Trace Element Analysis of Waste Water Reference Material and Eluates from Fly Ash by Benchtop Total Reflection X-ray Fluorescence Spectrometry

Atsushi Ohbuchi[1, 2], Wataru Matsuda[1], Hikari Takahara[1], Satoshi Ikeda[1], Yoshiyuki Kataoka[1],
Kengo Fujii[3], Yuya Koike[3]

1: Rigaku Corporation, 14-8 Akaoji, Takatsuki, Osaka 569-1146, Japan
2: Applied Rigaku Technologies, Inc, 9825 Spectrum Drive, Bldg 4, Suite 475, Austin, Texas 78717, USA
3: Meiji University, 1-1-1 Higashimta, Kawasaki, Kanagawa 214-8571, Japan

Abstract

A benchtop TXRF spectrometer with a 600 W X-ray tube, double-stacked multilayer mirror and a silicon drift detector (SDD) having a 50mm^2 active area was used for waste water analysis. Quantitative results were obtained using the internal standard method. The results obtained for a number of harmful elements present in a wide range of concentrations were in good agreement with standard values in waste water reference samples. The lower limits of detection (LLDs) were found to be in the low μg/L range for many elements. The LLD for Cd was calculated to 25 μg/L due to K line excitation by high energy X-ray excitation of 30 keV. The TXRF method was also used to study the leaching of hazardous elements from municipal solid waste incineration (MSWI) fly ash. The results obtained by TXRF show that an aqua seal coating could suppress the elution of harmful elements from MSWI fly ash.

Keywords: benchtop TXRF spectrometer, high energy excitation, waste water, elution from MSWI fly ash

1. Introduction

X-ray fluorescence spectrometry (XRF) is a non-destructive and widely applicable method to elemental analysis in industrial and R&D uses. Total reflection X-ray fluorescence (TXRF) spectrometry is a kind of XRF techniques using the phenomenon of total reflection of X-rays. The incident X-ray beam is irradiated on a flat and smooth substrate at a glancing angle less than the critical angle, and the penetration depth is approximately several nm. By utilizing the TXRF phenomenon, TXRF spectrometry has been applied to surface sensitive analysis, the TXRF application has been well established in semiconductor industry to control trace metallic contaminations on silicon wafers with high power dedicated equipment (Fabry *et al.*, 2001; Funabashi *et al.*, 1997; Tsuji *et al.*, 1997).

On the other hands, TXRF spectrometry has also been applied to the environmental and biological fields. Many papers report on a variety of applications such as analysis of liquids (e.g. water and oil), pharmaceutical drugs and environmental samples (Kunimura and Shinkai, 2017; Towett *et al*., 2013; Cherkashina *et al*., 2014; Schirmacher *et al*., 1993; Dalipi *et al*., 2017; Reus *et al*., 1993). Compact benchtop and low power TXRF spectrometers are commercially available nowadays.

TXRF spectrometry has been considered as a possible alternative technique to induced couple plasma atomic emission spectrometry (ICP-AES) (Iwata *et al.*, 2001), ICP-mass spectroscopy (ICP-MS) (Mester *et al.*, 1999) and atomic absorption spectrometry (AAS) (Das *et al.*, 2001) for elemental analysis of liquid samples. Compared to such chemical analysis methods, TXRF

method is advantageous to the small sample amount, non-destructive nature, time and cost consumption for analysis; the carrier gas is not required during measurements. The internal standard method using relative sensitivity factors is effective for quantification, saving the time of setting up calibration curves. The simple sample preparation only requires pipetting the liquid onto a carrier.

In this study, a benchtop TXRF spectrometer was used for elemental analysis in waste water. There are a variety of waste water samples such as industrial waste water, domestic waste water, and mine drainage. They contain various concentration levels and various components depending on their histories and processes. Therefore, the wide concentration levels of solutions from few tens of µg/L (ppb) to several mg/L (ppm) were evaluated. Fly ash is a waste disposed from thermal power stations and municipal solid waste incineration (MSWI) plants. MSWI fly ash contains harmful elements such as Cr, Cu, Zn, As, Se, Cd and Pb, and the elution of the elements contacted with rain and environmental moisture in the landfill site becomes serious environmental problem. To prevent the elution of harmful elements, MSWI fly ash is effectively stabilized with cement or chelate compound. However, the volume increase of MSWI fly ash by the cement or chelate compound is an issue for the capacity of landfill site. Therefore, the suppression method by water-repellent agent without volume increase was applied to prevent elution of harmful elements from MSWI fly ash. In addition, commercially available water-repellent agents was used as the stabilizing compounds for MSWI fly ash due to having common characteristics, namely preventing water absorption, preventing elution, weather resistance, alkali and acid resistances, moisture permeability and salt preventive property. Among the various types of water-repellent agents, “aqua seal” (Daido Corporation) is an oligomer of silane type agent for water absorption inhibitor for concrete. A MSWI fly ash sample was coated with aqua seal and the elution test by Japanese leaching test No. 13 (JLT-13) (Ministry of the Environment, 2013) was performed. The harmful elements in the elution were analyzed with the TXRF method and the effect of the aqua seal coating is discussed.

2. Experimental

2.1 Apparatus

A benchtop TXRF spectrometer NANOHUNTER II (Rigaku, Osaka, Japan) was used for the analyses of waste water and elution from fly ash sample. The optical schematic diagram of the apparatus is shown in Fig.1. The excitation source consists of a fine focus 600 W Mo target X-ray tube operated at 50 kV and 12 mA and a double-stacked synthetic multilayer mirror. The double-stacked synthetic multilayer mirror with different d value layers was fabricated as a curved synthetic multilayer mirror. The double-stacked synthetic multilayer mirror reflects two excitation X-ray energies according to Bragg’s law ($n\lambda = 2d\sin\theta$) of X-ray diffraction phenomena: X-rays of 17.4 keV from the characteristic X-rays of Mo Kα and high energy X-rays of 30 keV from continuous X-rays. K lines of elements with atomic number from 40 to 50 are efficiency excited by 30 keV

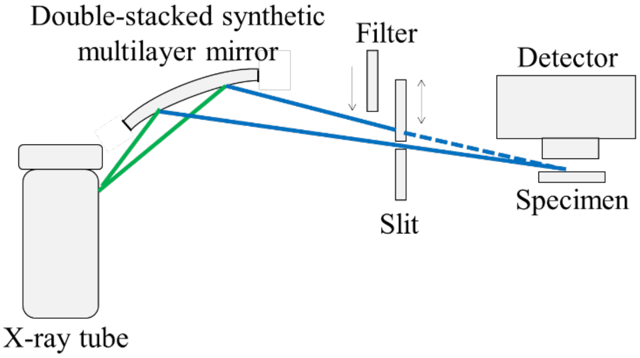

Fig. 1 Optical schematic diagram of NANOHUNTER II.

continuous X-ray. A specimen prepared for the waste water sample and elution from fly ash were measured with two different glancing angles of 0.010° and 0.025° since critical angles depend on the excitation energy. The angle of 0.010° was used for high energy excitation (30 keV with Al filter) to achieve lower background by preventing penetration of X-ray into dried sample and substrate. The angle of 0.025° was used for Mo Kα excitation to obtain high intensity. Measurement time was set to 1000 s for each energy range. An aluminum filter located between mirror and specimen was used to reduce Mo Kα X-rays, background and sum peaks from detected elements for the measurement in high energy excitation condition. A large area (50 mm^2) silicon drift detector (SDD) with an energy resolution of less than 150 eV at 5.9 keV was configured for the detection of elements from Al to U. The spectrometer was equipped with a horizontal 16 position sample changer.

2.2 Sample preparation

The reference material of waste water of 140-025-037 EnviroMAT supplied by SCP Science was used for validation of quantitative analysis and calculation of lower limits of detection (LLDs). As for the high concentration level sample, the reference material was used as the original solution. As for the low concentration level sample, the reference material was diluted 1:100 with 0.1 mol/L nitric acid solution (Fujifilm Wako Pure Chemical Co. guaranteed reagent). A distilled water (Fujifilm Wako Pure Chemical Co., for high performance liquid chromatography) was used for dilution of sample and each reagent. For quantification using internal standard method, Ga (Fujifilm Wako Pure Chemical Co., Ga standard solution of 1000 ppm) and Ag (Fujifilm Wako Pure Chemical Co., Ag standard solution of 1000 ppm) standard solutions were added to obtain final concentrations of 10 mg/L and 0.1 mg/L, respectively for high concentration and low concentration solutions. The internal standard of Ga is for the quantification for Mo Kα excitation and Ag is for high energy excitation. The sample solutions of 10 μL were pipetted on quartz glass carrier with 30 mm diameter and dried under reduced pressure for TXRF measurements. The carrier surface was made hydrophobic by pretreatment with silicone solution (Serva, for siliconizing glass and metal).

Fig. 2 Photograph of spray coating for aqua seal using the water-repellent agent.

2.3 Procedure to prepare eluted solution from the fly ash sample

The surface of MSWI fly ash collected at in a northern area of Japan was coated by spraying aqua seal as water-repellent agent 3 times for 30 sec to suppress elution of harmful elements. Fig. 2 shows a photograph of spray coating. The JLT-13 as used by the Ministry of the Environment in Japan for industrial waste was perfomed for elution from MSWI fly ash with and without coating treatment. The experimental procedure of the JLT-13 is

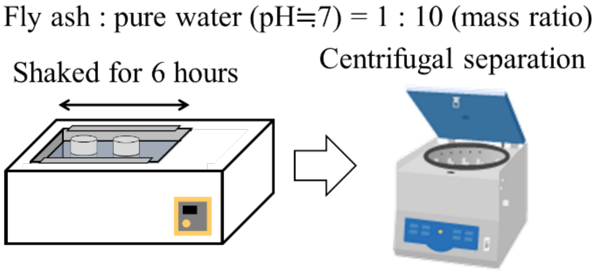

Fig. 3 Procedure of the JLT-13 according to the method of Ministry of Environment in Japan.

shown in Fig. 3. In the JLT-13, a mixture of pure water (pH≒7) and fly ash (Solid / Liquid ratio was set to 0.1) was subjected to continuous shaking for 6 h at 20 degree C in a shaker. After treatment, pH of elution was about 12. A mechanical shaker (Shaking Bath TBK 602DA, Advantec Inc.) was used to prepare eluted solutions from MSWI fly ash. The speed of the shaker was approximately 200 rpm. After shaking, pH of the elution was about 12 and was separated from the fly ash using a centrifugal separator (H-103N, Kokusan Co.). Elutions from MSWI fly ash with and without coating treatment were diluted 10 times at the time of analyzing process.

3. Results and Discussion

3.1 Quantitative analysis of waste water

Thirteen elements in the standard materials of 140-025-037 EnviroMAT-waste water were analyzed using internal standard method by adding solution of Ga and Ag.

Quantification was performed using relative sensitivity factors using the following equation (1).

$$C_A = \frac{S_{IS} \times I_A}{S_A \times I_{IS}} \times C_{IS} \times \frac{V_{IS}}{V_S} \,(1)$$

C_A is quantified concentration of sample and C_{IS} is concentration of internal standard element in internal standard solution. S_A and S_{IS} are relative sensitivity factors (eg. relative value of cps/μg) of analytical element and internal standard element. I_A and I_{IS} are net intensities of the lines of analytical and internal standard elements. V_S and V_{IS} are sampling volumes of sample and internal standard solution. The relative sensitivity factors are the sensitivity ratios between elements, which were theoretically calculated considering optical conditions and physical parameters.

Table 1 lists the analytical results of the waste water reference samples analyzed using the

Table 1 Analytical results of 140-025-037 EnviroMAT-waste water
Parenthesis: Relative standard deviation / %, n=6.
Measurement time: 1000 s at each excitation condition by Mo-Kα having 17.4 keV and 30 keV continuous X-ray.

(a) Original waste water of 140-025-037

	mg/L			
Elements	Analytical values	Standard values	LLDs	Recovery (%)
Cr	5.72 (3.3)	6.12	0.03	93
Mn	11.8 (1.8)	12.1	0.022	98
Fe	5.92 (3.8)	6.54	0.019	91
Co	7.41 (2.2)	8.05	0.018	92
Cu	9.96 (1.3)	10.7	0.017	93
Zn	2.45 (1.6)	2.92	0.015	84
As	8.45 (1.0)	7.92	0.0064	107
Se	2.71 (1.4)	2.65	0.0074	102
Cd	2.24 (12)	2.29	0.24	98
Tl	7.50 (3.0)	8.24	0.016	91
Pb	3.68 (2.2)	4.13	0.041	89
U	8.87 (0.76)	10.3	0.018	86

Recovery values were calulated as follows:

Recovery (%) = $\frac{Analytical\ value}{Standard\ value}$ ×100

(b) Waste water diluted 100 times

	mg/L			
Elements	Analytical values	Standard values	LLDs	Recovery (%)
Cr	0.052 (5.6)	0.0612	0.007	85
Mn	0.161 (13)	0.121	0.0029	133
Fe	0.076 (12)	0.0654	0.0022	116
Co	0.086 (9.9)	0.0805	0.0021	107
Cu	0.112 (8.1)	0.107	0.0018	105
Zn	0.032 (11)	0.0292	0.0014	110
As	0.107 (15)	0.0792	0.0008	135
Se	0.037 (18)	0.0265	0.0009	140
Cd	N. D.*	0.0229	0.025	-
Tl	0.094 (17)	0.0824	0.0021	114
Pb	0.057 (19)	0.0413	0.0029	138
U	0.089 (5.5)	0.103	0.0037	86

* : Not detected

internal standard method. Analytical Elements except for Cd were excited by Mo-Kα having 17.4 keV and Cd was excited by 30 keV continuous X-ray. Table 1 (a) is for high concentration of the original solution and Table 1 (b) for low concentration of the 100 times diluted sample. The selected analytical lines were $L\beta_1$ for Pb and Kα for the other elements. The recovery values are 84-140 % in the original and diluted solutions. The TXRF results would be appropriate comared to the TXRF results of wine (Dalipi *et al.*, 2016) with high matrix as well as waste water.
The detection limits (LLDs) in the tables were obtained using equation (2).

$$LLD = 3 \times \frac{C}{I_{NET}} \times \sqrt{\frac{I_{BG}}{t}} \dots (2)$$

where C is concentration (mg/L), I_{NET} is net intensity (cps), I_{BG} is background intensity (cps) and t is measurement time (s). The LLDs in the diluted sample are smaller than those in the original samples because of lower background intensities due to less matrix in the diluted solution. LLD value of Cd was calculated to 25 μg/L by excitated K line using high energy X-ray reflected from the double-stacked multilayer mirror although Cd analysis in several ppm to ppb level used L line was difficult due to overlapping peaks and deficient sensitivity in previous benchtop type TXRF spectrometer.

3.2 Elution analysis for fly ash with and without water-repellent treatment
The limits of elution for harmful elements from waste are regulated in the JLT-13 by Ministry of the Environmental in Japan as described in the experimental section. Regulated elements are Be, V, Cr, Ni, Cu, Zn, As, Cd, and Pb. Among them, regulated values of As, Se, Cd and Pb are enacted to below 0.3 mg/L and Cr (VI) is below 1.5 mg/L. Standard analysis methods for elution

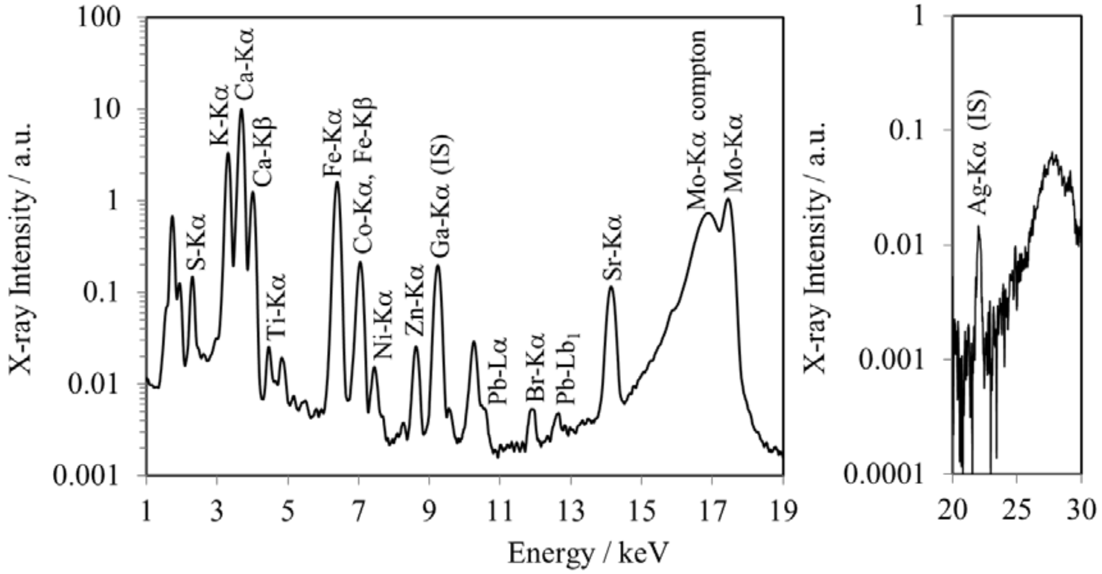

Fig. 4 TXRF Spectrum of elution from MSWI fly ash diluted 10 times.
IS: Internal standard
Measurement time: 1000 s at each excitation condition by Mo-Ka having 17.4 keV and 30 keV continuous X-ray.

from waste are defined with ICP-AES and AAS in the JLT-13. The LLDs in Table 1 obtained by the diluted waste water standard sample showed lower values of the regulatory limits in all regulated elements except for Be.

Spectrum of elution from untreated MSWI fly ash diluted 10 times is shown in Fig. 4. Cobalt, Zn, and Pb as harmful elements and Fe were eluted from untreated MSWI fly ash under conditions of the JLT-13. LLDs calculated by the equation (2) of eluted 4 elements from untreated MSWI fly ash diluted 10 times were 0.0060 mg/L for Fe, 0.0051 mg/L for Co, 0.0023 mg/L for Zn and 0.0053 mg/L for Pb respectively. Elution behavior of Fe in addition to 3 harmful elements from MSWI fly ash with and without water-repellent treatment is shown in Fig. 5. Elution amounts of 4 elements from treated MSWI fly ash were decreased by water-repellent agent. Especially, elution amounts of Fe, Co and Pb were exceedingly decreased compared to results of the untreated MSWI fly ash. On the other hand, elution amounts of Zn from treated fly ash were slightly decreased than the other 3 elements. Coating of Zn particles is considered less well compared to other elemental particles. SEM images of MSWI fly ash surface with and without water-repellent treatment are shown in Fig. 6. The fibers of needle shape were observed on surface of MSWI fly ash without water-repellent treatment. With water-repellent treatment, the fibers of needle shape were not observed due to change surface condition of MSWI fly ash. A part of heavy elements in MSWI fly ash might be formed with chloride compounds (Verhulst *et al.*, 1996) having high solubility in water. Therefore, their elements are eluted to environment from MSWI fly ash contacted with water or rainwater. With spray coating, water-repellent layer on the sample surface is formed covering MSWI fly ash particles. As the results, it was considered that elution of harmful elements was suppressed by preventing contact with water by coating on surface of MSWI fly ash particle although elucidating the details of coating treatment by water-repellent is future topics of discussion.

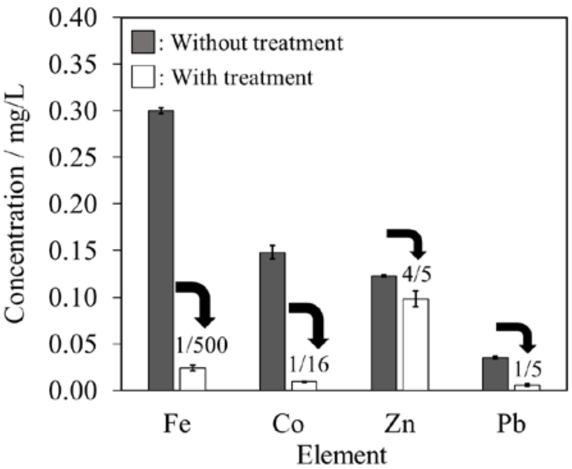

Fig. 5 Observation of elution behavior of harmful elements with and without water-repellent treatment.
Error bar: Standard deviations, n=6.

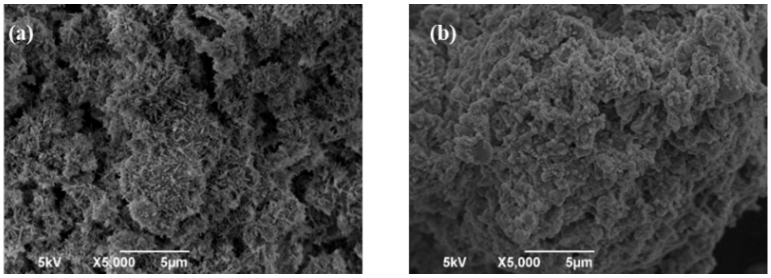

Fig. 6 SEM images of fly ash surface with and without water-repellent treatment.
(a): Without water-repellent treatment. (b): With water-repellent treatment.

4. Conclusions

Waste water and elution analysis with a benchtop TXRF system equipped with high power X-ray tube (600W), double-stacked multilayer mirror and SDD of large detection area for higher sensitivity analysis were investigated. Quantitative analysis was performed by internal standard method without preparing calibration curve. Analytical values of all elemets of the original and diluted sample showed good agreement with standard values compared to the TXRF results of wine with high matrix same with waste water. The LLDs of analytical elements in the diluted standard sample gave lower values from part per billion to sub part per billion. The LLD value of Cd was calculated to 25 μg/L by excitated K line using high energy X-ray reflected from the double-stacked multilayer mirror. The JLT-13 defined in Japananese regulation was used for preparation of elution from MSWI fly ash. The aqua seal using water-repellent treatment by spray coating was used to prevent elution of harmful elements due to form water-repellent layer on fly ash particles, and its elution was evaluated by the TXRF spectrometer. TXRF spectrometer can be applied as analysis method of harmful components in environmental water such as waste water and components in a wide concentration range from part per billion to part per million. TXRF spectrometer should have large potential as an screening method or alternative method of AAS and ICP-AES in water analysis.

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