combustion and the time for cooling were set in accordance with the previous studies.[37] After

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(39) Perkin Elmer-SCIEX, Elan version 3.0, Software Guide, 1006920 A, 2003, Thornhill, Canada.

(40) Spectro Ciros CCD, software version 01/March 2003, Spectro Analytical Instruments GmbH & Co. KG: Kleve, Germany.

(41) Gouveia, S. T.; Silva, F. V.; Costa, L. M.; Nogueira, A. R. A.; Nóbrega, J. A. *Anal. Chim. Acta* **2001**, *445*, 269–275.

digestion, the pressure of each vessel was carefully released. In this work, each run was performed with a minimum of four vessels. The resultant solution was diluted with water and transferred to 30 mL polypropylene vials. Cleaning of vessels and holders was carried out with 6 mL of concentrated HNO_3 in the microwave oven at 1400 W for 5 min and 0 W for 20 min for cooling. The concentration of ammonium nitrate solution, the minimum volume for the ignition process, as well as the mass of paper filter were based on previous works.[36,37] Final digests were analyzed by IC, ICP OES, ICPMS, and ISE.

RESULTS AND DISCUSSION

Microwave-Induced Combustion of Coal. Initial studies were performed for the evaluation of the safety aspects of the coal combustion process. The maximum pressure achieved during the combustion of 250 and 500 mg of coal samples, using 2 MPa as the initial oxygen pressure, was 3 and 4 MPa, respectively. The maximum pressure is 50% of the maximum working pressure recommended by the manufacturer (8 MPa). Therefore, the combustion process can be considered safe for the coal combustion procedure even with a sample mass as high as 500 mg. The maximum temperature achieved during the combustion was around 1400 °C for 500 mg of coal using the initial oxygen pressure at 2 MPa. During the combustion, a white and bright light was emitted that also confirms the high temperature attained. However, despite the high temperature, no damages were observed in the holders and vessels.

Influence of Absorbing Solution and Reflux Step on Bromide, Chloride, Fluoride, and Iodide Recoveries. The absorbing solution has an important role because the type and the concentration of the solution are not the same for different analytes as well as the time for absorption.[16,32] In some cases, a reducing agent must be added in order to prevent the formation of free halogen that could be lost when the vessel is opened.[33] In this work, the time for analyte absorption (26 and 31 min, with and without reflux, respectively) was chosen based on the time currently used for digestion using combustion bombs and oxygen flask techniques and further halogens determinations.[7,16,19,32]

A noncertified Brazilian coal sample was used, and spikes of Br, Cl, F, and I were made in the pellets (500 mg) for subsequent determination by IC. The recoveries after microwave-induced combustion using water or 10, 50, 100, and 200 mmol L^{-1} ammonium carbonate as the absorbing solution are shown in Figure 1. These preliminary tests were carried out without the reflux step, and the time for analyte absorption was set at 30 min. Water recoveries below 80% were obtained for F and I. Better values were obtained for Br (87%) and for Cl (92%). Moreover, for all analytes the relative standard deviation (RSD) was higher than 11%. With the use of a 10 mmol L^{-1} ammonium carbonate solution, an increase of 5% was obtained for F and I recoveries. However, practically the same values using water were obtained for Br and Cl. With an $(NH_4)_2CO_3$ solution of 50−200 mmol L^{-1}, recoveries higher than 92% were obtained for all analytes. For these conditions, the RSD was always higher than 4% but the maximum recovery was 97% for I.

Tests with 5 min reflux after the combustion step with the same absorbing solutions were also carried out. Results are shown in Figure 2. Recoveries better than 87% were obtained for all analytes with water as the absorbing solution, and the RSD was lower than 6%. However, the maximum value of 96% was only obtained for Cl. With the use of the 10 mmol L^{-1} $(NH_4)_2CO_3$ as the absorbing solution, an improvement of 5% was observed for I. With the use of 50 mmol L^{-1} $(NH_4)_2CO_3$, the recoveries were close to 100% and a RSD below 3% was obtained for all analytes. With higher concentrations of $(NH_4)_2CO_3$, the results were practically the same as with 50 mmol L^{-1} $(NH_4)_2CO_3$. The effect of the reflux step could be explained with the higher efficiency of washing of the holder and the internal vessel walls when compared to other processes such as, e.g., manual shaking. This aspect can be considered as the main difference to other combustion systems where a reflux step cannot be applied.[21,22] On the other hand, 50 mmol L^{-1} $(NH_4)_2CO_3$ as the absorbing solution provided a suitable medium for determinations by IC. In addition, the use of reflux minimizes the use of more concentrated solutions. Absorbing solutions as diluted as possible are generally desirable to ensure lower blank values. Then, the proposed MIC procedure could provide a convenient method that allows the simultaneous determination of all halogens by IC.

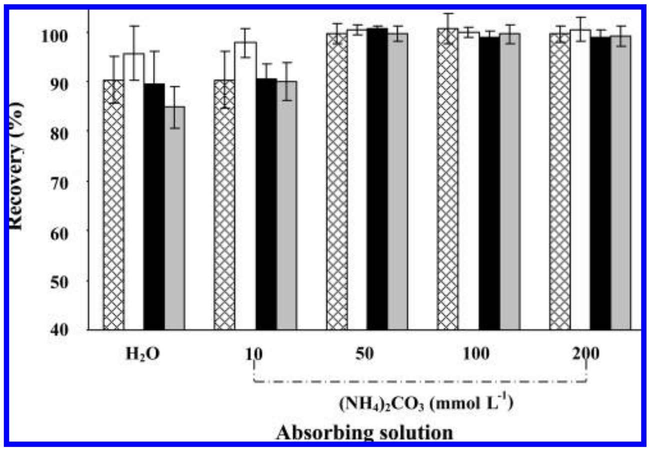

Figure 1. Influence of the absorbing solution for Br, Cl, F, and I (checkerd, white, black, gray, respectively) determination in coal using the proposed microwave-induced combustion procedure without the reflux step and determination by IC (error bars represent the standard deviation, $n = 3$).

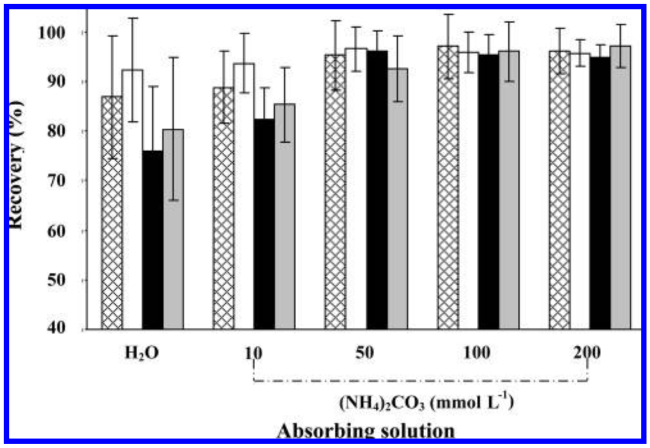

Figure 2. Influence of the absorbing solution for Br, Cl, F, and I (checkered, white, black, gray, respectively) determination in coal using the proposed MIC procedure with the reflux step and determination by IC (error bars represent the standard deviation, $n = 3$).

Determination of Bromide, Chloride, Fluoride, and Iodide in Coal After the MIC Procedure. With the use of 50 mmol L^{-1}

Table 2. Determination of Br, Cl, F, and I by IC, ICP OES, ICPMS, and ISE in Coal Certified References Materials Using the MIC Procedure[a]

		concentration (μg g^{-1} ± standard deviation)				
element	sample	IC	ICPMS	ICP OES	ISE	certified value (μg g^{-1})
Br	NIST 1632c	18.5 ± 0.2	18.9 ± 0.1	≤20.0	nd[b]	18.7 ± 0.4
	SARM 19	≤2.5	2.02 ± 0.08	≤20.0	nd[b]	2[b]
	Brazilian coal	≤2.5	0.70 ± 0.03	≤20.0	nd[b]	
Cl	BCR 181	1424 ± 42	nd[b]	1373 ± 45	nd[b]	1380 ± 50
	NIST 1632b	1228 ± 31	nd[b]	1241 ± 35	nd[b]	1260[b]
	NIST 1632c	1119 ± 27	nd[b]	1150 ± 38	nd[b]	1139 ± 41
	Brazilian coal	206.9 ± 4.6	202.3 ± 14.1	196.7 ± 12.5	nd[b]	
F	BCR 40	110.3 ± 3.1	nd[b]	nd[b]	110.8 ± 3.4	111.4 ± 8.5
	NIST 1632b	40.9 ± 1.9	nd[b]	nd[b]	41.9 ± 1.7	41.7 ± 3.2
	NIST 1632c	71.5 ± 2.3	nd[b]	nd[b]	71.7 ± 2.9	72.7 ± 6.8
	Brazilian coal	175.2 ± 7.2	nd[b]	nd[b]	170.5 ± 8.3	
I	Brazilian coal	≤3.0	0.26 ± 0.03	≤4.5	nd[b]	

[a] $n = 3$, 6 mL of 50 mmol L^{-1} $(NH_4)_2CO_3$ absorbing solution, 5 min 1400 W, 20 min cooling. [b] Informed value; nd: not determined

$(NH_4)_2CO_3$ as the absorbing solution, well-defined peaks with a stable baseline were observed for the IC chromatograms. In view of the low concentration, the signal for iodide was not observed. In spite of the presence of relatively high concentrations of sulfate and nitrate ions, in this work even using coal samples as high as 1.6% S, no influence was observed for all halogen signals by IC. A peak for nitrite was also identified in digests. However, this peak did not interfere for halogen determination either.

In addition to IC, nowadays, some plasma optical emission spectrometers also allow the determination of halogens (with the exception of F). Moreover, depending on the laboratory conditions it would be desirable to analyze the obtained digests by other determination techniques as ICPMS, ICP OES, and ISE. Table 2 presents the results for Br, Cl, F, and I determination by IC, ICP OES, ICPMS, and ISE in coal samples after MIC digestion with reflux using 50 mmol L^{-1} ammonium carbonate as the absorbing solution. Generally, results were in agreement with the certified or informed values for all analytes. Current Br concentration in coal is low[42] and, in particular, the bromide concentration in Brazilian coal was lower than the quantification limit (10σ) obtained by IC and ICP OES. In this case, Br determination was carried out by ICPMS. Spiked samples were used for evaluating the accuracy and recoveries, which were from 97.5 to 102%. For CRM, the results using ICPMS or ICP OES (for NIST 1632c) were in agreement with the certified or recommended values. For the determination of chloride, IC and ICP OES were used and the results for both techniques agreed with reference values (no statistical difference, 95% confidence level). In this case, the use of ICPMS was avoided due to the excessively high chloride concentration in the samples. Fluoride was determined only by IC and ISE because ICP OES and ICPMS are not able to measure this element. The results for the certified or recommended values were in agreement better than 98%.

Because of the low iodide concentration in Brazilian coal, the determination was only possible with ICPMS. Certified or recommended values were not available for iodide in the coal CRMs evaluated. Therefore, accuracy was evaluated using the spiked solution. In addition, a mixture of coal and certified reference milk powder (IRMM BCR 150-spiked skim milk powder, low level) was prepared. The pellets of this mixture were combusted by the proposed MIC procedure, and I determination was performed by IC, ICP OES, and ICPMS. For both kinds of spikes, the recoveries were better than 97%.

It is important to point out that iodide memory effects were observed in the initial determinations by ICPMS if reference solutions or digests were prepared in water or acidic medium. This fact has been also reported in the literature, and this effect can be thought to arise from the volatile iodine species (I_2 and HI) mainly in the spray chamber.[43−45] This problem was solved by preparing all the solutions in 10 mmol L^{-1} $(NH_4)_2CO_3$ and also using an ammonium carbonate solution to wash the sample introduction system (tubing, spray chamber, nebulizer).

Blanks for the proposed procedure were always low, probably due to the high cleaning efficiency of the holders and vessels by the reflux step and by the use of low-concentrated ammonium carbonate solutions.

Investigation of the Presence of Bromate, Chlorate, and Iodate in Digests after the Combustion Step. It was found in literature that some works have indicated that bromate and iodate may be generated after combustion,[46,47] and the addition of hydrazine sulfate[48] or hydrazine hydrate and ammonium vanadate in the absorbing solution[46] has been proposed to catalyze the conversion of bromate and iodate into the respective bromide and iodide. In the present work, a systematic study was carried out to evaluate the possible formation of bromate, chlorate, and iodate in a combustion step. Then, standard reference solutions of these anions were added to the digests, and they were determined by IC. The retention times of iodate, bromate, and chlorate were 3.6, 5.1, and 7.7 min, respectively. With the use of spikes in the digests, the presence of additional peaks was observed that were further identified as bromate and chlorate. Therefore, it was accepted that these species were not formed during the combustion. For iodate,

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(42) Spears, D. A. *Int. J. Coal Geol.* **2005**, *64*, 257−265.

(43) Al-Ammar, A.; Reitznerová, E.; Barnes, R. M. *Fresenius J. Anal. Chem.* **2001**, *370*, 479−482.

(44) Gelinas, Y.; Krusheveska, A.; Barnes, R. M. *Anal. Chem.* **1998**, *70*, 1021−1025.

(45) Fecher, P. A.; Goldmann, I.; Nagengast, A. *J. Anal. At. Spectrom.* **1998**, *13*, 977−982.

(46) Burns, D. T.; Maitin, B. K. *Analyst* **1983**, *108*, 452−456.

(47) Belcher, R.; Fildes, J. E. *Anal. Chim. Acta* **1961**, *25*, 34−41.

(48) Mázor, L.; Pápay, K. M.; Klatsmányi, P. *Talanta* **1963**, *10*, 557−560.

Table 3. Comparison between Coal Digestion Conditions for Subsequent Halogens Determinations Using the Proposed MIC and Recommended Combustion Techniques by ASTM

	digestion technique	
parameter	combustion bomb (ASTM)[21,22]	MIC
sample mass (g)	1.0	0.5
absorbing solution	5 mL of 0.75 mol L^{-1} $(NH_4)_2CO_3 \cdot H_2O$ (Cl) 5 mL of 1 mol l^{-1} NaOH (F)	6 mL of 50 mmol L^{-1} $(NH_4)_2CO_3$ (Br, Cl, F, and I)
determination technique	potentiometric titration (Cl) ISE (F)	IC (Br, Cl, F, and I) ICP OES, ICPMS (Br, Cl, I) ISE (F)
no. of digestions by hour	1−2 samples	up to 16 samples
reflux step	not available	available
pressure and temperature control	not available	available

its elution time is generally coincident with fluoride and conductivity detection is not selective to determine each species separately. Thus, if iodate was generated its presence could interfere in the fluoride determination by IC. However, it could be supposed that iodate was not present because the measurement of fluoride by IC and ISE were in agreement. Moreover, the agreement for Br, Cl, and F with the certified values was close to 100%, indicating that BrO_3^-, ClO_3^-, and IO_3^- were not formed by using the proposed MIC procedure.

Comparison of the Proposed Procedure with ASTM Procedures. The digestion of coal recommended by American Society for Testing and Materials is the bomb combustion for subsequent determination of Cl and F by potentiometric titration and ISE, respectively. A comparison of ASTM and the proposed MIC techniques is shown in Table 3. In the ASTM procedure, 1 g of sample is burnt in a bomb loaded with 2−3 MPa oxygen and different absorbing solutions. For Cl, 5 mL of 0.75 mol L^{-1} $(NH_4)_2CO_3 \cdot H_2O$ and for F, 5 mL of 1 mol L^{-1} NaOH are recommended. Therefore, two different digestions are necessary to determine these elements by different techniques. Consequently, a low sample throughput is observed. When compared to the ASTM procedure, MIC combined with IC enables the application of one single digestion and determination procedure for the determination of these two analytes and, additionally, Br and I. Moreover the analysis of different coal samples by means of the proposed procedure with good agreement to CRM values assures its robustness. In the MIC procedure, up to eight samples can be processed simultaneously that allow higher sample throughput of up to 16 samples per hour. One of the main aspects is related to the digest's compatibility to other determination techniques like ICP OES and ICPMS for Br, Cl, and I and ISE for F. Consequently, the proposed MIC digestion procedure can be used by different laboratories according to their available instrumentation for halogen determination. In addition, the reflux step, not available for combustion bombs, improves the absorption of analytes assuring quantitative recoveries. Moreover, MIC procedure allows pressure and temperature control which is important for safety reasons and for the accompaniment of the combustion reaction.

The limits of detection (LODs) using the proposed MIC procedure (3σ) were 2.5, 0.8, 0.25, and 3.0 $\mu g\ g^{-1}$ for Br, Cl, F, and I by IC, respectively. The LODs using ICPMS were 0.02, 6.1, and 0.001 $\mu g\ g^{-1}$ for Br, Cl, and I, respectively. The corresponding LODs for ICP OES determinations were 20.0, 8.4, and 4.5 $\mu g\ g^{-1}$. For the determination of F by ISE, the LOD was 3.5 $\mu g\ g^{-1}$.

Residual Carbon Content in Coal Digests. In this work, the residual carbon content was used to evaluate the efficiency of coal digestion procedures.[41] The RCC values were below 0.5% for coal samples using MIC procedures with or without the reflux step. The low RCC obtained with the proposed procedure could be related to the high temperature (about 1400 °C) during coal combustion. Under this condition practically all the organic matrix is completely oxidized, which prevents interferences with ISE, ICPMS, or IC by residual organic compounds.

CONCLUSIONS

With dependence on the analyte, the proposed MIC procedure for coal digestion was considered suitable for halogen determinations by IC, ICP OES, ICPMS, or ISE. Contrary to other combustion techniques, MIC allows a reflux step that minimizes potential losses due to analyte adsorption. In general, MIC procedure showed good performance for coal digestion due to complete oxidation of the organic matrix, safety, and high throughput, which is important for routine analysis.

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