Measurement of Trace Amount of Cadmium Using a Portable Total Reflection X-Ray Fluorescence Spectrometer

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This note describes a method for detecting Cd L-lines from a trace amount of cadmium using a portable total reflection X-ray fluorescence spectrometer. When the measurement was carried out in vacuum, the Ar K-lines (Ar Kα line: 2.96 keV, Ar Kβ line: 3.19 keV) that overlap with the Cd L-lines (Cd Lα line: 3.13 keV, Cd Lβ line: 3.32 keV) were remarkably reduced and the Cd L-lines from an analyte containing 1 ng of cadmium were detected. Although the K Kα line (3.31 keV) also overlaps with the Cd L-lines, solid-phase extraction for removing potassium from a sample solution containing both cadmium and potassium led to significant reduction in the intensity of the K Kα line. A combination of solid-phase extraction and measurement in vacuum makes it possible to analyze a trace amount of cadmium using the portable spectrometer.

KEY WORDS: cadmium; portable; total reflection; trace; X-ray fluorescence.

1. Introduction

In total reflection X-ray fluorescence (TXRF) analysis,1) a high power X-ray source is usually used to improve the detection limit. At synchrotron radiation facilities, absolute detection limits were obtained in the femtogram range.2-4) When using a TXRF spectrometer with a few-kW X-ray tube, an absolute detection limit of 0.7 pg was achieved for rubidium.5) On the other hand, portable TXRF spectrometers6-8) with low-power X-ray tubes for trace elemental analysis have been developed since 2006. Although a tungsten-target X-ray tube has been operated at 5 W in the portable spectrometer described in this note, an absolute detection limit of 8 pg was achieved for chromium when the measurement was performed in low vacuum.9) However, it was difficult for such portable spectrometers to detect the Cd K-lines from a trace amount of cadmium because the maximum tube voltage of the X-ray tube in such portable spectrometers7,8) was 50 kV and the intensities of the incident X-rays above the Cd K-edge absorption energy (26.7 keV) were weak. A previously reported absolute detection limit of cadmium was 1 ng.10) In that study, a silicon PIN detector was used and an X-ray waveguide acting as a collimator restricted the incident X-ray beam to a height of 10 μm. On the other hand, in the portable spectrometer described, a silicon drift detector is used and the X-ray waveguide restricts the incident X-ray beam to a height of 20 μm. However, this change may not lead to an improvement in the cadmium detection limit obtained from the measurement of the Cd Kα line. When the Cd L-lines (Cd Lα line: 3.13 keV, Cd Lβ line: 3.32 keV) are measured in air, the Ar K-lines (Ar Kα line: 2.96 keV, Ar Kβ line: 3.19 keV) from air containing 0.9 vol.% of argon and the K Kα line (3.31 keV) overlap with them. The reference value of cadmium in the leaching solution of blast-furnace slag aggregate for general-purpose concrete, as prescribed in JIS A 5011-1, is ≤0.01 mg/L. Potassium should be removed before measuring the Cd L-lines from cadmium in a leaching solution of blast furnace slag aggregate that contains potassium oxide.10) The intensities of the Ar K-lines are significantly reduced when the measurements are performed in vacuum. Measuring under a nitrogen11) atmosphere and replacing the air between an analyte and the detector with nitrogen12) or helium13) also reduce the intensities of the Ar K-lines. Solid-phase extraction makes it possible to remove potassium and to concentrate cadmium. In this note, we show that a combination of solid-phase extraction and measuring the Cd L-lines from an analyte in vacuum makes it possible to analyze a trace of cadmium using the portable spectrometer described.

2. Experimental

A previously reported portable TXRF spectrometer9) was used for measurements. White X-rays (i.e. both the characteristic and the continuum X-rays) from a 50-kV Magnum X-ray tube (Moxtek Inc., Orem, USA) with a tungsten target, operated at 25 kV and 200 μA, were collimated by an X-ray waveguide and then the collimated beam irradiated an analyte on a sample holder. A silicon drift detector VITUS-SDD (Ketek GmbH, Munich, Germany) having an active area of 7 mm² was used. A collimator was attached to the detector to protect the beryllium window of the detector. A quartz glass substrate having a flatness of λ/20 (λ = 632.8 nm) (Sigmakoki Co., Ltd., Hidaka, Japan) was used as the sample holder. A diaphragm pump with a base pressure of 2.7×10⁻⁴ Pa was used. Although an aluminum housing was used as a vacuum chamber in the previous study,9) here an acrylic resin housing was used, with a width of 61 mm, a depth of 45 mm, a height of 30 mm, and a slit acting as an entrance for the incident X-rays. The size of the slit was 15 mm in width and 2.5 mm in height, and it was sealed with an 8-μm-thick Kapton film. A 1 000-ppm cadmium standard solution (996 mg/L at 20°C) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was diluted by ultra-pure water for ultra-trace analysis (Wako Pure Chemical) to prepare a 1-mg/L cadmium standard solution. A 1-μL portion of the 1-mg/L cadmium standard solution was pipetted out and dried on the sample holder for preparing an analyte containing 1 ng of cadmium. To prepare a solution containing 0.01% of potassium and 0.1 mg/L of cadmium (solution A), 0.028 g of KCl was dissolved in 150 mL of distilled water, and then a 15-μL portion of the 1 000-ppm cadmium standard solution was added to this KCl solution.

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A 1-μL portion of solution A was pipetted out and dried on the sample holder. A solid-phase extraction column NOBIAS Chelate PA-1 (Hitachi High-Tech Fielding Co., Tokyo, Japan) was used for the high-efficiency removal of potassium. Sakamoto et al.14) reported a procedure of solid-phase extraction using this column, which we have used as a reference. The column was washed with 10 mL of acetone, 10 mL of 3-mol/L HNO₃, and 20 mL of distilled water. After washing, 10 mL of 0.1 mol/L of ammonium acetate solution was passed through the column. The pH of the ammonium acetate solution was adjusted to be same as the reported pH of a sample solution.14) However, the pH of ammonium acetate solution was not adjusted in this study. Then 150 mL of solution A was passed through the column. Chemical species trapped on the column were eluted and cadmium was concentrated with 1.5 mL of 3-mol/L HNO₃ after the column was washed with 15 mL of distilled water. When 150 mL of solution A, 15 mL of distilled water, and 1.5 mL of 3-mol/L HNO₃ were passed through the column, the pressure of the bottom side of the column was reduced by using a diaphragm pump. A 1-μL portion of the eluted solution (solution B) was pipetted out and dried on the sample holder.

3. Results and Discussion

Figure 1 shows a TXRF spectrum of the analyte containing 1 ng of cadmium measured in air. The Cd L-lines from the trace amount of cadmium were not detected because of the strong overlapping Ar K-lines. The Si Kα line from the quartz glass sample holder was also detected. The W L-lines detected were due to the W L-characteristic X-rays from the X-ray tube. The Ni Kα line may be due to a component of the portable spectrometer.

Figure 2 shows TXRF spectra of the dry residues of ultra-pure water for ultra-trace analysis and of the analyte containing 1 ng of cadmium measured in vacuum. As shown in Figs. 2(a) and 2(b), the Cl Kα line and the Ca Kα line were weak in intensity, and as shown in Fig. 2(a), the K Kα line was weakly detected. These three elements may be from a contamination during sample preparation. The intensities of the Ar K-lines were significantly reduced when the spectra were measured in vacuum. The peak intensity of the Ar Kα line in Fig. 2(a) was 218 times lower than that in Fig. 1, because of which the Cd L-lines from 1 ng of cadmium were detected as shown in Fig. 2(b). The detection limit of cadmium was calculated using the following equation:

\[
\text{Detection limit} = \frac{3m}{I_{\text{Net}}t} \sqrt{\frac{I_{BG}}{t}}
\]

where \(m\) is the amount of cadmium (ng or mg/L), \(I_{\text{Net}}\) is the net intensity of the Cd Lα line (counts/s), \(I_{BG}\) is the background intensity (counts/s), and \(t\) is the measuring time (s).

The absolute detection limit and the relative detection limit of cadmium were calculated to be 0.2 ng and 0.2 mg/L, respectively. As described earlier, the reported detection limit of cadmium was 1 ng when the Cd Kα line was measured in air;9) the cadmium detection limit in this note was about one-fifth of that. Figure 3 shows TXRF spectra of the dry residues of solutions A and B, measured in vacuum. The K K-lines and Cl Kα line were strongly detected in Fig. 3(a). The Cd L-lines were not detected in Fig. 3(a) because of the strong K Kα line. Solid-phase extraction led to significant reduction in the intensities of the K K-lines and the Cl Kα line, as shown in Fig. 3(b). The Cd Lα line was clearly detected in Fig. 3(b) because of the reduction...
in the intensity of the K Kα line. A relative detection limit of cadmium obtained from Fig. 3(b) was 0.02 mg/L, better than that obtained from Fig. 2(b), although the measurement time in Fig. 3(b) was one-third of that in Fig. 2(b). Solid-phase extraction improved the relative detection limit of cadmium by the portable spectrometer. The recovery rate of cadmium can be enhanced by optimizing conditions of solid-phase extraction.

4. Conclusions

A combination of solid-phase extraction and measuring in vacuum using a portable TXRF spectrometer was effective in detecting the Cd L-lines from a trace amount of cadmium in a sample solution containing both cadmium and potassium. On-site measurements under vacuum condition using the portable spectrometer can be performed using a small vacuum pump. Solid-phase extraction is comparatively simple and rapid; therefore, this extraction technique can be used for on-site analysis. According to JIS A 5011-1, the amount of cadmium eluted from blast furnace slag aggregate for general-purpose concrete must be \( \leq 0.01 \) mg/L. Although a relative detection limit of cadmium obtained from a sample solution in this study was 0.02 mg/L, the relative detection limit can be improved further by increasing the volume of sample solution dropped on the sample holder and the concentration factor of solid-phase extraction.

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