

## Multielement Determination and Distributions of Major-to-Ultratrace Elements in Industrial Waste Incineration Bottom Ash as Studied by ICP-AES and ICP-MS

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The multielement determination of major-to-ultratrace elements in industrial waste incineration bottom ash was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) after alkali fusion using LiBO<sub>2</sub>. The concentrations of 50 elements in bottom ash could be determined over the concentration range from 192 mg g<sup>-1</sup> of Si to 0.072 µg g<sup>-1</sup> of In. Silicon, Al, Fe, Ca, Na, and Ti, which except for Fe are lithophile elements, were major elements of industrial waste incineration bottom ash. The distributions of major-to-ultratrace elements in incineration bottom ash were evaluated by the enrichment factors. The enrichment factors of major elements in incineration bottom ash indicated that their relative contents were quite similar to those in the continental crust. It was also found that most minor and trace elements in the lithophile element group provided almost the same enrichment factors as those of major elements. On the other hand, Cu, Zn, Cd, and Pb in the chalcophile element group as well as some of the siderophile ones, such as Co and Ni, provided the significantly larger enrichment factors, although they were more enriched in fly ash than in bottom ash. Such large abundances of many transition elements in industrial waste incineration ashes may reflect the large amounts of metal use in industry as well as in modern society.

These days, waste management is becoming one of the most important social requirements for environmental conservation. In Japan, industrial and municipal wastes are mostly incinerated in order to reduce the volume of wastes as well as to maintain the public hygiene.<sup>1</sup> After all, 20 Mt (mega tons) of waste incineration bottom ashes and fly ashes are dumped in landfills every year. It is well known that industrial waste incineration ashes contain various kinds of elements, including toxic and hazardous ones at rather high concentration levels. Thus, many researchers have analyzed the incineration ash samples, especially municipal solid waste incineration fly ash samples, for the purpose of assessment of the environmental impacts.<sup>2–8</sup> So far, the concentrations, distributions and leachabilities of toxic and hazardous elements such as Cr, As, Se, Cd, Hg, and Pb in municipal solid waste incineration fly ash have been mainly investigated in order to prevent the environmental pollution caused by such elements. However, there have been few reports on the analysis for industrial waste incineration ash, although the total amount of industrial waste is 10-times more than that of municipal waste. Moreover, the multielement determination of major-to-ultratrace elements in industrial waste incineration ash samples has seldom been carried out due to the difficulties of detection of trace and ultratrace elements contained in complicated matrices.

The present authors reported the multielement determination of major-to-ultratrace elements in the fly ash samples such

as industrial waste incineration fly ash, municipal waste incineration fly ash, and coal fly ash,<sup>9</sup> in which about 50 elements over the concentration range from % to sub-µg g<sup>-1</sup> were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, the leaching behaviors of major-to-ultratrace elements from industrial waste incineration fly ash were investigated in association with the pH dependence of their leachabilities.<sup>10</sup> According to the results examined as the enrichment factor of each element,<sup>9</sup> coal fly ash provided elemental distributions almost identical to those in the continental crust. On the contrary, Cu, Zn, Ag, Cd, In, Sn, Sb, and Pb, which belong to the chalcophile element group in geochemical classification, were concentrated several orders of magnitude higher in industrial waste incineration fly ash than in the continental crust. The leachabilities of the elements from industrial waste incineration fly ash were significantly dependent on the final pH of the leachate, and their leaching behaviors could be categorized into several groups, reflecting their chemical properties.<sup>10</sup> However, the characterization of industrial waste incineration bottom ash on the multielement basis has not been investigated yet.

In the present study, hence, the concentrations of major-to-ultratrace elements in industrial waste incineration bottom ash collected from a rotary kiln furnace for industrial waste treatment were determined by ICP-AES and ICP-MS. In addition,

the elemental distributions in bottom ash were also evaluated as the enrichment factors as well as the melting temperature of the elements, and compared with the average elemental abundances in the continental crust.

### Experimental

**Instruments:** An ICP-MS instrument of model SPQ 8000A (Seiko Instruments, Chiba, Japan), consisting of a quadrupole-type mass spectrometer, was used for the determination of trace and ultratrace elements. An ICP-AES instrument of model Plasma AtomComp Mk II (Jarrell-Ash, Franklin, MA, USA) with a polychromator was also used for the simultaneous multielement determination of major and minor elements. An ICP-AES instrument model SPS 1500V (Seiko Instruments) with a N<sub>2</sub>-purge type of a monochromator was also used for the determination of sulfur at 180.7 nm. The instrumental components and their operating

conditions are summarized in Table 1. In the ICP-MS measurement, the internal standard method<sup>11</sup> and the correction coefficient method<sup>12</sup> were applied to correct matrix effects and polyatomic ion interferences, respectively.

**Samples:** The industrial waste incineration bottom ash sample was collected from a rotary kiln-type of industrial waste incinerator, by courtesy of a private waste treatment company. In this incinerator, waste oil, waste paint, waste petrochemical materials, and other industrial solid wastes were incinerated daily; the desulfurization treatment by a NaOH solution spray method was carried out. The fly ash sample collected from an electrostatic precipitator installed in the same incinerator and the coal fly ash standard reference material (SRM 1633b) issued from National Institute of Standards and Technology (NIST, USA) were also analyzed for comparative investigation with industrial waste incineration bottom ash. The industrial waste incineration bottom and fly

Table 1. Operating Conditions for ICP-AES and ICP-MS Instruments

ICP-AES: Jarrell-Ash Plasma AtomComp Mk II	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 17 L min <sup>-1</sup>
Auxiliary gas flow rate	Ar 1.0 L min <sup>-1</sup>
Carrier gas flow rate	Ar 0.48 L min <sup>-1</sup>
Observation height	18 mm above load coil
Nebulizer:	cross-flow type
Sample uptake rate	1.2 mL min <sup>-1</sup>
Polychromator:	Paschen-Runge mounting
Focal length	75 cm
Grating	2400 grooves/mm
Entrance slit width	25 μm
Exit slit width	50 μm
ICP-AES: Seiko Instruments SPS 1500V	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 L min <sup>-1</sup>
Auxiliary gas flow rate	Ar 0.5 L min <sup>-1</sup>
Carrier gas flow rate	Ar 0.48 L min <sup>-1</sup>
Purge gas	N <sub>2</sub> 5 L min <sup>-1</sup>
Observation height	10 mm above load coil
Nebulizer:	concentric type
Sample uptake rate	1.0 mL min <sup>-1</sup>
Monochromator:	Czerny-Turner mounting
Focal length	100 cm
Grating	3600 grooves/mm
Entrance slit width	20 μm
Exit slit width	30 μm
ICP-MS: Seiko Instruments SPQ 8000A	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 L min <sup>-1</sup>
Auxiliary gas flow rate	Ar 1.0 L min <sup>-1</sup>
Carrier gas flow rate	Ar 1.0 L min <sup>-1</sup>
Sampling depth	12 mm from load coil
Nebulizer:	concentric type
Sample uptake rate	0.7 mL min <sup>-1</sup>
Data acquisition:	
Dwell time	10 ms/point
Data point	3 points/peak
Number of scans	100

ash samples were dried at 60 °C for 24 h, and then ground in powder with an agate mortar.

**Chemicals:** Lithium metaborate ( $\text{LiBO}_2$ ) of ultrapure grade, purchased from Spex (Metuchen, NJ, USA), was used for alkali fusion of the ash samples. Nitric acid ( $\text{HNO}_3$ ) of electronics industry grade was purchased from Kanto Chemicals (Tokyo, Japan). The multielement standard solutions for making the working calibration curves were prepared, in a manner similar to the previous work,<sup>13</sup> by mixing aliquots of the single-element stock solutions ( $1000 \mu\text{g mL}^{-1}$ ) for atomic absorption spectrometry; the solutions were purchased from Wako Pure Chemical Industries (Osaka, Japan). They were adjusted to 1 M ( $\text{M} = \text{mol L}^{-1}$ )  $\text{HNO}_3$  solution, after the internal standard elements (Rh and Re;  $5 \text{ ng mL}^{-1}$  each) were added. Pure water used throughout the present experiment was prepared by a Milli-Q water purification system (Nihon Millipore Kogyo, Tokyo, Japan).

**Sample Decomposition Procedure:** The ash samples were dried at 105 °C for 2 h. Then, about 0.3 g of ash sample was decomposed with ca. 0.9 g of  $\text{LiBO}_2$  in a platinum crucible.<sup>9,13</sup> It should be stressed that the use of  $\text{LiBO}_2$  gave advantages of lower matrix effects over other fusion reagents, because it consisted of only light elements (Li and B). The residue was dissolved with 7.5 mL of conc.  $\text{HNO}_3$  and diluted with 50 mL of pure water. The decomposed sample solution was filtrated with a 5C filter paper and diluted to 100 mL with pure water. In the case of the ICP-MS measurement, the filtrated sample solution was further diluted to 20 times with 1 M  $\text{HNO}_3$ , after the internal standard elements (Rh and Re;  $5 \text{ ng mL}^{-1}$  each) were added.

## Results and Discussion

**Multielement Determination of Major-to-Ultratrace Elements in Industrial Waste Incineration Bottom Ash:** The major-to-ultratrace elements in the industrial waste incineration bottom ash sample were determined by ICP-AES and ICP-MS after alkali fusion using  $\text{LiBO}_2$ . The analytical method used here was applied to the analysis of the coal fly ash reference material (NIST SRM 1633b) in order to evaluate its analytical feasibilities; it was found to be quite accurate and precise enough for the multielement analysis of incineration ash samples.<sup>9</sup> The analytical results are summarized in Table 2, together with those for industrial waste incineration fly ash and the concentration ratio of each element in fly ash to that in bottom ash. The analytical results for the fly ash sample, which were newly obtained in the present experiment, were almost the same as those reported in the previous paper,<sup>9</sup> although the concentrations of some elements were slightly different from those reported previously because of the different sampling date. In the present experiment, 50 elements in industrial waste incineration bottom ash could be determined over the concentration range from  $192 \text{ mg g}^{-1}$  of Si to  $0.072 \mu\text{g g}^{-1}$  of In.

Major elements in incineration bottom ash were Si, Al, Fe, Ca, Na, Ti, and K, which were contained at the %-levels; the sum of them were more than 45% of the total content. As is seen in Table 2, all major elements provided the concentration ratios of  $C_F/C_B$  ( $C_F$ ; concentration in fly ash,  $C_B$ ; concentration in bottom ash) smaller than 1. These results indicate that the concentrations of such major elements were 1.5–7 times more in bottom ash than in fly ash, except for Na and K. According to the geochemical classification,<sup>14</sup> major elements in the bot-

tom ash samples are categorized as the lithophile and siderophile elements. Since the lithophile and siderophile elements have relatively large affinities to oxygen, they are generally found as oxides in the continental crust. Thus, it is considered that major elements may produce some stable oxides during the incineration process, and they may form some core materials of bottom ash particulates. Magnesium, Zr, Hf, Th, U, and rare earth elements (REEs) among minor and trace elements, which are also belonging to the lithophile elements, were also more abundant in bottom ash than in fly ash. These results suggest that the lithophile elements even at the minor and trace concentration levels behave in a manner similar to the major elements. In addition, it should be pointed out here that La, Ce, and Eu, which are widely used as the components of functional materials in various industries, were contained slightly more in fly ash than in bottom ash, while other REEs were significantly enriched in bottom ash.

It is seen in Table 2 that alkali elements such as Na, K, and Cs, and the chalcophile elements such as S, Zn, Cu, Pb, Sn, As, Cd, Bi, and In provided the rather large values of  $C_F/C_B$  ratio. These results indicate that these elements were contained significantly more in fly ash than in bottom ash. Since alkali elements belong to the lithophile elements, they were expected to distribute more in bottom ash than in fly ash. However, alkali elements were contained more in fly ash. These facts can be ascribed to the NaOH spray used for desulfurization of exhaust gas in the incinerator. The higher abundances of other alkali elements such as K and Cs in fly ash might be due to the impurities in the NaOH reagent. As mentioned earlier, S also distributed more in fly ash than in bottom ash. Since S is easily oxidized into gaseous compounds such as  $\text{SO}_x$  during the combustion process in an incinerator, gaseous  $\text{SO}_x$  in exhaust gas may react with NaOH to produce sodium salts such as  $\text{Na}_2\text{SO}_4$  through the desulfurization process. Then, it is reasonably considered that S was collected on the electrostatic precipitator. In fact, the content of S in fly ash was ca. 10 times larger than that in bottom ash. Since the chalcophile elements have the relatively large affinities to sulfur, they may produce mainly sulfides during the incineration process. The sulfides of the chalcophile elements generally vaporize easily, so that they may be adsorbed on the surfaces of fly ash particulates, which results in greater abundances of them in fly ash. Other minor and trace elements such as Cr, Mo, Ni, Co, W, and Y were almost at the same concentration levels in both bottom and fly ashes.

**Enrichment Factors of the Elements in Industrial Waste Incineration Bottom Ash:** In addition to the relative concentrations in bottom and fly ashes, shown in Table 2, the elemental distributions in industrial waste incineration bottom ash were investigated by estimating the enrichment factors (EFs) of analyte elements in bottom ash. The enrichment factor is defined as a normalized concentration ratio of an element in the ash sample to that in the continental crust, as shown in Eq. 1;

$$\text{EF} = \frac{[\text{M}]_{\text{sample}} / [\text{Al}]_{\text{sample}}}{[\text{M}]_{\text{crust}} / [\text{Al}]_{\text{crust}}} \quad (1)$$

where the analyte concentrations are normalized to aluminum concentrations in both bottom ash and the continental crust, re-

Table 2. Analytical Results for Industrial Waste Incineration Bottom Ash and Fly Ash Obtained by ICP-AES and ICP-MS

Element <sup>a)</sup>	Observed value <sup>b)/</sup> $\mu\text{g g}^{-1}$				Ratio <sup>c)</sup> ( $C_F/C_B$ )	EF <sub>bottom</sub> <sup>d)</sup>
	bottom ash ( $C_B$ )		fly ash ( $C_F$ )			
Si <sup>†</sup>	192000	± 3000	27500	± 700	0.14	0.60
Al <sup>†</sup>	88100	± 700	23600	± 500	0.27	1.0
Fe <sup>†</sup>	81200	± 1800	39500	± 4100	0.48	1.7
Ca <sup>†</sup>	51400	± 1100	34100	± 1200	0.67	1.2
Ti <sup>†</sup>	24300	± 200	10600	± 1200	0.43	5.5
Na <sup>†</sup>	21700	± 100	233000	± 1000	11	0.83
K <sup>†</sup>	11000	± 1000	47000	± 3000	4.3	0.46
Mg <sup>†</sup>	6100	± 100	2200	± 600	0.36	0.25
P <sup>†</sup>	5800	± 200	24300	± 1400	4.2	6.9
S <sup>†</sup>	5500	± 240	56200		10	7.1
Zn <sup>†</sup>	4230	± 60	21500	± 900	5.0	59
Cr	4150	± 290	4860	± 70	1.2	30
Cu <sup>†</sup>	3150	± 210	22400	± 200	7.1	110
Mo	2300	± 100	1940	± 10	0.83	1890
Ba <sup>†</sup>	1960	± 50	2180	± 110	1.1	3.0
Ni	1660	± 80	2590	± 320	1.6	27
Mn <sup>†</sup>	909	± 14	616	± 85	0.67	1.2
Pb	278	± 17	4160	± 120	15	17
Co	258	± 3	427	± 39	1.7	9.7
Zr	209	± 6	90.3	± 5.4	0.43	0.93
Sb	183	± 13	402	± 32	2.2	550
Sr	180	± 3	166	± 1	0.91	0.49
Sn	136	± 2	1060	± 60	7.7	53
W	56.1	± 0.9	84.8	± 2.8	1.5	51
Rb	27.5	± 1.2	19.1	± 0.1	0.71	0.32
Ce	24.4	± 2.0	38.2	± 0.5	1.6	0.37
Y	17.9	± 0.3	26.5	± 0.6	1.5	0.67
La	14.3	± 1.0	25.6	± 3.2	1.8	0.43
Ga	12.9	± 0.2	5.27	± 0.14	0.42	0.78
Nd	9.86	± 0.46	7.81	± 0.25	0.77	0.33
As	7.5	± 0.3	44.6	± 1.1	5.9	4.0
Hf	4.02	± 0.12	1.82	± 0.13	0.45	0.74
Th	3.53	± 0.29	0.770	± 0.068	0.22	0.38
Cd	3.39	± 0.18	10.4	± 0.1	3.0	31
Bi	3.38	± 0.29	28.8	± 0.3	8.3	36
Pr	2.53	± 0.17	2.44	± 0.05	1.0	0.34
Ge	1.91	± 0.04	2.81	± 0.06	1.5	1.2
Cs	1.83	± 0.09	19.2	± 0.4	10	0.49
Sm	1.60	± 0.10	0.761	± 0.018	0.48	0.22
Gd	1.32	± 0.01	0.433	± 0.012	0.33	0.78
Dy	1.26	± 0.04	0.374	± 0.024	0.29	0.30
U	1.04	± 0.02	0.301	± 0.002	0.29	0.55
Er	0.819	± 0.039	0.170	± 0.008	0.21	0.35
Eu	0.791	± 0.012	1.58	± 0.01	2.0	0.55
Yb	0.769	± 0.035	0.144	± 0.007	0.19	0.35
Tb	0.311	± 0.017	0.213	± 0.012	0.67	0.43
Ho	0.267	± 0.007	0.0538	± 0.0034	0.20	0.30
Tm	0.110	± 0.005	0.0183	± 0.0003	0.17	0.33
Lu	0.105	± 0.003	0.0217	± 0.0036	0.21	0.27
In	0.072	± 0.010	3.25	± 0.10	45	1.3

a) The elements with <sup>†</sup> were determined by ICP-AES and others by ICP-MS.b) Mean ± SD ( $n = 3$ ), but the value for S in fly ash is the mean of two-times measurements ( $n = 2$ ).

c) The concentration ratios of the elements in fly ash to those in bottom ash.

d) The enrichment factors for analyte elements in bottom ash.

spectively.<sup>9,10,12,14–17</sup> Aluminum is a chemically inactive element, and so it can be used as an indicator element to measure

the relative activities and reactivities of other diverse elements in a sample as well as those in the continental crust. Thus, it is

considered that the EF values on the basis of Al content indicate the relative enrichments of analyte elements in industrial waste incineration bottom ash, compared to those in the continental crust. The EF values for analyte elements calculated are summarized in Table 2. They are also plotted in Fig. 1, where the elements are arranged in the order of the groups in the periodic table of elements. In Fig. 1, the EF values of analyte elements in industrial waste incineration fly ash and coal fly ash standard reference material (NIST SRM 1633b)<sup>9</sup> are also illustrated for comparison.

As can be seen in Fig. 1, the enrichment factors of most elements in coal fly ash standard reference material were almost equal to 1, while a few trace elements such as As, Ge, Mo, Sb, and Bi provided large EF values. These results indicate that the relative concentrations of the main constituents in coal fly ash are quite similar to those in the continental crust. On the contrary, the EF values of analyte elements in industrial waste incineration bottom and fly ashes widely extend up to ca. 10000. These results indicate that a variety of elements are accumulated in industrial waste incineration ashes during the incineration process, depending on their chemical properties, although the EF values for incineration fly ash are significantly larger than those for incineration bottom ash.

According to the results in Table 2, the enrichment factors of Zn, Cr, Cu, Mo, Ni, Pb, Sb, Sn, W, Cd and Bi are larger than 10 in industrial waste incineration bottom ash. In addition, Ti, P, S, Ba, Co and As provided the EF values larger than 3. The large EF values of the elements listed here indicate that these

elements are concentrated in industrial waste incineration bottom ash, compared to the continental crust. On the other hand, other elements in incineration bottom ash provided the EF values close to or smaller than 1. These facts are clearly seen in Fig. 1. It should be noted here that the elements in incineration bottom ash can be generally divided into two groups, depending on the enrichment factors shown in Fig. 1; one is a group of the elements with relatively small EF values, and the other is a group of those with relatively large EF values. The elements of Groups 1–4 in the periodic table, Mn and Fe of Groups 7 and 8, Al, Ga, and In of Group 13, and Si and Ge of Group 14 are categorized into the former group, whose EF values are smaller than 2. The relative concentrations of these elements on the basis of Al content in bottom ash were quite similar to those in the continental crust. All the lithophile elements in bottom ash, including trace elements, belong to this group. These facts suggest that major elements as well as minor and trace elements of the lithophile element group in bottom ash easily form very stable oxides in the incineration process.

As is seen in Fig. 1, Ti and Ba among the lithophile elements were concentrated about 3 times more in bottom ash and about 10 times more in fly ash, compared to their concentrations in the continental crust, although other lithophile elements were not so much concentrated in incineration ashes. Titanium is extensively used for paints, catalysts, and polishing particles, and Ba is largely used for the additives for glasses, ceramics, pigments, rubber products etc. Such wide uses of Ti and Ba in industrial materials might result in large accumu-

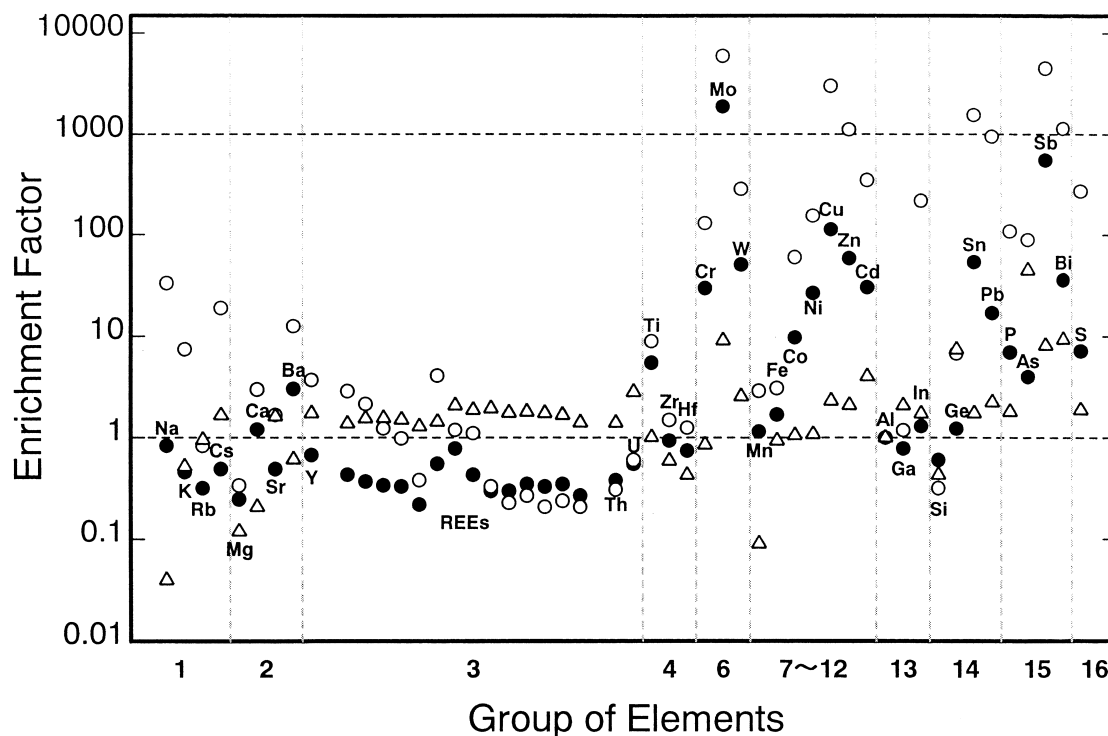


Fig. 1. Enrichment factors of analyte elements in industrial waste incineration bottom ash, industrial waste incineration fly ash, and coal fly ash standard reference material (NIST SRM 1633b).

●: industrial waste incineration bottom ash, ○: industrial waste incineration fly ash, △: coal fly ash standard reference material (NIST SRM 1633b).

lation of these elements in industrial waste incineration ashes.

On the contrary, it was found that the chalcophile elements and some siderophile elements (Co and Ni) belonging to Groups 6 and 9–15 in the periodic table were concentrated 10–1000 times higher in bottom ash than in the continental crust. The high concentrations of the chalcophile elements in industrial waste incineration bottom ash can certainly be ascribed to huge amounts of usage of such elements in the modern industry and society. These results thus indicate that the elemental concentrations in industrial wastes can be the good indicators to measure human activities.<sup>18</sup> For example, Sb and Mo provided the largest EF values in the bottom ash sample, in which they were concentrated 3 orders of magnitude more in bottom ash than in the continental crust. Although Sb and Mo are rare elements in the continental crust, they are extensively and widely used for industrial materials; Sb is used for catalysts and polymer composites as flame-retardants, and Mo is added into lubricant oil for engines.

It is also clearly seen from Fig. 1 that the EF values of the chalcophile elements in incineration fly ash are generally 10–100 times more than those in incineration bottom ash. The chalcophile elements in industrial wastes were easily evaporated and significantly condensed in fly ash during incineration processes because of the low vaporization temperatures of most of their compounds such as metals, oxides, sulfides, halides, etc.

**Distributions of the Elements between Industrial Waste Incineration Bottom and Fly Ashes:** In order to investigate the partitionings of the elements between bottom ash and fly ash during the incineration process, the concentration ratios of

$C_F/C_B$  of the analyte elements, listed in Table 2, were further discussed in association with their melting temperatures. Since industrial wastes are combusted in high-temperature media (ca. 1200 K), the melting temperature of the element may also be an indicator of the partitioning between bottom and fly ashes. Then, the  $C_F/C_B$  values versus melting temperatures of the elements<sup>19</sup> are plotted in Fig. 2. It is seen in Fig. 2 that analyte elements with low melting temperatures are enriched in fly ash rather than in bottom ash, while those with higher ones abundantly distributed in bottom ash. For example, In with melting temperature of ca. 430 K distributed 300-times more in fly ash than in bottom ash. On the contrary, Mo with melting temperature of ca. 3000 K was almost at the same level in both the bottom and fly ashes, although Mo is much more enriched in both the bottom and fly ash samples, compared to the continental crust. It is also noted here from the results in Fig. 2 that the lithophile and siderophile elements, which are shown as black squares (■) in Fig. 2, generally provide the small  $C_F/C_B$  values, while the chalcophile elements, shown as open circles (○), give the large  $C_F/C_B$  values. In particular, the  $C_F/C_B$  values of major elements such as Si, Al, Fe, Ca, and Ti were very close to each other regardless of their melting temperatures. These results suggest that these major elements probably form similar stable compounds which become core materials of ash particles in bottom ash as well as in fly ash during the incineration process because of high-temperature combustion.

However, some exceptions are found in Fig. 2; W particularly distributed almost at the same concentration level in the bottom and fly ashes, although its melting temperature is the high-

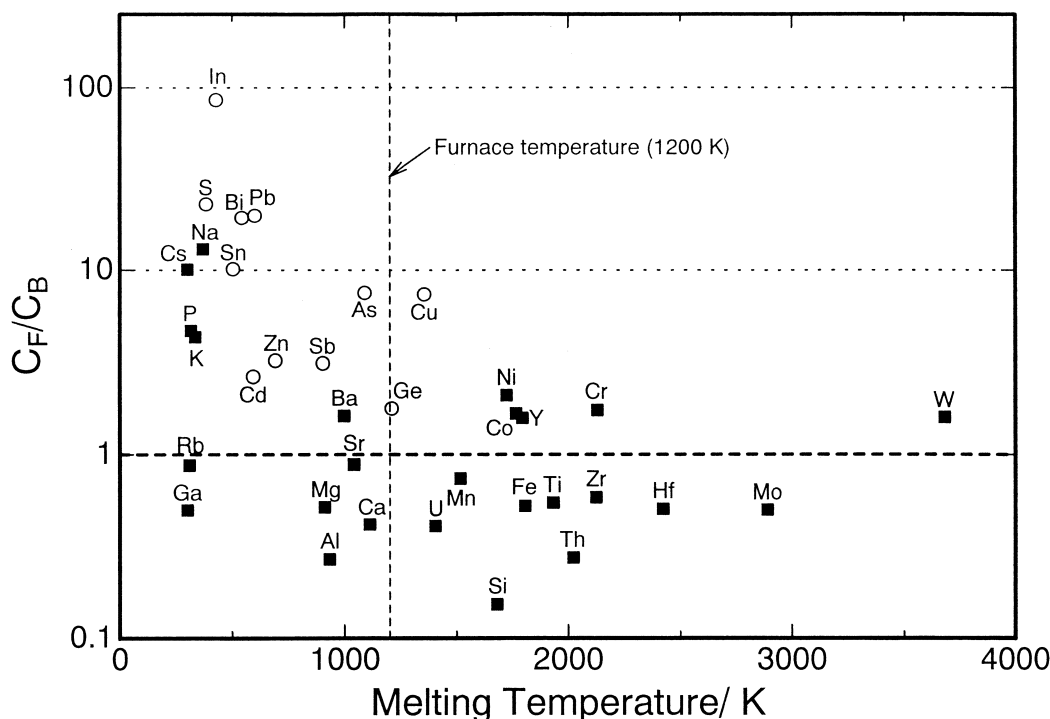


Fig. 2. Relationship between the concentration ratio of analyte elements in fly ash ( $C_F$ ) to those in bottom ash ( $C_B$ ) and their melting temperatures.

■: lithophile and siderophile elements, ○: chalcophile elements.

est, about 3700 K among the elements investigated here. These results suggest that W may volatilize to a certain extent in spite of its high melting temperature, in the form of some volatile compounds such as  $\text{WCl}_6$  (boiling temperature 620 K), which is easily produced under the chlorine-present conditions.

Trace siderophile elements (Ni and Co) were distributed more in fly ash than in bottom ash, although their melting temperatures are higher than the furnace temperature (1200 K). Nickel can form  $\text{NiSO}_4$  at low temperature during an incineration process, if S is available.<sup>20</sup> In fact, S was particularly abundant, 100-times more, in fly ash than in bottom ash. Thus, it may be considered that most Ni was distributed more in fly ash than in bottom ash in the forms of sulfate or sulfide.

Among the chalcophile elements, Ga particularly provided the small  $C_F/C_B$  value, while it has an extremely low melting temperature (ca. 300 K). Furthermore, as can be seen in Fig. 1, the EF values of Ga in both bottom and fly ashes were almost equal to 1. These results may indicate that Ga was mostly contained as stable oxides in the core materials of incineration ashes, and so it behaved in a manner similar to major lithophile elements.

It is generally concluded from the results in Fig. 2 that there is the inverse correlation between the concentration ratios of the elements and the melting temperatures of the elements, even though some exceptions were found.

### Conclusion

The concentrations of 50 elements in industrial waste incineration bottom ash collected from a rotary kiln-type of industrial waste incinerator could be determined by ICP-AES and ICP-MS, and the enrichment factors and the distributions of analyte elements were evaluated to discuss their enrichment and partitionings in bottom and fly ashes. The enrichment factors of major elements (Si, Fe, Ca, Na, and Ti) in bottom ash showed that their abundances are very similar to those in the continental crust. These results suggest that these major elements (lithophile and siderophile elements) produce mainly stable oxides in incineration processes; such oxides may form some core materials of ash particulates in bottom ash. The lithophile and siderophile elements at the minor and trace concentration levels distributed much more in bottom ash, in a manner similar to major elements. On the other hand, Cu, Sb, Sn, Zn, Pb, Bi, and Cd, which were at the minor and trace concentration levels, were concentrated 10-to-1000 times more in bottom ash than those in the continental crust, while they dis-

tributed remarkably more in fly ash than in bottom ash. These results for the chalcophile elements may reflect huge amounts of industrial usage of such elements, which results in their large accumulation in industrial waste as well as in the environment.

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