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Short communication

Simultaneous determination of halogens (F, Cl, Br, and I) in coal using pyrohydrolysis combined with ion chromatography

Bingxian Peng, Daishe Wu *, Jinhu Lai, Huayun Xiao, Ping Li

Department of Environmental Science and Engineering, Nanchang University, Nanchang 330031, China

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ABSTRACT

A method for the determination of halogens (F, Cl, Br, and I) in coal using pyrohydrolysis for sample digestion and ion chromatography is proposed. The pyrohydrolysis conditions and the types and concentrations of the absorption solutions are optimized. The limits of detection of the method are 0.045, 0.072, 0.15, and 0.25 μg g^{-1} for F, Cl, Br, and I, respectively. With its simplicity, precision, accuracy, and economy, the proposed method can be widely used for the routine analysis of all four halogens in coal.

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1. Introduction

Monitoring the halogen levels in coal is important because of their effects on human health and the environment. Few methods can be adopted to determine halogens in coal simultaneously. F can only be determined through ion chromatography (IC) and ion-selective electrode (ISE), whereas instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS) can only analyze Cl, Br, and I [1–4]. Sample decomposition is a critical step in halogen analysis. Halogens are volatile and readily lost when the sample is treated; furthermore, the reagents used for sample digestion may interfere with the determination process itself. To eliminate these drawbacks, pyrohydrolysis and microwave-induced combustion (MIC) have been proven effective and reliable digestion methods for determining halogens in coal and oil [2–9]. MIC combined with IC, a routine and classic analytical method for determining halogens in water [10], has been successfully used to determine halogens simultaneously in coal [4]. However, about 15% of Chinese coal has less than 2.5 μg g^{-1} Br and 75% have less than 3.0 μg g^{-1} I. Therefore, the limits of detections (LODs) for Br and I (2.5 and 3.0 μg g^{-1}, respectively) obtained using IC coupled with MIC is relatively high [4].

To lower the LODs of Br and I further, the present study establishes a quantitative method for determining F, Cl, Br, and I in coal using the IC system after pyrohydrolysis. The pyrohydrolysis conditions, as well the types and concentrations of the absorption solutions are optimized. The method is validated using certified reference coals (for F) or spikes (for Cl, Br, and I).

2. Experimental

2.1. Apparatus

The pyrohydrolysis apparatus was developed as mentioned in our previous study [5]. An IC system, the 861 Advanced Compact IC with an 838 Advanced Sample Processor (Metrohm AG, Herisau, Switzerland), was used for analysis. A mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ at a flow rate of 1 mL min^{-1} served as the eluent. A solution of 50 mM H_2SO_4 was used as the regenerant. The volume of the sample injection loop was 10 μL.

2.2. Reagents, samples, and certified reference materials

The Na_2CO_3 and $NaHCO_3$ were of analytical reagent grade (Merck, Darmstadt, Germany). Standard stock solutions containing 1000 mg L^{-1} F^-, Cl^-, Br^-, and I^- were prepared by dissolving an appropriate amount of their corresponding sodium salts at 99.9% purity (Merck, Darmstadt, Germany) in water. Ultrapure water, with a resistance of 18.2 MΩ cm, was used to prepare the solutions.

The four samples were collected and prepared in accordance with the Chinese standard method for coal preparation [11]. To determine the accuracy of the analysis of the actual coal samples, four Chinese soil reference materials (SRMs) for F, Cl, Br, and I (GBW07403, GBW07404, GBW07405, and GBW07407) and three

* Corresponding author. Tel./fax: +86 791 83969595.
E-mail address: dswu@ncu.edu.cn (D. Wu).

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coal reference materials for F (GBW11121, GBW11122, and GBW11123) were adopted.

2.3. Procedures

A 1.0 g coal sample (100 mesh) was evenly mixed with 0.25 g silica (20–50 mesh), placed in a porcelain boat, and then covered with 1.5 g silica. A tube furnace was heated to preset temperatures of 500–1100 °C. The oxygen flow rate was preset to 20–120 mL min^{-1}. A 15 mL absorption solution was placed into a 60 mL volumetric flask and then placed in an ice bath (<25 °C) to absorb the halogens released from the coal samples. The charged porcelain boat within the silica boat was gradually moved to the center of the high-temperature zone within 10 min. The coal was maintained in the high temperature zone for a preset time of 10–20 min. The other operations were the same as in our previous study [5].

2.4. Calibration and sample analysis

The standard working solutions were prepared fresh daily by serially diluting stock standard solutions using ultrapure water. Appropriate amounts of the standard working solution were placed in Metrohm autosampler tubes, and filled to 10 mL with ultrapure water. The solutions were then analyzed through IC. The method was calibrated with standard solutions of F^-, Cl^-, Br^-, and I^- prior to the determinations. A 10 mL sample of the absorption solution was pipetted into a Metrohm autosampler tube, and then analyzed via IC.

For comparative purposes, the F content in coal was determined by ISE. The I content in the coal was determined through catalytic spectrophotometry (CS) [5].

3. Results and discussion

3.1. Optimization of the pyrohydrolysis conditions and the absorption solution

Pyrohydrolysis was adopted to digest the coal samples and separate the halogens from the sample matrix. The separation depended mainly on the variations in temperature, time, oxygen flow rate, and the volume and concentration of the absorption solution. The pyrohydrolysis conditions were optimized specifically as follows: pyrohydrolytic temperature of 1050 °C, pyrohydrolytic time of 25 min, and oxygen flux of 90 mL min^{-1}.

The literature reports that a mixture of Na_2CO_3 and $NaHCO_3$ solutions, tetramethyl ammonium hydroxide (TMAH), NaOH, and Na_2SO_3, could be used to absorb the released halogens when the samples were digested through pyrohydrolysis [2,4,5,12]. The effects of the species in the absorption solution on the halogen analysis are shown in Table 1. A mixture of 7.2 mM Na_2CO_3 and 6.8 mM $NaHCO_3$, a pH buffer solution (pH = 10.3), was found to be the best absorption solution. The matrix effects were also minimized during the IC analysis.

3.2. Limits of detection

The LODs of F, Cl, Br, and I (S/N = 3) during the pyrohydrolysis with IC determination were 0.045, 0.072, 0.15, and 0.25 μg g^{-1}, respectively.

3.3. Accuracy and precision

The accuracy of the proposed method was evaluated by determining the Chinese SRMs with certified halogen values and analyzing the recoveries in the coal samples that had been spiked with SRMs. The measured results are in reasonable agreement with the certified concentrations and the *F* and *I* values determined through ISE and CS, respectively. The recoveries ranged from 96.6–105%, 93.4–108%, 92.3–107%, and 93.6–103% for F, Cl, Br, and I, respectively, with corresponding mean values of 102%, 98.5%, 102%, and 97.3%. The relative standard deviations of the six repeated analyses of the four coal samples ranged from 0.30% to 0.79% for F, with an average value of 0.51%. The values for Cl ranged from 0.18% to 0.69%, with an average value of 0.41%. The values for Br ranged from 0.30% to 2.40%, with an average value of 1.11%. The values for I ranged from 1.88% to 4.24%, with an average value of 3.22%. This method is thus accurate for determining the halogen content in coal.

3.4. Analysis of coals with very low bromine and iodine levels

The proposed method is accurate for the determination of F and Cl in all coal samples and for the determination of Br and I in most coal samples. However, in a fraction of coal samples, the levels of Br and I were too low (Br < 0.15 μg g^{-1}, I < 0.25 μg g^{-1}) to be detected by the proposed method. For these samples, 5.0 g was collected to improve the concentration of the final solution. The results show that even relatively low Br levels in coal can be accurately determined via IC combined with pyrohydrolysis using larger samples. The concentration of the final solution for I in coal with low sulfur (S) content can also be improved by increasing the mass of the sample. Considering the SO_4^{2-} peak is just in front of the I^- peak in the chromatogram, this may interfere with the I^- peak in certain coal that have high S levels. The I content of these coals, the I content of which is less than 0.25 μg g^{-1} and with the SO_4^{2-} peak overlapping the I^- peak in the chromatogram, can be determined using CS, which can be adopted for analyzing coals with I levels as low as 0.04 μg g^{-1} [13].

3.5. A comparison of the proposed method with other methods for simultaneously determining halogens in coal

A comparison of the methods for simultaneously determining halogens in coal is shown in Table 2. The LODs for the halogens in the proposed method are lower than that of the method that uses MIC digestion combined with IC. The LODs for Br and I in the proposed method using IC are comparable those using NAA

Table 1
Determination of F, Cl, Br, and I in Chinese SRM GBW07404 through IC using various absorption solutions after pyrohydrolysis (n = 6; uncertainties are standard deviations).

Halogen	Determined value (μg g^{-1})				Certified value (μg g^{-1})
	0.05 M NaOH	50 μg mL^{-1} Na_2SO_3	0.5% (v/v) TMAH	Mixture of 7.2 mM Na_2CO_3 and 6.8 mM $NaHCO_3$	
F	502 ± 2.5	541 ± 3.1	565 ± 2.9	543 ± 2.7	540 ± 25
Cl	30.0 ± 0.1	35.0 ± 0.2	37 ± 0.2	40 ± 0.2	(39)[a]
Br	nd[b]	3.20 ± 0.35	nd[b]	3.80 ± 0.42	4.0 ± 0.7
I	nd[b]	nd[b]	nd[b]	9.00 ± 0.30	9.4 ± 1.1

[a] Informed value.
[b] nd: Not determined.

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Table 2
Comparison of methods for simultaneously determining halogens in coal.

Parameter		Literature sources				
		Flores et al., 2008 [4]		Landsberger et al., 1989 [1]	Bettinelli et al., 2002 [2]	This work
Sample mass (g)		0.5		0.75	0.5	1.0
Digestion technique		MIC		None	Pyrohydrolysis	Pyrohydrolysis
Absorbing solution		6 mL of 50 mM $(NH_4)_2CO_3$		None	20 mL of 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$	15 mL of 7.2 mM Na_2CO_3/6.8 mM $NaHCO_3$
Determination technique		IC	ICP-MS	Epithermal NAA	IC and ICP-MS	IC
LODs ($\mu g\ g^{-1}$)	F	0.25		–	1[a]	0.045
	Cl	0.80	6.1	5	10[a]	0.072
	Br	2.5	0.02	0.2	0.1[b]	0.15
	I	3.0	0.001	0.03	0.1[b]	0.25

[a] Determined by IC.
[b] Determined by ICP-MS.

and ICP-MS. IC is more accessible and more economical compared with the nuclear reactor required for NAA and ICP-MS.

4. Conclusions

A method that combines pyrohydrolysis digestion with IC has been developed to simultaneously determine F, Cl, Br, and I in coal. Better LODs, which were 0.045, 0.072, 0.15, and 0.25 $\mu g\ g^{-1}$ for F, Cl, Br, and I respectively, were achieved, which met the analytical requirements for quantifying trace halogens in most coal types. The lower Br and I levels in some coal can be determined by increasing their mass (with the exception of I in certain coal that have high S content). The proposed method was confirmed to be accurate and precise. An additional advantage of this method is that it employs instrumentation, which can be acquired and maintained at lower costs compared with those used in INAA and ICP-MS.

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References

[1] Landsberger S, Vermette VG, Wolfe M, Powell MA. Determination of halogens in coal using thermal and epithermal neutron activation analysis. J Coal Qual 1989;8:95–7.
[2] Bettinelli M, Spezia S, Minoia C, Ronchi A. Determination of chlorine, fluorine, bromine, and iodine in coals with ICP-MS and I.C. Atom Spectrosc 2002;23:105–10.
[3] Dressler VL, Pozebon D, Flores ELM, Paniz JNG, Flores EMM. Determination of fluoride in coal using pyrohydrolysis for analyte separation. J Braz Chem Soc 2003;14:334–8.
[4] Flores EMM, Mesko MF, Moraes DP, Pereira JSF, Mello PA, Barin JS, et al. Determination of halogens in coal after digestion using the microwave-induced combustion technique. Anal Chem 2008;80:1865–70.
[5] Wu D, Deng H, Wang W, Xiao H. Catalytic spectrophotometric determination of iodine in coal by pyrohydrolysis decomposition. Anal Chim Acta 2007;60:183–8.
[6] Antes FG, Dos Santos MDFP, Loureno Guimarães RC, Gottfried Paniz JN, Moraes Flores EMM, Dressler VL. Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination. Anal Methods 2011;3:288–93.
[7] Pereira JSF, Mello PA, Moraes DP, Duarte FA, Dressler VL, Knapp G, et al. Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion. Spectrochim Acta B 2009;64:554–8.
[8] Pereira JSF, Mello PA, Duarte FA, Santos MDFP, Guimaraes RCL, Knapp G, et al. Feasibility of microwave-induced combustion for digestion of crude oil vacuum distillation residue for chlorine determination. Energy Fuel 2009;23:6015–9.
[9] Antes FG, Duarte FA, Paniz JNZ, Santos MDFP, Guimaraes RCL, Flores EMM, et al. Chlorine determination in petroleum coke using pyrohydrolysis and DRC-ICP-MS. Atom Spectrosc 2008;29:157–64.
[10] López-Ruiz B. Advances in the determination of inorganic anions by ion chromatography. J Chromatogr A 2000;881:607–27.
[11] State Bureau of Technical Supervision. GB 474-1996, Standardization Administration of the People's Republic of China. Beijing; 1996. < http://www.sac.gov.cn>.
[12] Chai JY, Muramatsu Y. Determination of bromine and iodine in twenty-three geochemical reference materials by ICP-MS. Geostand Geoanal Res 2007;06–07:143–50.
[13] Wu D, Deng H, Zheng B, Wang W, Tang X, Xiao H. Iodine in Chinese coals and its geochemistry during coalification. Appl Geochem 2008;23:2082–90.

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