



# Determination of uranium in immersion liquid of demolition waste using total reflection X-ray fluorescence analysis<sup>☆</sup>



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## ABSTRACT

In this study, we proposed a novel methodology based on total reflection X-ray fluorescence (TXRF) analysis for rapid evaluation of uranium radioactivity concentration in water samples, which will be found in the decommissioning field of Fukushima Daiichi Nuclear Power Plant containing various impurities. Sample solutions were prepared by mixing a multi-element standard solution containing uranium and thorium with an immersion liquid of the demolition debris in order to examine the effect of components of the demolition debris. An indium standard solution was added to the samples as an internal standard. Since the Rb  $K_{\alpha}$  peak overlapped with the U  $L_{\alpha}$  and Th  $L_{\alpha}$  peaks, Gaussian fitting was performed to determine the net intensity of the U  $L_{\alpha}$  peak. Moreover, due to the largely different contents of uranium and rubidium, reducing the number of fitting parameter made the Gaussian fitting easier. To determine the widths of the peaks, long-time TXRF measurement of the standard solutions for each element was performed. In the Gaussian fitting, only the peak intensities were considered as fitting parameters because the peak widths and peak energies could be fixed. The relative intensity of the U  $L_{\alpha}$  peak was calculated as the net intensity of the U  $L_{\alpha}$  peak normalized by that of the In  $K_{\alpha}$  peak. The relative intensity was directly proportional to the uranium concentration. The estimated minimum detection limit of uranium with a measurement time of 15 min was significantly lower than the effluent standard value for uranium concentration in drainage water as defined by the Japanese Water Pollution Prevention Law, 20 mBq/cm<sup>3</sup>. All in all, we believe that this method will be useful in determining the uranium concentration in drainage water in the decommissioning field of Fukushima Daiichi Nuclear Power Plant.

## 1. Introduction

A nuclear accident occurred at the Fukushima Daiichi Nuclear Power Plant (FDNPP) of the Tokyo Electric Power Company (TEPCO) after the Tohoku earthquake and tsunami on 11th March 2011. In the reactor pressure vessel, the fuel and structural materials reacted and melted at high temperature. The resulting product, melted fuel, should be removed in the decommissioning process of FDNPP. Moreover, since the melted fuel is cooled by water, radionuclide analysis of the cooling water will be required in near future. Generally, the radionuclide in the contaminated water obtained from the decommissioning field of FDNPP is analyzed by radiation measurement methods such as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -spectrometry. As the uranium in the nuclear fuel, mainly <sup>238</sup>U and <sup>235</sup>U, rarely emits  $\gamma$ -rays, the uranium concentration in the contaminated water is usually determined by  $\alpha$ -spectrometry. However, the low

specific radioactivity of uranium requires long-time sample preparation, such as drying several liters of contaminated water for half a day, and long-time measurement, such as  $\alpha$ -spectrometry conducted for 2 or 3 h. This procedure, therefore, requires a large amount of sample solution. As for other methods, inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) have been employed to analyze uranium in water samples [1–4]. However, these devices are very expensive, and in many cases their chemical pretreatments takes time. Also, in addition to large amounts of sample solutions, samples for remeasurement may be required due to sample losses during measurements. Therefore, it is difficult to measure the uranium content in contaminated water using these methods when the amount of sample is small, or when it is necessary to measure a large number of samples.

Recently, we have focused on total reflection X-ray fluorescence

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(TXRF) analysis [5] for the rapid and simple evaluation of uranium in contaminated water, because it does not require a chemical pretreatment of the sample and yields a low background signal. In traditional X-ray fluorescence (XRF) analysis, a non-negligible background signal derived from scattered incident X-rays appears in the measured spectrum, because the incident angle of the incoming X-ray beam is  $\sim 45^\circ$ , and the secondary X-rays emitted from the excited individual atoms are detected by a detector, i.e., a silicon drift detector (SDD) or a Si-PIN detector at an angle of  $\sim 45^\circ$  on the opposite side. On the other hand, TXRF spectrometry is an advanced technique [6–9] that uses the total reflection phenomenon of an incident X-ray having a low glancing angle (i.e.,  $90^\circ -$  incident angle), as reported by Compton in 1923 [10]. Since the refractive index of X-rays in quartz glass is below 1, the incident X-ray, which has a slightly low glancing angle, is thus totally reflected from the smoothly shaped material. This implies that only a small amount of incident X-rays are scattered, and the background signal in the TXRF spectrum derived from the scattered X-ray is much lower than that in the traditional XRF spectrum when the sample is smoothly shaped. In the case of quartz, the critical angle for total reflection is less than  $0.11^\circ$  for the Mo  $K_\alpha$  line (17.48 keV) [11]. Thus, in contrast to traditional XRF analysis, TXRF analysis usually uses an incident X-ray beam with a glancing angle of  $\sim 0.1^\circ$ , with the SDD or Si-PIN detector being placed just above the sample surface. To provide a smoothly shaped sample for TXRF analysis, a small amount of sample solution is dropped onto the sample holder (e.g., a flat polished quartz plate) and dried. In recent years, TXRF analysis has been widely applied for related purposes such as the detection of uranium in seawater [12], as well as the analysis of drinking water [13,14], wine [15,16], blood [17], and leaching solutions from plastic toys [18], with the minimum detection limit (MDL) ranging from several parts per billion (= ng/g) to sub-parts per million (=  $\mu\text{g/g}$ ).

In our previous study, we performed TXRF measurements of several concentrations of uranyl acetate solutions by using a portable TXRF device, with an MDL for uranium of  $\sim 0.3$  ppm. When the abundance of  $^{238}\text{U}$  and  $^{235}\text{U}$  were 95% and 5%, respectively, an MDL of approximately  $4.7 \text{ mBq/cm}^3$  could be achieved by using each half-life time. This value was significantly lower than the effluent standard value ( $20 \text{ mBq/cm}^3$ ) for uranium in drainage water in Japan [19]. In our previous study, ultra-pure water was used as a solvent; however, the contaminated water that will be found around the fuel reactor of FDNPP will contain other elements derived from structural materials.

Therefore, in the present study, we used an immersion liquid comprising demolition debris as a solvent of uranium-contaminated water, and applied TXRF analysis to the prepared solution. Rubidium, which is generally present in concrete, was included in the contaminated water of FDNPP. Since energies of the Rb  $K_\alpha$  line (mainly 13.41 keV) and U  $L_\alpha$  line (mainly 13.61 keV) are very close [20], each XRF peak in the TXRF spectrum would overlap with each other. Therefore, to determine the uranium concentration in drainage water, the Rb  $K_\alpha$  and U  $L_\alpha$  peaks must be separated. In an effort to separate these two peaks in the measured TXRF spectra, a peak fitting method using Gaussian function was constructed. The net intensity of the U  $L_\alpha$  peak was calculated by the Gaussian fitting, and the relationship between the net intensity and uranium concentration was obtained. Finally, the MDL of uranium in this method was calculated.

## 2. Materials and methods

### 2.1. Sample preparation

To produce a model sample solution of uranium-contaminated immersion liquid comprising demolition debris, which will be found in FDNPP in near future, some of the elemental standard solutions were added to the immersion liquid of the debris collected in the demolition field of an old building in our institute (National Institute of Radiological Sciences). First, an immersion liquid of the collected

**Table 1**

Abundance of immersion liquid, XSTC-1407 standard solution, and ultra-pure water.

Concentration of uranium (ppm)	0	1	2	3	4
Five-times concentrated immersion liquid containing demolition debris <sup>a</sup> (mL)	4	4	4	4	4
XSTC-1407 standard solution (mL)	0	2	4	6	8
Ultra-pure water (mL)	16	14	12	10	8

<sup>a</sup> The rubidium content was set to 1 ppm before the concentration process.

debris was prepared by placing the debris in ultra-pure water and then filtering with a  $0.1 \mu\text{m}$  pore size hydrophilic (polyvinylidene difluoride) membrane. Although the immersion liquid comprising demolition debris in FDNPP might contain rubidium, the produced model immersion liquid did not contain any. Therefore, a small amount of 1000 ppm rubidium standard solution (Wako pure chemical, Osaka, Japan) was added to the model immersion liquid to achieve a rubidium concentration of 1 ppm (i.e., 0.1% rubidium standard solution (v/v)). Thereafter, the model immersion liquid was concentrated five times. A multielement standard, XSTC-1407, which is a solution containing 10 ppm of uranium, thorium, copper, cesium, and cobalt was purchased from Spex CertiPrep Inc., (NJ, USA). The XSTC-1407 standard solutions (16 mL) diluted with ultra-pure water were mixed with 4 mL of the five-times concentrated model immersion liquid. The final concentrations of uranium and thorium in the sample solutions were 0, 1, 2, 3, and 4 ppm, and the concentration of rubidium was 1 ppm (Table 1). Since the produced sample solution contained one-fifth of the five-times concentrated immersion liquid, the same amount of matrix element as that in the immersion liquid was present in the sample solution. Twenty samples were prepared in total, with four sample solutions prepared for each uranium concentration. In the TXRF measurement, a 1000-ppm indium standard solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was mixed as an internal standard. Since the mixing ratio of the sample solution and indium standard solution was 190:10 ( $\mu\text{L}$ ), the concentration of indium in the measurement solution was 50 ppm. Ten microliters of the internal standard containing sample solution were dropped onto a fluorine-coated quartz optical flat and dried for 20 min.

### 2.2. TXRF measurement using portable TXRF device

The uranium concentration in the sample solution was measured using a portable TXRF spectrometer 200TX (Ourstex Co., Ltd., Neyagawa, Osaka, Japan), which employed an air-cooled X-ray tube with W anode and was operated at a tube voltage and tube current of 40 kV and 200  $\mu\text{A}$ , respectively. The incident white X-rays containing both continuum and characteristic X-rays from the tube were collimated by a waveguide placed between the tube and sample. The glancing angle of the incident X-ray was set to  $0.05^\circ$ , and the height and width of the X-ray beam were  $10 \mu\text{m}$  and 10 mm, respectively. The TXRF spectra were measured using an SDD having an effective detection area of  $7 \text{ mm}^2$ . A quartz optical flat (Sigmakoki Co., Ltd., Hidaka, Saitama, Japan) with a diameter, thickness, and flatness of 30 mm, 5 mm, and  $\lambda/20$  ( $\lambda = 632.8 \text{ nm}$ ), respectively, was used as a sample holder and was coated with fluorine resin before dropping the sample solution onto it. The TXRF signals were accumulated for 180 s, and the TXRF measurement was performed once for each of the 20 sample solutions.

## 3. Results and discussion

### 3.1. Widths of the peaks

The XRF peak of an element can be described in first-order approximation by the Gaussian function. The Gaussian curve,  $f_{net}(x)$ , can be defined as a function of the following:

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