IMPROVEMENT OF DETECTION LIMITS OF A PORTABLE TXRF 
BY REDUCING ELECTRICAL NOISE

Susumu Imashuku\textsuperscript{1}, Deh Ping Tee\textsuperscript{1}, Yasukazu Nakaye\textsuperscript{1}, Osami Wada\textsuperscript{2}, and Jun Kawai\textsuperscript{1}

\textsuperscript{1}Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
\textsuperscript{2}Department of Electrical Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

ABSTRACT
The sensitivity of the portable total reflection X-ray fluorescence (TXRF) spectrometer we had previously developed was improved by reducing electrical noise of TXRF spectrometer, and measurement of solutions containing cesium was carried out with the improved TXRF spectrometer. Spectral background of the TXRF spectrometer decreased by keeping the detector away from analog-to-digital convertor, electromagnetic shielding of X-ray tube with ethylene propylene electric conductive rubber tape, and grounding all instrument cases of the TXRF spectrometer. As for cesium measurement, the improved TXRF spectrometer is about 10 times as sensitive as an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instrument.

INTRODUCTION
In recent years, total reflection X-ray fluorescence (TXRF) analysis is widely applied to various fields such as environmental, biological, and food analysis which were previously performed with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instruments or atomic adsorption spectroscopy (AAS) instruments (von Bohlen, 2009). There are two major reasons for this trend. One is that the size of TXRF spectrometers has become smaller and that the manufacturing cost has become lower. The other is that TXRF spectrometers do not need either argon gas required for ICP-AES instruments or acetylene gas required for AAS instruments. As for sensitivity of TXRF spectrometer, detection limits of TXRF spectrometer were achieved to femtogram ($10^{-15}$ g) order using a monochromatic synchrotron radiation (Wobrauschek \textit{et al.}, 1997; Ortega \textit{et al.}, 1998; Pianetta \textit{et al.}, 2000; Sakurai \textit{et al.}, 2002). On the other hand, Kunimura \textit{et al.} (2007; 2009; 2010a; 2010b) developed a portable TXRF spectrometer using continuous X-rays of a low power X-ray tube. The detection limit of 14 pg for cobalt (Co) was achieved with the portable TXRF spectrometer. This value is four orders magnitude higher than TXRF spectrometer using monochromatic synchrotron radiation which is impractical for routine analysis. The portable TXRF spectrometer still has a potential to reduce the detection limits. There is a high possibility that electrical noise in the TXRF spectrometer hinders the improvement of sensitivity. Thus, in the present study, we reduced the electrical noise of the portable TXRF spectrometer. Also, as an example of measurement with the improved TXRF spectrometer, measurements of solutions containing cesium, which is a weak point for ICP-AES measurement, were carried out.

EXPERIMENTAL
The details of the TXRF spectrometer before improvement were reported by Kunimura \textit{et al.} (2010b), and improved points are summarized in this section. Photos of the TXRF spectrometer before and after the improvement are shown in figure 1. Analog-to-digital convertor was integrated into silicon PIN detector (X-123, Amptek Inc.) we used before the improvement. In
in order to decrease the electric noise from the analog-to-digital convertor, the silicon PIN detector was replaced with high purity silicon detector (Xerophy, Horiba) which does not include analog-to-digital convertor inside, and an external analog-to-digital convertor Nakaye et al. (2011) developed was connected to the high purity silicon detector. The electric cable of X-ray tube with a tungsten target (50 kV Magnum, Moxtek) was shielded with ethylene propylene electric conductive rubber tape (Semi-conducting tape, 3M Scotch) in order to reduce electromagnetic emissions. All instrument cases of the TXRF spectrometer were connected to the same ground terminal in order to reduce the electrical noise from each instrument part. As for a sample stage, a round quartz optical flat with the diameter of 10 mm (HMPQP-30C10-20, Shiguma Koki) was replaced by a square quartz optical flat with the size of 10 mm $\times$ 10 mm (OPSQ-30S05-20-2, Shiguma Koki) in order to reduce a scattering of incident X-rays at the edge of the optical flat.

The following solutions were analyzed with the improved TXRF spectrometer: a) commercially available mineral water which is underground water of Mt. Fuji containing vanadium, b) diluted mixed standard solutions containing 50 ppm K, Sc, V, Mn, Co and Cu, and c) diluted cesium solutions. One microlitter of the mineral water was dropped on optical flats with a micropipette. After the droplet was dried, another 1 $\mu$L of the mineral water was dropped on the optical flats. This procedure was repeated until the total amount of the mineral water became 20 $\mu$L. Potassium, scandium, vanadium, manganese, cobalt, and copper standard solution (Wako Pure Chemical Industries, Ltd.) was diluted with ultrapure water whose total organic carbon is less than 4 ppb (Wako Pure Chemical Industries, Ltd.) to become 50 ppm. Then, 2 $\mu$L of the mixed diluted standard solutions was dropped on the square optical flat in the same way as the mineral water. Cesium standard solution (Wako Pure Chemical Industries, Ltd.) was diluted with approximately 100 ppm potassium standard solution to become 5 ppm. Then, 5 $\mu$L of the diluted cesium solutions was dropped on the square optical flat in the same way as the mineral water. The X-ray tube was operated at 25 kV and 50 $\mu$A for the TXRF spectrometer before the improvement and at 25 kV and 80 $\mu$A for the TXRF spectrometer after the improvement. Grazing angle was fixed to 0.05°. The height of sample stage was adjusted to obtain the highest intensities of Ca K$\alpha$ line in the mineral water, Co K$\alpha$ line in the mixed diluted standard solution, and K K$\alpha$ line in the diluted cesium solutions. Measurements were performed in air for 600 seconds except for the measurement of the mineral water with the TXRF spectrometer after the improvement. The measurement duration of the mineral water with the TXRF spectrometer after the improvement was 3600 seconds.
RESULTS AND DISCUSSION

Figure 2 shows EDX spectra of the commercially available mineral water before and after the improvement of the TXRF spectrometer. The EDX spectra were normalized by the intensities of W Lα line. At the same measurement condition, the integrated intensity of W Lα line obtained after the improvement was lower than that before the improvement because the distance from the sample to the detector crystal of the high purity silicon detector was greater than that of the silicon PIN detector. Thus, the current of the X-ray tube was increased from 50 to 80 µA, and the measurement duration was extended to 3600 seconds in order that the intensity of W Lα line after the improvement became as strong as that before the improvement. Fe Kα and Ni Kα lines came from stainless steel in the X-ray detectors. Si Kα, Ar Kα, and W L lines were attributed to optical flats, air, target of the X-ray tube, respectively. Cl Kα, K Kα, Ca Kα, and V Kα lines came from the mineral water. Spectral background below 8 keV decreased by the improvement of the TXRF spectrometer. Spectral background above 10 keV increased after the improvement. This is because the high purity silicon detector is more sensitive to higher energy X-rays than silicon PIN detector due to the difference of thickness of detector layers (Van Grieken et al., 2002) (300 µm for silicon PIN detector and 3050 µm for high purity silicon detector). We also measured the mixed diluted standard solution with the improved TXRF spectrometer and evaluated the sensitivity of each element, and the result is shown in figure 3. As shown in the figure, intensities of Kα lines increased with the increase of the atomic number until Co Kα line, then decreased. Thus, Co is the most sensitive element for the improved TXRF spectrometer.

![Figure 2](image1.png)

Figure 2. EDX spectra of 20 µL of the mineral water before and after the improvement of the TXRF spectrometer. The EDX spectra were normalized to become the same intensities of W Lα line.

![Figure 3](image2.png)

Figure 3. EDX spectrum of 2 µL of diluted standard solution containing 50 ppm K, Sc, V, Mn, Co and Cu.

It is known that the detection limit of cesium for ICP-AES is 40 ppm which is much higher than the detection limit of other elements (Imashuku et al., 2012; *). We measured solutions containing cesium with the improved TXRF spectrometer. We can detect cesium Lα line of solution containing 5 ppm cesium with the improved TXRF spectrometer as shown in figure 4. Thus, As for cesium measurement, the improved TXRF spectrometer was about 10 times as sensitive as ICP-AES instrument.
CONCLUSIONS
Spectral background below 8 keV in the TXRF spectrometer we had previously developed was reduced by keeping the detector away from analog-to-digital convertor, electromagnetic shielding of X-ray tube with ethylene propylene electric conductive rubber tape, and grounding all instrument cases of the TXRF spectrometer. Cobalt was the most sensitive element for the improved TXRF spectrometer. The improved TXRF spectrometer was about 10 times more sensitive than ICP-AES as for cesium measurement.

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REFERENCES


