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Single-step microwave digestion with HNO_3 alone for determination of trace elements in coal by ICP spectrometry

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Abstract

A microwave digestion method with HNO_3 alone was conducted at a temperature as high as 250 °C for determination of 19 trace elements (Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, Cs, Ba, Hg, and Pb) in coal jointly by inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and flow injection ICP-MS (FI-ICP-MS). The validity of determination was assessed by using three standard coals, SRM 1632c, BCR 180, and SARM 19. It was found that the high-temperature digestion led to an extensive decomposition of the organic matrix and clay in coal, and no dissolved and solid carbon remained in the final solution after evaporation. Good recoveries were observed for all trace elements in three coals, with the exception of V, Rb, and Cs in high-ash SARM 19. Additionally, FI-ICP-MS combined with the present digestion without evaporation pretreatment was proved to be a rapid and efficient approach for determination of ultra-trace elements such as Se, Cd, and Hg in coal.

Keywords: Microwave digestion; Nitric acid; Coal; Trace elements; Inductively coupled plasma optical emission spectrometry; Inductively coupled plasma mass spectrometry; Flow injection inductively coupled plasma mass spectrometry

1. Introduction

Multi-elemental ICP-OES and ICP-MS techniques have been applied to determine diverse trace elements in coal [1–5]. These analytical techniques normally require that coal sample be dissolved in an acidic solution through decomposition of the organic and mineral matrices. Broadly, three coal dissolution approaches are categorized as [6]: (1) the open wet ashing dissolution carried out on a hot plate, which uses the combination of acids to destroy carbonaceous material and to dissolves minerals; (2) the dry ashing dissolution in which carbonaceous material is burnt out in air, then the ash was molten with lithium metaborate, and finally dissolved with nitric acid; (3) the closed vessel dissolution assisted by microwave irradiation. Compared to the former two methods, microwave digestion provides a rapid and efficient method, and it also possesses an advantage of reducing volatilization loss and contamination.

To date, however, the microwave digestion is still a state-of-the-art method. No procedures have been standardized for coal digestion. Fadda et al. [2] used a mixture of HF/aqua regia/$HClO_4$ as a digestion reagent. $HClO_4$ acts as a strong oxidant to destroy the organic matrix but it raises a safety concern. A mixture of aqua regia and HF without $HClO_4$ is thus widely employed [1,3,7,8] but this digestion does not completely destroy the organic matrix in the case of using the conventional low-pressure vessels. A successive treatment is generally required to neutralize the extra hydrofluoric acid with the addition of boric acid and to remove the organic remainder by evaporation [1]. However, boric acid is unfavorable for ICP-MS because of the matrix effect and spectrometric interferences. In addition, the solution containing Cl-based acids also has a negative impact on ICP-MS because they induce the Cl-combined polyatomic interference. Therefore, it is desired to develop a coal digestion method without HF and Cl-based acids so that the digestion solution can simply be used for ICP-MS. Some researchers explored this kind of digestion but the digestion using the conventional low-pressure vessels was not validated for dissolution of many trace elements [9–11].

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We carried out the microwave digestion with HNO_3/H_2O_2 using a high-temperature fluoropolymer vessel (maximum temperature, 230 °C; maximum pressure, 3.5 MPa), and found that the temperature could be a critical factor facilitating the dissolution of trace elements in the case of the HF-free digestion [12]. Here, we intend to investigate a more rigorous microwave digestion with HNO_3 alone. Moreover, since less abundant Se, Cd, and Hg in coal can be difficult to determine with common ICP-MS [9,12], quantification of these elements usually needs use of other analytical techniques, for example, hydride generation inductively plasma mass spectrometry (HG-ICP-MS) for determination of Se and cold vapor atomic adsorption spectrometry (CVAAS) for determination of Hg [13,14]. In this paper, simultaneous determination of these elements has been implemented by means of FI-ICP-MS.

2. Experimental

2.1. Coal samples and reagents

One bituminous coal (SRM 1632c) and two sub-bituminous coals (BCR 180 and SARM19) were used in this study. All three coals were the standard reference materials that were described previously [12]. The ash contents of SRM 1632c, BCR 180, and SARM19 were 9.2, 7.2, and 29.6%, respectively. The particle sizes of the samples were less than 250 μm.

Nitric acid (60%) was of ultrapure grade (Kanto Chemical Co. Inc., Japan). A XSTC-13 solution (SPEX Certiprep Inc., USA) containing $10\,\mu g\,ml^{-1}$ of 31 elements was used for the calibration. Ultrapure water from a Milli-Q system was used throughout the solution preparation.

2.2. Microwave digestion

The digestion was performed on a commercial Microwave Digestion System (Multiwave 3000, Anton Paar) using a high-pressure quartz vessel (XQ80). The HF-free digestion made the quartz vessel applicable. This vessel could stand a temperature up to 260 °C (via IR sensor) and a pressure up to 8 MPa. In each digestion, an accurately weighed amount of 0.05 g coal sample was mixed with 3 ml of HNO_3 in a cleaned vessel. After the cap assembles were sealed, the four liners were stuck inside the vessel jackets and then mounted on the rotating tray in a symmetrical pattern to ensure a uniform irradiation. The heating profile was controlled by the predetermined power program. Typically, the temperature rose from room temperature to 200 °C in the first 30 min, and then to about 250 °C in the later 30 min with the autogeneous pressure of about 7.5 MPa.

After the vessel was cooled down and depressurized, the solution was carefully transferred to a Teflon beaker. Unless stated otherwise, the solution was evaporated in an evacuated bench to a small drop of thick liquid (∼0.1 g) at a temperature below 60 °C by heating with two infrared radiation lamps. This procedure typically took 5 h. The residue was dissolved with 1 M HNO_3, and then passed through a PTFE filter with a pore size of 0.45 μm (Sterile Millex-HV Millipore), and finally diluted with 1 M HNO_3 for the instrumental analysis. Since the decomposition degree of HNO_3 upon the digestion was unknown, the evaporation procedure allowed the digestion solution to be easily adjusted on the background HNO_3 concentration and consequently, the solution could be analyzed by an external calibration method. In all experiments, the polypropylene bottles used for storing the solutions were immersed in 1 M HNO_3 overnight, and rinsed with ultrapure water, and then dried in a Class 100 bench.

2.3. Instrumental analyses

Six major elements (Na, Mg, Al, K, Ca, and Fe) and 15 trace elements (Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Sr, Cd, Ba, and Pb) were determined by ICP-OES (Optima 4300 DV, Perkin-Elmer, USA). The above trace elements together with Rb and Cs were determined by ICP-MS (Agilent 7500a, Agilent Technologies Inc., Japan). The external calibration method was used in these analyses. Signal drift was monitored using the standard solution at intervals of three samples. More detailed instrumentations were described previously [12].

Se, Cd, and Hg were determined by FI-ICP-MS. In this analysis, 1 M HNO_3 was used as a carrier solution at a flow rate of $1.0\,ml\,min^{-1}$. The carrier solution was flowed using a peristaltic pump. The standard calibration solution or sample solution was introduced by a flow injection (100 μl). The signal intensity was continuously measured over time, and the accumulated peak area obtained after subtracting a background was used for calculating the elemental concentration by the external calibration method or by the standard addition calibration method.

Carbon in the solid residue derived from digestion was determined with a Total Organic Carbon Analyzer (TOC-V SSM-5000A, Shimadzu). For determination of carbon in the solution, the solution was first neutralized with a concentrated sodium hydroxide solution, and then analyzed on an elemental analyzer (EALLK Element Analyzer CE Instruments ThermoQuest Italia).

3. Results and discussion

3.1. Limit of quantification

Table 1 shows the limits of quantification (LOQs) of trace elements in coal by ICP-OES and ICP-MS. The LOQ is calculated as the concentration equal to 10 times the standard deviation of the background signal (the signal of 1 M HNO_3), multiplied by the dilution factor (DF). The LOQ means the lowest concentration of an element in coal that is quantifiable using the referred instrument. It was shown in expectation that the amounts of LOQ by ICP-MS were one to two orders of magnitude lower than those by ICP-OES for most trace elements at an identical DF (150). In the practical measurement, the solutions (DF = 3000) used in ICP-MS except for those used in FI-ICP-MS (DF = 150) were more dilute than those used in ICP-OES (DF = 150) for the purpose of ensuring the operational stability of ICP-MS. Even at a DF of 3000, the LOQs of Ga, As, Rb, and Cs by ICP-MS were much lower than those by ICP-OES. Note that for relatively concentrated Ba and Sr in three coals as well as Mn in SARM 19,

Table 1
Limits of quantification in coal by ICP-OES and ICP-MS

Element	ICP-OES		ICP-MS		
	Wavelength (nm)	LOQ ($\mu g\, g^{-1}$) (DF = 150)	Isotope (*m*/*z*)	LOQ ($\mu g\, g^{-1}$) (DF = 3000)	LOQ ($\mu g\, g^{-1}$) (DF = 150)
Li	670.78	0.02	7	0.05	0.002
Be	313.11	0.04	9	0.03	0.002
V	290.88	0.5	51	0.05	0.002
Cr	267.72	0.4	53	1.4	0.07
Mn	257.61	0.01	55	0.2	0.01
Co	228.62	0.09	59	0.08	0.004
Ni	231.60	0.9	60	1.0	0.05
Cu	324.75	0.3	63	0.4	0.02
Zn	213.86	0.3	66	0.8	0.04
Ga	294.36	0.8	71	0.02	0.02
As	188.98	1.5	75	0.4	0.02
Se	196.03	1.4	82	1.0	0.05
Rb	420.19	23	85	0.06	0.003
Sr	407.77	0.02	88	0.02	0.001
Cd	228.80	0.1	111	0.10	0.005
Cs	455.53	104	133	0.02	0.001
Ba	455.40	0.04	137	0.06	0.003
Hg	194.17	0.4	202	0.8	0.04
Pb	220.35	0.3	208	0.2	0.01

a larger dilution factor was used in the ICP-OES and ICP-MS analysis.

3.2. *ICP-OES and ICP-MS results of trace elements*

Tables 2 and 3 show the results of trace elements determined by ICP-OES and ICP-MS, respectively. All the digestions were controlled at a temperature of 250 ± 10 °C and a pressure of 7.5 ± 0.5 MPa. The instrumental relative standard deviation (I.R.S.D.) represents the instrumental precision, which is the result of measuring a single solution in triplicate. The total relative standard deviation (T.R.S.D.) represents the reproducibility of the sample preparation and instrumental analysis, which is obtained by analysis of three solutions prepared separately.

ICP-OES results showed that the measured values of Li, Be, Cr, Mn, Co, Ni, Cu, As, Sr, and Ba in all three coals were well consistent with the certified or reference values, with amounts of T.R.S.D. smaller than 10%. The results of V for SRM 1632c and BCR 180 were satisfactory but that for SARM 19 was slightly lower. The values of Zn and Pb were virtually in agree-

Table 2
ICP-OES results of three standard coals by microwave digestion with HNO_3 alone at 250 ± 10 °C and 7.5 ± 0.5 MPa (results in $\mu g\, g^{-1}$)

Element	SRM 1632c				BCR 180				SARM 19			
	Certified[a]	Found	I.R.S.D. (%)	T.R.S.D. (%)	Certified	Found	I.R.S.D. (%)	T.R.S.D. (%)	Certified[b]	Found	I.R.S.D. (%)	T.R.S.D. (%)
Li	(8)	9.3	0.7	1.4	(15.5)	15.4	0.7	1.1	(37)	38.8	1.0	1.1
Be	(1)	0.90	0.8	4.2	(0.81)	0.70	1.2	7.3	2.8 +0.3, −0.5	2.40	0.7	0.9
V	(23.7 ± 0.5)	21.4	0.8	1.4	19.3 ± 0.6	17.5	0.8	1.7	35 ± 2	25.9	0.9	0.9
Cr	(13.7 ± 0.1)	12.9	0.4	1.1	(13.5)	11.6	0.7	2.8	50 +8, −3	46.2	0.5	1.0
Mn	(13.0 ± 0.5)	11.6	0.5	2.3	34.3 ± 1.1	33	0.7	8.0	157 +11, −14	138	0.5	1.6
Co	(3.5 ± 0.2)	3.7	0.6	9.0	(3.3)	3.2	0.5	6.2	5.6 +0.6, −0.4	5.37	0.3	1.3
Ni	(9.3 ± 0.5)	9.9	0.4	2.1	(9.5)	8.2	0.7	1.4	16 +4, −3	14.1	0.7	3.6
Cu	(6.0 ± 0.2)	5.9	1.1	2.2	(9.1)	8.6	0.8	1.7	13 ± 1	11.2	1.0	2.9
Zn	(12.1 ± 1.3)	13.5	0.3	4.2	27.4 ± 1.1	29	0.4	12	12 +4, 3	20	0.5	21
Ga	(3)	4.04	9.8	2.3	(3.9)	3.8	13	9.1	14 ± 1	13.4	2.2	2.4
As	(6.2 ± 0.2)	5.5	3.4	5.2	4.23 ± 0.19	4.2	1.7	8.9	7 ± 1	6.8	4.0	4.2
Se	(1.33 ± 0.03)	<LOQ			1.32 ± 0.06	<LOQ			(1)	<LOQ		
Rb	7.5 ± 0.3	<LOQ			(8.3)	<LOQ			9 ± 1	<LOQ		
Sr	(63.8 ± 1.3)	57.9	0.7	0.1	(113)	98	0.4	4.0	126 +16, −1	111	0.6	4.3
Cd	(0.071 ± 0.007)	0.14	16	6.8	0.21 ± 0.01	0.24	10	5.5	(0.25 ± 0.03)	0.24	10	5.5
Cs	(0.59 ± 0.01)	<LOQ			(0.69)	<LOQ			1.4 +0.6, −0.1	<LOQ		
Ba	41.1 ± 1.6	37.3	0.6	2.2	(157)	152	0.6	2.0	304 +14, −9	241	0.7	3.1
Pb	(3.79 ± 0.08)	3.8	5.2	6.6	17.5 ± 0.5	16.1	5.5	5.5	20 ± 3	16	1.6	15

[a] Data in parentheses are reference values.

[b] Figures presented as $x + a, -b$ means a value of x with 95% certainty from $x - b$ to $x + b$.

Table 3
ICP-MS results of three standard coals by microwave digestion with HNO_3 alone at 250 ± 10 °C and 7.5 ± 0.5 MPa (results in $\mu g\,g^{-1}$)

Element	SRM 1632c				BCR 180				SARM 19			
	Certified[a]	Found	I.R.S.D. (%)	T.R.S.D. (%)	Certified	Found	I.R.S.D. (%)	T.R.S.D. (%)	Certified[b]	Found	I.R.S.D. (%)	T.R.S.D. (%)
Li	(8)	7.3	2.0	5.7	(15.5)	15.4	1.0	1.6	(37)	36.0	1.4	9.6
Be	(1)	0.92	10	6.7	(0.81)	0.75	9.5	3.5	2.8 +0.3, −0.5	2.5	3.6	8.9
V	(23.7 ± 0.5)	22.1	1.4	6.4	19.3 ± 0.6	18.4	1.3	4.8	35 ± 2	28.8	1.5	7.1
Cr	(13.7 ± 0.1)	14.3	3.6	6.6	(13.5)	13.7	4.2	6.0	50 +8, −3	53	1.5	11
Mn	(13.0 ± 0.5)	12.2	2.1	2.6	34.3 ± 1.1	36	1.1	8.1	157 +11, −14	141	0.8	2.3
Co	(3.5 ± 0.2)	3.4	3.1	11	(3.3)	3.0	4.4	2.9	5.6 +0.6, −0.4	5.7	1.8	5.0
Ni	(9.3 ± 0.5)	9.8	3.6	3.4	(9.5)	8.4	1.9	3.4	16 +4, −3	15.1	3.6	3.3
Cu	(6.0 ± 0.2)	6.1	1.0	8.2	(9.1)	9.2	4.0	0.4	13 ± 1	11.6	1.5	7.9
Zn	(12.1 ± 1.3)	11.5	4.7	12	27.4 ± 1.1	24	2.4	16	12 +4, 3	16	3.6	31
Ga	(3)	3.6	3.2	7.1	(3.9)	3.6	3.9	3.9	14 ± 1	12.9	1.9	7.2
As	(6.2 ± 0.2)	5.5	3.4	10	4.23 ± 0.19	4.4	15	4.8	7 ± 1	5.94	4.9	4.4
Se	(1.33 ± 0.03)	1.7	16	21	1.32 ± 0.06	1.7	15	14	(1)	2.0	6.7	14
Rb	7.5 ± 0.3	6.6	1.8	4.7	(8.3)	7.2	2.3	3.6	9 ± 1	4.2	1.7	5.4
Sr	(63.8 ± 1.3)	57.3	1.4	1.8	(113)	91	0.7	4.3	126 +16, −1	102	1.2	5.2
Cd	(0.071 ± 0.007)	<LOQ			0.21 ± 0.01	0.1	44	43	(0.25 ± 0.03)	<LOQ		
Cs	(0.59 ± 0.01)	0.51	13	6.5	(0.69)	0.6	22	41	1.4 +0.6, −0.1	1.04	3.6	4.8
Ba	41.1 ± 1.6	37.2	1.6	4.5	(157)	150	2.0	3.6	304 +14, −9	244	2.5	4.9
Pb	(3.79 ± 0.08)	3.8	5.0	1.0	17.5 ± 0.5	16.5	2.3	10	20 ± 3	18	2.0	15

[a] Data in parentheses are reference values.

[b] Figures presented as $x + a, -b$ means a value of x with 95% certainty from $x - b$ to $x + b$.

ment but T.R.S.D. amounts of these analytes were significantly greater than I.R.S.D. amounts in some cases. This implied a possible contamination of Zn and Pb during the sample preparation. Previous studies [2,9,12] also reported that Zn and Pb were readily susceptible to the contamination. However, the contamination source has not been defined. Ga in SARM 19 was determined accurately and precisely, while the measurement of Ga in SRM 1632c and BCR 180 exhibited a greater I.R.S.D. This was because the concentrations of Ga in SRM 1632c and BCR 180 were too close to the LOQ. For a similar reason, the determination precisions of Cd were poor for all three coals. In addition, ICP-OES was insensitive enough for determination of Se, Rb, Cs, and Hg.

As shown in Table 3, good precisions of Ga, Rb, and Cs determination were obtained by ICP-MS, and this was due to the enhanced sensitivity by ICP-MS compared to ICP-OES. Lower values of Rb and Cs for SARM 19 indicated that recovery of the two elements from this coal was likely to be incomplete. Hg, Cd, and Se could not precisely be quantified even with ICP-MS. For the rest of trace elements, the results obtained by ICP-MS were consistent with those obtained by ICP-OES.

3.3. *FI-ICP-MS results of Se, Cd, and Hg*

FI-ICP-MS has recently been used for measurement of Hg in fish tissue [15] and metallic elements in human serum [16]. In this study, it is for the first time applied to simultaneously determine ultra-trace elements in coal. In the ICP-MS analysis, since a higher dilution factor (3000) was used, the concentrations of Se, Cd, and Hg in the coals were lower than the LOQ amounts. As shown in Table 1, reduction of dilution factor (namely use of a less dilute solution) can be a straightforward way to reduce LOQ. However, the solution derived from coal contains concentrated inorganic components. The continuous introduction of a thick solution may cause serious deposition of the matrix on the cones, as well as the memory effect of mercury [15]. This problem is overcome by means of FI-ICP-MS that injects only small aliquots of the sample solution into the instrument.

Table 4 shows the results of Se, Cd, and Hg obtained by FI-ICP-MS using a low dilution factor of 150. The external calibration method was used for the solutions prepared after the evaporation, and the standard addition method for the solutions without undergoing evaporation. In contrast to the common ICP-MS, FI-ICP-MS achieved accurate results of Se and Cd with reasonable amounts of T.R.S.D. In addition, no significant differences in the concentration were observed with and without the evaporation, indicating that little of these two elements were vaporized. It should be noted that isotope ^{82}Se was chosen in analysis because the most abundant isotope ^{80}Se were susceptible to the isobaric interference by $^{40}Ar^{40}Ar$. On account of a possible spectrometric overlapping of ^{82}Kr on ^{82}Se, the data have been corrected according to the following equation:

$$(^{82}\mathrm{Se})_{\mathrm{corrected}} = (^{82}\mathrm{Se})_{\mathrm{measured}} - 1.0 \times (^{83}\mathrm{Kr})_{\mathrm{measured}}$$

For comparison, the uncorrected data are shown in parentheses. It could be seen that all uncorrected data of Se were appreciably greater than the certified or reference values, whether using the external calibration method or using the standard addition method.

Hg is regarded as a highly volatile metallic element. It was actually demonstrated that the concentrations of Hg measured through the evaporation were lower than the certified or reference values for BCR 180 and SARM 19 coal, whereas without evaporation, the concentrations of Hg in all three coals were in

Table 4
FI-ICP-MS determination of Se, Cd, and Hg in three standard coals by the microwave digestion with HNO_3 alone at 250 ± 10 °C and 7.5 ± 0.5 MPa followed by evaporation or wihout evaporation (results in $\mu g\,g^{-1}$)

Coal	Element	Certified	By evaporation			Without evaporation[a]		
			Found[b]	I.R.S.D. (%)	T.R.S.D. (%)	Found	I.R.S.D. (%)	T.R.S.D. (%)
SRM 1632c	Se	(1.33 ± 0.03)	1.28(1.44)	1.3	3.2	1.34(1.9)	6.6	5.3
	Cd	(0.071 ± 0.007)	0.064	7.3	1.4	0.073	9.9	5.7
	Hg	0.0983 ± 0.004	0.10	7.7	7.4	0.105	4.3	1.2
BCR 180	Se	1.32 ± 0.06	1.33(1.6)	2.8	9.7	1.29(2.3)	1.7	1.6
	Cd	0.21 ± 0.01	0.20	5.0	5.8	0.22	3.2	1.3
	Hg	0.123 ± 0.008	<LOQ			0.14	4.6	4.3
SARM 19	Se	(1)	1.01(2.1)	5.9	3.5	0.89(1.87)	4.1	2.1
	Cd		0.25	5.8	12	0.17	5.8	5.9
	Hg	(0.2)	0.12	8.8	8.7	0.19	3.4	1.0

[a] Using standard addition method.
[b] Figures in parentheses are not corrected for the interference from ^{82}Kr.

good agreement with the certified or reference values. This suggested that unlike other elements, Hg was easily susceptible to a vaporization loss. But it is unclear why Hg in BCR 180 coal was mostly vaporized, whereas no obvious vaporization occurred for SRM 1632c coal. If the evaporation procedure was terminated before a thick liquid drop formed, we observed no loss of Hg for all three coals.

Determination of Se, Cd, and Hg in coal generally requires the ramified digestion and instrumental methods [13,14]. This study has proposed a rapid and efficient method for simultaneous determination of such ultra-trace analytes in coal by FI-ICP-MS analysis of the non-evaporated solution prepared from the present digestion. Although a standard addition method is needed in the instrumental analysis, the total analytical procedure is simple and time-saving. It should be mentioned that in principle, FI-ICP-MS are also suitable for determination of other elements in coal if the elements are present in ultra-trace amounts. However, FI-ICP-MS is not suitable for simultaneous determination of many elements because spectrometric scanning of many analytes can spoil their shape of the FI time profile. For determination of a large number of trace elements of higher concentrations, it is preferable to use a common ICP-MS by the external calibration method.

3.4. Coal decomposition

Coal consists of carbonaceous and mineral matrices, both of which host a wide variety of trace elements. Therefore, it is generally required to thoroughly destroy the organic structure and inorganic minerals for ensuring total dissolution of trace elements. The use of $HClO_4$ and aqua regia in the conventional digestion serves to accelerate the decomposition of the carbonaceous and mineral matrices under the mild conditions. When using HNO_3 alone or HNO_3/H_2O_2, a significant part of carbonaceous material and silicates remained after the microwave digestion [9,10].

The residual organic carbon in the solution can negatively influence the ICP-OES and ICP-MS analyses [17]. In a previous study [12], we visibly observed that digestion with HNO_3/H_2O_2 at 220 °C resulted in a yellowish solution. Here, we have quantitatively examined the decomposition degree of coal with HNO_3 at different temperatures. Fig. 1 shows the residual carbon amounts in the solutions collected after digesting 50 mg of coal sample with 3 ml of HNO_3 at different temperatures followed by filtration and/or evaporation, where the percentage of carbon remaining is calculated based on the carbon fed from raw coal. It is supposed that the coal organic matrix is oxidized with HNO_3 as the following equation:

$$\text{Coal} + HNO_3 \rightarrow NO_2 + H_2O + CO_2 + \text{dissolved organics} + \text{solid organic residue}$$

The dissolved fraction of carbon is determined from the solution obtained after filtration. Because a tiny solid residue cannot be quantitatively collected upon the filtration, the solid frac-

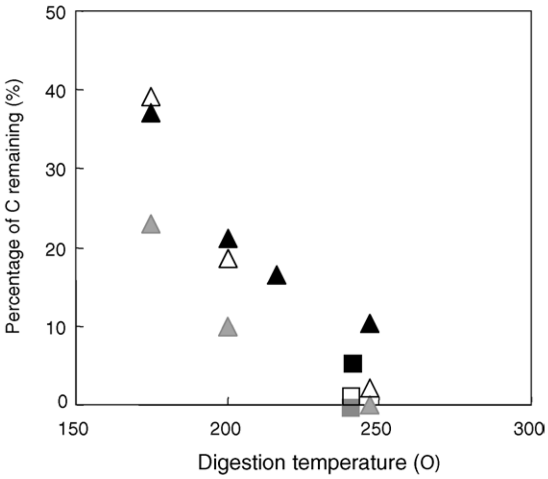

Fig. 1. Percentage of carbon remaining in the solutions obtained by the digestion with HNO_3 alone at different temperatures. Triangle symbols, SRM 1632c; square symbols, SARM 19. Black symbols, carbon in the solution obtained by filtration; void symbols, carbon in the solid residue obtained by evaporation; ash symbols, carbon in the solution obtained by dissolution of the solid residue with 1 M HNO_3 and then by filtration.

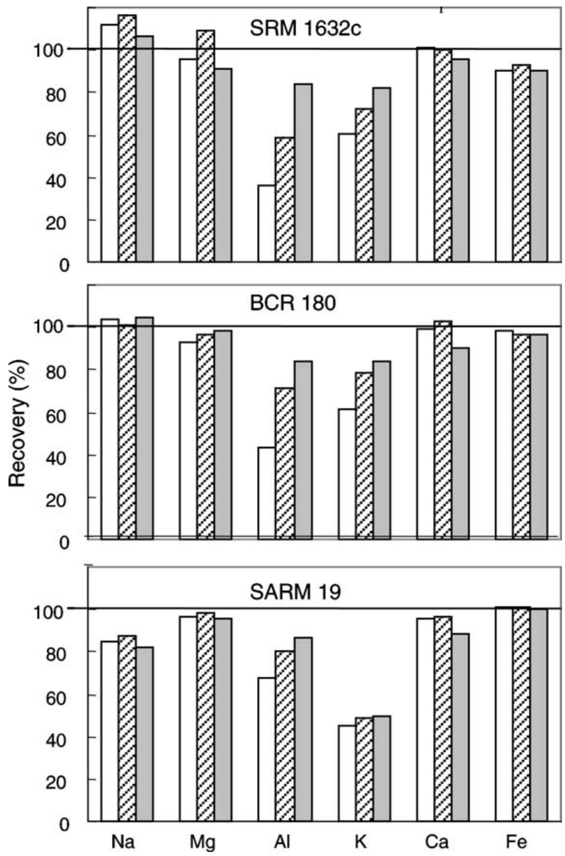

Fig. 2. Recovery of major elements from three standard coals by the digestion with HNO_3 alone at different temperatures. Void bar, 175 ± 5 °C; slash bar, 200 ± 10 °C; ash bar, 250 °C.

tion of carbon is estimated by measuring the carbon in the solid residue remaining after evaporation. Since some dissolved carbon is possibly precipitated during the evaporation, this part of carbon is roughly estimated by measuring the carbon in the solution obtained sequentially by evaporation, dissolution with 1 M HNO_3, and filtration (named the EDF treatment below).

At 180 °C (a maximum temperature permitted for the conventional low-pressure vessels), approximately 38% of dissolved carbon and some solid carbon remained for SRM 1632c. As the temperature increased, both the dissolved carbon and the solid carbon decreased. At 250 °C, the percentage of dissolved carbon decreased down to 12% for SRM 1632c, with almost no solid carbon remaining. After the EDF treatment, the solution was almost free of any carbon. At high temperature, not only was the oxidation of the solid carbon facilitated but also the dissolved organics degraded to smaller molecular organic compounds. The light organic compounds were prone to be volatilized and thus most of them could be removed by the evaporation. The final solution obtained at 250 °C was colorless and transparent, and it was very amenable to the instrumental analysis. Possible influences of the organic carbon could be minimized.

Fig. 2 shows the recoveries of major elements in three coals by the digestion with HNO_3 alone at different temperatures. Good recoveries were obtained for Na, Mg, Ca, and Fe even at 175 °C. Dissolution of Al and K relied strongly on the temperature and coal. At 175 °C, significant part of Al was not dissolved out, whereas at 250 °C, the recoveries of Al in all three coals reached greater than 85%. This indicated that most clay in coal was decomposed at the elevated temperature even in the absence of HF. The recovery of K showed a trend similar to Al, implying that some K was associated with clay. However, more than half of K in SARM 19 was not dissolved even at 250 °C; this was probably due to the existence of acid-resistant K-bearing feldspar in this coal [20]. It should be stated that quartz in coal was insoluble in the hot HNO_3, forming a white solid suspension. It is thus needed to purify the solution by filtration before the instrumental analysis.

3.5. Dissolution of trace elements

Fig. 3 shows the recoveries of some trace elements obtained after the digestion at different temperatures followed by ICP-OES. It could be seen that the recoveries of Li, V, Cr, Ga, and As were improved at the elevated temperature depending on coal, while Mn, Co, and Ni in all three coals appeared to be well recovered even at 175 °C. Low recoveries of Li, V, Cr, and Ga were also observed in the conventional low-temperature digestion [9,10].

For clarity, the recoveries of all the trace elements from three coals obtained by the digestion at a temperature of 250 °C and

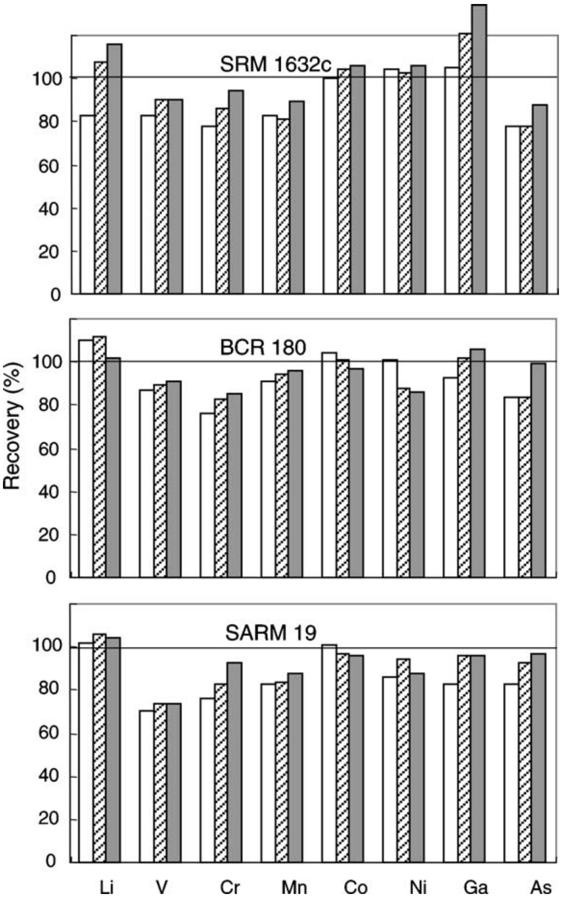

Fig. 3. Recovery of some trace elements from three standard coals by the digestion with HNO_3 alone at different temperatures. Void bar, 175 ± 5 °C; slash bar, 200 ± 10 °C; ash bar, 250 °C.

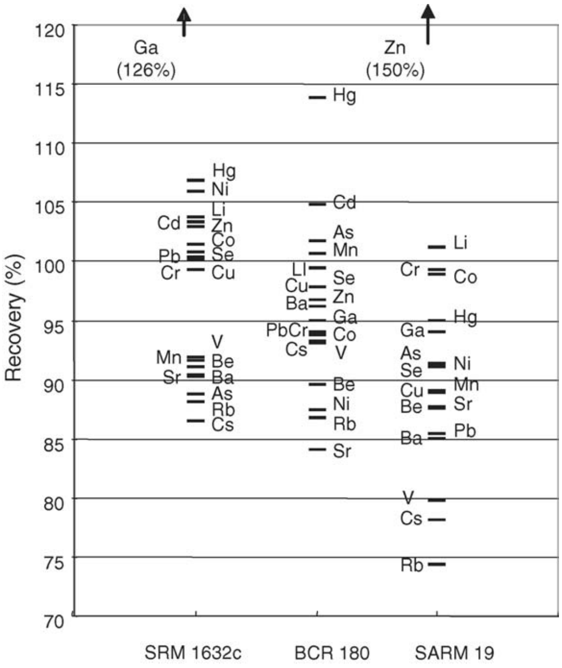

Fig. 4. Recovery of trace elements from three standard coals by the digestion with HNO_3 alone at 250 °C and 7.5 MPa.

a pressure of 7.5 MPa followed by ICP-MS and FI-ICP-MS are depicted in Fig. 4. The recoveries of all the trace elements in SRM 1632c and BCR 180 except Ga in SRM 1632c and Sr in BCR 180 were ranged within 100 ± 15%. Good recoveries were also verified for most trace elements in SARM 19, but low recoveries of V, Rb, and Cs were observed for this high-ash coal. Alkali elements, Rb and Cs, were likely to be combined partly with insoluble K-bearing feldspar. The overmuch recoveries of Ga from SRM 1632c and Zn from SARM 19 were probably ascribed to less precise reference values.

In general, trace elements in coal are present as carbonate, chalcophite, ion-exchanged, organically bound, and silicate-associated forms [18]. The dissolution of trace element varies with their modes of occurrence in coal. Carbonate, chalcophite, and ion-exchanged trace elements are soluble in HNO_3, and these forms of trace elements can readily be recovered. However, the organic matrix and clay are enriched with many lithophite trace elements [19,20], and these forms of trace elements can not be well recovered unless the organic and clay matrices were thoroughly decomposed. This accounts for the incomplete dissolution of many trace elements in HNO_3/H_2O or HNO_3 alone under the low-temperature condition [9,10]. At the elevated temperature and pressure, because the organic matrix and clay in coal were tended to be extensively decomposed even with HNO_3 alone, the digestion is validated for total dissolution of a wide range of trace elements. Although quartz and some minor refractory rocks are not dissolved with HNO_3 alone, they generally contain less trace elements of importance.

4. Conclusion

The severe microwave digestion with HNO_3 alone (250 °C, 7.5 MPa) was validated for quantitative dissolution of all 19 trace elements (Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Cd, Cs, Ba, Hg, and Pb) in three standard coals, with the exception of V, Rb, and Cs in the high-ash SARM 19 coal.

ICP-MS with the conventional sample introduction required a greater dilution factor and this led to an insufficient sensitivity for determination of less abundant trace elements such as Se, Cd, and Hg in coal. These elements could be simultaneously determined by FI-ICP-MS using a smaller dilution factor.

The coal organic matrix was oxidized to gaseous products with fractional part of light dissolved organics under the rigorous digestion condition. Through the subsequent evaporation, nearly no carbon remained in the final solution. Clay in coal was also substantially dissolved with HNO_3 alone. Thorough decomposition of the coal organic matrix and clay contributed to good recoveries of numerous trace elements from coal.

Hg was lost during the evaporation. The evaporation procedure should be avoided for assay of this element. The loss was insignificant for all other trace elements during the evaporation.

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