

Feature Article

Masao Horiba Award

Development of Portable Total Reflection X-ray Fluorescence Spectrometer with Picogram Sensitivity

Shinsuke Kunimura

A high power X-ray source was usually used for ultra trace elemental determination with total reflection X-ray fluorescence (TXRF) analysis, and femtogram (10^{-15} g) detection limits were achieved with synchrotron radiation. On the other hand, we have developed portable TXRF spectrometers with a low power (1-5 W) X-ray tube since 2006, and a 10 pg (10^{-11} g) detection limit was achieved with the present portable spectrometer. This result shows that using a low power X-ray tube in TXRF analysis makes it possible to perform ultra trace elemental determination. In the present paper, a summary of the present portable spectrometer is introduced.

Introduction

X-rays are totally reflected on a specular surface at a glancing angle below a critical glancing angle for total reflection (e.g. 0.1°). In total reflection X-ray fluorescence (TXRF) analysis, incident X-ray beams illuminate a sample on a sample holder (X-ray reflector) at a glancing angle below a critical angle, and incident and reflected X-rays excite fluorescent X-rays from the sample. Various types of samples such as a Si wafer, river water, aerosol particles, and a biological tissue are analyzed with TXRF analysis, and this spectrometric method makes it possible to analyze ultra trace elements in a small amount of a sample (e.g. microliters of a solution). In 1971, Yoneda and Horiuchi^[1] first proposed TXRF analysis and reported that a 1 ng detection limit is obtained with this spectrometric method. Detection limits obtained by TXRF analysis are improved compared with those obtained by X-ray fluorescence analysis without using total reflection because the use of X-ray total reflection leads to a decrease in the spectral background due to scattering of incident X-rays from a sample holder and the sample itself. However, an amount of a sample measured with TXRF analysis was large in 1970s and 1980s and therefore scattering from the sample itself became strong. When using a high power X-ray source such as synchrotron radiation, strong scattering reaching a detector causes detector saturation. In 1984, Iida and Gohshi^[2] reported that monochromatization of incident

X-ray beams significantly reduces the spectral background. Monochromatization led to a decrease in a total count rate of a detector and made it possible to use high power X-ray sources without detector saturation. Detection sensitivity has been improved with the use of high power monochromatic X-rays since Iida and Gohshi reported TXRF analysis with monochromatic excitation in 1984, and detection limits down to femtograms (1 femtogram = 10^{-15} g)^[3-5] were obtained in 1990s and 2000s. In 2002, Sakurai et al.^[6] reported that a 0.3 fg detection limit is achieved with wave-length dispersive TXRF analysis using a monochromatic synchrotron radiation. Nishihagi et al.^[7] developed TXRF spectrometers with a rotating anode X-ray tube and a monochromator, and these spectrometers have widely been used for semiconductor analysis. A detection limit of a few hundred femtograms (10^9 atoms/cm²) was achieved with these spectrometers, and these spectrometers made it possible to perform non-destructive analysis of surfaces of Si wafers. For the purpose of a reduction of the intensity of diffracted X-rays from Si wafers as well as the purpose of a decrease in the spectral background, monochromatic excitation was used in Si wafer analysis. Recently, detection limits down to 10^8 atoms/cm² are required in production process of semiconductor devices, and a pre-concentration technique is used in order to achieve these low detection limits. In 2000s, detection limits ranging from a few to a few tens of picograms (1 picogram = 10^{-12} g) were obtained with

table-top TXRF spectrometers using a 40-50 W X-ray tube with a monochromator^[8, 9] or a low-pass filter^[10]. Using these table-top spectrometers, ppb (10^{-9} g/g) concentrations of elements in food and environmental samples were detected.

On the other hand, we have developed portable TXRF spectrometers^[11, 12] using white X-rays (characteristic and continuum X-rays from an X-ray tube) from a 1-5 W X-ray tube since 2006. The use of white X-rays improved detection limits compared with the use of monochromatic X-rays when a low power X-ray tube was used^[12], and the present portable spectrometer using weak white X-rays achieved a detection limit of 10 pg^[13]. In the present paper, an overview of the present portable spectrometer is shown.

Portable Spectrometer

Figure 1 shows the present portable spectrometer. This spectrometer is lightweight (6 kg) as shown in Figure 1 and consists of an air-cooled X-ray tube (Rh or W target),

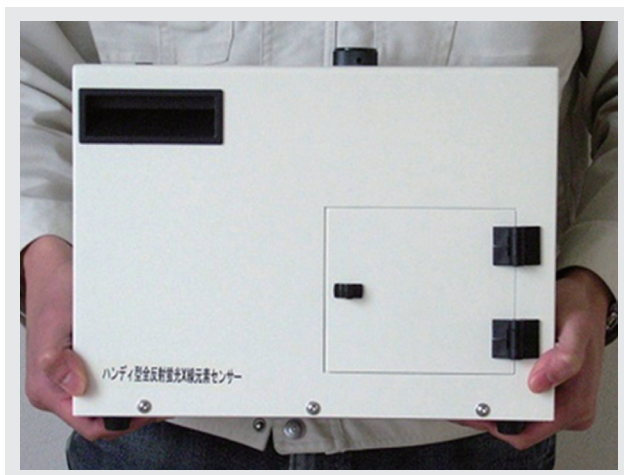


Figure 1 Portable total reflection X-ray fluorescence spectrometer.

a Si-PIN detector, an X-ray waveguide, and a quartz sample holder. White X-rays are used as an excitation source. Measurements are performed in air. In TXRF analysis, a collimator with a length of about 10 cm was usually used in order to obtain parallel incident X-ray beams. On the other hand, a 1 cm length X-ray waveguide for collimation has been developed and has been used in the portable spectrometers. Figure 2 shows a photograph and a schematic view of the waveguide. As shown in Figure 2, this waveguide consisted of two parallel Si wafers. The use of the waveguide resulted in a short distance between an X-ray tube and a center of a sample holder (~3 cm), and this short distance led to downsizing of TXRF spectrometers. Furthermore, this short distance contributed to a decrease in absorption of incident X-rays from air, leading to an increase in excitation power. An angler divergence of incident X-ray beams became smaller with the decrease in a distance between Si wafers in the waveguide and therefore the spectral background due to scattered X-rays was reduced with the decrease in the distance between Si wafers^[14]. In the present portable spectrometer, the waveguide restricts incident X-ray beams to 10 μ m in height and 1 cm in width, and an area on a sample holder where the incident X-rays illuminate is about 1 cm².

White Beam Excitation Improves Detection Limits Compared with Monochromatic Excitation

When a low power X-ray tube is used, the use of white X-rays improves detection limits in TXRF analysis compared with the use of monochromatic X-rays^[12]. Figure 3 shows schematic views of TXRF analyses with or without a monochromator and TXRF spectra obtained by the portable spectrometer with or without a

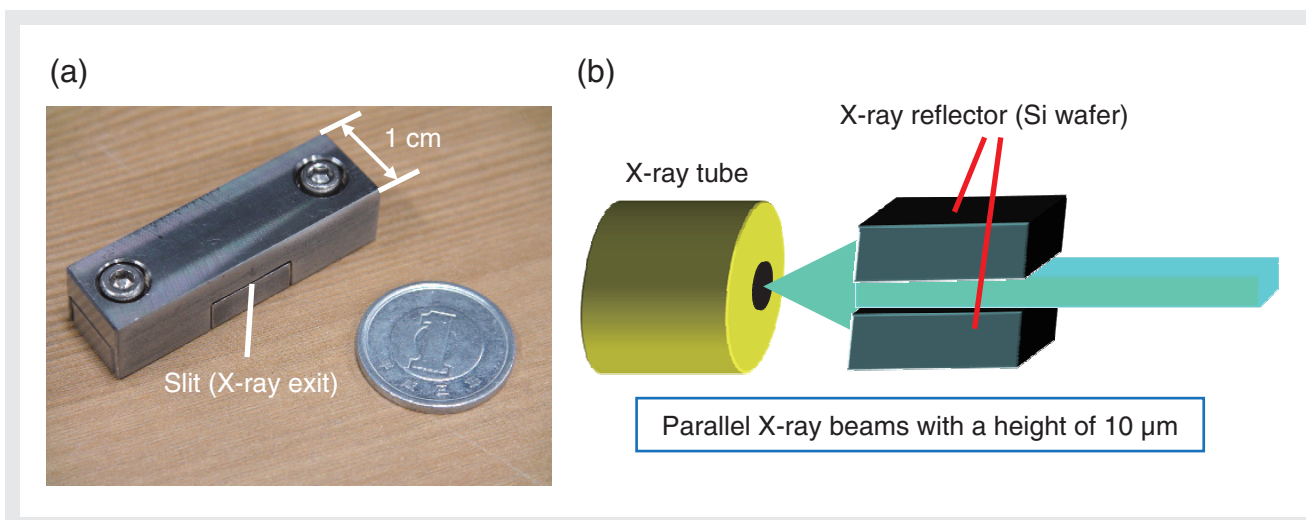


Figure 2 (a) Photograph of an X-ray waveguide and 1 Japanese yen, (b) schematic view of the waveguide.

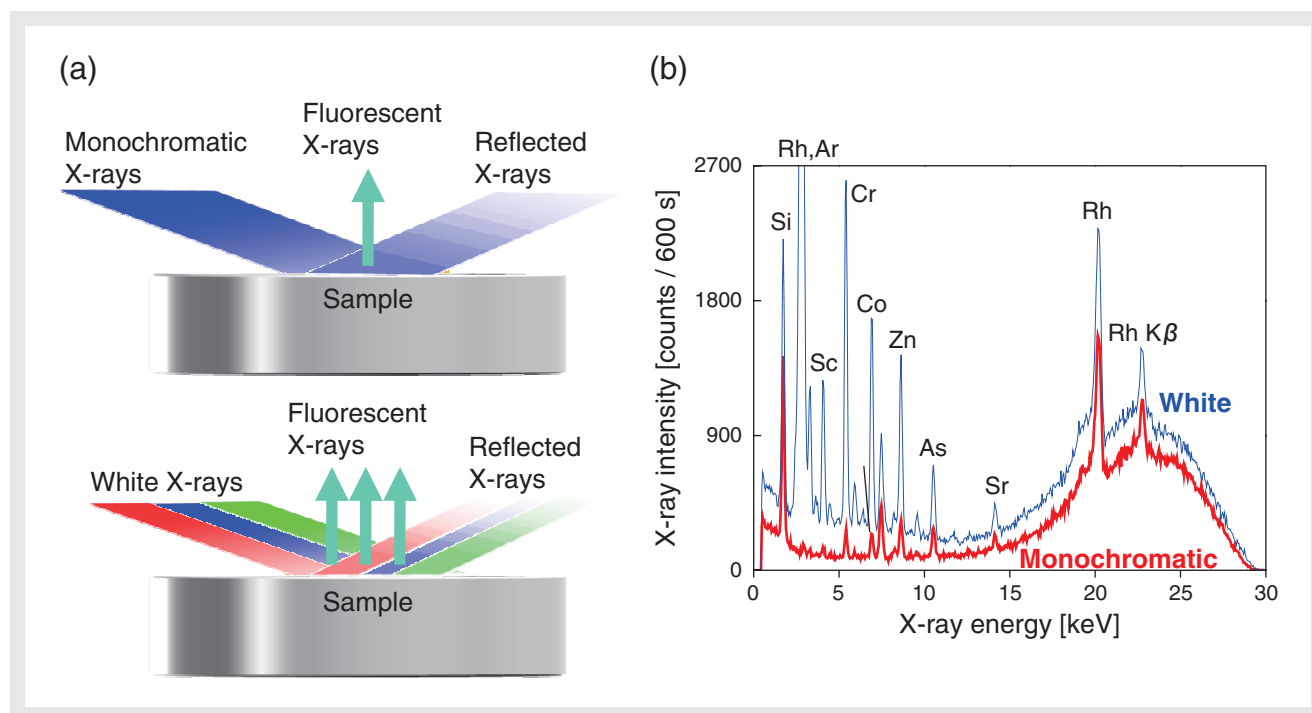


Figure 3 (a) Schematic views of total reflection X-ray fluorescence (TXRF) analyses with monochromatic and white beam excitation, (b) spectra of 5 ng each of Sc, Cr, Co, Zn, As, and Sr obtained by a portable TXRF spectrometer with or without a monochromator. A Rh X-ray tube was operated at 30 kV and 100 μ A. A 500 μ m thick Al plate was placed in front of the X-ray tube in order to obtain monochromatic X-rays. In b, the Si K α line was due to a quartz sample holder, and the Ar K α line was because of air containing 0.9 % Ar. The Rh K-lines were due to the characteristic X-rays from the X-ray tube.

monochromator. As shown in Figure 3, the spectral background became higher when white X-rays were used. However, white beam excitation enhanced fluorescent X-ray intensities compared with monochromatic excitation because the integral intensity of incident X-rays above absorption edge energies of each element was higher when using white X-rays, and the enhancement of fluorescent X-ray intensities led to an improvement in detection limits obtained by the portable spectrometer.

Measurement of a Small Amount of a Sample Improves Detection Limits

When white X-rays are used as an excitation source, the intensity of scattered X-rays can be reduced when a small amount of a sample is measured^[15]. Figure 4 shows schematic views of TXRF analyses of a large amount and a small amount of a sample and TXRF spectra of 35 and 65 μ L portions of a certified reference material of river water (JSAC0302-3). As shown in Figure 4, the spectral background was reduced with the decrease in a sample amount, and the background reduction led to an improvement in detection limits obtained by the portable spectrometer.

Application

The portable spectrometer was applied to analyses of urine^[13], a leaching solution of soils^[16], river water^[17], a leaching solution of a plastic toy^[17], wines^[18], and commercial bottled drinking water^[19]. Figure 5 shows a TXRF spectrum of a leaching solution of a mug measured with the portable spectrometer. Screening for toxic elements such as Pb in a leaching solution of a cup for daily is useful for safety assessment. This mug was painted with blue, red, green, and white as shown in Figure 5. This mug was measured with a portable X-ray fluorescence spectromicroscope in a previous paper^[20], and Pb was detected in green, blue, and red areas. As shown in Figure 5, Pb, S, K, Ca, Ba, Co, and Zn were detected from the leaching solution of the mug.

Conclusion

Lightweight portable TXRF spectrometers have been developed since 2006. Although a 5 W X-ray tube was used in the present portable spectrometer, detection limits down to 10 pg were achieved with the following methods:

1. Using white incident X-rays (characteristic and

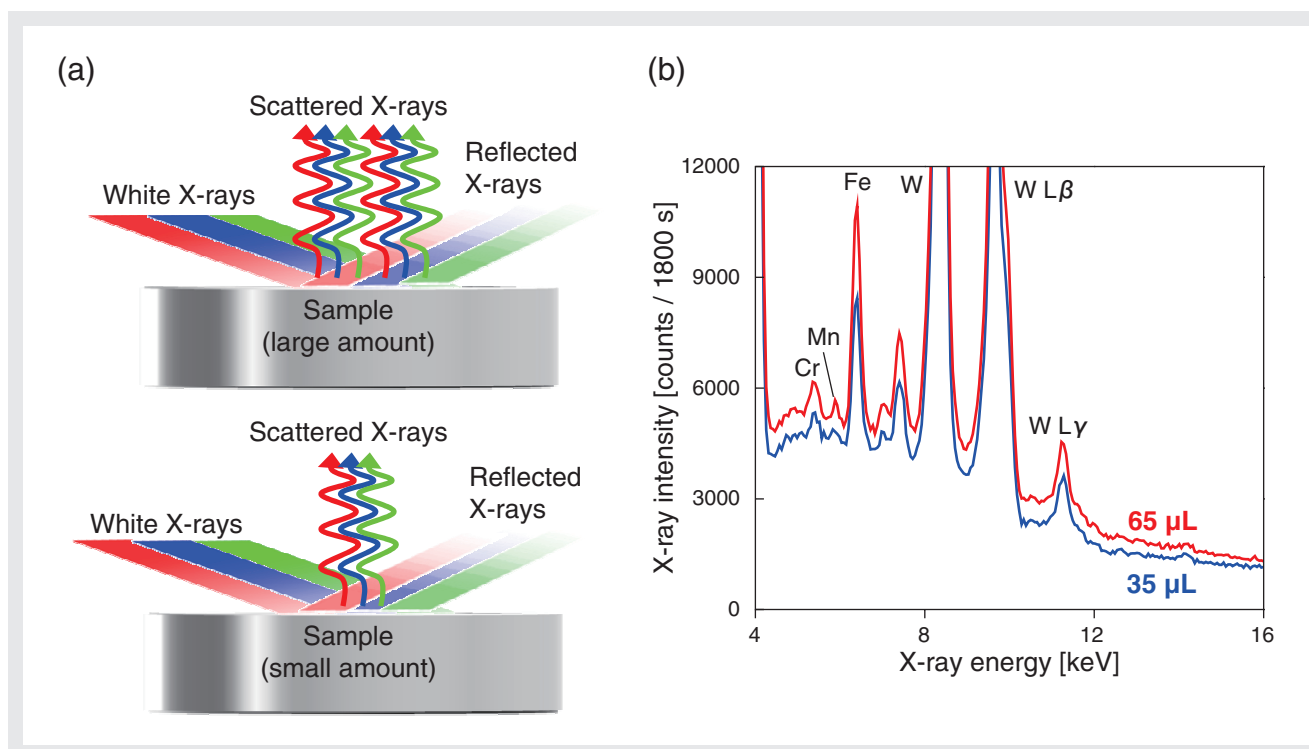


Figure 4 (a) Schematic views of total reflection X-ray fluorescence (TXRF) analyses of a large amount and a small amount of a sample, (b) spectra of 35 and 65 μL portions of a certified reference material of river water (JSAC0302-3) obtained by a portable TXRF spectrometer. The certified concentrations of Cr, Mn, and Fe were 10, 5, and 58 ppb, respectively. A W X-ray tube was operated at 25 kV and 200 μA . The W L-lines in b were because of the characteristic X-rays from the X-ray tube.

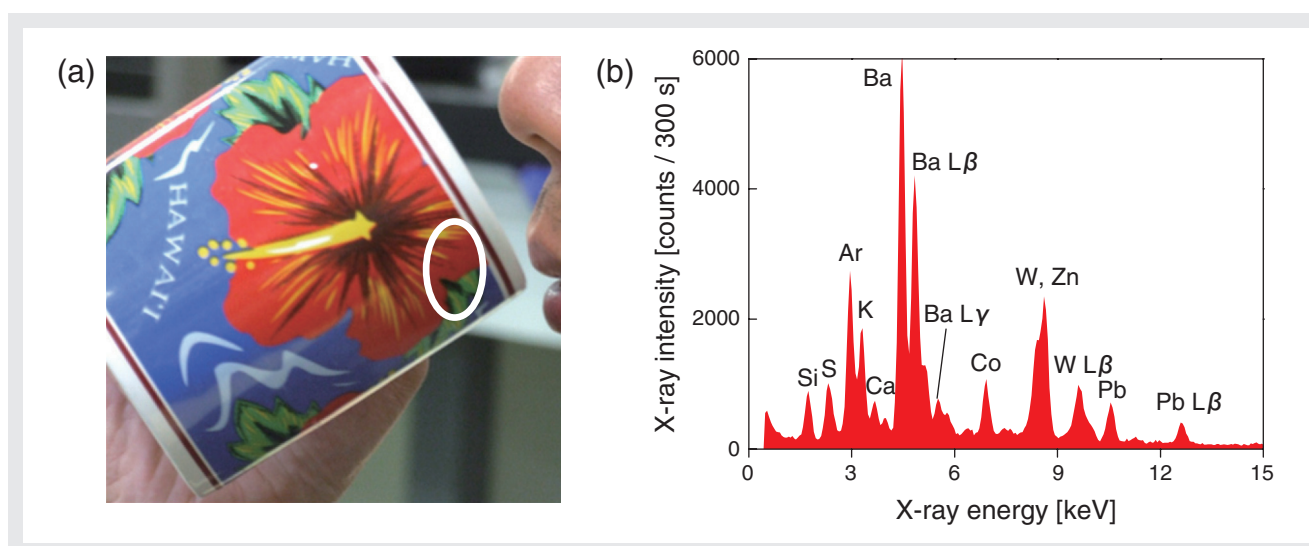


Figure 5 Total reflection X-ray fluorescence spectrum of a leaching solution of a mug measured with a portable spectrometer. A W X-ray tube was operated at 25 kV and 200 μA . In sample preparation, a 50 μL portion of 1 mol/L HNO_3 was pipetted onto the mug, and contents of the mug was eluted with HNO_3 for 5 min. An area where HNO_3 was pipetted is shown in a white circle in a. A 10 μL portion of the leaching solution of the mug was pipetted and dried onto a quartz sample holder.

- continuum X-rays from an X-ray tube)
2. Measuring a small amount of a sample
3. The use of a small X-ray waveguide

This kind of highly sensitive and lightweight spectrometer can be applied to on-site ultra trace elemental analysis of a sample of which sampling chance is limited (e.g. space dust). We have reported that ultra trace elemental determination is performed even when a low power X-ray

tube is used. This result indicates that detection limits obtained by a high power X-ray source such as synchrotron radiation can be further improved with optimization of a measurement condition (e.g. instrument geometry). The further improvement of detection limits in TXRF analysis will make it possible to perform non-destructive ultra trace elemental analysis of semiconductors.

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Shinsuke Kunimura

Materials Fabrication Laboratory,
RIKEN (The Institute of Physical and Chemical
Research)
Special Postdoctoral researcher, Ph. D.