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Comparative Study on the Distributions of Precious Metals (Ru, Rh, Pd, Ir, Pt, and Au) in Industrial Waste Incineration Ashes as Determined by Tellurium Coprecipitation and ICP-MS

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The multielement determination of precious metals (Ru, Rh, Pd, Ir, Pt, and Au) in industrial waste incineration ashes was examined by inductively coupled plasma mass spectrometry (ICP-MS) with external calibration. Precious metals in the incineration ash samples were preconcentrated by Te coprecipitation after sample decomposition by acid digestion. By using the present Te coprecipitation method, precious metals could be recovered almost quantitatively, while the elements causing polyatomic interferences in the determination of precious metals by ICP-MS were more than 96% removed. The analytical detection limits of precious metals were 0.05, 0.004, 0.03, 0.02, 0.05, and 0.05 ng g^{-1} for Ru, Rh, Pd, Ir, Pt, and Au, respectively, when 0.3 g of ash sample was used for analysis. It was found that the concentration levels of precious metals in coal fly ash and city waste incineration ash certified reference materials were at the ng g^{-1} levels, which were at the same levels as those in the continental crust. On the other hand, the concentrations of precious metals in industrial waste incineration ashes were in the range from ng g^{-1} to μg g^{-1}, which were a few to several-hundreds of times higher than those in coal fly ash and city waste incineration ash reference materials.

As is well known, the platinum group metals (Ru, Rh, Pd, Os, Ir, and Pt) and Au are called "precious" or "noble" metals. Precious metals provide unique properties of high electronic conductance and catalytic activities, which results in their wide use for modern industrial production.[1] Since the late 1970's, the demand for Rh, Pd, and Pt has increased in automobile catalysts for cleaning exhaust gases. As a result, annual use of Rh, Pd, and Pt for automobile catalysts run up to 14.4, 139, and 49.6 t, respectively, which corresponds to 86.0, 57.5, and 29.1% of their total production.[1] Thus, the anthropogenic emission of Rh, Pd, and Pt into the environment from automobile catalysts has been increasing for the last few decades.[2–4] On the other hand, ca. 10–20% of total Rh, Pd, and Pt produced are used for other industrial products, such as functional materials in electrical and electronics industry, catalysts in various chemical processes, and drugs in chemotherapy. On considering the current circumstances, there is a possibility that precious metals may be further emitted into the environment from various anthropogenic sources such as industrial particulate emissions and waste incineration. Therefore, a reliable and practical analytical method for precious metals in environmental samples should be established to investigate the kinetic behaviors of precious metals in the environment.

Nowadays, ICP-MS is one of the most reliable methods for the determination of precious metals at ultratrace concentration levels. However, the determination of precious metals by ICP-MS is still difficult because of their low concentrations in environmental samples as well as spectral interferences due to concomitant elements. Therefore, preconcentration together with matrix separation is necessary to obtain reliable analytical results for precious metals. Various pretreatment techniques such as fire assay, anion exchange, cation exchange, and coprecipitation have thus been employed for preconcentration/matrix separation in the determination of precious metals.[2,5] Among them, the tellurium coprecipitation technique is commonly used as the pretreatment method for geological samples,[6–10] but the Te coprecipitation method often provides poor recoveries of precious metals. The isotope dilution (ID) technique could be used to overcome the problem of low recoveries of precious metals in the ICP-MS measurements.[7,10] The ID technique is no doubt a very accurate method, but this technique cannot be applied to the mono-isotopic elements (Rh and Au). Therefore, an external calibration method is preferable for practical analysis, if good recoveries can be achieved.

As described earlier, waste incineration is considered to be a possible source of anthropogenic emission of precious metals into the environment. The present authors have investigated the multielement determination of major-to-ultratrace elements in industrial waste incineration ashes by using ICP-AES and ICP-MS.[11–14] It was found from those analytical results that industrial waste incineration ashes, especially fly ashes, enrich various kinds of heavy metals such as Cu, Zn, Sb, and Pb, which are widely used in industrial production. It is thus considered that precious metals may also be enriched in industrial waste incineration ashes. However, there has been no report on precious metals in industrial waste incineration ashes.

The present paper describes an analytical method for the determination of precious metals (Ru, Rh, Pd, Ir, Pt, and Au) in industrial waste incineration ashes by ICP-MS with external calibration. The incineration ash samples were decomposed by acid digestion, and precious metals were preconcentrated by

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the Te coprecipitation method. The feasibilities of the present analytical method were assured by analyzing a certified reference material of WPR-1. Then, precious metals in industrial waste incineration ashes, as well as in coal fly ash and city waste incineration ash reference materials, were determined with quite good analytical precision. In addition, the distributions and the partitionings of precious metals in industrial waste incineration ashes were evaluated using their enrichment factors and concentration ratios between fly and bottom ashes.

Experimental

Instrumentation. An ICP-MS instrument (model HP-4500, Agilent Technologies, Yokogawa Analytical Systems, Tokyo, Japan) was employed for the determination of precious metals. Since the present ICP-MS instrument was composed of a low-resolution quadrupole mass spectrometer, polyatomic interferences derived from concomitant elements may cause some analytical errors in the determination of precious metals. Therefore, the operating conditions of the ICP-MS instrument, summarized in Table 1, were set to minimize polyatomic interferences due to oxide ions (e.g., ${}^{87}\mathrm{Sr}^{16}\mathrm{O}^+ \rightarrow {}^{103}\mathrm{Rh}^+$, ${}^{89}\mathrm{Y}^{16}\mathrm{O}^+ \rightarrow {}^{105}\mathrm{Pd}^+$, and ${}^{177}\mathrm{Hf}^{16}\mathrm{O}^+ \rightarrow {}^{193}\mathrm{Ir}^+$). In the present work, the oxide formation rate (R) was estimated by measuring a Pr standard solution (10 ng mL^{-1}) so as to keep $R_{\mathrm{PrO/Pr}}$ less than 0.5%. When necessary, polyatomic interferences were corrected by the interference correction coefficient method.[11] The internal standard method was used to correct matrix effects due to major elements.[15]

Chemicals. Nitric acid and hydrochloric acid of electronics industry grade (Kanto Chemicals, Tokyo, Japan), perchloric acid of analytical grade (Kanto Chemicals), and hydrofluoric acid of Suprapur grade (Merck, Darmstadt, Germany) were used for sample decomposition. Tellurium stock solution ($\mathrm{TeCl_4}$ in 6 M HCl, 1000 μg mL^{-1}) for atomic absorption spectrometry, which was purchased from Wako Pure Chemicals (Kyoto, Japan), was used as a coprecipitant. Tin(II) chloride solution (4.6%) in 1 M HCl was prepared from $\mathrm{SnCl_2 \cdot 2H_2O}$ (Wako Pure Chemicals). The standard solutions for precious metals for making the working calibration curves were prepared by diluting aliquots of 1000 μg L^{-1} single-element stock solutions of Pd, Pt, and Au purchased from Wako Pure Chemicals, Rh from Kanto Chemicals, and Ru and Ir from Aldrich (Milwaukee, WI, USA). Deionized water was prepared with a Milli-Q plus water purification system (Nihon Millipore Kogyo, Tokyo, Japan).

Samples. Certified reference material of altered peridotite platinum group element material (WPR-1), issued from CANMET (Canadian Center for Mineral and Energy Technology, Ontario, Canada), was used for the evaluation of the present analytical method. Coal fly ash certified and standard reference materials of JCFA-1 issued from GSJ (Geochemical Survey of Japan, Tsukuba, Japan) and SRM 1633b from NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA), and city waste incineration ash certified reference material of CRM 176 issued from BCR (Community Bureau of Reference, Brussels, Belgium) were analyzed for the comparisons of the analytical data.

Table 1. Operating Conditions for ICP-MS Instrument

Plasma conditions:	
Incident power	1.4 kW
Coolant gas flow rate	Ar 15.0 L min^{-1}
Auxiliary gas flow rate	Ar 1.0 L min^{-1}
Carrier gas flow rate	Ar 1.2 L min^{-1}
Sampling depth	9 mm from load coil
Nebulizer:	Babington-type
Sample uptake rate	0.4 mL min^{-1}
Data acquisition:	
Measurement mode	Peak jumping
Dwell time	20 ms/point
Data point	3 points/peak
Number of scans	100

The industrial waste incineration fly ash (IWIFA) and bottom ash (IWIBA) samples were collected at the same time from three different types of incinerators (hereafter referred to as incinerators A, B, and C),[13,14] by courtesy of private industrial waste treatment companies. The IWIFA and IWIBA samples obtained from incinerators A, B, and C are referred to as IWIFA A and IWIBA A, IWIFA B and IWIBA B, and IWIFA C and IWIBA C, respectively, which are the same samples used in previous works.[13,14] In incinerator A, petrochemical wastes such as oils, solvents, and paints were mainly incinerated with a rotary kiln-type of furnace (average furnace temperature 850 °C). In incinerator B, waste papers, waste plastics, and sludges in almost the same amounts were processed in a slagging incinerator using a rotary kiln as the furnace (1200 °C). In incinerator C, food wastes from supermarkets and waste plastics were mainly incinerated in a stoker-type incinerator (900 °C) equipped with a rotary kiln as the preburning furnace.

Sample Decomposition Procedure. About 0.3 g of sample was taken in a Teflon® beaker (100 mL in volume), into which 10 mL of HF and 10 mL of *aqua regia* were added. It is noted here that 1 mL of NaCl solution (1%) was also added to form chloro complexes of precious metals ($[\mathrm{RuCl_6}]^{2-}$, $[\mathrm{RhCl_6}]^{3-}$, $[\mathrm{PdCl_4}]^{2-}$, $[\mathrm{IrCl_6}]^{3-}$, $[\mathrm{PtCl_6}]^{2-}$, and $[\mathrm{AuCl_4}]^{-}$) in order to prevent a possible loss of precious metals by hydrolysis during the digestion procedure.[6] Then, the sample was heated for 8 h on a hot plate at 150 °C to decompose silicate minerals, and heated to dryness in order to evaporate excess HF. After cooling, 7 mL of $\mathrm{HClO_4}$ and 2 mL of concd $\mathrm{HNO_3}$ were added, and it was heated again for 8 h at 230 °C. Then, 12 mL of *aqua regia* was added and heated for 4 h to decompose the sample completely, and heated to dryness again. Furthermore, the procedure of adding 5 mL of HCl to the residue and heating to dryness was repeated two times to ensure complete conversion of precious metal salts to chloro complexes. Finally, the residue was dissolved in 50 mL of 1 M HCl.

Preconcentration of Precious Metals by Tellurium Coprecipitation. A 40 mL aliquot of digested sample solution obtained by the method described above was transferred to a borosilicate glass beaker (100 mL in volume). After adjusting the concentration of HCl in the sample solution to 6 M, 1.5 mL of 1000 μg mL^{-1} of Te solution (1.5 mg as Te) was added all at once as a carrier for precious metals. Then, 10 mL of 4.6% $\mathrm{SnCl_2}$ solution was dropwise added to the sample solution as a reducing agent and boiled for 90 min at 150 °C until the black precipitate coagulated and the supernatant liquid became clear. After cooling, the black precipitate was filtered with a 0.45 μm cellulose nitrate membrane filter (ADVANTEC), and washed with a small amount of deionized water. The precipitate was transferred to a Teflon® beaker (100 mL in volume) together with the filter. Then, the precipitate and the filter were dissolved with 4 mL of *aqua regia* and heated to dryness. Finally, the residue was dissolved with 5 mL of 1 M *aqua regia*, in which internal standard elements (Cd and Tl; 5 ng mL^{-1} each) were contained.

Results and Discussion

Recovery Values and Analytical Detection Limits of Precious Metals. In order to obtain reliable analytical results, good recoveries of precious metals should be achieved in coprecipitation preconcentration. Thus, the effect of the amount of Te carrier on the recovery values of precious metals was investigated by using the test solution, in which precious metals (Ru, Rh, Pd, Ir, Pt, and Au) were added to be 1 ng mL^{-1}. Then, the precious metals were concentrated by 8-fold according to the procedure described in the experimental section, where the amount of Te carrier was varied in the range of 0.3–2.4 mg. The results are shown in Fig. 1. As can be seen in Fig. 1, the recovery values of precious metals were more than 90% when the amount of Te was larger than 1.5 mg. Therefore, the amount of Te carrier was chosen as 1.5 mg in the present work.

Next, the recovery values of precious metals from the real sample solution were examined by Te coprecipitation. Precious metals were added to be 1 ng mL^{-1} in the digested solution of WPR-1, and concentrated by 8-fold as described in the experimental section. The recovery values of the precious metals are summarized in Table 2. As can be seen in Table 2, the recovery values of all of the precious metals were in the range of 93.7–100.1%. In addition, the relative standard deviations of the recovery values were less than 5% when three replicate experiments were carried out. These results indicate that the present Te coprecipitation procedure is reproducible enough to apply to the determination of precious metals by ICP-MS.

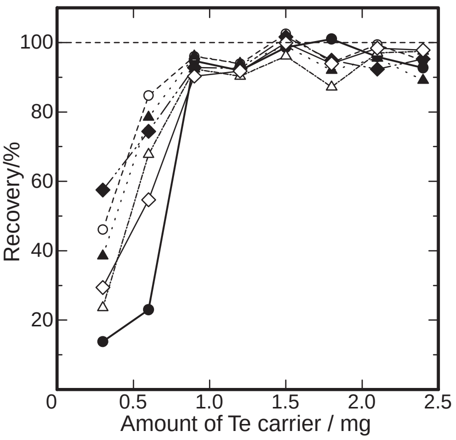

Fig. 1. Recovery values of precious metals as a function of the amount of Te carrier. ●: Ru, ○: Rh, △: Pd, ▲: Ir, ◆: Pt, and ◇: Au.

The analytical detection limits, which were estimated by dividing the instrumental detection limits with the concentration factor (=8) and the recovery values obtained in the preconcentration procedure, are also listed in Table 2. The analytical detection limits of precious metals were 0.05, 0.004, 0.03, 0.02, 0.05, and 0.05 ng g^{-1} for Ru, Rh, Pd, Ir, Pt, and Au, respectively, when 0.3 g of incineration ash sample was used for analysis. These analytical detection limits were low enough to determine precious metals in incineration ash samples. In addition, the blank values for all of the precious metals were below analytical detection limits, where the blank test was carried out by employing the same experimental procedure used for incineration ash samples.

Removal Efficiencies of Interferent Elements by Te Coprecipitation. Table 3 shows the possible polyatomic interferences in the determination of precious metals in incineration ash samples by quadrupole-type ICP-MS. Therefore, separation of these interferent elements is indispensable to minimize analytical errors due to polyatomic interferences. In Table 3, the removal efficiencies of interferent elements are summarized, when the test solution (Ni 50 ng mL^{-1}, Cu 100 ng mL^{-1}, Zn 100 ng mL^{-1}, Rb 50 ng mL^{-1}, Sr 50 ng mL^{-1}, Y 10 ng mL^{-1}, Hf 10 ng mL^{-1}, Ta 10 ng mL^{-1}, Pb 100 ng mL^{-1}) was concentrated 10-fold by Te coprecipitation. It can be seen from Table 3 that interferent elements were efficiently removed by Te coprecipitation. As a result, the polyatomic interferences listed in Table 3 could be reduced to almost the negligible levels.

Table 2. Recovery Values and Analytical Detection Limits of Precious Metals by Te Coprecipitation and ICP-MS

Element	m/z	Recovery value[a) /%	Analytical detection limit /ng g^{-1}
Ru	99	96.2 ± 0.5	0.05
Rh	103	97.8 ± 0.9	0.004
Pd	105	98.0 ± 3.5	0.03
Ir	193	100.1 ± 2.3	0.02
Pt	195	99.7 ± 1.4	0.05
Au	197	93.7 ± 3.9	0.05

a) Mean ± SD ($n = 3$).

Table 3. Removal Efficiencies of the Interferent Elements by Te Coprecipitation

Interferent	Possible polyatomic interference	Removal efficiency[a) /%
Ni	$^{62}\mathrm{Ni}^{37}\mathrm{Cl}^+ \rightarrow {}^{99}\mathrm{Ru}^+$, $^{64}\mathrm{Ni}^{35}\mathrm{Cl}^+ \rightarrow {}^{99}\mathrm{Ru}^+$, $^{61}\mathrm{Ni}^{38}\mathrm{Ar} \rightarrow {}^{99}\mathrm{Ru}^+$	96.4 ± 1.8
Cu	$^{63}\mathrm{Cu}^{40}\mathrm{Ar}^+ \rightarrow {}^{103}\mathrm{Rh}^+$, $^{65}\mathrm{Cu}^{40}\mathrm{Ar}^+ \rightarrow {}^{105}\mathrm{Pd}^+$	99.6 ± 0.2
Zn	$^{64}\mathrm{Zn}^{35}\mathrm{Cl}^+ \rightarrow {}^{99}\mathrm{Ru}^+$	99.5 ± 0.4
Rb	$^{87}\mathrm{Rb}^{16}\mathrm{O}^+ \rightarrow {}^{103}\mathrm{Rh}^+$	99.8 ± 0.02
Sr	$^{87}\mathrm{Sr}^{16}\mathrm{O}^+ \rightarrow {}^{103}\mathrm{Rh}^+$, $^{88}\mathrm{Sr}^{16}\mathrm{O}^{1}\mathrm{H}^+ \rightarrow {}^{105}\mathrm{Pd}^+$	98.5 ± 0.04
Y	$^{89}\mathrm{Y}^{16}\mathrm{O}^+ \rightarrow {}^{105}\mathrm{Pd}^+$	98.6 ± 0.5
Hf	$^{177}\mathrm{Hf}^{16}\mathrm{O}^+ \rightarrow {}^{193}\mathrm{Ir}^+$, $^{179}\mathrm{Hf}^{16}\mathrm{O}^+ \rightarrow {}^{195}\mathrm{Pt}^+$	99.9 ± 0.03
Ta	$^{181}\mathrm{Ta}^{16}\mathrm{O}^+ \rightarrow {}^{197}\mathrm{Au}^+$	97.3 ± 0.9
Pb	$^{206}\mathrm{Pb}^{++} \rightarrow {}^{103}\mathrm{Rh}^+$	99.5 ± 3.8

a) Mean ± SD ($n = 3$).

Table 4. Analytical Results for Precious Metals in WPR-1 Obtained by ICP-MS with and without Te Coprecipitation (unit: ng g^{-1})

Element	Analytical values[a),b)]		Certified value
	Without Te coprecipitation	With Te coprecipitation	
Ru	20.7 ± 2.9 (0.94)	21.4 ± 3.7 (0.97)	22 ± 4
Rh	16.7 ± 0.4 (1.25)	13.6 ± 0.4 (1.01)	13.4 ± 0.9
Pd	237 ± 16 (1.01)	233 ± 9 (0.99)	235 ± 9
Ir	16.5 ± 3.9 (1.22)	14.1 ± 1.0 (1.04)	13.5 ± 1.8
Pt	285 ± 14 (1.00)	288 ± 3 (1.01)	285 ± 12
Au	41.2 ± 1.3 (0.99)	42.4 ± 1.7 (1.01)	42 ± 3

a) Mean ± SD ($n = 3$). b) Values in the parentheses are the ratios of the analytical values to the certified values.

Table 5. Analytical Results for Precious Metals in Incineration Ash Certified Reference Materials (unit: ng g^{-1})

Element	Coal fly ash		City waste incineration ash	Continental crust	
	JCFA-1	SRM 1633b	CRM 176	Wedepohl[a)]	Lide[b)]
Ru	1.69	2.62	1.07	0.1	1
Rh	0.476	1.29	3.79	0.06	1
Pd	4.37	5.58	5.88	0.4	15
Ir	0.21	0.35	0.30	0.05	1
Pt	2.04	4.17	4.63	0.4	5
Au	3.89	14.1	66.7	2.5	4

a) Cited form Ref. 16. b) Cited from Ref. 17.

Determination of Precious Metals in Certified Reference Material of WPR-1. In the present work, the certified reference material of WPR-1 was analyzed to validate the present method. First, in order to evaluate the sample decomposition procedure, the precious metals in WPR-1 were determined directly, without Te coprecipitation, by ICP-MS with external calibration. The analytical results are shown in the second column of Table 4, where the analytical results were shown as the mean values and standard deviations (SDs) obtained from three replicated experiments. The values in the parentheses are the ratios of the analytical values and the certified values. It can be seen in Table 4 that the analytical results without Te coprecipitation were almost consistent with the certified values, except for Rh and Ir. These results indicate that there were no losses of precious metals during the sample decomposition step. It was thus considered that the addition of NaCl was very helpful to prevent some losses of precious metals during the sample decomposition procedure by forming their stable chloro complexes.[6] The positive errors for Rh and Ir might be attributed to incomplete correction of polyatomic interferences (e.g., $^{87}Sr^{16}O \rightarrow {}^{103}Rh$, $^{177}Hf^{16}O \rightarrow {}^{193}Ir$), because the interfering elements, such as Sr and Hf, were not removed here.

Next, the precious metals in WPR-1 were determined after Te coprecipitation to evaluate the entire analytical procedure. The analytical results with Te coprecipitation are summarized in the third column of Table 4. As can be seen in Table 4, the observed values of precious metals with Te coprecipitation were in quite good agreement with the certified values. It is noted here that the analytical results for Rh and Ir were very much improved with Te coprecipitation by removing the above interfering elements. In consequence, precious metals were quantitatively recovered through the whole analytical procedure, including sample decomposition and Te coprecipitation. Therefore, it was concluded that the present sample decomposition and Te coprecipitation were applicable as the pretreatment method for the determination of precious metals in incineration ash samples by ICP-MS with external calibration.

Determination of Precious Metals in Incineration Ash Samples. The present analytical method was applied to the determination of precious metals in incineration ash samples. The analytical results for coal fly ash certified reference materials (JCFA-1 and SRM 1633b) and city waste incineration ash certified reference material (CRM 176) are summarized in Table 5. As can be seen in the table, the concentrations of precious metals in coal fly ash and city waste incineration ash certified reference materials were at the ng g^{-1} to sub-ng g^{-1} levels. For comparison, the concentrations of precious metals in the continental crust, which were cited from two references,[16,17] are also listed in Table 5. As can be seen in Table 5, the concentrations of precious metals in coal fly ashes were almost at the same levels as those in the continental crust, although the concentrations of precious metals in the continental crust still have some uncertainty. In the case of city waste incineration ash, the concentration of Au was significantly higher than those in coal fly ashes, while other precious metals were at the same levels as those in coal fly ashes.

The analytical results for precious metals in the IWIFA and IWIBA samples are listed in Table 6. In Table 6, the results for IWIFA A and IWIBA A are expressed as mean value ± SD ($n = 3$), which were obtained from three replicated experiments, and the others are the results obtained from a single experiment. As can be seen in Table 6, the concentrations of precious metals in IWIFA A and IWIBA A had rather large variations, which may be attributed to the heterogeneous distributions of precious metals in the industrial waste incineration ash samples. The concentrations of precious metals in the

Table 6. Analytical Results for Precious Metals in Industrial Waste Incineration Ashes (unit: $\mathrm{ng\,g^{-1}}$)

Element	Concentration[a)]					
	Incinerator A[b)]		Incinerator B[c)]		Incinerator C[d)]	
	IWIFA A	IWIBA A	IWIFA B	IWIBA B	IWIFA C	IWIBA C
Ru	13.2 ± 1.7	5.4 ± 1.0	15.5	12.3	8.6	11.6
Rh	13.4 ± 1.1	4.70 ± 0.43	46.8	29.8	3.86	7.29
Pd	161 ± 15	245 ± 4	2360	1850	125	517
Ir	1.63 ± 0.42	7.55 ± 1.68	2.79	2.44	0.90	0.72
Pt	83.9 ± 19.4	393 ± 94	301	212	60.9	73.7
Au	70.7 ± 18.2	54.0 ± 3.6	254	129	89.4	195

a) The results for IWIFA A and IWIBA A are expressed as mean value ± SD ($n = 3$), and the others are the results obtained from a single experiment. b) Oil and petrochemical wastes were mainly incinerated. c) Solid wastes were mainly incinerated. d) Food wastes were mainly incinerated.

IWIFA and IWIBA samples were at 1–1000 $\mathrm{ng\,g^{-1}}$ levels, which were 1 or 2 orders of magnitude higher than those in coal fly ashes. In addition, the differences of their concentrations were within a factor of 20, even though these samples were collected from different incinerators with different kinds of input waste materials. These results may reflect the wide use of precious metals in industrial production.[18,19] For example, Pd, Pt, and Au are used as electronics device materials, while Ru, Rh, and Ir are used as ingredients for alloy materials of other precious metals to increase their mechanical strength. In addition, Rh, Pd, and Pt are used for various catalytic materials in petrochemical industry.

Enrichment Factors of Precious Metals in Incineration Ash Samples. In order to compare the elemental distributions in each sample in previous works, the enrichment factors (*EF*s) of the elements, which are defined as normalized concentration ratios of the elements in the samples to those in the continental crust, were used.[11–14] However, the concentrations of precious metals in the continental crust are still uncertain, as described earlier. Thus, in the present work the concentrations of precious metals in coal fly ash (CFA) certified reference material (JCFA-1) were used as the references for normalization instead of their abundances in the continental crust, because the elemental composition of CFA was generally very similar to that of the continental crust.[11] The *EF* values of precious metals in incineration ash samples, compared to their abundances in CFA (JCFA-1), are expressed by Eq. 1;

$$EF_{\mathrm{CFA}} = \frac{[\mathrm{M}]_{\mathrm{sample}}/[\mathrm{Al}]_{\mathrm{sample}}}{[\mathrm{M}]_{\mathrm{CFA}}/[\mathrm{Al}]_{\mathrm{CFA}}}, \tag{1}$$

where $[\mathrm{M}]_{\mathrm{sample}}$ and $[\mathrm{Al}]_{\mathrm{sample}}$ are the concentrations of M (precious metal) and Al in the sample, and $[\mathrm{M}]_{\mathrm{CFA}}$ and $[\mathrm{Al}]_{\mathrm{CFA}}$ are their concentrations in CFA (JCFA-1). The EF_{CFA} values of precious metals in the incineration ash samples are shown in Fig. 2. As can be seen in the figure, the EF_{CFA} values of all precious metals in SRM 1633b (coal fly ash) were smaller than 3. These results indicate that the concentrations of precious metals in SRM 1633b are not so much different from those in JCFA-1. In the case of city waste incineration ash (CRM 176), Rh and Au were slightly enriched ($EF_{\mathrm{CFA}} > 10$) compared with those in coal fly ash. On the other hand, the EF_{CFA} values for precious metals in the IWIFA and IWIBA samples were from 10 up to 1000. These results may reflect that various precious metals are widely used in modern industrial production. Among precious metals, Au is widely used as an electrical device material such as for circuit boards, electrodes, and IC chips.[19] As a result, the EF_{CFA} values of Au in all IWIFA and IWIBA samples were larger than 50. Rh and Pd are commonly used in various catalysts along with Pt,[19] which resulted in their similar distributions in each sample. However, the distribution patterns of Rh and Pd were different from that of Pt, as can be seen in Fig. 2. On the other hand, the distribution pattern of Ir, which is used as an alloy material for Pt in electronic devices to increase their mechanical strength,[18] is similar to that of Pt. These results suggest that Pt in industrial waste incineration ashes was mostly derived from electronic device materials, rather than catalytic materials.

Partitionings of Precious Metals in Different Industrial Waste Incineration Ashes. It can also be seen in Fig. 2 that the EF_{CFA} values of some precious metals in fly ashes were larger than those in bottom ashes; precious metals were more abundant in fly ashes than in bottom ashes. Therefore, the concentration ratios of $C_{\mathrm{F}}/C_{\mathrm{B}}$ (C_{F}; concentration in fly ash, C_{B}; concentration in bottom ash) for precious metals were estimated to evaluate their partitionings during the incineration processes.[13] In the previous work, it was found that the elements that were more partitioned in fly ashes than in bottom ashes during the incineration processes provided $C_{\mathrm{F}}/C_{\mathrm{B}}$ values larger than that of Al.[13] Therefore, the $C_{\mathrm{F}}/C_{\mathrm{B}}$ values of precious metals in industrial waste incineration ashes were normalized to that of Al in each incineration ash. The normalized $C_{\mathrm{F}}/C_{\mathrm{B}}$ values ($C_{\mathrm{F}}/C_{\mathrm{B,norm}}$) are illustrated in Fig. 3. As can be seen in Fig. 3, the $C_{\mathrm{F}}/C_{\mathrm{B,norm}}$ values of precious metals were close to 1 with some exceptions. These results indicate that precious metals are mechanically transferred to fly ashes during the incineration processes.[13] However, the $C_{\mathrm{F}}/C_{\mathrm{B,norm}}$ values of Ru and Rh in incineration ashes A and C and Pd in incineration ashes A were larger than 2. As described earlier, these metals are mostly used as catalytic materials, in which precious metals are used in the forms of very fine particles (submicron particles) adsorbed on the surface of support materials such as alumina and zeolite.[20] These fine particles of precious metals might be desorbed from support materials and transferred to fly ashes by the convection flows in the incinerators, which resulted in their higher distributions in fly ashes than in bottom ashes. In the case of Au, its $C_{\mathrm{F}}/C_{\mathrm{B,norm}}$ values

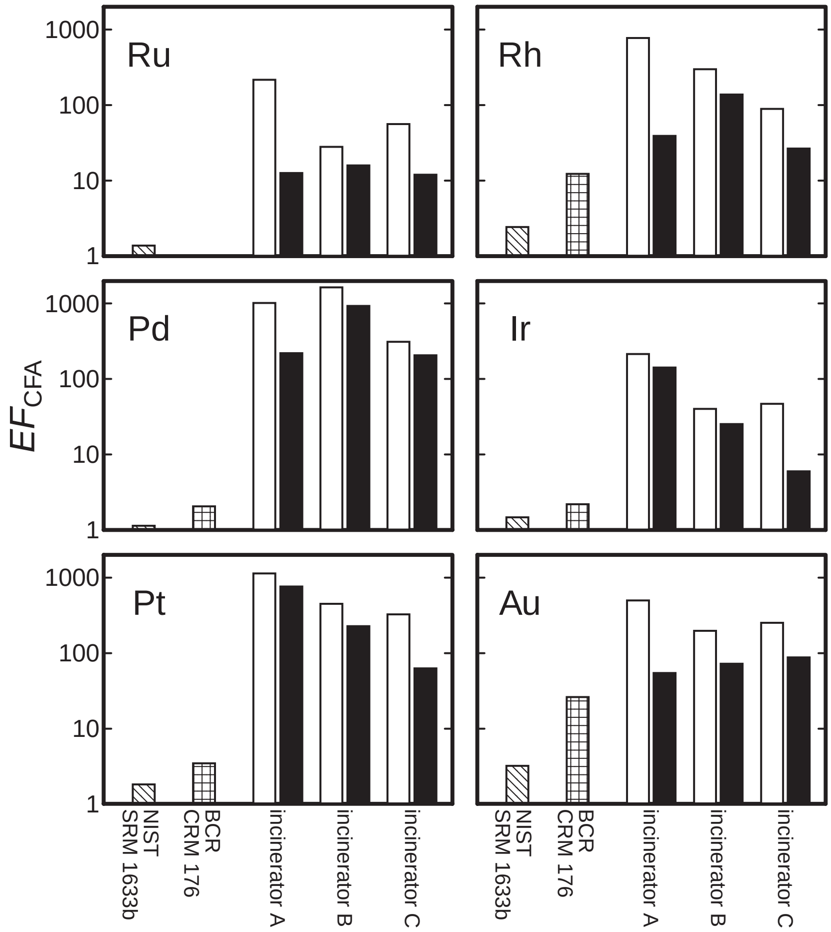

Fig. 2. Comparison of enrichment factors of precious metals in incineration ash samples. ▧: Coal fly ash, ⊞: city waste incineration ash, □: IWIFA, and ■: IWIBA.

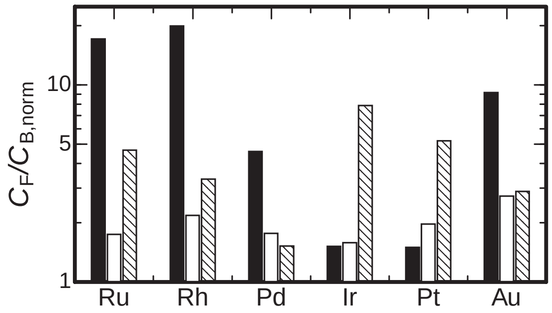

Fig. 3. Concentration ratios of C_F/C_B (C_F; concentration in fly ash, C_B; concentration in bottom ash) for precious metals in industrial waste incinerators, normalized to those for Al in each incinerator. ■: Incinerator A, □: incinerator B, and ▧: incinerator C.

were larger than 2 in all of the incinerators. Gold is extensively used in electronic devices in its metallic form whose melting temperature (1064.43 °C) is close to the incineration temperatures (850–1200 °C). Therefore, the large $C_F/C_{B,norm}$ values of Au suggest the formation of its volatile compounds (e.g., $AuCl_3$: boiling temperature 265 °C) during the incineration processes. The reason for the large $C_F/C_{B,norm}$ values of Pt and Ir in incinerator C is not known, but this fact supports the idea that Pt in the IWIFA and IWIBA samples was mostly derived from electronic devices (same as Ir), not from catalytic materials.

Conclusion

Precious metals in industrial waste incineration ashes could be successfully determined the first time. It was found from the analytical results that the present sample preparation method, including sample decomposition and Te coprecipitation, was useful for the determination of precious metals by ICP-MS with external calibration. The concentrations of precious metals in coal fly ash and city waste incineration ash reference materials were several ng g^{-1}, which were at the same levels as those in the continental crust. On the other hand, the IWIFA and IWIBA samples contained precious metals in the range of 1–1000 ng g^{-1}, reflecting the wide use of precious metals in modern industrial production. These days, the anthropogenic emission of precious metals (Rh, Pd, and Pt) from automobile catalysts attracts extensive attention. The analytical results obtained here suggest that the industrial waste incinerator may be another possible source of anthropogenic emission of precious metals into the environment, even though it is considered that the dust in flue gases could be more than 99% captured by air pollution control devices. Such investigations are now in progress.

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References

1 C. R. M. Rao and G. S. Reddi, *TrAC, Trends Anal. Chem.*, **19**, 565 (2000).

2 M. Moldovan, M. A. Palacios, M. M. Gómez, G. Morrison, S. Rauch, C. McLeod, R. Ma, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, M. Zischka, C. Pettersson, U. Wass, M. Luna, J. C. Saenz, and J. Santamaría, *Sci. Total Environ.*, **296**, 199 (2002).

3 L. Bencs, K. Ravindra, and R. Van Grieken, *Spectrochim. Acta, Part B*, **58**, 1723 (2003).

4 K. Pyrzyńska, *J. Environ. Monit.*, **2**, 99N (2000).

5 M. Balcerzak, *Anal. Sci.*, **18**, 737 (2002).

6 J. G. Sen Gupta, *Talanta*, **36**, 651 (1989).

7 J. Enzweiler, P. J. Potts, and K. E. Jarvis, *Analyst*, **120**, 1391 (1995).

8 K. Oguri, G. Shimoda, and Y. Tatsumi, *Chem. Geol.*, **157**, 189 (1999).

9 X. Jin and H. Zhu, *J. Anal. At. Spectrom.*, **15**, 747 (2000).

10 M. B. Gómez, M. M. Gómez, and M. A. Palacios, *J. Anal. At. Spectrom.*, **18**, 80 (2003).

11 E. Fujimori, K. Ichikawa, H. Takata, K. Asai, K. Chiba, and H. Haraguchi, *Environ. Sci.*, **11**, 363 (1998).

12 E. Fujimori, K. Ichikawa, R. Shiozawa, K. Asai, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **74**, 2045 (2001).

13 E. Fujimori, S. Iwata, K. Minamoto, K.-H. Lee, A. Itoh, K. Chiba, and H. Haraguchi, *Anal. Sci.*, **20**, 189 (2004).

14 E. Fujimori, K. Minamoto, S. Iwata, K. Chiba, and H. Haraguchi, *J. Mater. Cycles Waste Manage.*, **6**, 73 (2004).

15 E. Fujimori, H. Sawatari, K. Chiba, and H. Haraguchi, *Anal. Sci.*, **12**, 465 (1996).

16 K. H. Wedepohl, *Geochim. Cosmochim. Acta*, **59**, 1217 (1995).

17 "Handbook of Chemistry and Physics," ed by D. R. Lide, CRC Press, Florida (1998).

18 "Kikinzoku no Kagaku (Science of Noble Metal, in Japanese)," Tanaka Kikinzoku Kogyo, Tokyo (2001).

19 "Material Flow of Mineral Resource," Mineral Resource Information Center, Metal Mining Agency of Japan (2001).

20 "Kankyo Shokubai (Environmental Catalyst, in Japanese)," ed by the Surface Science Society of Japan, Kyoritsu Shuppan, Tokyo (1997).