



Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176

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ABSTRACT

Sequential extraction procedures and the high-pressure digestion method were selected to determine the element constituents of fly ash samples. Sequential extraction is one of the most useful methods used to measure the various elements from municipal solid waste incineration ash and contaminated soils. The extract from each step is analyzed using various techniques and equipments, and the results are then evaluated. In this work, a six-step extraction procedure modified from that of Tessier et al. and Wang et al. was performed and applied to the certified reference material BCR 176 (city waste incineration ash). Analyses were carried out by various techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), and X-ray powder diffraction (XRPD) to evaluate the characteristics of fly ash. The extraction efficiency of many elements was higher than 80%, and the relative standard deviations (RSD) for recovery of most elements were within 10%. In addition, an $\text{H}_2\text{O}_2 + \text{HNO}_3 + \text{HF}$ mixed acid digestion solution processed using a low-temperature evaporation procedure was selected as the optimal process for fly ash digestion. The results of this work provide information on the chemical composition, distribution, and potential mobility of the investigated elements.

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1. Introduction

In recent decades, due to the growth of urbanization and industrialization, solid wastes have not only increased in quantity but also undergone changes in properties and composition. Therefore, the problem of solid waste disposal has become a major challenge to environmentalists and scientists. At present, various treatment methods, including landfills, resource recycling, and incineration, have been applied and investigated [1]. In many developed countries, combustion has become a common management strategy for solid waste treatment and disposal. In Japan, about 80% of municipal solid waste (MSW) generated is treated by incineration, and only 20% is processed by composting or landfill [2]. In Taiwan, about 60% of MSW is treated by incineration, 20% by landfill, and 17% by reuse and recycle.

With incineration, the volume and mass of solid wastes can be reduced by 90% and 70%, respectively. Incineration also produces

by mass nearly 70% fumes, 27% bottom ash and 3% fly ash [3–8]. In addition, incineration can destroy pathogenic agents and generate thermal energy that can be recovered for reuse [9,10]. Despite the advantages of solid waste combustion, incineration residues, including bottom ash and fly ash, are a significant source of inorganic pollution. The behavior of many pollutant elements such as As, Cd, Cu, Cr, Hg, Ni, Pb and Zn of incineration residues have been described [9,11–13], and the release of such elements during storage can have deleterious effects on the environment, including groundwater and surface water resources, as well as on human health [5,14].

Due to element toxicity, it is important to determine the concentration and distribution of pollutants from incineration residues in order to mitigate their impact on the environment. Extraction methods show promise as a means to address the above-mentioned problem. Numerous extraction procedures have been developed [15] and reported in the literature, based on various sequence schemes and carried out under various operating conditions [7,16,17]. Sequential extraction procedures have been applied to sediments [18,19], contaminated soils [20–22], incinerated sludge ash [23,24] and municipal solid waste ash [25,26].

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Recently, this step-by-step procedure has been applied to bottom ash and fly ash from municipal solid waste incinerators (MSWI) to determine the distribution of elements [7,25,27,28]. Determining the elemental content in the fly ash requires systematic studies under the different conditions associated with the various methods.

Although some literature has focused on the composition of SRM BCR 176, most does not provide detailed sequential extraction information. Therefore, this study was aimed at using the sequential extraction method for fly ash to measure the residual characteristics (especially in toxic metal content) under different environment conditions (e.g., pH variation) [29–32]. In addition, the sequential extraction method has not been applied to measure the element fraction of BCR 176 in detail.

This work focuses on the methods (sequential extraction procedures and high-pressure digestion method) to investigate the characteristics of reference material BCR 176 (city waste incineration ash) [33,34], which not only has wide interest in the analytical field but also generates data comparable to that of other studies. The six-step extraction procedure was modified from the original sequential extraction method by Tessier et al. [35] and Wang et al. [36], and a variety of techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) and X-ray powder diffraction (XRPD) were used to determine the concentration and the morphological and mineralogical phases in each step. In addition, the characteristics of high-pressure digestion methods (four-digestion solution) and six-step sequential extraction procedures are compared in this study.

2. Experimental

2.1. Apparatus and material

Concentrations of the major elements such as Al, Ca, Fe, K, Mg, Na, and S in the extracts were measured by inductively coupled plasma atomic emission spectrometry (PerkinElmer Optima 3000DV). Other trace elements were measured by inductively coupled plasma-mass spectrometry (PerkinElmer Elan 5000). The operating conditions of ICP-AES and ICP-MS are shown in Table 1.

Morphological investigations were carried out on a scanning microscopy analyzer (SEM, JOEL JSM-6300F), coupled with an energy-dispersive X-ray analyzer (EDX, OXFORD INCAENERGY 400). The typical accelerating voltage of SEM was kept at 30 kV, and the EDX was run with a lithium drifted silicon detector at a resolution of 133 eV.

Mineralogical phases presented in the solid residues were identified using X-ray powder diffraction (MAC Science XXP 18) with Cu K α radiation and a position-sensitive detector. The accelerating voltage was kept at 30 kV and the current at 20 mA. A divergent slit (1°), a scattering slit (1°) and a receiving slit (0.3 mm) were used to produce the best spectrum. Scans were conducted from 20° to 70° at the rate of 1°–2 θ /min. Data were digitally recorded, and peak position and intensity were determined either on screen or using the smoothed and peak finder feature in the software. Identification of compounds was made by manual search of the JCPDS – International Center for Diffraction Data (ICDD) as a reference database. The signal of the XRPD diagram filtered out the noise; generally, if the signal to noise ratio is larger than 3, the peak can be regarded as a signal. A horizontal and mechanical water bath shaker was used for the extraction steps, and the centrifuge was used to separate the solid phase from the extraction liquid.

2.2. Reference material

The procedure was tested on city waste incineration ash BCR 176-certified reference material [33,34]. The fly ash was collected at the electrostatic filter of a city waste incinerator without any combustion additives. The material was then separated and sieved to reduce the particle size to less than 40 μm for the following analytical processes.

2.3. Reagents

All chemicals used for the study were supplied by Merck (analytical pure grade). The extraction solutions were prepared with de-ionized water (high purity water of resistance >16 M Ω cm). Nitric acid was used to adjust the pH, and standard calibration solutions of the elements of interest (1000 $\mu\text{g ml}^{-1}$) were prepared from stock concentrations by diluting to volume with de-ionized water. The polytetrafluoroethylene (PTFE), polyethylene, and propylene containers were cleaned by immersing the vessels in concentrated HNO₃ overnight and then washing successively with de-ionized water.

2.4. Sequential extraction procedure

The six-step sequential extraction applied in this study is described in Table 2. The extraction method of this study is mainly modified from Tessier et al. (steps b, c, d and e); de-ionized water extraction for step a is added in this study, and a study by Wang et al. is used as a reference for the final step f. First, a water-soluble fraction was investigated, followed by ion-exchangeable, carbonate, oxide, organic and residue steps. The detailed procedures were as follows:

- (a) Water-soluble: 10 ml of de-ionized water was added to 50 mg of the reference material [36–38] in a 15-ml polyethylene centrifuge tube. The mixed sample was extracted by shaking at a speed of 150 rpm for 3 h at ambient temperature with no delay between the addition of the leaching solution and the shaking process. Then the extract was separated from solid residues by centrifugation for 5 min. The supernatant was then removed and stored in a polyethylene tube at 4 °C for analysis. The obtained residue was added to 5 ml of the same leaching agent, shaken for 15 min, and centrifuged (extracted again) (the procedure was done in other steps). The supernatant was then transferred into the previous polyethylene tube. In both solid–liquid separation processes, it is necessary to filter out the solid residues, which must be retained for the next step.
- (b) Ion exchange: 10 ml of 0.1 M MgCl₂ was added to the residues from step a in the centrifuge tube and extracted by shaking for 3 h at ambient temperature. Extraction and solid–liquid separations as well as extract storage were carried out as described above.
- (c) Bound to carbonates: 10 ml of 0.1 N NaOAc/HOAc was added to the residues from step b in the centrifuge tube and extracted by shaking for 3 h at ambient temperature. Extraction and solid–liquid separation as well as extract storage were carried out as described in step b.
- (d) Bound to metal oxides: 10 ml of 0.1 N NH₂OH·HCl was added to the residues from step c in the centrifuge tube and extracted by shaking for 3 h at 60 °C. Extraction and solid–liquid separation as well as extract storage were carried out as described above.
- (e) Bound to organic metal complex or sulfides: 10 ml of mixed solution (2% of HNO₃ + H₂O₂ = 3 ml:7 ml) was added to the residues from step d in the centrifuge tube and extracted by shaking for

Table 1
Operation conditions for ICP-AES and ICP-MS instrument

ICP-AES (PE-Optima 3000DV)		ICP-MS (PE-Sciex Elan 5000)	
RF power	1300 W	RF power	1100 W
Nebulizer	Cross-flow	Gas flow rate	
Gas flow rate		Coolant	Ar 14.0 (1 min ⁻¹)
Plasma	Ar 15.0 (1 min ⁻¹)	Auxiliary	Ar 0.8 (1 min ⁻¹)
Auxiliary	Ar 0.5 (1 min ⁻¹)	Carrier	Ar 0.8 (1 min ⁻¹)
Carrier	Ar 0.8 (1 min ⁻¹)	Ion sampling depth	Adjusted to obtain maximum signal intensity
Sampling uptake rate	1.0 (ml min ⁻¹)	Ion lens setting	Adjusted to obtain maximum signal intensity and signal to noise ratio
Sampling uptake time	15 s	Dwell time (ms)	20
Delaying time	30 s	Resolution	300 ^a
Integration	Peak area	Readings/replicate	50
		Sweeps/reading	1
Elements (analytical wavelength) and observation axis		Scanning mode	Peak hopping transient
Al (369.152 nm)	Axial view	Sampling cone	Nickel (1.1 mm) ^b
Ca (317.933 nm)	Axial view	Skimmer	Nickel (1.1 mm) ^b
Fe (259.940 nm)	Radial view	Isotopes	As-75 (100% abundance)
K (766.491 nm)	Radial view		Ba-137 (11.2% abundance)
Mg (279.079 nm)	Axial view		Cd-114 (28.7% abundance)
Na (589.592 nm)	Radial view		Cr-52 (83.8% abundance)
S (180.669 nm)	Axial view		Cu-65 (30.9% abundance)
			Mn-55 (100% abundance)
			Ni-60 (26.2% abundance)
			Pb-208 (52.4% abundance)
			Sb-121 (57.4% abundance)
			Se-77 (7.58% abundance)
			Sr-86 (9.86% abundance)
			V-51 (99.76% abundance)
			Zn-66 (27.8% abundance)

^a The peak width at 10% of peak maximum is about 0.832 mass units.

^b Data in parentheses are the aperture diameter.

3 h at 85 °C. Extraction and solid–liquid separation as well as extract storage were carried out as described in step d.

(f) Residues, bound to silicate and silico-aluminate: The final residues were digested in the high-pressure bomb with 10 ml of mixed acid (HNO₃ + H₂O₂ + HF = 3 ml:5 ml:2 ml) at 190 °C. After digestion, the sample solution was transferred into a PTFE beaker and gently heated (85–90 °C) on a hot plate to evaporate the residual acid. The residues were then diluted to 50 ml for the analysis.

The morphological and mineralogical phases after the extraction step were examined by SEM and XRPD, respectively. The elemental constituents of the solutions extracted during the various steps were measured by ICP-AES and ICP-MS.

2.5. High-pressure bomb digestion

Fifty milligrams of BCR 176 was digested in a high-pressure bomb system with various digested solutions to determine elemental constituents. Prior to the ICP-AES and ICP-MS measurements, the following procedures were performed: (a) HNO₃ + HClO₄: 50 mg BCR 176 was digested with an 8-ml mixture of HClO₄ and HNO₃ (5:3,

v/v). After the digestion, the sample solution was transferred into a PTFE beaker and heated gently (85–90 °C) on a hot plate to allow the residual acid to evaporate. The residue was diluted to 50 ml by HNO₃ for ICP-AES and ICP-MS analysis. (b) HNO₃ + HClO₄ + HF: The method used was similar to that in (a) except that the samples were digested with a 10-ml mixture of HNO₃, HClO₄ and HF (5:3:2, v/v). (c) HNO₃ + H₂O₂: The method used was similar to that in (a) except that the HClO₄ was replaced by H₂O₂. (d) HNO₃ + H₂O₂ + HF: The method used was similar to that in (b) except that the HClO₄ was replaced by H₂O₂.

3. Results and discussion

3.1. Morphology analysis with SEM/EDX

SEM was carried out on the original and solvent leaching samples, and their elemental compositions were semi-qualitatively analyzed with EDX spectrometry (data not shown). Fig. 1 shows the morphology of BCR 176 for raw material and solvent leaching samples by SEM. Due to the agglomeration of the particles, an accurate quantitative measurement could not be made by surface analysis.

Table 2
Sequential extraction steps

Step	Fraction	Operation conditions ^b			
		Reagents ^a	pH	Temperature	Shaken time (h)
a	Water-soluble	De-ionized water (18.2 MΩ)	~6	Room temperature: 25 °C	3
b	Ion-exchangeable cations	0.1 M MgCl ₂	~6	Room temperature: 25 °C	3
c	Carbonates	0.1N NaOAc/HOAc	~5	Room temperature: 25 °C	3
d	Metal oxide	0.1N NH ₂ OH·HCl	~3	60 °C	3
e	Organic complex or sulfide	2% HNO ₃ + H ₂ O ₂ (3:7, v/v)	~2	85 °C	3
f	Silicate and silico-aluminate	HNO ₃ /H ₂ O ₂ /HF (3:5:2, v/v)		190 °C Acid vaporization: 85–90 °C	5

^a 10 ml reagents were added into samples for every extracted procedure.

^b All extracted solutions were centrifuged at 3000 rpm for 3 min before ICP-AES and ICP-MS analysis. Extracted solution was diluted to 50 ml by 2% HNO₃.

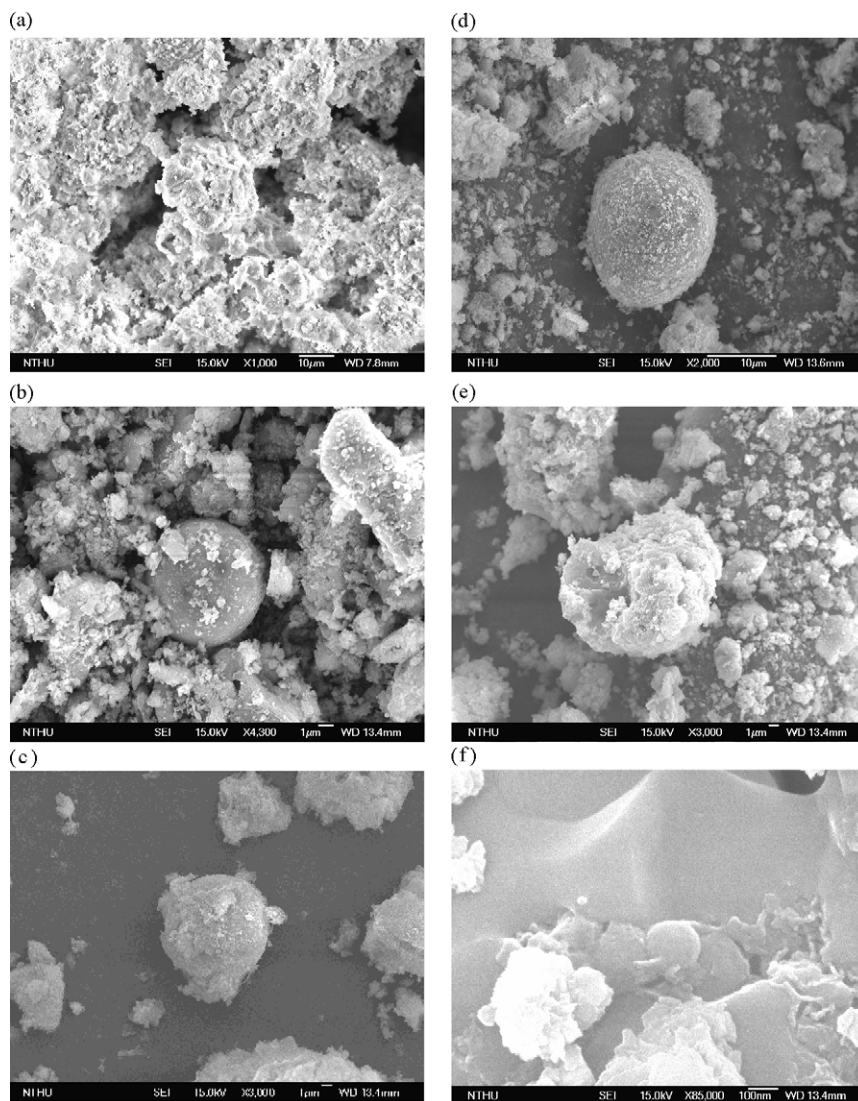


Fig. 1. Scanning electron microscopy of BCR 176. (a) Non-leached sample, (b) water-leached residue, (c) MgCl_2 -leached residue, (d) NaOAc/HOAc -leached residue, (e and f) $\text{NH}_2\text{OH}\cdot\text{HCl}$ -leached residue.

The SEM images indicate that BCR 176 consists of huge agglomerated particles in a wide range (Fig. 1a). Along with some roughly hollow spheres ranging in size from 5 to 100 μm , the samples were highly agglomerated, and small particles adhered to each other to form large ones. This suggests that many particles of 50–100 nm intertwined together to form larger ones (~ 0.1 – $10 \mu\text{m}$) and accumulated on the surface of the sphere. The EDX spectrum showed mainly silicates and silico-aluminates from BCR 176 in the no-leaching samples (residues). Mostly Ca-, K-, Mg-, Na- and Cl-containing compounds were found on the surface.

Fig. 1b depicts the water-leached BCR 176, where the agglomerated matter on the surface disappeared, compared to Fig. 1a. The salts aggregated on the original fly ash surface have been washed by de-ionized distilled water. The signals corresponding to Cl, K, and Ca substantially decreased, indicating that the agglomerated matter covering the fly ash was composed of water-soluble salts such as CaCl_2 , KCl , MgCl_2 , which were easily formed during the condensation process of exhaust gas and aggregation on the particle surface. The aggregation of salts of this type in fly ash has been reported elsewhere [39–41].

Fig. 1c reveals the results of the other extracted step, i.e., the extraction of water-leaching residues with MgCl_2 solution. Most of

the agglomerated matter on the surface observed on Fig. 1b is not seen in Fig. 1c.

In addition, the residues obtained from the previous step were extracted by a slightly acid solution (NaOAc/HOAc , $\text{pH} \approx 5$); some matter was extracted, and the shape of the sphere surface became irregular (Fig. 1d).

It was found that most of the metal oxides remained in the residues and could be dissolved with a slightly reducing reagent ($\text{NH}_2\text{OH}\cdot\text{HCl}$, $\text{pH} \approx 3$). As shown in Fig. 1e, the shape of the sphere surface becomes irregular, with some holes found in the particles. Results suggest that some evaporated elements and compounds adhere in the smaller sphere during the incineration process. The larger spheres were hollow and filled with some smaller silicate spheres (Fig. 1f). The small and broken sphere particles were primarily observed in Fig. 1f; EDX showed that they consist of Si, Al and Na (data not shown).

In addition, the morphology pictures of steps e and f are not mentioned because the stronger acid ($\text{HNO}_3 + \text{H}_2\text{O}_2$ used in step e ($\text{pH} \approx 2$) and $\text{HNO}_3 + \text{H}_2\text{O}_2 + \text{HF}$ used in step f) destroyed the structure of the residues. In particular, in step f, the residues are digested completely.

3.2. Mineralogical phase analysis with XRPD

Mineralogy is the primary way to understand the binding element status in the ash. The toxicity of MSW incineration fly ash is dependent not only on the concentration of the polluting elements, but also on the speciation of pollutant elements and the nature of the chemical combination [39–41]. The crystalline phases are very important in considering the potential effects on health of inhaled particles and in determining the physical and chemical properties of the ash. Data from the crystalline phases may be useful for developing methods of resource recovery from ash utilization and disposal.

The mineralogy phases of BCR 176 for raw materials and solvent-leached samples are illustrated in Fig. 2. The peaks of major compounds in BCR 176 such as SiO_2 , Na_2S , $\text{NaAlSi}_3\text{O}_8$, CaCl_2 , K_2S , CaS_2O_7 , $\text{K}_{0.4}\text{Na}_{0.6}\text{Cl}$, CaSO_4 , CaCO_3 and NaCl are shown in Fig. 2a.

After the water-soluble step, some compounds from BCR 176 such as Na_2S , CaCl_2 , K_2S , CaS_2O_7 , $\text{K}_{0.4}\text{Na}_{0.6}\text{Cl}$, CaSO_4 , CaCO_3 and NaCl substantially decreased. The results also indicated that the agglomerated matter covering the fly ash formed water-soluble salts such as CaCl_2 , KCl , and MgCl_2 by the condensation and aggregation processes on the particulate surface. The peaks of the water-leached BCR 176 are illustrated in Fig. 2b.

The residue of BCR 176 was extracted by MgCl_2 solution and then by a slightly acidic (NaOAc/HOAc) solution. After these two steps, it was found that most of the peaks of SiO_2 , $\text{NaAlSi}_3\text{O}_8$ (Fig. 2c and d) and some of the CaS_2O_7 (Fig. 2c) were on the particle surfaces. This phenomenon could be explained by the fact that the silicate and albite in the ash could not be dissolved in the above-mentioned solutions. Most of the compounds bonding metal oxide can be dissolved in a slightly reducing reagent ($\text{NH}_2\text{OH}\cdot\text{HCl}$). However, the peaks shown in Fig. 2e are similar to those in Fig. 2d.

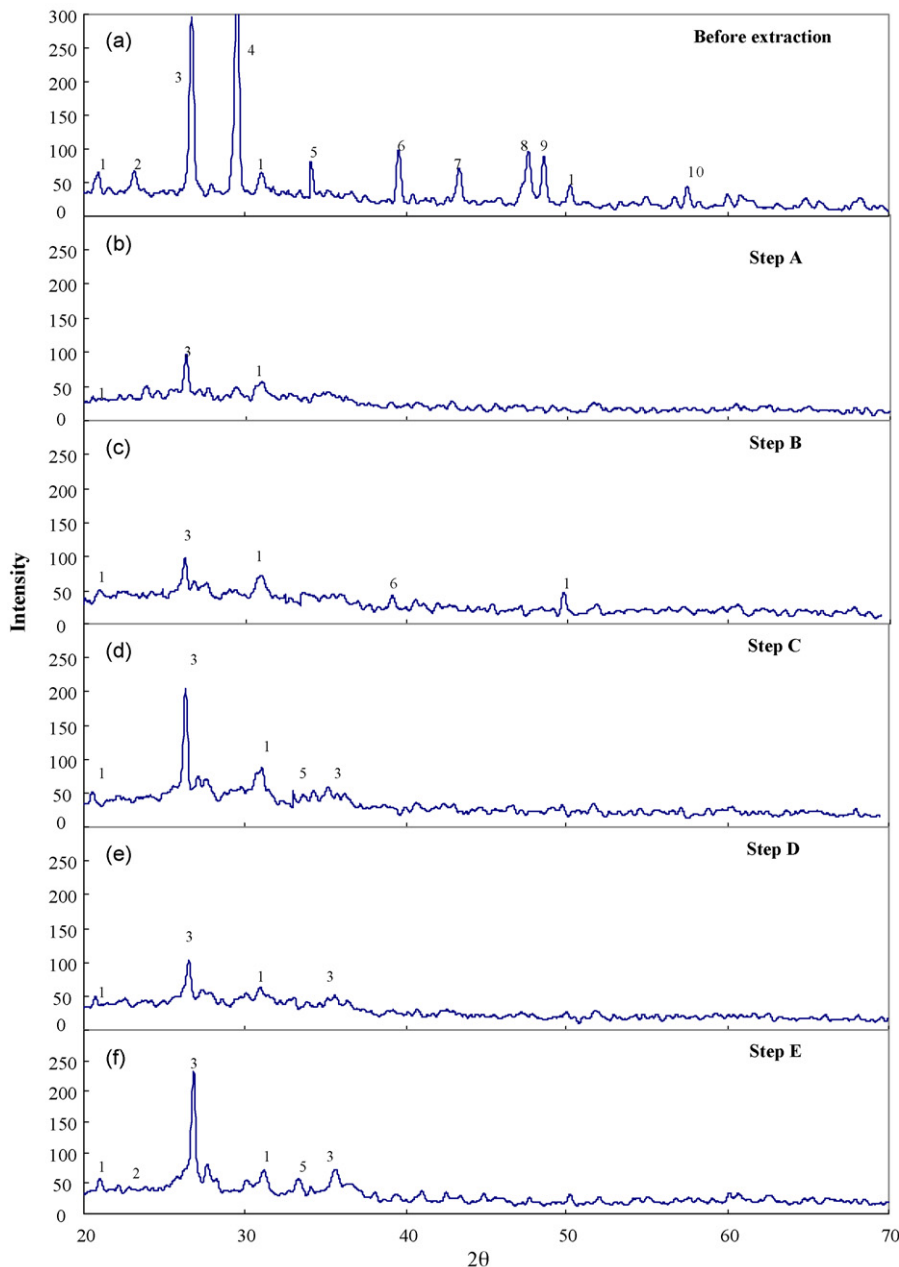


Fig. 2. X-ray powder diffraction of BCR 176. (a) Non-leached sample, (b) water-leached residue, (c) MgCl_2 -leached residue, (d) NaOAc/HOAc -leached residue, (e) $\text{NH}_2\text{OH}\cdot\text{HCl}$ -leached residue, (f) $\text{HNO}_3/\text{H}_2\text{O}_2$ -leached residue. (1) SiO_2 ; (2) Na_2S ; (3) $\text{NaAlSi}_3\text{O}_8$; (4) CaCl_2 ; (5) K_2S ; (6) CaS_2O_7 ; (7) $\text{K}_{0.4}\text{Na}_{0.6}\text{Cl}$; (8) CaSO_4 ; (9) CaCO_3 ; (10) NaCl .

Table 3Chemical composition between certified and found values in BCR 176 determined under sequential extraction ($n = 5$)

Element ^b	BCR 176 (mg/g)	Recovery ^a (%)						Sum	RSD (%) ^d
		(a) ^a	(b)	(c)	(d)	(e)	(f)		
Al ^b	101.6	1.3 ± 0.1	1.1 ± 0.1	2.9 ± 0.1	1.7 ± 0.3	38 ± 2	43 ± 1	88 ± 2	2.4
Ca	88.02	29 ± 1	8.1 ± 0.8	18 ± 1	7.4 ± 0.2	28 ± 2	4.3 ± 0.5	95 ± 2	2.5
Fe	21.3 ± 1.1	1.0 ± 0.1	0.7 ± 0.1	1.0 ± 0.1	2.9 ± 0.3	28 ± 1	56 ± 2	89 ± 2	2.7
K	44.99	45 ± 1	3.2 ± 0.1	4.0 ± 0.1	1.0 ± 0.1	17 ± 1	13 ± 1	83 ± 1	1.7
Na	42.92	46 ± 1	2.5 ± 0.3	ND ^c	ND ^c	ND ^c	ND ^c	49 ± 1	1.4
Mg	21.72	2.6 ± 0.1	ND ^c	ND ^c	ND ^c	ND ^c	ND ^c	2.6 ± 0.1	3.8
S	44.6	66 ± 3	10 ± 1	6.1 ± 0.2	0.7 ± 0.1	1.7 ± 0.1	0.4 ± 0.1	86 ± 3	3.4
As	0.093	5.7 ± 0.3	DL ^c	42 ± 1	6.5 ± 0.3	30 ± 1	8.1 ± 0.9	92 ± 2	2.1
Ba	4.5 ± 0.2	4.1 ± 0.2	10 ± 1	5.9 ± 0.3	13 ± 2	57 ± 4	7.6 ± 0.7	98 ± 5	4.9
Cd	0.470 ± 0.009	26 ± 2	12 ± 1	38 ± 1	4.4 ± 0.2	4.6 ± 0.1	DL ^c	84 ± 2	2.5
Cr	0.863 ± 0.034	DL ^c	DL ^c	2.0 ± 0.6	DL ^c	16 ± 2	66 ± 2	84 ± 5	6.0
Cu	1.302 ± 0.026	3.3 ± 2.5	2.9 ± 0.2	55 ± 1	9.6 ± 0.5	23 ± 1	11 ± 1	105 ± 3	2.8
Mn	1.50 ± 0.20	0.5 ± 0.1	0.9 ± 0.1	6.5 ± 0.3	10 ± 1	55 ± 3	16 ± 1	89 ± 3	3.9
Ni	0.124 ± 0.004	DL ^c	DL ^c	3.1 ± 1.3	1.4 ± 1.7	21 ± 1	67 ± 5	92 ± 6	6.3
Pb	10.87 ± 0.17	3.5 ± 0.1	2.2 ± 0.1	58 ± 1	6.2 ± 0.5	23 ± 1	3.5 ± 0.2	97 ± 1	1.1
Sb	0.412 ± 0.018	4.3 ± 0.5	3.1 ± 0.8	5.6 ± 0.8	4.4 ± 0.2	15 ± 1	52 ± 4	84 ± 6	7.0
Se	0.041 ± 0.002	11 ± 1	DL ^c	35 ± 2	DL ^c	28 ± 1	6.8 ± 0.4	81 ± 2	2.7
Sr	0.433 ± 0.020	18 ± 0.3	9.3 ± 0.1	11 ± 0.4	8.7 ± 0.8	35 ± 2	6.8 ± 0.2	88 ± 3	2.8
V	0.041 ± 0.001	2.4 ± 0.2	DL ^c	3.8 ± 0.2	6.0 ± 1.8	43 ± 2	25 ± 1	81 ± 3	3.5
Zn	25.77 ± 0.38	3.4 ± 0.2	2.5 ± 0.3	37 ± 1	6.9 ± 0.3	17 ± 1	14 ± 1	82 ± 2	2.2

Bold values indicates the recovery are out of criteria (80–120%).

^a (a) Water-soluble; (b) ion-exchangeable; (c) bound to carbonates; (d) bound to metal oxides, (e) bound to organic metal complex; (f) residues.

^b Al, Ca, Fe, K, Mg, Na and S were measured by ICP-AES, and others were measured by ICP-MS, Al, Ca, K, Mg, Na, S, and As have no certified range.

^c ND (not determined): due to the reagent interference, the element concentration was not applicable. DL: the concentration was less than the method determination limit.

^d Relative standard deviation (RSD) = (standard error/mean) × 100%.

In this case, the slightly destructive reagent (a mixture of $\text{HNO}_3 + \text{H}_2\text{O}_2$ solution) could dissolve the compounds bonding the organic complex. While the original silicate and albite still resisted, part of the compounds on the particle surface did dissolve. After the $\text{HNO}_3 + \text{H}_2\text{O}_2$ mixture extraction, the alkaline metal sulfides (K_2S , Na_2S) appeared on the particle surface, as indicated by XRPD measurements. The peaks of these compounds are shown in Fig. 2f.

3.3. Chemical composition with sequential extraction by ICP-AES and ICP-MS

Although semi-qualitative determination of the sample compound composition was rapidly determined by EDX and XRPD, instrument limitations required that the amount of the composition needed to be greater than 3% for analysis. Therefore, the quantities of minor and trace elements in the ash were analyzed not by EDX and XRPD but by sequential extraction with ICP-AES and ICP-MS.

Table 3 shows the elemental recovery fraction of the municipal waste incineration ash reference material (BCR 176) under sequential extraction by ICP instruments. The results are expressed as the measured values of the elements determined in each step, corresponding to the mean of five sample measurements. In addition, the recovery for each of the elements was reported as follows: Recovery = (measured value/certified value) × 100%. The measured values were the addition of the extraction percentage obtained for each step, except for Mg and Na due to reagent interference in the first and second sequential steps. The recovery of other elements was in the range of 81% (V, Se) to 105% (Cu), which is acceptable in terms of quality assurance and quality control criteria [39,42].

In addition, microwave digestion at $175 \pm 5^\circ\text{C}$ for 10 min with hydrochloric acid and nitric acid mixed solution was used for BCR 176; results indicated the element recovery of BCR 176 was low, especially for Ba, Ti, Cr, Al, Mg, Na, S, Sb, Ni, K, and Sr (< 80%). On the other hand, As, Cd, Ca, Co, Cu, Fe, Pb, Mn, Hg, Se, Ag, V and Zn

were in the acceptable range (84–101%) [43]. The performance of different methods has to be compared on an element-by-element and matrix-by-matrix basis.

Results of the sequential extraction procedure are presented in Table 3. The following summarizes the results for each element:

Aluminum (Al): Al was the major element in the ash. Fractions a, b, c and d contained a relatively low concentration of Al, and the highest concentration of this element was found in the two last steps. In the ash, Al almost binds to the organic metal complex (38%) and to the silicates (43%). This indicates that Al was tightly bound into the matrices and would not be easily released under natural conditions. Similar results have been observed and reported in the literature [25].

Calcium (Ca): In contrast to Al, Ca seemed to be released from ash under all of the conditions mentioned above. Specifically, 29% of Ca was released during the water-soluble step, 8.1% from ion exchange, 18% from bound to carbonate, 7.4% from slightly metal oxide, 28% from organic metal complex, and 4.3% from silicate fractions.

Iron (Fe): As in the case of Al, Fe did not release easily in the first four steps and dissolved easily in the last two steps. The Fe bound to the organic metal complex (28%) and to the silicates (56%). Smeda and Zyrnicki [25] found that Fe occurred in the ash under the oxide forms such as magnetite or hematite and was also present in amorphous forms.

Potassium (K): About 45% of K was released from the ash in the water-soluble step (fraction a), but it was not easily dissolved in the ion-exchangeable, bound to carbonates, and bound to metal oxide steps. Parts of K were bound to the organic complex (17%) and silicates (13%), indicating that the K compounds released easily into the natural environment.

Sodium (Na): As shown in Table 3, about 46% of Na was released from the water-soluble step. Only 2.5% of Na was released from the second step and, due to the reagent interference, the Na concentration could not be determined in the last four steps.

Magnesium (Mg): Mg was poorly dissolved in the water-soluble step (2.6%). Similar to Na, Mg was not detected in the last extraction steps due to reagent interference.

Sulfur (S): Under slightly acidic conditions, more than 85% of S was released from the first three extraction steps. In particular, more than 66% of S was released from the water-soluble step, and it was found in all the extraction steps of this study. S was poorly bound to oxides, organic metal complexes, and silicates, and its compounds were easily released into the natural environment.

Arsenic (As): Most of the As compounds were bound to carbonate (42%) and organic compounds (30%).

Barium (Ba): Ba was almost bound to the organic metal complex (57%). Ba was found in all the fractions, from the water-soluble to the bound to silicate and silico-aluminates. Ba was poorly dissolved in water and not easily released into the natural environment.

Cadmium (Cd): Water-soluble (26%) and carbonate (38%) fractions were mainly cadmium species for BCR 176. In addition, there was about 10% ion-exchangeable species; other species were less than 5%.

Chromium (Cr): Most chromium compound was silicate and silico-aluminate fraction (66%), and there was about 16% organic complex and sulfide. Other fractions were less than 2%.

Copper (Cu): 55% copper was bound with carbonate, 23% was in the organic complex and sulfide, 11% was silicate and silico-aluminate compound, and 10% was metal oxides. Others were less than 3.3%.

Manganese (Mn): Mn was almost bound to the organic metal complex (55%). Mn was not easily dissolved in water and MgCl₂ solution, suggesting that Mn was strongly bound to the matrix and would not be easily released into the environment under natural conditions.

Nickel (Ni): A very small amount of Ni was released in the first four steps. The highest concentration was found in fractions of the last two steps, i.e., 21% of Ni in the organic metal complex and 67% of Ni in silicates.

Lead (Pb): Over 50% lead was bound with carbonate, and 23% was organic complexes or sulfide. Other fractions were less than 6%.

Antimony (Sb): Similar to Ni, Sb was not easily dissolved in the first four steps of extraction. Sb was almost bound to the organic metal complex (15%) and silicates (52%). Results indicated that Ni and Sb were tightly bound to the matrix and would not be easily released into the environment under natural conditions during the utilization of fly ash in civil engineering.

Selenium (Se): Se is found in only trace amounts in the ash. As shown in Table 3, the highest concentration of this element was found in fractions c and e. Se mainly bound to the carbonate (35%) and the organic metal complex (28%), and these compounds were easily released together as acid rain into the environment.

Strontium (Sr): Sr seems to be released at all the extraction steps. Sr was easily dissolved in water (18%) and the organic metal complex (35%) and was slightly dissolved at the other steps.

Vanadium (V): Over 70% vanadium compound was bound with organic, sulfur, silicate and silico-aluminate. Other fractions were less than 6%.

Zinc (Zn): Carbonate compound was the dominant fraction in the BCR 176. Organic metal complex and silicate and silico-aluminate compounds were about 14%. Other fractions were less than 7%.

Based on the sequential extraction procedures of BCR 176, a large fraction of the toxic elements (As, Cd, Cu, Pb, Zn) could be extracted at pH 5 (which is similar to the acid rain condition in the environment); therefore, it is important that fly ash be disposed of carefully.

In addition, the linkage of the element fraction of XRPD and sequential extraction could not be provided in detail because few crystalline compounds could be measured (most of them were Si, Na, Ca, Al and K that were *crystal* elements). In contrast, the leaching solution of every sequential extraction step measured 21 elements. Therefore, most of the elemental species could not be compared between the two analysis methods. Based on the XRPD diagram (Fig. 2), the intensity of NaAlSi₃O₈, CaCl₂, K₂S, CaS₂O₇, CaSO₄, CaCO₃ and NaCl was significantly reduced after the de-ionized water extraction. The results could be compared to the sequential extraction step (Table 3); the leaching of step a yielded a high fraction of Ca, K, Na, and S.

Table 4
Elemental recovery of BCR 176 under different high-pressure bomb digestion solutions ($n=5$)

Element ^a	BCR 176 (mg/g)	Recovery (%)				
		HClO ₄ + HNO ₃	HClO ₄ + HNO ₃ + HF	H ₂ O ₂ + HNO ₃	H ₂ O ₂ + HNO ₃ + HF	HCl + HNO ₃ ^c
Al	101.6	85 ± 1	86 ± 3	91 ± 2	102 ± 2	56.2
Ca	88.02	89 ± 0.2	87 ± 2	97 ± 1	102 ± 1	94.3
Fe	21.3 ± 1.1	94 ± 3	88 ± 1	93 ± 2	101 ± 1	88.6
K	44.99	68 ± 1	69 ± 2	76 ± 1	86 ± 1	70.3
Mg	21.72	80 ± 0.4	79 ± 2	87 ± 1	95 ± 1	54.0
Na	42.92	58 ± 1	62 ± 2	70 ± 1	97 ± 3	60.7
S	44.6	81 ± 2	84 ± 2	86 ± 1	94 ± 4	65.1
As	0.093	500 ± 50	270 ± 95	92 ± 2	94 ± 1	91.3
Ba	4.5 ± 0.2	68 ± 3	79 ± 9	78 ± 1	97 ± 1	29.5
Cd	0.470 ± 0.009	65 ± 1	88 ± 3	78 ± 3	85 ± 4	89.9
Cr	0.863 ± 0.034	113 ± 11	104 ± 20	52 ± 7	97 ± 1	24.4
Cu	1.302 ± 0.026	43 ± 3	69 ± 11	68 ± 1	96 ± 3	88.6
Mn	1.50 ± 0.20	53 ± 4	75 ± 9	74 ± 2	94 ± 3	84.6
Pb	10.87 ± 0.17	59 ± 1	73 ± 9	105 ± 2	97 ± 1	93.3
Se	0.041 ± 0.002	ND ^b	ND ^b	81 ± 1	86 ± 12	101.1
Sr	0.433 ± 0.020	52 ± 2	71 ± 6	69 ± 1	90 ± 2	77.4
V	0.041 ± 0.001	ND ^b	ND ^b	95 ± 6	90 ± 2	91.3
Zn	25.77 ± 0.38	54 ± 3	76 ± 13	72 ± 2	97 ± 1	92.6
Out of criteria (#)		10	10	9	0	8

Bold values indicates the recovery are out of criteria (80–120%).

^a Al, Ca, Fe, K, Mg, Na and S were measured by ICP-AES and others were measured by ICP-MS, Al, Ca, K, Mg, Na, S, and As have no certified range.

^b ND (not determined): due to the polyatomic interference, the data of Se and V was not applicable.

^c BCR 176 was digested by a closed vessel in the microwave [43].

3.4. High-pressure bomb digestion

The digestants selected included HNO_3 , HClO_4 , H_2O_2 , and HF ; the digested solutions are similar to those used in a previous study by the authors [25,44,45]. A two-step closed-vessel acid mixture digestion process ($\text{HNO}_3 + \text{HClO}_4/\text{HF}$) for multi-element analysis of the airborne particles had been studied in our previous work [46–48]. The four-digestion solution was used for the determination of As and V content in urban particles, soil, coal fly ash and city waste incineration ash [36] and of Pb, Zn, Cu and Cd in city waste incineration ash [49].

The reference material was dissolved, and the solution thus obtained was analyzed to validate the sample preparation techniques. Elemental contents determined under different digestion conditions are summarized in Table 4. As clearly presented in Table 4, digestion using H_2O_2 instead of HClO_4 had better recovery. The recovery criteria were in the range of 80–120%. There were 9–10 elements out of the recovery criteria in $\text{HClO}_4 + \text{HNO}_3$, $\text{HClO}_4 + \text{HNO}_3 + \text{HF}$ and $\text{H}_2\text{O}_2 + \text{HNO}_3$ solutions. Only $\text{H}_2\text{O}_2 + \text{HNO}_3 + \text{HF}$ solution could completely digest the samples and fit the recovery criteria for most elements.

HClO_4 and H_2O_2 are commonly used as oxidants in digestion. In general, the strength of oxidation of HClO_4 is higher than that of H_2O_2 . But the boiling point of chlorinated metal oxide is lower than that of metal oxide. Therefore, the chlorinated metal oxide was more easily lost than the metal oxide during the vaporization process, which increased the uncertainty of the metal concentration when analyzed via ICP. Therefore, the recovery of Cu, Mn, Pb, Sr and Zn was low after the $\text{HClO}_4 + \text{HNO}_3$ digested sample. In addition, inherent problems arise with the determination of As and V during the chloride acid content digestion solution. An erroneous, excessive recovery was observed for both As and V data involving the addition of HClO_4 to the digestion process. This could be attributed to the ArCl^+ interference for As determination and ClO^+ or ClN^+ interference for V determination. However, interference problems due to the acid-derived background ions formed during the ion extracting process of ICP-MS can significantly degrade the sensitivities of many elemental determinations, especially those of ^{75}As and ^{51}V [50,51]. Previous studies revealed that chloride, introduced via reagents or samples, could give rise to the formation of $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{37}\text{Cl}^{14}\text{N}^+$ and $^{35}\text{Cl}^{16}\text{O}^+$, which may seriously inhibit the deviation of $^{75}\text{As}^+$ and $^{51}\text{V}^+$ [52,53].

In addition, the polyatomic interference of $^{25}\text{Mg}^{35}\text{Cl}^-$, and $^{23}\text{Na}^{37}\text{Cl}^-$ could affect the analysis of ^{60}Ni [54], which may also cause Na recovery to be low in the HClO_4 addition solution. In addition, many references in the literature have reported the volatility effect on Cr(IV), e.g., from CrO_2Cl formation and the digestion and evaporation procedures. In addition, the interference problems could be caused by argon gas (i.e., $^{40}\text{Ar}^{12}\text{C}^+$ and $^{38}\text{Ar}^{14}\text{N}^+$ interfere with ^{52}Cr), and acid-derived background ions (i.e., $^{35}\text{Cl}^{16}\text{OH}^+$ and $^{35}\text{Cl}^{17}\text{O}^+$ ions inhibit detection of the $^{52}\text{Cr}^+$ isotope). Therefore, the use of low-resolution ICP-MS to determine the Cr content could result in a significant overestimation [55]. This may be the reason for the overestimation of Cr recovery in the HClO_4 addition digested solutions.

If H_2O_2 was used as the oxidizing agent to substitute for HClO_4 in the digestion solution, recovery of most of the elements, except for Cr, could be improved. Generally, the presence of the Cr compound in the H_2O_2 acid solution could easily result in the formation of CrO_5 [56,57], which may inhibit determination of the Cr content.

In addition, for the ICP-MS measurement, the main advantage of utilizing H_2O_2 as the oxidizing reagent is the limited formation of polyatomic (acid-derived) interference, which may be significantly improved by the instrument sensitivity [37]. The addition of HF is necessary to destroy the scarcely dissolved silicate matrix to obtain

Table 5

Recovery of the optimal high-pressure bomb digestion and sequential extraction procedures

Element	BCR 176 (mg/g)	Recovery (%)	
		High-pressure bomb digestion $\text{H}_2\text{O}_2 + \text{HNO}_3 + \text{HF}$	Six-step sequential extraction procedures
Al ^a	101.6	102 ± 2	88 ± 2
Ca	88.02	102 ± 1	95 ± 2
Fe	21.3 ± 1.1	101 ± 1	89 ± 2
K	44.99	86 ± 1	83 ± 1
Mg	21.72	95 ± 1	2.6 ± 0.1
Na	42.92	97 ± 3	49 ± 1
S	44.6	94 ± 4	86 ± 3
As	0.093	94 ± 1	92 ± 2
Ba	4.5 ± 0.2	98 ± 1	98 ± 5
Cd	0.470 ± 0.009	85 ± 4	84 ± 2
Cr	0.863 ± 0.034	97 ± 1	84 ± 5
Cu	1.302 ± 0.026	96 ± 3	105 ± 3
Mn	1.50 ± 0.20	94 ± 3	89 ± 3
Ni	0.124 ± 0.004	ND ^b	92 ± 6
Pb	10.87 ± 0.17	97 ± 1	97 ± 1
Sb	0.412 ± 0.018	ND ^b	84 ± 6
Se	0.041 ± 0.002	86 ± 12	81 ± 2
Sr	0.433 ± 0.020	90 ± 2	88 ± 3
V	0.041 ± 0.001	90 ± 2	81 ± 3
Zn	25.77 ± 0.38	97 ± 1	82 ± 2

Bold values indicates the recovery are out of criteria (80–120%).

^a Al, Ca, Fe, K, Mg, Na and S were measured by ICP-AES and others were measured by ICP-MS, Al, Ca, K, Mg, Na, S, and As have no certified range.

^b ND: not determined.

a reasonable recovery. Therefore, a $\text{HNO}_3 + \text{H}_2\text{O}_2 + \text{HF}$ mixed digestion was proposed as the optimal digestion procedure for city waste incineration fly ash (BCR 176).

As Table 5 shows, the sum of the concentrations obtained during the sequential extraction procedure was in good agreement with the results gained by the high-pressure bomb digestion. Most of the elements of BCR 176 measured by the two methods were in the acceptable range (recovery: 80–120%), except Mg and Na in sequential extraction method due to the interference of extraction solutions (MgCl_2 solution for step b and NaOAc solution for step c). The recovery efficiency of elements in BCR 176 by the high-pressure bomb method ($\text{H}_2\text{O}_2 + \text{HNO}_3 + \text{HF}$ solution) and sequential extraction procedures were in the range of the established criteria. Results indicated that the two methods could be applied to measure the elemental concentrations of BCR 176. After each extraction step, the mixture was first centrifuged, and then the supernatant and a small amount of solids were removed. This may be the main reason that lower concentrations were found in the subsequent steps, resulting in the low total composition measured by the sequential extraction procedure. The advantage of sequential extraction procedures is that they can measure the fraction of different compounds; however, they are more time consuming. In contrast, the high-pressure digestion method can save time and is an effective way to measure the elemental content but not the speciated compound fraction. However, when compared to high-pressure bomb digestion, the sequential extraction procedure was more time consuming and much more complex to operate. Therefore, if one is interested in the total concentration or needs a rapid analysis, the high-pressure bomb digestion with the $\text{H}_2\text{O}_2 + \text{HNO}_3 + \text{HF}$ mixture is recommended; when there is a need to know the composition, sequential extraction is recommended.

4. Conclusion

Based on the recovery of BCR 176, results indicated that the six-step sequential procedure could be applied to identify the ele-

ment contents and fit the certified values *except* for Mg and Na. Neither of these elements could be determined because of interference from extracted reagents (MgCl₂ solution in step b and NaOAc solution in step c). Actually, the difficulty of the sequential extraction procedure is that the extraction from each step depends on the previous step, and some factors can influence the extracted amount of metals. However, the six-step sequential extraction can help to show a trend concerning the release of the elements under different conditions, and the characteristics of residues can be confirmed by SEM/EDX and XRPD. In addition, substituting H₂O₂ for HClO₄ can result in a reduction of polyatomic interference and HF added in the digested solution to destroy the silicate matrix. Therefore, H₂O₂ + HNO₃ + HF was selected as the optimal digestion solution for BCR 176. A comparison of the two methods suggests that the high-pressure digestion method can save time and enable measurement of the elemental content but can not classify the speciated compound fraction, which can be accomplished with the six-step sequential extraction procedure. In addition, integration of the two methods could provide more detailed information, as they are complementary. Based on the element recovery and the relative standard error of BCR 176, two pretreatment methods can be applied to determine the element content of fly ash reference materials; the choice of method depends on the application requirements.

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