

Note

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 α line (Ar K α line: 2.96 keV, Ar K β line: 3.19 keV) that overlap with the Cd L-lines (Cd L α line: 3.13 keV, Cd L β 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 K α 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 K α 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 spectrometers^{6–8)} 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.⁸⁾ 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 spectrometers^{7,8)} 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.⁹⁾ In that study, a silicon PIN detec-

tor 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 K α line. When the Cd L-lines (Cd L α line: 3.13 keV, Cd L β line: 3.32 keV) are measured in air, the Ar K-lines (Ar K α line: 2.96 keV, Ar K β line: 3.19 keV) from air containing 0.9 vol.% of argon and the K K α 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 spectrometer⁸⁾ 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 $\lambda/20$ ($\lambda = 632.8$ nm) (Sigmakoki Co., Ltd., Hidaka, Japan) was used as the sample holder. A diaphragm pump with a base pressure of 2.7×10^2 Pa was used. Although an aluminum housing was used as a vacuum chamber in the previous study,⁸⁾ 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- μ L 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- μ L 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 K α 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 K α line may be due to a component of the portable spectrometer.

Figure 2 shows TXRF spectra of the dry residue 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 K α line and the Ca K α line were weak in intensity, and as shown in Fig. 2(a), the K K α 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 K α 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:

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

where m is the amount of cadmium (ng or mg/L), I_{Net} is the net intensity of the Cd L α 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 K α 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 K α line were strongly detected in Fig. 3(a). The Cd L-lines were not detected in Fig. 3(a) because of the strong K K α line. Solid-phase extraction led to significant reduction in the intensities of the K K-lines and the Cl K α line, as shown in Fig. 3(b). The Cd L α line was clearly detected in Fig. 3(b) because of the reduction

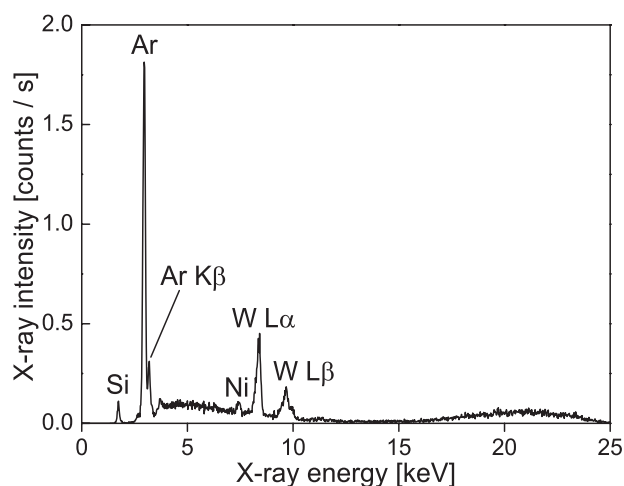


Fig. 1. Total reflection X-ray fluorescence spectrum of an analyte containing 1 ng of cadmium measured in air for 600 s.

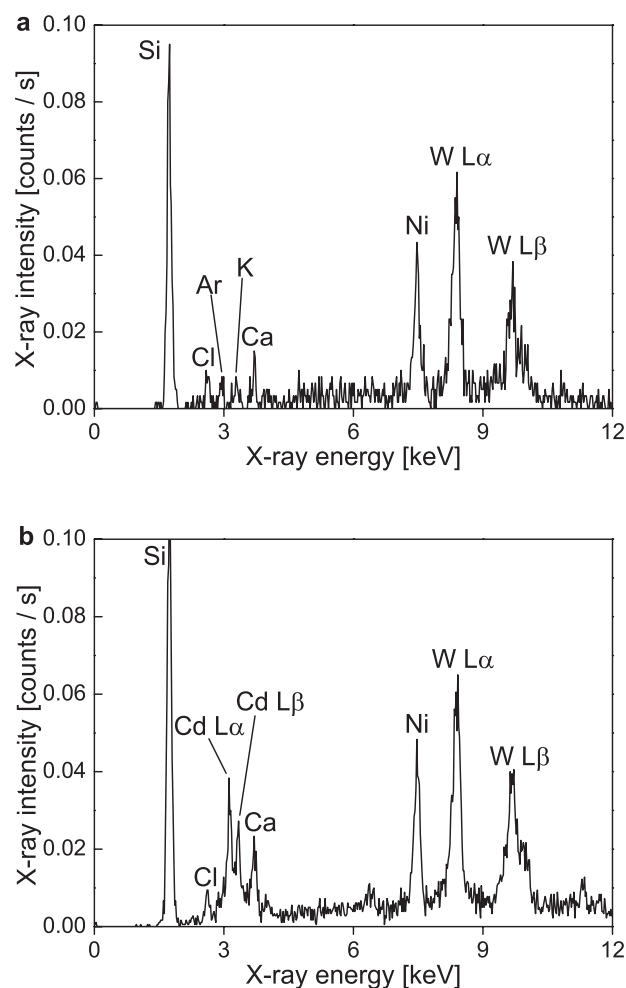


Fig. 2. Total reflection X-ray fluorescence spectra of (a) the dry residue of ultra-pure water for ultra-trace analysis and (b) the analyte containing 1 ng of cadmium. The measurement in Fig. 2(a) was performed in vacuum for 600 s, and that in Fig. 2(b) was performed in vacuum for 1 800 s.

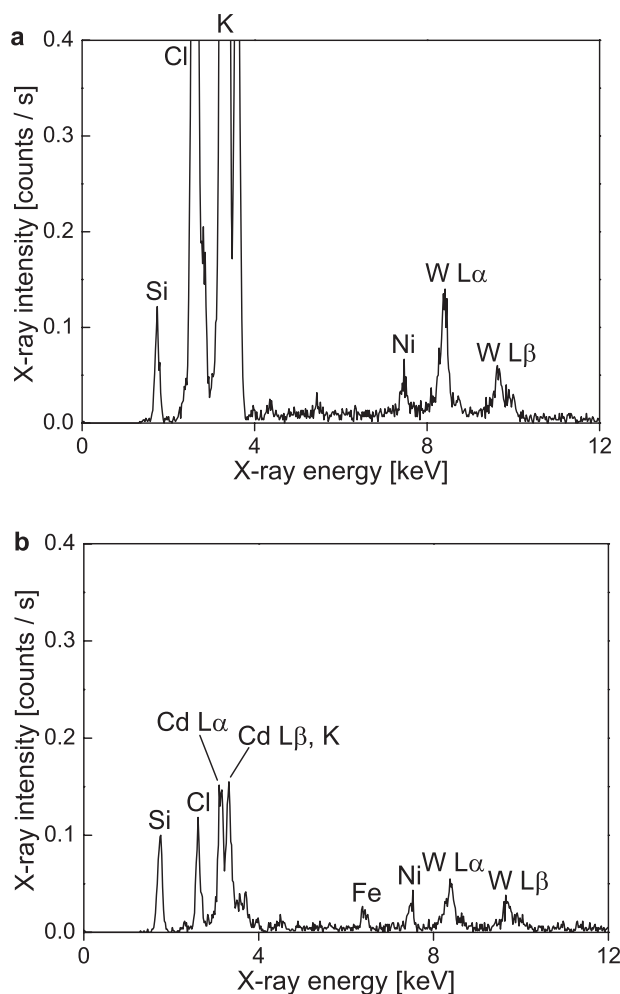


Fig. 3. Total reflection X-ray fluorescence spectra of (a) the dry residue of solution A and (b) that of solution B. These spectra were measured in vacuum for 600 s.

in the intensity of the K $K\alpha$ 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 ≤ 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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