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Talanta 66 (2005) 58–64

Talanta

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Effect of HF addition on the microwave-assisted acid-digestion for the determination of metals in coal by inductively coupled plasma-atomic emission spectrometry

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Received 17 February 2004; accepted 23 September 2004
Available online 5 November 2004

Abstract

The microwave-assisted acid-digestion for the determination of metals in coal by ICP-AES was investigated, especially focusing on the necessity of adding HF. By testing five certified reference materials, BCR-180, BCR-040, NIST-1632b, NIST-1632c, and SARM-20, it was found that the two-stage digestion without HF ($HNO_3 + H_2O_2$ was used) was very effective for the pretreatment of ICP-AES measurement. Both major metals (Al, Ca, Fe, and Mg) and minor or trace metals (Co, Cr, Cu, Mn, Ni, Pb, and Zn) in coal gave good recoveries for their certified or reference values. The possibility of 'HF-memory effect' was cancelled by the use of a set of vessels which had been never contacted with HF. Twenty-four Japanese standard coals (SS coals) were analyzed by the present method, and the concentrations of major metals measured by the present method provided very high accordance with those from the authentic JIS (Japanese Industrial Standard) method.

Keywords: Microwave-assisted digestion; Inductively coupled plasma-atomic emission spectrometry; Coal; Metal concentration; Trace metals; Addition of HF

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1. Introduction

Coal is mainly a cluster of organic high molecular compound which consists of C, H, O, N, and S. However, coal is one of the components of crust, so that it contains many kinds of mineral matter elements including metals derived from its generation. The behavior of mineral matter elements during coal combustion process is very important because they not only cause slugging and fouling, but also gives great influence upon the combustion characteristics due to positive or negative catalytic effect. Further, recently the existence of hazardous trace elements, such as heavy metals, in coal has been a considerable problem on the viewpoint of environmental safety [1–5]. Some of these hazardous elements will be released into air while some of them are distributed in bottom ash, fry ash, and desulfurization residues. The development of precise and easy determination method for the metals in coal is the essential factor for the study of above problems which are caused by the existence of metals in coal.

Recently, the metals in coal have been frequently determined by atomic spectrometry, such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS). For the sample intro-

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doi:10.1016/j.talanta.2004.09.018

Table 1
Recent reports of the microwave-assisted acid-digestion of coal

Literature	Number of coal samples	Composition of acid mixture	Analytical method
[6]	1	$HNO_3 + HF$	GFAAS
[7]	2	HNO_3 or $HNO_3 + HF$	GFAAS
[8]	7	$HNO_3 + HF$	ICP-AES
[9]	2	$H_2SO_4 + HClO_4 + HF$[a]	ICP-MS
[10]	1	$HNO_3 + HClO_4 + HF$	ICP-MS
[11]	2	$HNO_3 + H_2O_2 + HF$	ICP-MS
[12]	2	$HNO_3 + HClO_4 + HF$	ICP-MS
[13]	3	$HNO_3 + HClO_4 + HF$	ICP-MS
[14]	3	$HNO_3 + H_2O_2$ or $HNO_3 + H_2O_2 + HF$	ICP-AES

[a] Acid-digestion was performed in a platinum crucible on a hot-plate.

duction system of these methods, usually solution nebulization is used. Therefore, the analyte is needed to transfer from solid phase into solution. In recent years, the acid-digestion assisted by microwave processing is popularly utilized for such a pretreatment of solid matters. The microwave-assisted acid-digestion offers some advantages in short reaction time, the prevention of vaporization, and the contamination control, compared to the conventional hot-plate digestion methods. Table 1 lists the recent reports which had studied on the microwave-assisted acid-digestion for the determination of metals in coal [6–14]. For the microwave-assisted acid-digestion of coal samples, the combination of HNO_3 and HF is usually adopted because coal contains considerable amount of inorganic matters (1–30%), which mainly consists of aluminosilicate matrix [6,8,10–13]. However, Ikavalko pointed that the use of HNO_3 alone provided quite good results for various heavy metals except for Cu; the recovery of Cu was greatly improved by the addition of HF in a small amount (HNO_3:HF, 50:1) [7]. Such a HF-lean microwave digestion was also performed [11]. Further, Wang et al. described that there was not essential difference between the HF-lean digestion and HF-free digestion in terms of the recoveries of many elements [14]. The utilization of HF is recommended to avoid if possible because of its negative effects on instrumental parts as well as safety considerations. However, the optimization of digestion conditions for coal sample has not yet fully done, especially for the effect of adding HF upon the recovery of metals.

Also, almost all studies shown in Table 1 have dealt with limited numbers of coals. The properties of coal are greatly dependent upon the brand of coal. However, there have been few studies about the application of the digestion method to many brands of coals.

In this study, we examined the microwave-assisted acid-digestion method for the determination of metals in coal by ICP-AES, focusing on the necessity of using HF as well as the number of digestion procedure. By use of five certified reference materials, we proved the effectiveness of the present method for major metals (Al, Ca, Fe, and Mg) as well as minor or trace metals (Co, Cr, Cu, Mn, Ni, Pb, and Zn). For the major metals, the accordance of the values from the present method with those derived from the authentic JIS (Japanese Industrial Standards) method (JIS M 8812 and M 8815) [15] was evaluated by the use of 24 brands of coals.

2. Experimental

2.1. Samples

Five certified reference materials for coal from National Institute of Standards & Technology, USA (NIST; 1632b and 1632c), Community Bureau of Reference, EC (BCR; 040 and 180), and SA Bureau of Standards, Republic of South Africa (SARM-20), were used. These coals were provided with certified or reference values for various elements, which include major, minor, and trace metals.

Also, 24 brands of Japanese standard coals (SS coals), which had been provided by the Center of Coal Utilization, Japan (CCUJ), were used. The content of metal oxide in the ash of coal after ashing had been determined according to JIS method [15]. Table 2 shows the ash contents (JIS M 8812) and the metal oxide contents in ash (JIS M 8815).

2.2. Reagents and instrumentation

Nitric acid (HNO_3, 61%), hydrogen peroxide solution (H_2O_2, 30%), and hydrofluoric acid (HF, 46%) were analytical grade reagents from Wako Pure Chemical India Ltd. Their mixture was employed in the microwave digestion. Distilled water was further purified by a Milli-Q system and used throughout the experiments. Multielement standard solution (1000 ppm, Merck) was used for ICP-AES measurement.

The microwave digestion was carried out by using a Milestone ETHOS1600, which was equipped with an evaporation module (SSM60). ICP-AES measurement was performed using a Perkin-Elmer Optima 3100RL equipped with pneumatic cross-flow type nebulizer, quartz torch, and alumina injector, which enabled us to detect samples containing HF in a small amount.

2.3. Digestion procedures and measurement

In the one-stage digestion, a 0.25 g portion of dried sample was weighed and transferred into a pressure-resistant PTFE vessel (volume 100 ml), and the mixture of acids ($HNO_3 + H_2O_2$, 5:3 ml or $HNO_3 + H_2O_2 + HF$, 5:2:1 ml) was added. The vessel was then sealed and mounted in a sleeve (outer vessel). A total of six samples were evenly spaced in the microwave oven carousel and the digestion program was set as listed in Table 3. The vessels were removed and carefully vented in a fume hood after cooling to room temperature in a water-bath.

The two-stage digestion was carried out as follows. The procedure and acid conditions of the first processing were the same as those for the one-stage digestion except for the digestion program (Table 3). After the venting procedure

Table 2
Data of SS coals in literature [15]

Coal (Country)	Ash content (%) (JIS M 8812)	Metal oxide content in ash (%) (JIS M 8815)				
		Al_2O_3	Fe_2O_3	CaO	MgO	MnO
SS001 (AUS)	14.97	32.61	5.14	7.66	1.33	0.05
SS002 (AUS)	14.52	28.46	2.23	2.01	0.74	0.02
SS003 (AUS)	8.56	30.87	2.18	0.86	0.37	0.04
SS004 (CHN)	9.68	20.39	15.95	2.68	0.89	0.13
SS005 (JPN)	12.08	23.54	6.24	9.55	1.95	0.10
SS006 (AUS)	11.92	21.26	5.60	5.73	1.45	0.05
SS007 (AUS)	15.00	26.31	0.90	0.33	0.26	0.02
SS008 (AUS)	11.90	26.01	3.07	0.87	0.50	0.02
SS009 (IND)	4.38	26.47	5.77	3.54	0.96	0.01
SS010 (IND)	5.14	25.98	9.90	1.95	1.74	0.26
SS011 (IND)	1.58	9.18	10.53	20.63	6.84	1.09
SS012 (IND)	3.38	18.98	11.87	11.89	4.28	2.46
SS013 (AUS)	13.70	28.97	4.24	1.99	0.92	0.06
SS014 (AUS)	13.60	28.12	5.48	7.65	1.67	0.10
SS015 (COL)	8.30	17.84	7.76	1.80	0.89	0.04
SS016 (USA)	8.80	20.47	3.81	5.19	1.21	0.01
SS017 (IND)	10.60	36.75	5.35	1.89	0.66	0.01
SS018 (CHN)	9.10	34.80	4.97	5.54	1.98	0.09
SS019 (ZAF)	13.70	31.33	3.74	8.14	2.21	0.06
SS020 (ZAF)	12.90	29.39	5.00	7.13	2.60	0.09
SS021 (ZAF)	14.43	32.90	2.93	8.54	1.69	0.64
SS022 (ZAF)	13.73	28.56	4.46	9.84	2.22	0.66
SS023 (USA)	6.80	12.06	5.06	8.40	1.64	0.02
SS024 (USA)	7.14	27.50	5.55	3.98	1.22	0.01

mentioned above, a mixture of $HNO_3 + H_2O_2$ (2:1 ml) was quickly added to each sample. The vessels were returned to the microwave oven and the second processing was applied to the samples under the conditions as described in Table 3.

When HF was not used, the reaction mixture was filtered, and the filtrate was diluted to a fixed volume (25 ml) with Milli-Q water. For the digestion with HF (both for one-stage digestion and two-stage digestion), the reaction mixture was subjected to an evaporation procedure by use of the evaporation module in order to remove the acids after the final digestion. Then the residue was dissolved in Milli-Q water and filtrated, and the filtrate was diluted to a fixed volume (25 ml). The ICP-AES measurement was performed for the diluted solutions.

For each run, samples were prepared at least triplicates, and the ICP-AES measurement for each digested sample was carried out twice. From these more than six measurements, mean value and standard deviation for the metal concentration were obtained.

3. Results and discussion

3.1. Various digestion conditions

For a certified reference material, BCR-180, various digestion conditions were attempted. Table 4 presents the values obtained by the microwave-assisted acid-digestion under various digestion conditions followed by the ICP-AES measurement. The variation of digestion conditions includes “with HF” and “without HF” (basic condition, $HNO_3 + H_2O_2$) as well as “one-stage” and “two-stage” (see Section 2).

Table 3
Microwave digestion program

Step	One-stage digestion			Two-stage digestion					
				Stage 1			Stage 2		
	Time (min)	Power (W)	Temperature ($^\circ$C)[a]	Time (min)	Power (W)	Temperature ($^\circ$C)[a]	Time (min)	Power (W)	Temperature ($^\circ$C)[a]
1	5	250	110	2	250	110	5	250	130
2	5	400	110	1	0	110	5	400	130
3	10	500	110	5	250	110	5	500	130
4	10	600	110	5	400	110	5	600	130
5	5	250	110	5	500	110	15	400	130
6				20	400	110			

[a] Temperature at the sleeve (outer vessel).

Table 4
Determination of metals in BCR-180 by various digestion methods

Metal	Certified[a]	One-stage digestion				Two-stage digestion			
		With HF		Without HF		With HF		Without HF	
		Measured	Recovery (%)[b]	Measured	Recovery (%)[b]	Measured	Recovery (%)[b]	Measured	Recovery (%)[b]
Al (mg/g)	(12.4)	0.30 ± 0.07	2	10.6 ± 0.3	85	3.1 ± 1.1	25	12.0 ± 0.3	97
Ca (mg/g)	NA	0.97 ± 0.23	–	3.40 ± 0.29	–	2.46 ± 0.31	–	3.44 ± 0.28	–
Fe (mg/g)	(11.7)	5.9 ± 1.6	50	10.4 ± 0.4	89	10.0 ± 0.8	85	11.3 ± 0.2	97
Mg (mg/g)	NA	0.03 ± 0.01	–	0.51 ± 0.03	–	0.13 ± 0.04	–	0.54 ± 0.02	–
Co (μg/g)	(3.3)	2.9 ± 0.2	88	3.4 ± 0.1	103	4.4 ± 0.4	133	4.3 ± 0.4	130
Cr(μg/g)	(13.5)	11.1 ± 0.8	82	11.4 ± 0.3	84	13.1 ± 1.1	97	12.9 ± 0.8	96
Cu(μg/g)	(9.1)	7.9 ± 0.3	87	7.8 ± 0.2	86	9.6 ± 0.6	105	9.3 ± 0.2	102
Mn(μg/g)	34.3 ± 1.1	31.9 ± 1.7	93	31.1 ± 1.6	91	35.4 ± 1.6	103	35.4 ± 1.4	103
Ni(μg/g)	(16)	7.2 ± 0.5	45	7.5 ± 0.4	47	7.8 ± 0.4	49	7.7 ± 0.3	48
Pb(μg/g)	17.5 ± 0.5	15.5 ± 1.2	89	15.2 ± 1.2	87	18.0 ± 1.3	103	18.1 ± 0.6	103
Zn(μg/g)	27.4 ± 1.1	25.5 ± 1.5	93	26.0 ± 1.2	95	26.2 ± 2.1	96	26.1 ± 1.3	95

[a] NA: not available; values in parentheses are not certified (reference value).

[b] Recovery (%) = ([mean measured values]/[certified or reference value]) × 100.

For Al, the addition of HF greatly reduced the recovery of metal; the recovery was 2% for the one-stage digestion and 25% for the two-stage digestion. From a comparison between the values obtained when HF was used and those when it was not used, it was found that the HF addition also largely lowered the recovery of Ca and Mg; BCR-180 does not have the certified or reference values of those metals. It is proposed that when HF is present, metal fluoride species are produced and these species are quite insoluble in the aqueous solution. It has been reported that when HF was added in digestion process for coal, boric acid was usually used to remove HF in the resulting solution to make BF_4^- complexes [6–8,10]. However, this method has a disadvantage in the use of high concentration of boric acid, which leads to a contamination of torch and other parts in ICP-AES instruments by boron-memory effect.

For Fe, the decrease in the recovery occurred to some extent when HF was used. The one-stage digestion without HF gave 85–89% recoveries for Al and Fe. Those recoveries were improved by use of the two-stage digestion, and good recoveries were obtained; “good” or “satisfied” recoveries mean 90–110% recoveries in this text. The results of the two-stage digestion without HF were about the same as those of the one-stage digestion for Ca and Mg.

For minor or trace metals, Co, Cr, Cu, Mn, Ni, Pb, and Zn, the addition of HF did not affect the recovery so much. The two-stage digestion provided considerable improvement in the recovery compared to the one-stage digestion. Thus, the two-stage digestion without adding HF gave good recoveries. When the two-stage digestion was conducted, the recovery of Co was ca. 130% with or without HF, while that of Ni was ca. 50%. For other certified reference materials (BCR-40, NIST-1632b, NIST-1632c, and SARM-20), the recoveries of Co and Ni were good (see Tables 5 and 6). Therefore, it is concluded that the reference values (not certified) of Co and Ni for BCR-180 presented by BCR are not accurate.

Table 5
Determination of metals in BCR-40 by various digestion methods

Metal	Certified[a]	One-stage digestion				Two-stage digestion			
		With HF		Without HF		With HF		Without HF	
		Measured	Recovery (%)[b]	Measured	Recovery (%)[b]	Measured	Recovery (%)[b]	Measured	Recovery (%)[b]
Al (mg/g)	NA	0.70 ± 0.18	–	17.2 ± 0.4	–	2.4 ± 0.2	–	17.3 ± 0.5	–
Ca (mg/g)	NA	0.27 ± 0.08	–	1.38 ± 0.12	–	1.14 ± 0.37	–	1.51 ± 0.11	–
Fe (mg/g)	NA	8.92 ± 0.14	–	8.65 ± 0.17	–	8.61 ± 0.80	–	9.58 ± 0.40	–
Mg (mg/g)	NA	0.03 ± 0.01	–	1.23 ± 0.09	–	0.10 ± 0.03	–	1.24 ± 0.07	–
Co (μg/g)	7.8 ± 0.6	8.4 ± 0.5	108	6.2 ± 0.4	79	8.2 ± 0.3	105	7.3 ± 0.2	94
Cr (μg/g)	31.3 ± 2.0	24.6 ± 1.6	79	21.9 ± 0.3	70	29.1 ± 1.4	93	29.7 ± 1.8	95
Cu (μg/g)	NA	30.1 ± 1.7	–	28.8 ± 2.4	–	34.5 ± 2.5	–	33.8 ± 1.8	–
Mn (μg/g)	139 ± 5	100 ± 4	72	109 ± 2	78	126 ± 7	91	129 ± 10	93
Ni (μg/g)	25.4 ± 1.6	19.3 ± 1.1	76	18.8 ± 1.6	74	23.6 ± 1.3	93	23.6 ± 1.1	93
Pb (μg/g)	24.2 ± 1.7	22.2 ± 1.6	92	23.8 ± 1.2	98	23.5 ± 2.0	97	24.8 ± 1.2	102
Zn (μg/g)	30.2 ± 1.9	26.4 ± 2.4	87	27.3 ± 2.3	90	27.2 ± 1.3	90	28.7 ± 0.7	95

[a] NA: not available.

[b] Recovery (%) = ([mean measured values]/[certified or reference value]) × 100.

Table 6
Determination of metals in three certified reference materials

Metal	NIST-1632b		NIST-1632c		SARM-20	
	Certified[a]	Measured	Certified[a]	Measured	Certified[a]	Measured
Al (mg/g)	8.55 ± 0.19	8.72 ± 0.24	(9.15 ± 0.14)	9.02 ± 0.22	5.97	5.58 ± 0.37
Ca (mg/g)	2.04 ± 0.06	2.13 ± 0.19	(1.45 ± 0.30)	1.43 ± 0.10	1.34	1.29 ± 0.11
Fe (mg/g)	7.59 ± 0.45	7.78 ± 0.16	(7.35 ± 0.11)	7.52 ± 0.27	8.18	7.78 ± 0.41
Mg (mg/g)	0.38 ± 0.01	0.37 ± 0.03	(0.38 ± 0.03)	0.35 ± 0.03	2.6	2.3 ± 0.2
Co (μg/g)	2.29 ± 0.17	2.5 ± 0.1	3.48 ± 0.20	3.7 ± 0.2	8.3	7.8 ± 0.3
Cr (μg/g)	(11)	11.8 ± 0.8	(13.73 ± 0.20)	13.4 ± 0.7	(67)	60.3 ± 1.2
Cu (μg/g)	6.28 ± 0.30	6.4 ± 0.3	(6.01 ± 0.25)	5.8 ± 0.3	18	17.1 ± 0.4
Mn (μg/g)	12.4 ± 1.0	11.6 ± 0.2	13.04 ± 0.53	12.4 ± 0.4	80	75.3 ± 2.4
Ni (μg/g)	6.10 ± 0.27	6.5 ± 0.3	(9.32 ± 0.51)	9.6 ± 0.3	25	25.3 ± 0.6
Pb (μg/g)	3.67 ± 0.26	3.5 ± 0.3	(3.79 ± 0.07)	3.9 ± 0.2	26	24.5 ± 1.0
Zn (μg/g)	11.89 ± 0.78	12.0 ± 1.0	12.1 ± 1.3	11.7 ± 0.5	17	16.6 ± 1.2

[a] Values in parentheses are not certified (reference value).

In Table 5, the values obtained for another certified reference material, BCR-40, are recorded. The influence of adding HF and that of multi-stage digestion upon the recovery were quite similar to those when BCR-180 was analyzed. The addition of HF resulted in a great diminution in the values obtained for Al, Ca, and Mg. The use of two-stage digestion lead to some measurable improvements in the recovery compared to the one-stage digestion, especially when minor or trace metals were analyzed.

As a result, the optimum method for the microwave-assisted digestion of coal is the two-stage digestion without HF, i.e., coal is digested with a mixture of $HNO_3 + H_2O_2$ (first processing), followed by the further addition of the fresh mixture, and then the second processing is performed. It is proposed that the mixture of $HNO_3 + H_2O_2$ can effectively extract these metals in coal during the microwave-assisted acid-digestion, and thus the complete decomposition of silicate matrix by adding HF is not necessary.

By use of the optimum digestion method followed by the ICP-AES measurement, other three certified reference materials, NIST-1632b, NIST-1632c, and SARM-20, were tested. As shown in Table 6, almost satisfied agreement between the certified or reference values and the measured values was obtained for all of metals examined.

3.2. HF-memory effect

It has been proved that the addition of HF is not necessary for the microwave-assisted digestion of coal. There is a possibility that a trace amount of HF remaining in the PTFE vessel will work for the digestion of coal (HF-memory effect), even when the external addition of HF is not performed. It has been said that HNO_3-memory effect really exists when the microwave-assisted digestion is carried out with a PTFE vessel; when one uses a newly bought vessel, the digestion cannot be satisfactorily performed, because a trace amount of HNO_3, which penetrates through the vessel, may effectively proceed the digestion.

To confirm the presence or absence of ‘HF-memory effect’, a set of newly bought vessels were used; the vessels had been aged by the HNO_3–H_2O_2 digestion procedure, and had been never contacted with HF. By use of the vessels, the microwave-assisted acid-digestion followed by the ICP-AES measurement was carried out for the two certified reference materials, BCR-180 and NIST-1632c. As shown in Table 7, the results obtained with the vessels (no contact with HF) were about the same as those in Tables 4 and 6 (without HF) for which the vessels used had been sometimes contacted with HF. Therefore, it is concluded that ‘HF-memory effect’ is absent in the microwave-assisted acid-digestion.

3.3. Determination of metals in SS coals

Japan is the world’s biggest coal-importing country, and thus many types of coals from various countries are imported and used in coal-fired power plants and industries. Those coals have been collected as standard samples and provided as “SS coals” from the Center of Coal Utilization, Japan (CCUJ). For the SS coals, some data according to JIS are provided from CCUJ. Those data include proximate analysis and elemental analysis as well as the analysis of ash content (JIS M 8812) and ash composition for major metals (Al, Ca, Fe, Mg, etc.), (JIS M 8815). However, those coals do not have the data for the concentrations of trace metals. To confirm the usefulness of the present digestion/ICP-AES method, 24 brands of SS coals were analyzed by the optimized method, in which the two-stage digestion without HF followed by the ICP-AES measurement was involved.

In the JIS method (JIS M 8815), after ashing coal at 815 °C in the air, an acid-digestion or an alkali fusion was carried out for the ash, and then the concentration of the metal oxides was determined by volumetric or colorimetric analysis. From the ash content (JIS M 8812) and the ash composition (JIS M 8815) obtained from the JIS methods [15], it is possible to calculate the concentration of metal in coal, if it can be assumed that no volatilization of metal occurs during the ashing process. The values of metal concentrations calculated in this way are called “JIS-value”. The correlation between the metal concentrations measured by the present digestion/ICP-AES method and those of JIS-value was investigated, and

Table 7
Determination of metals in BCR-180 and NIST-1632c[a]

Metal	BCR-180			NIST-1632c		
	Certified[b]	Measured	Recovery (%)[c]	Certified[b]	Measured	Recovery (%)[c]
Al (mg/g)	(12.4)	11.6 ± 0.5	94	(9.15 ± 0.14)	8.88 ± 0.37	97
Ca (mg/g)	NA	3.42 ± 0.32	–	(1.45 ± 0.30)	1.38 ± 0.03	95
Fe (mg/g)	(11.7)	10.9 ± 0.2	93	(7.35 ± 0.11)	7.15 ± 0.13	97
Mg (mg/g)	NA	0.52 ± 0.04	–	(0.38 ± 0.03)	0.35 ± 0.01	92
Co (μg/g)	(3.3)	3.8 ± 0.1	115	3.48 ± 0.20	3.7 ± 0.2	106
Cr (μg/g)	(13.5)	12.7 ± 0.2	94	(13.73 ± 0.20)	13.8 ± 0.4	101
Cu (μg/g)	(9.1)	8.6 ± 0.6	95	(6.01 ± 0.25)	5.5 ± 0.2	92
Mn (μg/g)	34.3 ± 1.1	32.7 ± 2.0	95	13.04 ± 0.53	12.7 ± 0.3	97
Ni (μg/g)	(16)	8.0 ± 0.3	50	(9.32 ± 0.51)	10.1 ± 0.4	108
Pb (μg/g)	17.5 ± 0.5	17.2 ± 1.5	98	(3.79 ± 0.07)	3.8 ± 0.3	100
Zn (μg/g)	27.4 ± 1.1	25.8 ± 1.3	94	12.1 ± 1.3	12.7 ± 0.5	105

[a] Newly bought PTFE vessels, which had been aged by the HNO_3–H_2O_2 digestion procedure (no contact with HF), were used.

[b] NA: not available; values in parentheses are not certified (reference value).

[c] Recovery (%) = ([mean measured value]/[certified or reference value]) × 100.

the results are shown in Fig. 1. As shown in Fig. 1, very good agreements were obtained between the concentrations of Al, Ca, Fe, and Mg measured by the present method and those of JIS-value ($y = a + bx$: $a = -0.02$–0.44, $b = 0.95$–1.05; $R^2 = 0.97$–0.99). For JIS-value, the analytical procedure is totally different from that used in the digestion/ICP-AES method. Accordingly, the fact that these two methods provide highly accordant values suggests that the present method can give very accurate determination for the metals in coal.

When the Mn concentrations obtained by the present method was plotted against those of JIS-value, a good correlation was observed except for five points, as shown in Fig. 2a. The CCUJ also provided the data of X-ray fluorescence (XRF) analysis for the SS coals [16]. When the values for the present method was plotted against those measured by XRF, a good correlation including the five points was obtained, although the slope obtained was 0.69 (Fig. 2b). Consequently, it is proposed that JIS-value cannot give accurate values for minor or trace metal concentrations, such as Mn, although it provides good values of major metal concentrations. Also for XRF, the literature described that higher values for recovery (110–130%) were obtained for NIST cer-

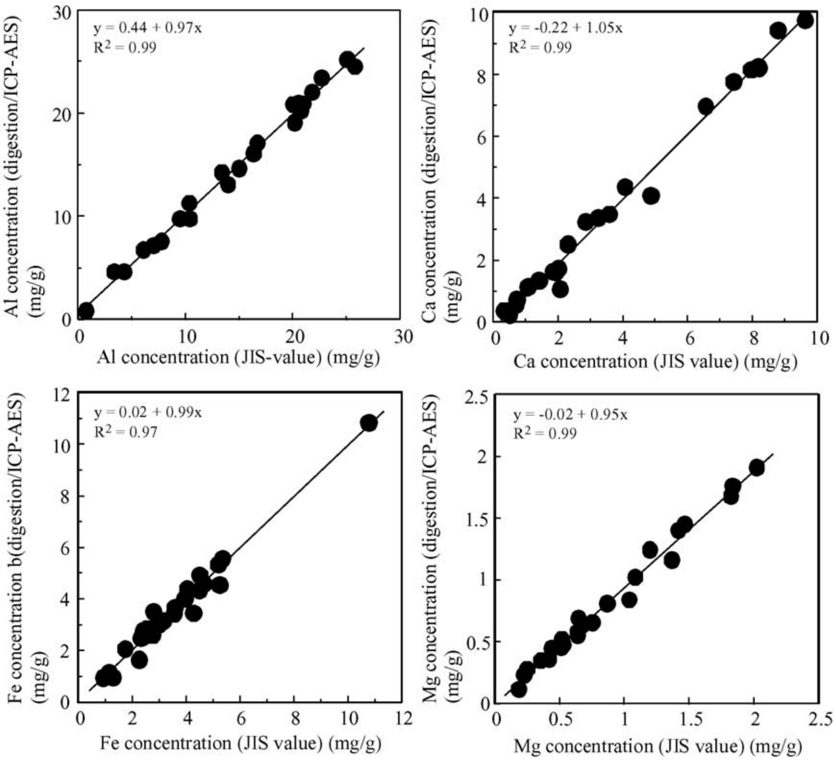

Fig. 1. Comparison between the values of metal concentrations in 24 SS coals measured by the digestion/ICP-AES method and those of JIS-value [15].

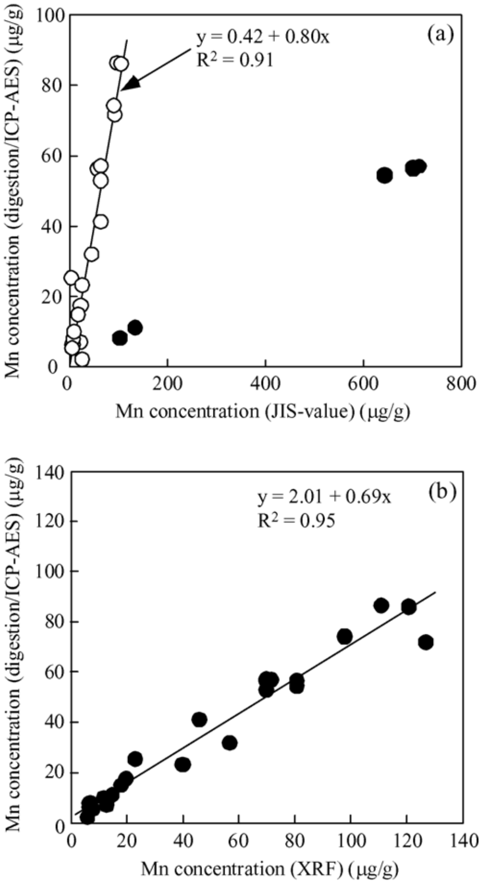

Fig. 2. Comparison between the Mn concentrations in 24 SS coals measured by the digestion/ICP-AES method and those of JIS-value [15] (a); comparison between the values measured by the digestion/ICP-AES method and those by XRF [16] (b).

tified materials (NIST-1632a and 1632b) when minor or trace metals, such as Cr, Mn, and Ni, were measured [16]. Thus, it appears that the slope 0.69 in Fig. 2b is ascribed to the tendency that XRF gives higher values of recovery.

4. Conclusion

The microwave-assisted acid-digestion for the determination of metals in coal by ICP-AES was investigated, especially focusing on the necessity of adding HF. By use of five references certified materials, it was proved that the optimum method is the two-stage digestion without HF, i.e., coal is digested with a mixture of $HNO_3 + H_2O_2$ (first processing), followed by the further addition of the fresh mixture, and then the second processing is performed. The addition of HF to the digestion system caused a great depression in the recoveries of Al, Ca, and Mg, while the two stage-digestion improved the metal recoveries, especially for minor and trace metals, compared to the one-stage digestion. The possibility of ‘HF-memory effect’ was cancelled by use of a set of vessels which had never been contacted with HF.

When 24 brands of SS coals were analyzed by the optimum digestion/ICP-AES method, very good agreements were obtained between the concentrations of Al, Ca, Fe, and Mg measured by the present method and those of JIS-value. It is hoped that the present method is useful in the practical determination of metals in various coals, which should deserve further exploration.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 10141239 from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors would like to thank the Center for Coal Utilization, Japan (CCUJ) for providing SS series coals and their data.

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