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Low Power Total Reflection X-Ray Fluorescence Spectrometry

Ying Liu
Ph.D. Thesis

Low Power Total Reflection X-Ray Fluorescence Spectrometry

by

Ying Liu

Department of Materials Science and Engineering
Graduate School of Engineering
Kyoto University
For my dearest mom, who is always my motivation.

And my beloved late father, who taught me the meaning of life.
Preface

Low power total reflection X-ray fluorescence (TXRF) technique is leading to a growing trend towards TXRF instrument miniaturization. Dr. Shinsuke Kunimura and Prof. Jun Kawai at Kyoto University have developed a low power portable TXRF spectrometer (less than 5 kg) with a 1~5 W X-ray tube. Although the weak non-monochromatic radiation was used in the portable spectrometer, a detection limit of 10 picogram was achieved, which can be compared to a high power benchtop TXRF spectrometer and even the synchrotron radiation induced TXRF analysis.

The aim of this thesis is to present the capability of low power portable TXRF technique in the determination of multi-element solutions and the new applications of this technique. In addition, a newly developed low power TXRF spectrometer using a diffractometer guide rail will be reported. The feasibility of modifying an X-ray diffractometer to a low power TXRF spectrometer will be proved.

This thesis is based on four published papers (Chapter 2~5), one review paper (Chapter 1) submitted to the journal “Advances in X-Ray Chemical Analysis, Japan”, and one research paper (Chapter 6) that submitted to the journal “Powder Diffraction” in June, 2014. The contents of these papers are described in detail in this thesis. Due to the independence of these works, reading the chapters in order is not necessary.

This thesis would not have been finished without the help and support I have received from many people. First and foremost, I would like to thank my supervisor, Prof. Jun Kawai of Kyoto University, for his guidance, advice and continuous support throughout my three years’ research. Secondly, I would like to give special thanks to Prof. Akio Itoh at the Department of Nuclear Engineering, Kyoto University and Prof.
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Deep gratitude goes to my great friends who have gifted me with their encouragement and support. Special thanks to my good friend Dr. Vedran Jovic for his kind help as well as useful and professional suggestions during my PhD study.

And most of all, I wish to thank my beloved family for their unfailing love, support, and my loved ones who have given my life shape and meaning.

June 9th, 2014

Ying Liu
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IV
Chapter 1

Introduction*

Total reflection X-ray fluorescence (TXRF) technique is a spectrometric method for micro and trace multi-elemental analysis. This technique has the ability to simultaneously detect almost all the elements (B-U) in the analyte within a few minutes. Detection limits of picogram range (relative concentration of ppb) can be easily achieved with laboratory TXRF spectrometers;\textsuperscript{1-4} while using synchrotron radiation induced TXRF analysis (SR-TXRF) allows the absolute detection limits further reduce to the femtogram range for several transition metals in semiconductor industry, such as Ni, Co and Fe.\textsuperscript{5-8}

1.1 Basic principles of TXRF technique

TXRF technique is a variation of energy-dispersive X-ray fluorescence (EDXRF) technique with a significant difference in the excitation and detection geometry. Unlike EDXRF (Fig. 1), the primary radiation excites the sample at an angle of about 40°, TXRF analysis uses the primary beam shaped like a strip of paper to strike the sample on a special sample carrier (\textit{e.g.} a flat polished quartz plate) at grazing incidence (usually less than 0.1°). Because of the grazing incidence, the primary beam is totally reflected. This means a totally reflected beam having nearly the same intensity as

* This introduction is based on a review paper submitted to the journal “\textit{Advances in X-Ray Chemical Analysis, Japan}” in June, 2014.
Fig. 1 Schematic view of the instrumental arrangement for (a) conventional EDXRF and (b) TXRF.
the primary beam is generated at the glancing angle smaller than the so-called critical angle. The critical angle $\alpha_{\text{crit}}$ of total reflection can be given by:

$$
\alpha_{\text{crit}}(\text{rad}) \approx \sqrt{2\delta}
$$

(1)

where $\delta$ is the real component of the complex index of X-ray refraction $n$ given by

$$
n = 1 - \delta + i\beta
$$

(2)

here $i^2 = -1$, $\beta$ is a measure of the absorption that can be expressed by

$$
\beta = \frac{\mu\lambda}{4\pi}
$$

(3)

and $\mu$ is the linear mass absorption coefficient, $\lambda$ is the wavelength of the primary radiation. $\delta$, called the decrement, is a measure of the deviation of the real part of the refractive index from unity. For X-rays, its value is of the order of $10^{-6}$. If the primary radiation’s energy is higher than the absorption edges of the elements in the substrate, $\delta$ is given by the following equation:

$$
\delta = \frac{N_A r_e \rho Z}{2\pi} \frac{Z^2}{\lambda^2}
$$

(4)

here $N_A$ is Avogadro’s number $= 6.022 \times 10^{23}$ atoms/mol, $r_e$ is the classical electron radius $= 2.818 \times 10^{-13}$ cm, $\rho$ is the density of the substrate (in g/cm$^3$), $Z$ is the atomic number, $A$ is the atomic mass (in g/mol), $\lambda$ is the wavelength of the primary radiation. Insertion of equation (4) in equation (1) gives the approximation

$$
\alpha_{\text{crit}}(\text{degree}) \approx 1.65 \frac{Z}{E} \sqrt{\frac{\rho}{A}}
$$

(5)

where $E$ is the energy of the primary radiation (keV), $\rho$ is the density of the substrate (g/cm$^3$). Thus, the critical angle of total reflection is dependent on the incident beam energy and the substrate material. For example, if a quartz glass substrate is used as a
sample carrier during analysis, the critical angles for X-rays of 17.44 keV and 35 keV energies are 0.10° and 0.050°, respectively. In the case of glassy carbon substrate, the critical angles for the same primary beams are 0.080° and 0.040°, respectively.\textsuperscript{1,2}

Although the incoming beam is totally reflected at the flat and smooth surface, there is still a small amount of the primary radiation that penetrates the substrate. Penetration depth, which is defined as the depth at which the primary beam intensity reduces to 1/e (37%) of its initial value, is down to a few nanometers below the critical angle. This is compared to the depth values on the order of micrometers without total reflection excitation. This indicates that in TXRF analysis, only a narrow zone in the substrate is penetrated by the incident X-rays and is interacted with the X-rays to contribute to the scattering background of the spectra. Therefore, a drastic reduction of spectral scattered background is observed in the XRF experiment with total reflection geometry. Except for the scattering background reduction, a second important advantage of TXRF is a thin sample on the substrate is excited twice, the first time by the incident and the second time by the totally reflected beam. The double excitation of the thin sample and the extremely low background resulted by the low penetration of the primary radiation into the substrate lead to a considerably improved signal-to-background ratio compared with conventional EDXRF, and allow the determination of elements in the picogram and even femtogram range.\textsuperscript{1-3}

Except for the powerful detection capability, a further advantage of TXRF is the easy way of quantification. The special excitation geometry in TXRF analysis allows only very small quantities of sample volume to be investigated. Therefore, samples deposited on the optical flat as dry residues can be taken as thin films, which means the matrix effects during analysis is negligible and the measured fluorescence intensities are
linear with concentrations. By adding an internal standard with known concentration in the sample (the internal standard should not include the elements of interest), a simple multi-element quantification can be carried out using the equation:

\[
C_X = \frac{S_{\text{std}}}{S_X} \times \frac{I_X}{I_{\text{std}}} \times C_{\text{std}}
\]

(6)

where \(C\) indicates the concentration, \(I\) is the net intensity of the fluorescence radiation, \(S\) is the relative sensitivity, \(X\) represents the element to be determined, \(\text{std}\) represents the added element served as an internal standard. Relative sensitivity can be determined experimentally after recording simultaneously X-ray fluorescence signals of standard samples or calculated theoretically if all parameters are known.\(^{1-4}\)

TXRF technique, as a powerful non-destructive analytical method, has been widely used in various research areas. Its applications can be generally divided into two areas: chemical analysis and surface analysis. With regard to the application of chemical analysis, four typical fields of application can be classified: environmental, medical, forensic and industrial. Environmental samples, such as water, soil, airborne particulate, can be analyzed by TXRF directly or after some pre-treatment, like separation of suspended matters and digestion in acidic. Biological tissue can be cut in thin sections (around 15 \(\mu\)m thick) by a microtome and be analyzed directly. TXRF is highly suitable for forensic science because of its non-destructive and microanalytical capabilities. Typical use in this field is the trace element determination of pigments and textile fibers. Some applications of TXRF in industrial field are the element impurity investigation of highly concentrated acids like HNO\(_3\), HCl, or HF and bases like NH\(_3\) solution.\(^{1,9}\) The application of most importance in the use of TXRF for surface analysis is the contamination investigation of Si wafer surface. Two ISO standards were
published for surface impurity examination of Si wafer using TXRF.\textsuperscript{10} A special set-up, allowing TXRF measurement without any surface contact and with the possibility of an angle scan, is required. Commercial TXRF instruments for this purpose have been available since about 1989.\textsuperscript{9} In 1999, more than 300 TXRF instruments were in use for Si wafer analysis all over the world.\textsuperscript{11} Recently, Klockenkämper has made a survey for worldwide distribution of TXRF devices and the applications of TXRF in different fields. According to the feedback from 38 users and 3 manufacturers, it is indicated that 283 working TXRF instruments (not include the big instruments in semiconductor industry) are mainly distributed in Germany (48), USA (26), Japan (18), Italy (13), Russia (12), Brazil (11), Austria (10), and Taiwan (10). The survey also represents about 200 applications of TXRF in 13 different fields, and the main application fields are environment, industry, chemical and biology.\textsuperscript{12}

1.2 Historical development of TXRF analysis and its instrumentation

In 1919, Stenström in Lund University theoretically predicted X-ray refraction and reflection phenomena in his doctoral thesis.\textsuperscript{13} Compton gave the first experimental evidence to prove the existence of total reflection of X-rays in 1923.\textsuperscript{14} Nearly fifty years later in 1971, Yoneda and Horichi in Kyushu University, Japan found the possibility of using X-ray total reflection phenomenon on an optical flat for trace elemental analysis in a small amount of sample. The absolute detection limits of four transition metals Cr, Fe, Ni and Zn were estimated to be 1.9 ng, 1.7 ng, 1.5 ng and 5.1 ng, respectively.\textsuperscript{15} This promising idea did not get any attention until the year 1974. In this year, Aiginger and Wobrauschek in Austria performed an experiment in which 5 \( \mu \)L aqueous solutions (5 ng to 100 ng) of Cr salts deposited on a fused silica reflector were measured in X-ray
total reflection geometry. The results well agree with the attainable sensitivity as evaluated by Yoneda and Horichi.\textsuperscript{16} Experimental set-up, more detailed results dealing with theoretical estimation, quantification and linearity of TXRF technique were published in 1975.\textsuperscript{17} In 1977, Knoth, Schwenke, Marten and Glauer published the analytical results of human blood serum utilizing a preliminary experimental setup with totally reflecting sample support. The detectable limit was about 1.5 mmol/L in 1000 s and the precision in the 20 mmol/L range of the metals was 3-5%.\textsuperscript{18} Realizing the suitability of X-ray total reflection phenomena for trace elemental analysis, the first spectrometer prototype for TXRF analysis was developed by Knoth and Schwenke at the same year, and the results were published in 1978.\textsuperscript{19} This prototype apparatus consisted of a fine structure tube with a molybdenum target (30 kV, 60 mA), a special module for TXRF analysis and a Si(Li)-detector with an efficient detection area of 80 mm\textsuperscript{2}. The detection limits achieved by this apparatus were near or below 1 ppb (0.05 ng) for 13 elements when specimens with low matrix content were measured. At the same time, a second reflector used to reflect the incident radiation prior to sample excitation was considering to suppress the high energy fraction of the Bremsstrahlung. Technical realization of this idea was in 1979 when Knoth and Schwenke developed an X-ray fluorescence spectrometer consisting of a molybdenum anode X-ray tube (60 kV, 13 mA), an aligned arrangement of two reflectors, a sample support, three diaphragms, and a Si (Li)-detector.\textsuperscript{20} In this spectrometer, the primary X-rays were reflected by quartz blocks twice before reaching the sample. The first reflector acting as a low-pass filter cuts off the higher energy part of primary radiation. The second reflector directs the X-ray beam towards the sample support, and then the incident beam was totally reflected on the quartz sample support. A further improvement of the sensitivity was
achieved by this spectrometer; the detection limits below $10^{-11}$ g or 0.1 ppb were achieved for about 20 elements with atomic numbers between 26 to 38 (Fe-Sr) and 74 to 83 (W-Bi). These values were achieved by the basic setting of the instrument without optimization with regard to experimental parameters, such as excitation power and incident angle. Based on the compact module developed by Knoth and Schwenke, the first commercially available TXRF spectrometer “Extra II” was supplied by Rich. Seifert & Co., Ahrensburg, Germany in 1980. This spectrometer equipped with two X-ray fine focus lines with molybdenum and tungsten anode. Detection limits for most detectable elements were in the low picogram range. With the molybdenum source operating at 50 kV and 5~30 mA or the tungsten source operating at 25 kV and 5~25 mA, a count rate of ~ 5000 cps in the measured spectra was acquired. A simple attachment module (WOBI-module) for TXRF analysis using existing high power X-ray tube and X-ray generator developed by Wobrauschek was available from Atominstitut, Vienna since 1986. This compact unit carrying all necessary components for high power TXRF analysis can be attached to standard X-ray diffraction tube housings. These modules have been distributed to about 50 countries through the cooperated program of the International Atomic Energy Agency (IAEA) by the year 2008. Except for Seifert Extra II and WOBI-module, other commercial high power TXRF instruments have also been available since 1980s, such as TX2000 of Italstructures (Italy), Model 3726 and TXRF 300 of Rigaku (Japan), TREX 600 of Technos (Japan), and TXRF 8010 of Atomika (Germany). These instruments such as the Model 3726, TXRF 300, TREX 600 and TXRF 8010 are especially suited for Si wafer analysis.
In 1984, Iida and Gohshi found that the spectral background of TXRF analysis can be efficiently reduced by using monochromatic X-ray beam from a high power X-ray tube. At the same time they considered the monochromatic synchrotron radiation source (available in Japan around 1982) might be much more suitable for this purpose. In the following year, the authors published a paper “Energy dispersive X-ray fluorescence analysis using synchrotron radiation”. They reported an experimental arrangement at Photon Factory in Tsukuba, Japan. Using the monochromatic synchrotron radiation beam as a radiation source, the detection limit down to 0.5 ppb or 1 picogram was obtained in total reflection excitation geometry. Since then, it has been believed that it is essential to use monochromatic incident radiation in order to improve detection limits. The lowest detection limits of TXRF analysis were obtained by Sakurai et al. using a synchrotron radiation induced wavelength-dispersive TXRF at SPring-8, Japan. The absolute and relative detection limit for Ni are $3.1 \times 10^{-16}$ g and 3.1 ppt, respectively. Although the detection limits were reduced to femtogram scale by SR-TXRF, these values were only achieved for several elements, such as Ni, Co and Fe in Si wafer analysis. In addition, limited access to synchrotron radiation facility makes it impractical for routine analysis.

1.3 Low power portable TXRF technique

Low power TXRF technique means air cooled X-ray tubes in a tube power range lower than 50 W. Emergence of this technique leads to a general trend in TXRF instrumentation from large size to small-scale, from floor-standing type to benchtop and portable type. Compared to high power (kW) TXRF spectrometers that widely used in Si wafer analysis, the compact low power desktop TXRF has been commonly used
in the field of environmental analysis.\textsuperscript{33-37} The low power TXRF can be classified into monochromatic and non-monochromatic type. A typical monochromatic benchtop TXRF spectrometer is around 40 kg, and mainly consisted of a 40~50 W X-ray tube, a multilayer monochromator and a liquid nitrogen-free silicon drift detector.\textsuperscript{33, 37} Elements in the picogram range can be detected using this type of spectrometer. But non-monochromatic type is possible only by a 1~5 W X-ray tube, and the sensitivity is comparable. Kunimura and Kawai at Kyoto University developed the non-monochromatic and low-power TXRF spectrometer (commercialized by OURSTEX Corp., Neyagawa, Japan and named OURSTEX 200TX) (Figs. 2 and 3), and pointed out that when a low power X-ray tube of a few watts was used, the non-monochromatic TXRF is more sensitive than monochromatic type.\textsuperscript{38, 39}

The first non-monochromatic and low-power TXRF spectrometer mainly incorporated a 1.5 W X-ray tube with a tungsten target (Hamamatsu Photonics, Hamamatsu, Japan), a waveguide slit restricting the incident beam to a parallel beam of 10 mm in width and 50 μm in height, and a Si-PIN photodiode detector X-123 (Amptek, Bedford, USA). This detector was cooled by a Peltier device and contained a preamplifier and a digital signal processor. The waveguide slit used in this spectrometer was proposed by Egorov and Egorov.\textsuperscript{40} It was formed by placing two 50 μm thick tungsten foils (at a distance of 10 mm) between two Si wafers. All the components of the spectrometer were included in a compact box made of Pb-containing acrylic slabs. The size of the box was 23 cm (height) × 30 cm (width) × 9 cm (length). Weight of the spectrometer was less than 5 kg. Although the weak white X-rays were used in the portable spectrometer, a detection limit of 1 ng for Cr was achieved.\textsuperscript{38} A further work was undertaken by Kunimura \textit{et al.} in the optimization of the glancing angle for this
Fig. 2 Low power portable TXRF spectrometer.

Fig. 3 Set-up of the low lower portable TXRF spectrometer.
spectrometer. The optimum glancing angle was reported to be 0.13 degrees (critical angle for total reflection is 0.20 degrees when accelerated voltage was 9.5 kV), achieving detection limits of sub- to 10 ng for elements Ca, Cr, Fe, Mn, Ni, Sc, Ti and V. The maximum energy of the incident X-rays in this spectrometer was 9.5 keV, which means toxic elements of interest in environmental filed, such as arsenic, cadmium, mercury and lead, could not be detected. In addition, the excitation efficiency of the 1.5 W X-ray tube for the transition metal elements of Ni and Cu was low, and Zn could not be detected. In order to overcome the shortcoming and to detect a wide range of elements, a 4 W X-ray tube with a rhodium target and a 5 W X-ray tube with a tungsten target (Moxtek, Orem, USA) were applied. A 10 picogram detection limit was achieved for Co by the portable TXRF with a 5 W “Magnum 50 kV” X-ray tube (tungsten target) under optimum excitation conditions. This value is only four orders of magnitude higher than that of a synchrotron radiation induced TXRF. However, such a low value was only achieved for one element, Co, in an ideal sample in which the spectral peaks of the analyte were free from interference. The portable TXRF (1.5 or 5 W) has been applied to analyze urine, rain, leaching solutions of toy, metal materials and soil, and wine. However, these applications only deal with the simple samples in which less than seven non-interfering elements were included. In addition, capability evaluation for the portable TXRF in the toxic element determination of a real environmental sample or daily food has not been carried out. As mentioned previously, the low power TXRF spectrometer is mainly used in environmental analysis where samples are characterized by multiple and/or interfering elements, some very low concentrations, and various matrices. This underscores the need for multi-element determination with high sensitivity or lower detection limits. Therefore, it is necessary
and of significance to evaluate the capability of the portable TXRF in multi-element analysis with regard to sensitivity, measurement time and detectable elements, and to apply it to real sample analysis in food quality and environmental investigation. Based on the above considerations of the issues, Chapter 2~5 of this thesis, using a 4 W non-monochromatic portable TXRF spectrometer, will fill these gaps.

The non-monochromatic and low-power excitation technique in the portable TXRF spectrometer is based on a commercial low power X-ray tube. This indicates the realization of this analytical technique relies on an appropriate X-ray source – a specially designed X-ray tube for low power load (< 10 watts). However, this limitation might be overcome if a high power X-ray source existing in a widely used laboratory instrument can switch its use to low power TXRF analysis. The WOBI-module developed by Wobrauschek uses an existing XRD tube for high power TXRF analysis.\textsuperscript{25,26} From the good hint brought up by this module, an XRD was modified to a low power TXRF by reducing the X-ray tube power (3 kW) down to 10 watts by a power supply. This study will be presented in Chapter 6, and will be published in a scientific journal.

Structure of this thesis is as follows:

Chapter 2 assessed the capability of low power portable TXRF spectrometer in multi-element determination. The experimental condition (glancing angle, operational voltage and current of X-ray tube, sample amount) dependencies of X-ray fluorescence signal and background with regard to the sample and sample holder were studied and discussed. The suitability of the portable TXRF in multi-element analysis was demonstrated.
Chapter 3 studied the influence of sample holder (substrate) direction on TXRF analysis by low power portable TXRF spectrometer. The spectra obtained in different substrate direction were tested by two-way analysis of variance. The significant influence of the substrate direction on TXRF analysis was demonstrated. Finally, optimum experimental conditions with regard to number of the measurement and the measuring time were given based on the comparison between the experimental and theoretical intensity.

Chapter 4 and Chapter 5 presented the applications of portable TXRF spectrometer in the analysis of potential toxic materials in laboratory environment and traditional Japanese food Hijiki seaweed, respectively.

Chapter 6 described a newly constructed low-power and non-monochromatic TXRF spectrometer using a diffractometer guide rail and the primary measurement results. The compact spectrometer used a 3 kW XRD tube that was reduced its operation power down to 10 watts by a power supply during analysis. The feasibility of modifying an X-ray diffractometer to a low power TXRF spectrometer was proved.

The closing chapter, Chapter 7, is a summary of the studies in this thesis and suggestions for future work. In addition, supplementary discussion of several issues that were not addressed in the main body of the thesis was made.
References


Chapter 2

Multi-Element Analysis by Portable Total Reflection X-Ray Fluorescence Spectrometer*

Abstract

Multi-element solutions containing the 11 elements S, K, Sc, V, Mn, Co, Cu, Ga, As, Br and Y were analyzed by a portable total reflection X-ray fluorescence (TXRF) spectrometer. The excitation parameters (glancing angle, operational voltage and current) and sample amount were optimized for the portable TXRF in order to realize the smallest possible detection limits for all elements. The excitation parameter dependencies of the fluorescence signal and background for the detected elements are explained in detail. Background contributed by the sample carrier is also discussed. Consequently, nine elements were detectable at sub-nanogram levels in a single measurement of 10 min under the optimal experimental conditions. The portable TXRF spectrometer was found to be suitable for simultaneous multi-element analysis with low detection limits. The features of high sensitivity, small sample amount required, and fast detection of a wide range of elements make the portable TXRF a valuable tool in various applications, such as field studies in environmental and geological investigations.

Key words: Portable total reflection X-ray fluorescence spectrometer, multi-element solution, optimize, detection limit

2.1 Introduction

Total reflection X-ray fluorescence (TXRF) analysis is a well-known trace elemental analysis method with high sensitivity and was first widely applied to Si wafer analysis in the semiconductor industry. However, the ultimate detection limits of femtogram order were only achieved for several elements by using monochromatic synchrotron radiation induced TXRF (SR-TXRF) in Si wafer analysis, such as Ni, Co and Fe. Since such experiments must be carried out at large-scale synchrotron radiation facility, it is very difficult to use SR-TXRF in practical industrial semiconductor applications. In TXRF analysis, monochromatic excitation is believed to effectively improve analytical sensitivity. But Kunimura et al. developed portable TXRF spectrometers using X-ray tubes of a few watts, and found that when a low power X-ray tube is used, non-monochromatic excitation improves the detection sensitivity compared with monochromatic excitation. A 10 picogram detection limit was achieved using the portable spectrometer in an interference-free sample comprising the four elements Sc, Cr, Co and As. However, this low value was only achieved for one element, Co, in the ideal sample for a half-hour (1800 s) measurement in which the spectral peaks of the analyte were free from interference. Similarly, the analytical features of portable spectrometers in different applications only applied to ideal samples containing three to five non-interfering elements. Although a 17 picogram detection limit of Co was achieved in a mixed standard solution containing 14 nanograms of S and 1 nanogram each of Sc, V, Cr, Mn, Fe, Co, As, Rb, Sr, Y and Zr, and all elements in the standard solution were detected in a single TXRF measurement, a long measurement time of 1800 s was also needed. In addition, the capability of the portable TXRF spectrometer in multi-element analysis was not
evaluated and discussed. The TXRF technique is currently primarily used for chemical micro- and trace analyses, especially in the fields of environment, geology and biology studies\textsuperscript{18–20} where samples are characterized by multiple elements and interferences, some very low concentrations, and various matrices. These applications reflect an increasing demand for rapid sample scanning at relatively low cost, while also underscoring the need for multi-element determination with high sensitivity or lower detection limits. Although the portable TXRF spectrometer has proven to be an economical tool for trace elemental determination, its versatility in practical applications of providing rapid multi-elemental profiles of a wide range of elements with high sensitivity has not been demonstrated yet. The present study was carried out to assess the capability of a portable TXRF spectrometer in multi-element determination. Multi-element solutions containing the 11 elements S, K, Sc, V, Mn, Co, Cu, Ga, As, Br and Y were prepared and studied in the present paper. The 11 elements chosen are very common in environmental, geological and biological studies in which Ga and Y are widely used as internal standards for TXRF analysis. The multi-element solutions cover not only almost all element categories in the metal-nonmetal range, but also include interfering elements since the energy differences between K\(\alpha\) and K\(\beta\) lines of some adjacent elements are less than the spectral resolution of the detector. Taking into account that the operating conditions can maximize the peak intensity and minimize the background, with the aim of achieving the smallest possible detection limits for all elements detected, the experimental condition dependencies of the present portable spectrometer in the multi-element solution analysis were studied and discussed in detail. Consequently, sub-nanogram detection limits were achieved for nine elements under optimal experimental conditions in a single measurement of 10 min. Finally, the
applicability of portable spectrometers to multi-element analysis with high sensitivity was demonstrated.

2.2 Experimental

2.2.1 Sample preparation

Commercially available 1000 mg L\(^{-1}\) K, V, Mn, Co, Cu, Ga, As, Br, Y and 100 mg L\(^{-1}\) Sc standard solutions were used (Wako Pure Chemical Industries, Osaka; Nacalai Tesque, Kyoto, Japan). Multi-element solutions containing 50 mg L\(^{-1}\) each of K, Sc, V, Mn, Co, Cu and 1 mg L\(^{-1}\) each of K, Sc, V, Mn, Co, Cu, Ga, As, Br and Y were prepared by mixing the standard solutions and diluting with the ultrapure water for LC/MS use (Wako Pure Chemical Industries). Because V and Cu standard solutions contained H\(_2\)SO\(_4\) and CuSO\(_4\), respectively, S was also included in the multi-element solutions. An optical flat made of synthetic fused silica (Sigma Koki, Tokyo, Japan) was used as the sample carrier (\(\lambda/10\) of surface flatness, \(\lambda = 632.8\) nm). 1-\(\mu\)L aliquot of the 50 mg L\(^{-1}\) solution, and 1, 5, 10 and 20 \(\mu\)L aliquots of the 1 mg L\(^{-1}\) solution were pipetted and dried separately on the optical flat. Cleanness of the optical flat before each use was checked by the same portable spectrometer.

2.2.2 Apparatus

A series of portable TXRF spectrometers with low power X-ray tubes were designed and developed by Kunimura and Kawai\(^{11-17, 21}\) at Kyoto University (financially supported by Development of Systems and Technologies for Advanced Measurement and Analysis Program of SENTAN, JST), and were commercialized by OURSTEX Corp. (Neyagawa, Japan) and named OURSTEX 200TX. The portable TXRF
spectrometers weighed less than 5 kg, and used non-monochromatic X-rays as excitation sources. The present portable TXRF spectrometer mainly consisted of a 4 W X-ray tube with a Rh target (40 kV Magnum, Moxtek, Orem, UT), a waveguide slit restricting the incident radiation to a parallel beam of 10 mm in width and 10 µm in height, and a Si-PIN photodiode detector (X-123, Amptek, Bedford, MA) that was cooled by a Peltier device and contained a preamplifier and a digital signal processor. All measurements were performed in air. The irradiated area of incident X-rays on the surface of the sample carrier was about 8 mm in length and 10 mm in width when glancing angle of 0.07° was used. Schematic views and detailed information on portable spectrometers were reported in detail by Kunimura et al.16

2.3 Results and Discussion

2.3.1 Glancing angle dependence of fluorescence signal

The dry residue containing 50 ng of K, Sc, V, Mn, Co, and Cu was measured at glancing angles of 0.00°, 0.02°, 0.04°, 0.07°, 0.10°, 0.12° and 0.14°. Figure 1 shows measured representative TXRF spectra at the glancing angles of 0.02°, 0.04° and 0.14°. All elements in the sample were simultaneously detected in 10 min. S was detected because it was contained in the sample as described in the Experimental section. Si and Ar were detected because the optical flat was composed of SiO₂ and air contains 0.93% Ar. The Kα peaks of potassium were partly overlapped by the Ar peaks, since the spectral resolution of the detector was not sufficient to separate the peaks.

Since the non-monochromatic X-rays from the X-ray tube operated at 25 kV and 50 µA were used as excitation radiation, energies of the incident X-rays were lower than
Fig. 1  Glancing angle $\phi$ dependence of measured TXRF spectra. $\phi = 0.02^\circ$ (■); $0.04^\circ$ (□); $0.14^\circ$ (△). X-ray tube was operated at 25 kV and 50 $\mu$A.

25 keV. The critical angle of total reflection was not clear for the non-monochromatic X-ray beam. However, the critical angle for monochromatic X-rays with 25-keV energy was theoretically calculated to be $0.07^\circ$ for the SiO$_2$ substrate. This indicates that the critical angles for the X-rays with energies less than 25 keV were greater than $0.07^\circ$ because the critical angle becomes larger as X-ray energy decreases. Thus, when glancing angles smaller than $0.07^\circ$ were used, X-rays with energies lower than 25 keV could be totally reflected. Therefore, at glancing angles of $0.02^\circ$ and $0.04^\circ$, the continuous incident beam was totally reflected. At $0.02^\circ$, the spectral background was lowest in the energy range of 1 – 9 keV as shown in Fig. 1, but each peak was much
weaker compared to that at $0.04^\circ$. At $0.14^\circ$, because the incident beam was not totally reflected, background in the energy range above 9 keV increased markedly, whereas each peak was suppressed. Such angle dependence indicates that the dry residue was less than $10^2$ nm in thickness.\textsuperscript{2} The glancing angle dependence of a portable TXRF spectrometer was also investigated in previous research,\textsuperscript{21} in which a 1.5 W X-ray tube with a tungsten target was operated at 9.5 kV and 150 $\mu$A, and the 3d transition metals of Sc, Ti, V, Cr, Mn, Fe and Ni were studied. Even if the measurement was carried out at the optimum glancing angle of $0.13^\circ$, the detection limit for Ni was 10 nanograms, which was much higher (worse) than those of the other elements (sub-nanograms to 2 nanograms). It is due to the fact that the maximum energy of the incident X-rays was 9.5 keV, then there were fewer X-ray photons with energies higher than the Ni K absorption edge energy (8.3 keV). This indicates that the excitation efficiency of the 1.5 W X-ray tube for the elements Ni and Cu was low, and Zn could not be detected because the maximum incident radiation energy of 9.5 keV was less than the Zn K absorption edge energy (9.7 keV). In contrast with the 1.5 W X-ray tube, the 4 W X-ray tube used in the present study was more suitable for the analyses of these elements. The detection limit for Cu was down to 1 nanogram at the optimum glancing angle of $0.04^\circ$ when the 4 W X-ray tube was operated at 25 kV and 50 $\mu$A.

Figure 2 shows the glancing angle dependence of fluorescence intensities of Sc, V, Mn, Co and Cu. At angles above $0.07^\circ$, the fluorescence signal decreases as the glancing angle. Such strong angle dependence can be understood as the reflectivity of the incident beam decreasing with an increase in the glancing angle, which results in
more radiation transferring into the substrate and then less radiation exciting the dry residue on the substrate.

### 2.3.2 Voltage and current dependencies of fluorescence signal and background

Figure 3 shows the fluorescence signal and background at voltages of 20, 25, 30 and 35 kV, and at currents of 20, 50, 80 and 100 μA. Both the signal and background increased with the tube voltage and current. This is because increasing the X-ray tube voltage or current can linearly increase the primary beam intensity. Further, more X-ray photons excite the dry residue and more scattering occurs. Consequently, more fluorescence signal and higher background were generated. The detection limit, however, does not improve linearly with increasing operational power of the X-ray tube.
when non-monochromatic X-rays are used. It is not only due to the increment of the background intensity, but also due to the detector saturation caused by the highly intense scattered X-rays of non-monochromatic X-rays from a high power X-ray source. Considering a typical X-ray tube working at 30 – 40 kV, it emits bremsstrahlung radiation at the order of a few units × 10^7 photons/μA s. The maximum count rate of a

![Graphs](image_url)

**Fig. 3** Signal (a, b) and background (c, d) dependence of Sc (●), V (◇), Mn (▲), Co (○) and Cu (△) on X-ray tube voltage and current. Glancing angle \( \phi \) was 0.04°. X-ray tube was operated at the current of 50 μA in (a) and (c), at the voltage of 25 kV in (b) and (d).
Si-drift detector is up to $10^6$ counts/s. Although the detector can be used for the non-monochromatic X-rays from the high power X-ray source, shaping time should be shortened in order to make a measurement at the maximum count rate. As a result, the energy resolution of the detector is degraded (worse), and XRF peaks become broader. This indicates the overlap between adjacent peaks becomes severe, detection sensitivities for the analyzed elements are decreased.\textsuperscript{12} Therefore, high power X-ray sources are usually used with monochromator. When continuous X-rays are used as excitation sources, non-monochromatic X-rays from a low power X-ray tube are more effective for improving the detection limits.\textsuperscript{11}

2.3.3 Excitation parameter dependencies of background contributed by the optical flat

In the TXRF analysis, the Si fluorescence peak was generated by the SiO\textsubscript{2} optical flat. The excitation parameter dependencies of the Si fluorescence signal are shown in Figure 4. It is found in Fig. 4(a) that the Si fluorescence signal increased with the glancing angle, especially for angles above 0.07° as the signal linearly increased. This angular dependence can be illustrated by the penetration depth of incident X-rays into the optical flat. At angles above 0.07°, the penetration depth of the primary beam into the substrate increased with the glancing angle, and the depth was in the order of sub- to several micrometers. Below the angle of 0.07°, because the incident beam was totally reflected, the penetration depth reached a constant level of only a few nanometers.\textsuperscript{2} This indicates that a thinner layer in the substrate was passed through with decreasing glancing angle, and consequently less fluorescence signal was produced. The
Fig. 4 Signal dependence of Si on: (a) glancing angle when X-ray tube was operated at 25 kV and 50 µA, (b) X-ray tube voltage (◊) and current (▲) at the glancing angle of 0.04°, where the X-ray tube was operated at the current of 50 µA for the voltage variation curve, and at the voltage of 25 kV for the current variation curve. Si fluorescence signal also increased with the tube voltage or current, as shown in Fig. 4(b), due to the enhancement of the primary beam intensity with increasing tube operational power.

2.3.4 Detection limits for all detected elements under optimal experimental conditions

The suitability of the portable spectrometer for determining elements in the multi-element solutions was evaluated by determination of the detection limits. The following equation was used to calculate the detection limits:

\[
\text{Detection limit} = 3m \frac{\sqrt{I_{BG}}}{I_{Net}}
\]
where \( m \) is the amount of a studied element (nanogram) in the sample, \( I_{\text{Net}} \) and \( I_{\text{BG}} \) are the net and background counts (counts/s), respectively, and \( t \) is the counting time (s).

Figure 5 shows the experimental condition dependencies of the detection limits. Sub-nanogram detection limits for Sc, V, Mn, Co, Cu, Ga, As, Br and Y were achieved in a single run at the glancing angle of 0.04°, voltage of 25 kV, current of 100 \( \mu \)A, and sample amount of 1 \( \mu \)L. The optimum voltage of 25 kV may be dependent on the energy range of the detector since efficiency of the detector is above 25% for the X-rays from 1.5 – 25 keV, and decreases outside this range. In Fig. 5(d), detection limits for As were much higher compared with those of the other elements when sample amounts of 5, 10 and 20 \( \mu \)L were used. This might be due to the volatilization of As during the drying processes, which was caused by the long heating time for the aqueous samples on the optical flat. Detection limits under the optimum experimental conditions are shown in Table 1. A 0.23 ng detection limit for Co was achieved, which corresponds to \( 24 \times 10^{11} \) atoms/cm\(^2\) if we assume that the irradiated area is 1 cm\(^2\). The detection limit for S was much higher in contrast to the others, because the efficiency of an energy-dispersive spectrometer strongly diminishes for photons below 2 keV energy.\(^2\) The K\(\alpha\) peaks of potassium strongly overlapped with the Ar peaks, so the detection limit for K was not considered here.

**Table 1** Detection limits obtained at the glancing angle of 0.04°, voltage of 25 kV, current of 100 \( \mu \)A, and sample amount of 1 \( \mu \)L

<table>
<thead>
<tr>
<th>Element</th>
<th>S</th>
<th>Sc</th>
<th>V</th>
<th>Mn</th>
<th>Co</th>
<th>Cu</th>
<th>Ga</th>
<th>As</th>
<th>Br</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits/ng</td>
<td>1.77</td>
<td>0.87</td>
<td>0.53</td>
<td>0.35</td>
<td>0.23</td>
<td>0.43</td>
<td>0.27</td>
<td>0.50</td>
<td>0.47</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Fig. 5 Detection limits of Sc (●), V (□), Mn (△), Co (×), Cu (×) as functions of: (a) glancing angle when X-ray tube was operated at 25 kV and 50 μA, (b) voltage at the glancing angle of 0.04° and X-ray tube current of 50 μA, and (c) current at the glancing angle of 0.04° and X-ray tube voltage of 25 kV. Detection limits as functions of (d) sample amounts of 1 (●), 5 (□), 10 (△) and 20 μL (∗) at the glancing angle of 0.04°, X-ray tube voltage of 25 kV and current of 100 μA.

2.4 Conclusions

This study illustrates the performance of a portable TXRF spectrometer in analyzing multi-element solutions containing 11 elements. Under the optimal experimental conditions, detection limits for nine elements were as low as sub-
nanograms in a single TXRF measurement of 10 min. The 0.23 ng detection limit for Co achieved in this study is higher than those reported in the previous research.\textsuperscript{12,17} The lower detection limits in the former studies are attributed not only to the ideal measurement sample and/or the long measurement time of 1800 s as indicated in the Introduction section, but also to the use of an X-ray tube with a tungsten target (50 kV Magnum, Moxtek). When the X-ray tube is operated at the voltage of 25 kV, W L-lines are emitted with energies between 8.3 and 11.3 keV. Since the energies of W L-lines are close to the K absorption edge energy of Co (7.7 keV) in contrast to the Rh K-lines (20.0–23.2 keV) that were used in the present study, the X-ray tube with a tungsten target is more suitable for Co analysis. However, the tungsten target X-ray tube is not well-suited for Cu and Zn analysis because of the interference of W L-lines with K-lines of Cu and Zn. Moreover, only W L-lines are generally used to excite samples in analysis. Therefore, the tungsten target X-ray tube may not be a good choice in multi-element solution determination, especially in the analysis of the environmental, geological and biological samples characterized by various elements and complex matrices. By contrast, the X-ray tube with a Rh target is more suitable for these applications. Because the atomic number of Rh is moderately high, a Rh target X-ray tube can produce good continuum intensity and both the K- and L-lines can be used to excite the samples.

The suitability of the portable TXRF spectrometer in multi-element analysis has been demonstrated in the present paper. The features of low detection limit, minute amounts of sample required, and fast detection of a wide range of elements in a single run make the portable spectrometer a valuable tool in versatile applications, such as
rapid monitoring in field environmental or geological investigations, as well as fast sample screening when a large number of samples must be dealt with in field studies.

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References


Chapter 3

Influence of Substrate Direction on Total Reflection X-Ray Fluorescence Analysis*

Abstract

We studied the substrate direction influence on total reflection X-ray fluorescence (TXRF) analysis by using portable TXRF spectrometer. Since a square optical flat made of synthetic fused silica was applied as sample substrate, spectra were measured for four substrate directions by rotating the substrate 90° clockwise three times on the sample stage. The spectra of the four directions were significantly different, because the significance was tested by two-way analysis of variance (ANOVA). Consequently, the significant influence of the substrate direction on TXRF analysis was demonstrated. The reason was an inhomogeneous dry residue formed in the drying process. Finally, based on the comparison between the measured intensity and the theoretically calculated intensity, the optimum number of the measurement and the measuring time in TXRF analysis were given.

Key words: Portable spectrometer, Total reflection X-ray fluorescence (TXRF), Substrate, Direction, Two-way analysis of variance (ANOVA)

3.1 Introduction

Total reflection X-ray fluorescence (TXRF) analysis is a non-destructive trace elemental analysis technique which was first proposed by Yoneda and Horiuchi to analyse small quantity of transition metal elements in 1971 \(^1\). In TXRF analysis, primary X-rays from an X-ray tube strike a specimen deposited on a polished flat reflector (substrate) at an incident angle below the critical angle. Under the special geometry of excitation, the incident beam can be totally reflected. Therefore, only a small amount of the primary X-rays penetrate into the substrate. The penetration depth of the incident X-rays into the substrate drastically decreases to sub-nanometres, which contrasts to that of micrometre depth for traditional XRF analysis. This indicates that the elastic and inelastic collisions of the primary photons with the substrate substances are greatly decreased, and as a result, the scattered background in a measured TXRF spectrum is deliberately low. In addition, a standing wave is formed in front of the substrate, and the specimen on the substrate is excited twice by the incoming and reflected X-rays. Consequently, an extremely low background spectrum with high signal to background ratios can be obtained in TXRF analysis, and detection limits are substantially decreased \(^2,3\). So far, ultimate detection limits of several femtograms have been achieved for silicon wafer analysis when monochromatic synchrotron radiation induced TXRF was used \(^4,6\). In TXRF measurement, since only a few micrograms or microliters of sample are required, the dry residue formed by heating aqueous solution on the substrate can be taken as a thin film. This means the matrix effects from absorption and secondary excitation can be neglected, and the relation between fluorescence intensity and sample amount is expected to be linear. Therefore, a simple quantification procedure can be performed through adding a certain element with
known concentration as an internal standard which is unusual in the original sample \(^2\).
The elements in the sample must be homogenously distributed in the dry residue and no
localisation of the deposition occurs. This is because of the extremely low angle of
incidence that the primary radiation is attenuated by the sample matrix along the
pathway through the sample spot, local accumulations of one distinct element in the
sample film would lead to a systematic error \(^7\).

In the year 1984, Iida \textit{et al.} reported that monochromatic X-rays are a more
effective way to improve the analytical sensitivity \(^8\). Recently, Kunimura \textit{et al.} found
when the X-ray tube of a few watts is used, non-monochromatic TXRF is a more
effective way to improve the analytical sensitivity \(^9\). Since the year 2007, Kunimura \textit{et al.} have developed a series of portable TXRF spectrometers using polychromatic X-rays
from low power X-ray tubes. The schematic views and detailed information of portable
spectrometers were reported elsewhere \(^10\)-\(^12\) and are briefly summarized here. The
portable spectrometer with compact design only weighed less than 5 kg. It mainly
consisted of a low-power X-ray tube, a waveguide slit, an adjustable sample stage, a
goniometer in order to rotate a sample, and a Si PIN photodiode detector. Because no
monochromator existed in the equipment, both continuous and characteristic X-rays
from the X-ray tube were used as excitation sources. The primary X-rays were restricted
to a parallel beam by the waveguide slit and then used to excite the sample. So far, a 10
picogram detection limit for Co was achieved by using a W anode X-ray tube (the
maximum operational voltage and current are 50 kV and 200 \(\mu\)A, respectively) under
optimum excitation conditions \(^13\), which is only four orders of magnitude higher (worse)
than that obtained from SR-TXRF analysis.
The importance of the substrate in TXRF analysis had often been underlined\(^2\). The chosen substrate should have many characteristics in order to take full advantages of the analytical technique, such as the mechanical properties, inertness and free of fluorescence lines over the energy range of interest. Imashuku et al. reported when a quartz optical flat of square shape is used instead of a round shape in TXRF analysis, the spectral background can be reduced\(^{14}\). We studied the substrate shape dependency in TXRF analysis by using 1 ppm cesium solution, and found that when the round-shaped substrate was used, the scattering background in the measured TXRF spectrum was much higher than that of square-shaped substrate, as shown in Fig. 1. This high

![Fig. 1 Substrate shape (round and square) dependence of the measured TXRF spectra.](image-url)
spectral background was attributed not only to the scattering by the residue, but also to the scattering of the incident X-rays at the edge of the disc shape substrate. The X-ray beam projection sometimes grazes the edge of the quartz substrate when it has a disc shape. However, if we use a square-shaped quartz substrate, the incident X-ray projection is within the surface. In the present portable TXRF spectrometer, the direction of the incident X-ray beam with respect to the sample stage was fixed, thus when a square shape substrate was used, the substrate could be put on the sample stage in four different directions. The aim of this work was to investigate the influence of the substrate direction on TXRF analysis.

3.2 Experimental

The portable TXRF spectrometer used in the study was about 25 cm in height, 30 cm in length and 12 cm in width. A Rh target X-ray tube of 4 W (40 kV Magnum, Moxtek Inc., Orem, UT, USA) was used as an excitation source. A waveguide slit which was placed between the X-ray tube and sample stage could restrict the incident X-rays to a parallel beam of 10 mm in width and 10 μm in height. Fluorescence signals were registered by a Si PIN photodiode detector X-123 (Amptek Inc., Bedford, MA, USA) which contained a preamplifier and a digital signal processor.

The multielement solution containing 50 mg L\(^{-1}\) each of K, Sc, V, Mn, Co and Cu was prepared from individual 1000 mg L\(^{-1}\) standard solutions except for Sc of 100 mg L\(^{-1}\) original concentration (Wako Pure Chemical Industries, Ltd., Osaka; Nacalai Tesque, Inc., Kyoto, Japan). As V standard solution contained H\(_2\)SO\(_4\) and Cu standard solution contained CuSO\(_4\), sulfur was also included in the solution. The water used
throughout the study was ultrapure water (Wako Pure Chemical Industries, Ltd., Osaka, Japan). An optical flat made of synthetic fused silica (Sigma Koki Co., Ltd., Tokyo, Japan) was used as the sample substrate (square shape, side length of 30 mm, thickness of 5 mm, $\lambda/10$ of surface flatness).

One $\mu$L aliquot of the multielement solution was placed onto the substrate, and dried on a heating plate. The dry residue containing 50 ng each of K, Sc, V, Mn, Co and Cu was not measured until it had totally cooled. The substrate was put on the sample stage in four different directions. Each direction was made by rotating the substrate 90° clockwise on the stage. Five measurements were performed in each direction. The two-way analysis of variance (ANOVA) test was applied to examine the significance of differences among the results obtained in the four substrate directions.

3.3 Results and Discussion

3.3.1 Irradiated area on the substrate in the TXRF measurements

In the TXRF analysis, the X-ray tube was operated at the voltage of 25 kV. Because polychromatic radiations were used in the portable spectrometer, the critical angle for total reflection could not be theoretically calculated. However, we assumed the incident X-rays were monochromatic, and then theoretically calculated the X-ray intensity dependence as the change of the glancing angle for the incident X-ray energy of 10, 15, and 20 keV. Through changing the $\beta$ value which was the imaginary part of the refractive index, it was found that the 20 keV incident X-rays were the best fit among the three energies. This 20 keV energy corresponded to the Rh K$\alpha$ energy ($K\alpha_1 = 20.214$ keV, $K\alpha_2 = 20.072$ keV). Thus the effective X-rays to excite the sample were the Rh K$\alpha$ lines $^{15}$. For 20 keV incident X-rays impinging on a silica substrate, the
critical angle for total reflection was theoretically calculated to be $0.085^\circ$. Thus when the glancing angle of $0.04^\circ$ was used, the incident beam was regarded to be totally reflected. At the glancing angle of $0.04^\circ$, the irradiated area of incident beam on the substrate was about $14 \times 10 \text{ mm}^2$ as shown in Fig. 2. This area was much larger than that of a dry residue which was usually several square millimeters. Therefore, the entire dry residue could be irradiated regardless of the changes in substrate direction in the TXRF analysis.

Fig. 2 Cross (a) and Top (b) sectional views of the irradiated area in the TXRF analysis.
3.3.2 Measured TXRF spectra in the four directions

TXRF spectra measured in the four directions are shown in Fig. 3. All elements in the dry residue were simultaneously detected in 10 minutes. Si from the substrate and Ar from air were also detected. Two-way ANOVA was carried out to ascertain the significance of difference among the peaks measured in the four directions with a probability of 95%. Results from the ANOVA showed that the peaks of all elements obtained in the four directions were significantly different. Although the irradiated areas on the substrate were identical, the measured spectra were significantly different in the four directions. The differences might have resulted from the inhomogeneous dry residue on the substrate as a possible consequence of the drying process. Because the

Fig. 3 Substrate direction dependence of the measured TXRF spectra. The X-ray tube was operated at the voltage of 25 kV and current of 80 µA; the glancing angle of incident X-rays was 0.04°.
heterogeneous distribution of the component elements could lead to different attenuation of the incident radiation and self-absorption of the fluorescence radiation.

3.3.3 Signal, background and signal-to-background ratio in the four directions

Fig. 4 shows the substrate direction dependences of signal, background, and signal-to-background ratio for the elements Sc, V, Mn, Co and Cu (a, b, c) and Si (d). For the elements Sc, V, Mn, Co and Cu, the differences of the XRF intensity, scattered background, and the signal-to-background ratio in the four directions were also

Fig. 4 Substrate direction dependences of signal (a), background (b) and signal-to-background ratio (c) for Sc, V, Mn, Co and Cu; substrate direction dependences of signal, background and signal-to-background ratio (d) for Si.
significantly different according to the two-way ANOVA with a probability of 95%.

Compared to the other elements in the sample, discrepancy for Mn was most evident. This might be due to the solubility, which caused Mn being present in the dry residue in a significantly different physical and chemical form than the other elements after the drying process. For example, Mn is very soluble when presents as the nitrate in the Mn standard solution \(^\text{16}\) and as a result it salts out late in the drying process, which causes it to form uneven distribution around the centre of the reflector surface. Co on the other hand is relatively insoluble \(^\text{16}\) when exists as the nitrate in the standard solution compared with the other elements and salts out early in the outer edge of the sample spot \(^\text{17}\). Compared with the elements contained in the dry residue, the signal, background, and signal-to-background ratio of the element Si in the four directions were almost the same, as shown in Fig. 4d. Because Si was the component element of the flat substrate and was homogeneously distributed in the substrate.

We calculated the X-ray intensity on the surface of the SiO\(_2\) substrate for the Rh K\(\alpha\) radiation (transmission coefficient of the X-ray beam through the interface) \(^\text{18}\). In the calculation, \(\delta = 1.12 \times 10^{-6}\), \(\beta = 3.98 \times 10^{-9}\) for Rh K\(\alpha\) radiation (\(\lambda = 0.61\) Å), the density of quartz glass was 2.20 g/cm\(^3\). The calculated transmission coefficient \(T\) plotted as a function of the glancing angle \(\phi\) is presented in Fig. 5. It is found in Fig. 5 that \(T = 0.87\) for Rh K\(\alpha\) radiation at the glancing angle of 0.04°. The measured Co intensities in the four substrate directions and the arithmetic mean of the four values were compared to the calculated intensities in Fig. 6. The Co intensity was proportional to the transmission coefficient \(T\) which represented the X-ray intensity just under the surface of the sample material. In order to compare the measured results with the theoretical results, and to obtain the best fit between the experiment and theory, the Co intensities
Fig. 5 Plot of the calculated transmission coefficient $T$ for SiO$_2$ substrate vs the glancing angle $\phi$ for the Rh K\textalpha radiation. The dashed vertical line represents the glancing angle used in this study.

Fig. 6 Comparison of the theoretical intensity (\(\bullet\)) to the measured Co intensities in the four substrate directions (\(\square\)) and the arithmetic mean of the four values (\(\Delta\)). The intensities of Co were divided by 5000.
in Fig. 6 were divided by 5000. It is demonstrated in Fig. 6 that the discrepancy between the theoretical value and the mean value was less compared to that from each direction.

3.4 Conclusions

The influence of the substrate direction on TXRF analysis was studied in this paper. The spectra measured in the four substrate directions were significantly different, which might be the reason that a heterogeneous dry residue is formed as a consequence of the drying process. Because the homogeneous distribution of detected elements in the dry residue is a prerequisite for precise and accurate quantification when an internal standard is used in TXRF analysis, the influence of the substrate direction on the analysis should attract particular attention in the measurement considering that it would cause large errors in quantification process. It is recommended that the dry residue should be measured at least one time in each direction, and the arithmetic mean calculated from the results of all the directions be used for further qualification and quantification analysis. It is also recommended that the measuring time in each direction could be set to $1/n$ of the total measuring time, in which $n$ represents the amount of the substrate direction that can be made in the TXRF analysis.

Acknowledgements

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References


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Chapter 4

Portable Total Reflection X-Ray Fluorescence Analysis in the Identification of Unknown Laboratory Hazards*

Abstract

In this study, a portable total reflection X-ray fluorescence (TXRF) spectrometer was used to analyze unknown laboratory hazards that precipitated on exterior surfaces of cooling pipes and fume hood pipes in chemical laboratories. With the aim to examine the accuracy of TXRF analysis for the determination of elemental composition, analytical results were compared with those of wavelength-dispersive X-ray fluorescence spectrometry, scanning electron microscope and energy-dispersive X-ray spectrometry, energy-dispersive X-ray fluorescence spectrometry, inductively coupled plasma atomic emission spectrometry, X-ray diffraction spectrometry (XRD), and X-ray photoelectron spectroscopy (XPS). Detailed comparison of data confirmed that the TXRF method itself was not sufficient to determine all the elements (Z > 11) contained in the samples. In addition, results suggest that XRD should be combined with XPS in order to accurately determine compound composition. This study demonstrates that at least two analytical methods should be used in order to analyze the composition of unknown real samples.

4.1 Introduction

Total reflection X-ray fluorescence (TXRF) analysis\textsuperscript{1, 2} has become an appealing technique for the determination of elemental composition in unknown samples due to its rapid and simultaneous multielement analysis ability with low detection limits (subpicogram). Using synchrotron radiation (SR) based TXRF analysis, the absolute detection limit can be further reduced to the femtogram scale for transition metals. To date, such low detection limits in the femtogram range were only achieved for several elements during the analysis of Si wafers.\textsuperscript{3–5} As access to SR facilities is limited, the use of SR-TXRF is impractical for routine and rapid analysis of unknown samples. Alternatively, a lab-scale X-ray tube (kW or 1–50 W) TXRF spectrometer is readily available for routine analysis. Compared to high-power (kW) TXRF spectrometers, routinely used in the semiconductor industry for the analysis of Si wafer surface contamination,\textsuperscript{6–8} the low-power (1–50 W) desktop TXRF has been commonly used in environmental studies for pollution investigation or environmental quality control, such as rain water,\textsuperscript{9} soil,\textsuperscript{10} and air aerosol.\textsuperscript{11} Low-power TXRF instruments are either monochromatic or non-monochromatic. The former requires a fan-cooled 50 W X-ray tube, while the latter requires only an air-cooled 1 W X-ray tube to achieve comparable sensitivities. This low-power and non-monochromatic type portable TXRF spectrometer was developed by Kunimura and Kawai. Details regarding the portable spectrometer can be found in previous reports.\textsuperscript{12, 13} Although weak white X-rays are employed in the portable TXRF spectrometer, detection limits down to 10 picogram have been achieved.\textsuperscript{14} This value is only four orders of magnitude higher than that of SR-TXRF. The portable TXRF featuring low detection limits, fast measurements with high sensitivity for a wide range of elements, and minimal sample preparation\textsuperscript{14, 15} has been
demonstrated as a valuable tool for composition evaluation of unknown samples. Accordingly, a low-power portable TXRF was used to determine the elemental composition of potentially toxic substances found in our chemical laboratories and offices. The potentially toxic, unknown substances precipitated on cooling pipes and fume hood pipes within the laboratories and offices are seen in Figs. 1 and 2, respectively. Taking into account their potentially hazardous nature and the need to protect the health and safety of laboratory personnel and office occupants, elemental analysis of the precipitates (especially to determine whether or not toxic elements such as Cd was included in the hazards, as the fume hood pipe inlets were in the laboratory where CdTe based compounds were used in experiments for up to 10 years) was mandatory.

Fig. 1 Yellow substances precipitated on the cooling pipe.
In order to examine the accuracy of TXRF analysis for the determination of elemental composition ($Z > 11$), analytical results were compared with those of wavelength-dispersive X-ray fluorescence spectrometry (WDXRF), scanning electron microscope and energy-dispersive X-ray spectrometry (SEM-EDX), energy-dispersive X-ray fluorescence spectrometry (EDXRF), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray diffraction spectrometry (XRD), and X-ray photoelectron spectroscopy (XPS). A variety of analytical methods can be employed for
elemental analysis. However, the practical analytical method selection concerning the present problem should take into consideration (1) availability, (2) analysis time, (3) detectable elements, and (4) sensitivity. WDXRF and EDXRF were selected as they are routinely employed to determine the presence of elements from Na to U with typical detection limits at ppm levels for medium- and high-Z elements, which are satisfactory for many analytical problems. In addition, WDXRF also allows efficient determination of low-Z elements down to atomic number 4 (Be). SEM-EDX was used as it provides rapid elemental determination without sample pretreatment. ICP-AES was applied to explore toxic elements, such as Cd, as this method is capable of performing highly sensitive analysis with detection limits down to ppb levels. XRD and XPS were employed as these techniques can be used not only for elemental analysis but also for identifying chemical compounds within the bulk and at the surface of the unknown samples. It is worthy to mention that not all the aforementioned techniques were applied to the determination of each unknown sample. SEM-EDX, WDXRF, and XRD, used to analyze cooling pipe samples, were not applied to fume hood pipe samples. This is due to the following restraints and considerations: (1) the unknown substances on the two kinds of pipes (cooling and fume hood) were not found at the same time. Therefore, unknown samples located on fume hood pipes were not characterized until cooling pipe samples were first identified; (2) chemicals which precipitated on laboratory cooling pipes also precipitated on cooling pipes above office ceilings. Taking into consideration that the chemicals might immerse to the offices from ceilings and directly affect the air quality of the offices, determination of the unknown chemicals' full profile is mandatory. Accordingly, structural characterization by XRD was applied to cooling pipe samples. As surface topography of the chemicals does not strongly influence the materials’
toxicity, SEM-EDX was used only for the purpose of elemental analysis. Elemental composition was also determined by WDXRF due to the reasons outlined earlier in the text. In addition, WDXRF was applied for the quantitative analysis of the cooling pipe sample; (3) fume hood pipes, on which the unknown precipitates were found, were only installed behind the walls of the chemical laboratories. In such cases, laboratory personnel are only exposed to potential toxins when doors exposing such areas are open. Accordingly, identification of potentially hazardous elements was one of the main objectives. Since toxic elements of interest have relatively high atomic numbers, low-Z element determination was not necessary. Therefore, WDXRF was not applied. Instead, EDXRF was applied for both qualitative and quantitative analyses of fume hood samples.

This paper describes the use of a portable TXRF spectrometer in the analysis of unknown laboratory hazards. Results are compared with those of WDXRF, SEM-EDX, EDXRF, ICP-AES, XRD, and XPS, to probe whether TXRF can be used as a sole technique for the determination of elemental composition (Z > 11) in unknown samples. So as to further discuss whether or not one analytical technique is sufficient in unknown real sample analysis.

4.2 Experimental

4.2.1 Sample

Samples for analysis were scraped from the surfaces of the cooling pipes and fume hood pipes (using microspatulas) into plastic sample containers (certified clean of all analytes of concern). In order to avoid contamination during sampling, the microspatulas were sterilized with 99.8% ethanol (Wako Pure Chemical Industries,
Osaka, Japan) prior to use. Special attention was paid to avoid manipulating any sample with hands. The amount of collected sample in each case did not exceed 0.5 g. Prior to analysis, samples were sealed and stored in a dry place at ambient temperature (20–25 °C).

Hazardous materials that precipitated on the silvery protection tape of the cooling pipe were yellow in color (Fig. 1). In contrast, hazardous materials that precipitated on the aluminum alloy paper (used to wrap the stainless-steel fume hood pipes) were grayish or dark brown (Fig. 2). They were visually inhomogeneous, sticky, and speckled with apparent rust/corrosion particles. As shown in Figs. 1 and 2, the precipitation of unknown substances was not localized to one spot. Therefore, for the purpose of obtaining representative and reproducible results, all unknown precipitates on each pipe were considered in the sampling. From one of the cooling pipes, a mixed sample was collected from all precipitated areas. Three samples in total were collected from fume hood pipes located in two different laboratories (A and B). One sample, a mixture of all the precipitates found on the fume hood pipe in laboratory B, was collected. In laboratory A, unknown substances precipitated on two different areas of the same fume hood pipe; thus, two samples, each of which was a mixture of the respective precipitated area, were collected. The same sampling procedure was applied to all other analytical methods.

4.2.2 TXRF analysis

TXRF analysis was performed using a portable total reflection X-ray fluorescence spectrometer. Details of the portable TXRF have been reported in previous papers15, 18 and are briefly summarized here. The spectrometer weighed less than 5 kg.
and mainly consisted of a 4 W X-ray tube with a Rh target (40 kV Magnum, Moxtek, Orem, USA), a waveguide slit (restrict the incident beam to a parallel beam of 10 mm in width and 10 μm in height), and a Si-PIN photodiode detector (X-123, Amptek, Bedford, USA). Measurements were performed in air at a glancing angle of 0.05° with respect to the synthetic fused silica optical flat (λ/10 of surface flatness, λ = 632.8 nm, Sigma Koki, Tokyo, Japan). The X-ray tube was operated at 30 kV and 80 μA.

All chemicals used during sample preparation were of analytical grade or better. Ultrapure water for LC/MS (Wako Pure Chemical Industries) was used throughout the experiments. A cooling pipe sample (0.0015 g) was pre-weighed and dissolved in ultrapure water (100 μL) within a 3-mL vial. Small bubbles were observed during the dissolution process. In addition, moisture was seen on the interior wall of the vial. The cooling pipe sample was easily dissolved in the ultrapure water within 10 min. The dissolved solution was yellowish and visually clear without the presence of any precipitation. A 5-μL aliquot of the dissolved solution was pipetted onto the optical flat and subsequently dried on a heating plate. Fume hood pipe samples (0.0050 g) were pre-weighed and dissolved in 100 μL ultrapure water and 100 μL 60% HNO₃ (Nacalai Tesque, Kyoto, Japan). Small bubbles were also observed during the dissolution process, which took around 20 min to complete. The dissolved solutions were colorless and also visually clear without the presence of any precipitation. A 1-μL aliquot of the dissolved solution was transferred onto the silica optical flat and allowed to dry on a heating plate. The pipetting and drying process was repeated five times. Thus, a total of 5 μL of the dissolved solution was used during TXRF analysis. Taking into consideration that volatile elements may be present within the precipitates, the samples were not exposed to heating for more than 30 s. Following the drying step, the optical flat carrying the
sample was transferred to a clean bench and allowed to cool to room temperature. These processes would allow the liquid sample on the optical flat to become a dry residue that was ready to be analyzed. In order to trace artificially introduced contamination during sample preparation, blank samples of ultrapure water were also prepared and analyzed at the same measurement conditions as the hazard samples.

A mixed solution containing 250 ppm each of Mn, As, Ag, and Cd was prepared from four 1000 ppm commercially available standard solutions for atomic absorption (Wako Pure Chemical Industries; Nacalai Tesque). The solution was used for energy calibration of measured TXRF spectra.

### 4.2.3 WDXRF, SEM-EDX, EDXRF, ICP-AES, XRD, and XPS analyses

WDXRF measurements were performed on a Rigaku ZSX-100e WDXRF spectrometer. The sample was finely ground and then pressed into a small tablet of 5 mm in diameter and 0.2 mm in thickness to be used for WDXRF analysis. A fundamental parameter method was used for WDXRF semiquantitative analysis. The same tablet was used during XRD analysis, which was performed using a Rigaku Ultima-IV XRD spectrometer. SEM-EDX analysis was performed on a JEOL SEM (JSM-5600LVS) equipped with an Ourstex silicon drift detector (SDD). The SDD was attached to the SEM using a blank flange, which was specially modified by our lab, as described in a previous publication. EDXRF analysis was performed on a Shimadzu EDX-800 XRF spectrometer with a Rh target. A fundamental parameter method was also used for EDXRF quantitative analysis. XPS measurements were performed on a JEOL TRXPS spectrometer (JPS9010 TRX). Wide scan measurements (1 eV/step) were carried out at the glancing angle of 10°. ICP-AES measurements were performed using
an SII SPS3000 (cooling pipe sample analysis) and a SPECTROBLUE (fume hood sample analysis) ICP-AES spectrometer. An external calibration curve method was used for quantitative determination during ICP-AES analysis.

4.3 Results and Discussion

With regard to the energy-dispersive techniques (TXRF, SEM-EDX, and EDXRF), spectral energy was calibrated by measuring standard samples of known composition. Figure 3 shows the energy versus channel number linearity plotted using characteristic X-ray peaks of Si, Mn, As, Ag, and Cd in a TXRF spectrum. The six peaks, applied to the energy calibration, were from the low, medium, and high energy region in the TXRF spectrum of the mixed standard solution of Mn, As, Ag, and Cd. Si was detected because of the quartz sample carrier. Since the energy versus channel number shows a high degree of linearity ($R^2 = 0.9999$), the energy calibration was applied to the following measured TXRF spectra.

Figure 4 shows a TXRF spectrum for the cooling pipe sample and the spectrum of the blank (ultrapure water). Table I summarizes the elements and compounds determined by TXRF and other analytical techniques. It can be seen from Fig. 4 that the K Kα peak strongly overlapped with the Ar peak. Ar was detected in both spectra due to the fact that measurements were performed in air. Ag and Sn possibly arise from the solder used in the spectrometer, which is consistent with the previous research. In total, three elements (Na, S, and K) were detected in the sample. The Si peak (coming from the optical flat) in the spectrum of the blank was more prominent than in the spectrum of the sample, indicating that the water residue on the optical flat was thinner than that of the sample. Therefore, under the same measurement conditions, the absorption of the
Fig. 3 Energy vs channel number calibration obtained by using the characteristic X-ray peaks of Si, Mn, As, Ag and Cd in a TXRF spectrum of the mixed standard solution containing Mn, As, Ag, and Cd.

Fig. 4 TXRF spectra of the cooling pipe sample (solid line) and the blank sample of ultrapure water (dotted line).
TABLE I. Determined elements and/or chemical compounds with each analytical technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Determined elements and/or compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling pipe sample</td>
<td>TXRF</td>
<td>Na, S, and K</td>
</tr>
<tr>
<td></td>
<td>SEM-EDX</td>
<td>Na, S, and K</td>
</tr>
<tr>
<td></td>
<td>WDXRF</td>
<td>C, O, Na, Mg, Si, P, S, Cl, K, and Ca</td>
</tr>
<tr>
<td></td>
<td>XRD</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;•H&lt;sub&gt;2&lt;/sub&gt;O and NaHCO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>XPS</td>
<td>C, N, O, Na, S, and SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>ICP-AES</td>
<td>Cd was not detected.</td>
</tr>
<tr>
<td>Fume hood sample</td>
<td>TXRF</td>
<td>Al, Cl, Ca, Mn, Fe, Co, Ni, Zn, Br, and Zr</td>
</tr>
<tr>
<td></td>
<td>EDXRF</td>
<td>Cl, Ca, Fe, Zn, Br, and Zr</td>
</tr>
<tr>
<td></td>
<td>XPS</td>
<td>C, N, O, Al, Cl, and Zn</td>
</tr>
<tr>
<td></td>
<td>ICP-AES</td>
<td>14 ppm Cd and 92–162 ppm Pb</td>
</tr>
</tbody>
</table>

Water residue to the incident and emitted radiation was weaker compared to the sample residue. Consequently, more incident X-ray photons could go through the water residue and penetrate into the optical flat; thus, more Si X-ray fluorescence was generated and emitted. Meanwhile, the thick residue of the sample absorbed more incident X-ray photons resulting in more scattering, which increased the spectral background in the energy range of 4–11 keV compared to what was seen in the spectrum of the blank. Na, S, and K in the sample were also detected by both SEM-EDX and WDXRF. In addition, WDXRF also detected Mg, Si, P, Cl, Ca, and the low-Z elements C and O. Among the elements detected by WDXRF, the Ca intensity was much lower compared to the others. For instance, the intensity was one thirtieth of the K intensity. Therefore, Ca was not considered in WDXRF semi-quantification analysis. If C and O were also not considered in the semi-quantification, the results suggest that 79.0 wt. % of Na, 13.1 wt. %
of S, and 6.0 wt. % of K were included in the sample. The relative standard deviations for Na, S, and K were 1.5%, 1.6%, and 2.2%, respectively. The weight percentages of Mg, Si, P, and Cl were below 1.0%. Based on the analytical results of TXRF, SEM-EDX, and WDXRF, it is found that the major elements Na, S, and K in the sample could be detected by all the three methods; however, the minor composition Mg, Si, P, Cl, and Ca could only be detected by WDXRF. Si could not be detected by TXRF due to the quartz sample carrier. Possible reasons as to why TXRF could not detect Mg, P, Cl, and Ca may be due to: (1) their characteristic K-lines are between 1.2 and 4.0 keV, whereas the detection efficiency of an energy dispersive spectrometer strongly diminishes for X-ray photons below 2 keV; (2) the characteristic peaks of Si and Ar in the TXRF spectra as well as the three peaks of the major elements Na, S, and K could strongly overlap with the Ka peaks of Mg, P, Cl, and Ca; (3) Cl is a highly volatile element. Even though drying time during the sample preparation was controlled, it might still volatilize. XRD results demonstrate that the major and minor components in the sample were thermonatrite (Na$_2$CO$_3$$\cdot$H$_2$O) and nahcolite (NaHCO$_3$), respectively. Furthermore, a small amount of sodium carbonate sulphate (Na$_4$CO$_3$SO$_4$) may also be present within the sample. However, the corresponding component of K whose presence had been demonstrated by TXRF, WDXRF, and SEM-EDX could not be identified by XRD analysis. The presence of sulphate (SO$_4^{2-}$) in the sample was confirmed by observing the chemical shift of the S 2p peak from XPS analysis. XPS results also show the presence of Na, N, and C at the surface of the sample. However, C and O signals in the XPS analysis may be mixture of sample and surface contamination. This is because C and O peaks could be detected not only from sample, but also from surface contamination. Toxic elements of interest, such as Cd, were not found in the cooling
pipe sample by any of the employed techniques. ICP-AES analysis also suggests that no Cd was present in the sample. Accordingly, there was no conclusive evidence for the presence of Cd in the unknown cooling pipe sample. However, Cl, which is poisonous for all living organisms at high concentrations, was found in the sample by WDXRF. In contrast, Cl could not be found by TXRF or SEM-EDX.

Representative TXRF spectra of the fume hood pipe samples are displayed in Fig. 5. As stated in the Sec. II, three samples in total were collected from the fume hood pipes, two of which came from laboratory A. TXRF spectra of the two samples show the same elemental composition; therefore, only one TXRF spectrum from laboratory A was shown in Fig. 5. The TXRF results show that, apart from the two inherent peaks of Si and Ar, light metal Al, alkaline earth metal Ca, transition metals Mn, Fe, Co, Ni, Zn, and Zr, and halogens Cl and Br were detected in both the samples. Furthermore, sum peaks of Zn were observed in both spectra due to the high concentration of Zn within the samples. Ag and Sn (possibly arising from the solder) were also detected. Ca and Ti were detected in the blank samples, possibly the result of contamination during sample preparation. Although the two samples were collected from different fume hood pipes in two separate laboratories (as described in Sec. II), the elemental compositions of the two samples were the same. This indicates that the two fume hood pipes were exposed to identical environments which ultimately resulted in the formation of the hazardous precipitates. As shown in Table I, Cl, Ca, Fe, Zn, Br, and Zr were also detected by EDXRF. However, EDXRF could not detect light metal Al and transition metals Mn, Co, and Ni because of the lower sensitivities of EDXRF for these elements compared to TXRF. The EDXRF quantitative results (with relative
Fig. 5 Representative TXRF spectra of the fume hood pipe samples collected from laboratory A (a) and B (b) (solid line), and the blank samples of ultrapure water (dotted line). The spectra were plotted by using the mean values of four TXRF measurements.
standard deviation of 0.2%) suggest that 76.8–78.4 wt. % of Zn was included in the fume hood samples. Detected elements by XPS were C, N, O, Al, Cl, and Zn. The analysis depth of XPS is shallower than 10 nm. As a result, XPS may detect different elements from EDXRF. This can be seen from Table I, which shows that Ca, Fe, Br, and Zr detected by EDXRF were not detected by XPS. Additionally, lower detection limits of XPS are about 0.1 at. %. Elements lower than the detection limits could not be detected. C and O signals in the XPS analysis may also be mixture of sample and surface contamination due of the reasons outlined earlier. Compared to the TXRF, EDXRF, and XPS results, ICP-AES analysis (with relative standard deviation of 10%) shows that the toxic elements, Cd (14 ppm) and Pb (92–121 ppm), were also present in the samples. As demonstrated by Fig. 5 and Table I, Cd and Pb could not be detected by TXRF, EDXRF, and XPS. The elements Al, Ca, Mn, Fe, Co, Ni, Zn, Zr, and Pb within the unknown samples most likely come from the stainless-steel fume hood pipes and the Al alloy paper used to wrap the pipes, because these elements are often applied as alloying elements in the steel and Al alloy industries. In this respect, Ca,21 Mn, and Zn (Ref. 22) are common alloying elements in Al alloys; Mn (Ref. 23) and Ni (Ref. 24) are often used to increase the strength of steel; Co (Ref. 24) increases the hardness and tempering resistance of steel; Zn (Ref. 23) and Zr (Ref. 25) are applied to protect steel from rust or corrosion; and Pb (Ref. 26) may be added to steel to improve its machinability. However, how the substances precipitated on the pipes is yet to be determined. In addition, the reason why toxic elements such as Cl, Br, and Cd were present in the substances is also an open question. Since toxic elements such as Cl, Cd, Br, and Pb were found, the existence of the hazards in the laboratory cannot be neglected. Periodical checking and monitoring of the hazards as well as assessing
indoor air quality of the laboratories on a regular basis should be conducted with the aim of protecting the health and safety of laboratory personnel and office occupants.

4.4 Summary and Conclusions

A portable TXRF spectrometer was applied in response to an urgent analytical requirement regarding the identification of unknown laboratory hazards that precipitated on exterior surfaces of cooling pipes and fume hood pipes. By comparing TXRF results with those of WDXRF, SEM-EDX, EDXRF, ICP-AES, XRD, and XPS, it was found that the detection sensitivity of TXRF analysis was not sufficient to detect all the elements in the unknown sample, in particular, the toxic elements Cd and Pb. The minimum detection limits (MDLs, absolute amount) of the present TXRF spectrometer were estimated to be 33 ng for Cd and 11 ng for Pb. When 5 μL of the dissolved solution was used during TXRF analysis, the MDLs (relative concentration) were 6.6 ppm for Cd and 2.2 ppm for Pb. The MDLs were lower than the concentrations of Cd and Pb determined by ICP-AES, which were 14 ppm for Cd and 92–162 ppm for Pb. However, Cd and Pb could still not be detected by TXRF. This is because the MDLs of the spectrometer were evaluated by using standard solutions, which can be regarded as ideal samples because the spectral peaks of the analyte were free from interference, and the spectral background was low. Accordingly, the evaluated MDLs could not represent the sensitivity of a spectrometer in real unknown sample analysis, because real sample analysis is usually characterized by multiple elements, interferences, and high background, like the analysis of the unknown hazards studied in this paper. ICP-AES was sensitive enough for the present problem, but it is not always easy to know the overall tendency of elements. TXRF was also unable to detect the presence of the toxic
element Cl and minor elements Mg, Si, P, and Ca in the cooling pipe sample due to insufficient detection efficiency, two inherent Si and Ar peaks and spectral overlaps in the energy range below 4.0 keV, and the possible volatilization of Cl during the sample preparation. Thus, TXRF itself was not sufficient to provide full elemental profiles (Z > 11) in an unknown sample. It was also found that XRD method itself was unable to accurately determine all the chemical components in the sample, and the existence of sulphate had to be confirmed by XPS. These results demonstrate that in unknown sample identification, final conclusions should not be drawn based on the results from one analytical method. At least two analytical methods should be considered when analyzing the composition of unknown real samples.

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References


Chapter 5

Trace Elemental Analysis of Leaching Solutions of Hijiki Seaweeds by a Portable Total Reflection X-ray Fluorescence Spectrometer*

Abstract

A portable total reflection X-ray fluorescence spectrometer (TXRF) was used to analyze leaching solutions of hijiki seaweeds. S, Cl, K, Ca, Ti, Fe, Ni, As and Br were detected in the solutions. Arsenic quantification results were compared to those from ICP-AES. The TXRF quantification results of arsenic were not significantly different from those of ICP-AES, as two-way analysis of variance (ANOVA) method was applied to the significance test. This kind of small and high sensitive TXRF spectrometer can be used in food quality and environmental pollution investigation.

Key words: Portable spectrometer, Total reflection X-ray fluorescence spectrometry, Hijiki, Nutrition elements, Arsenic

*This chapter is based on Y. Liu, S. Imashuku, and J. Kawai, Adv. X-Ray. Chem. Anal., Japan, 45, 203 (2014). (This paper is originally published in Japanese. In order to realize the linguistic consistency of this thesis, it is translated into English.)
5.1 Introduction

In the development of X-ray fluorescence spectrometer, there is a trend towards small-scale (bench-top and hand-held) type from large floor-standing model. Bench-top total reflection X-ray fluorescence spectrometer (TXRF) with a 40~50 W X-ray tube (employs a forced air-cooled design) and a monochromator/low-pass filter has been developed since the year 2000. The detection limits ranging from a few to a few tens of picograms have been achieved using the beach-top TXRF. On the other hand, Kuminura et.al have developed a portable TXRF with a low power X-ray tube (1~5 W) since the year 2006. Although weak X-rays were applied, elements in picogram range could be detected. At the beginning, a 1 W X-ray tube (Hamamatsu Photonics, Hamamatsu, Japan) was used in the portable TXRF as an excitation source.1, 2 and a detection limit of 1 ng was achieved for Cr. However, because the maximum operational voltage of the X-ray tube was 10 kV, toxic elements, such as arsenic, cadmium, mercury and lead, could not be detected. Therefore, a 40~50 kV X-ray tube (Moxtek, Orem, USA) was applied since 2008 in order to detect a wider range of elements. A 10 picogram detection limit was achieved by the portable TXRF. This value is only four orders of magnitude higher than that obtained by synchrotron radiation induced TXRF. The portable TXRF has been applied to the elemental analysis (ppm or ppb level) of urine,1 drinking water,5 wine,6 rain,7 leaching solutions of toy,8 metal materials,9 soil,9 and aqueous solution containing a small amount of cadmium.10

The high sensitive portable TXRF is considered suitable to performing trace elemental analysis in hijiki seaweed. Hijiki seaweed, which belongs to the Sargassum genus, is a brown sea vegetable growing wild on rocky coastlines around Japan, Korea, and China. Hijiki seaweed is a traditional food in Japan. It is known to be rich in
essential elements such as calcium, potassium, and iron. However, hijiki contains potentially toxic quantities of inorganic arsenic (about 50\% of the total arsenic). Therefore, the food safety agencies of several countries such as Canada, the United Kingdom, and New Zealand have advised against its consumption. Since tens of ppm arsenic is contained in dried hijiki, fast detection of arsenic and the other elements in tens of ppm range can be carried out on site by hand-held XRF. However, it is not easy for hand-held XRF to detect the elements less than 10 ppm. In order to detect these elements, ICP-MS, ICP-AES, and AAS methods are commonly used. But these methods require dissolving samples in acid, and the long and laborious sample pre-treatment step results in possible analyte loss and contamination. In addition, the on-site analytical results of dried hijiki obtained by a hand-held TXRF cannot represent the actual intake of the people who consume hijiki. This is because dried hijiki is usually soaked in water as a pre-cooking treatment. During the soaking, 28-60\% of total arsenic is removed from dried hijiki at room temperature.\textsuperscript{11,12} Although water-soaking process can elute arsenic from dried hijiki, other nutrition elements may also be eluted into the water. Accordingly, it is of importance to analyze the water extract. Analytical results of the water extract not only show water-soluble elements including arsenic in dried hijiki, but also show the lost nutrition elements during soaking process. Furthermore, the results can provide references with respect to food nutrition. In this study, we analyzed the leaching solutions of four commercially available hijiki seaweed products (made in Japan or South Korea) using a portable TXRF. Arsenic quantification results were compared to those from ICP-AES, in order to evaluate the accuracy of the results obtained by the portable TXRF. The suitability of the portable TXRF for the qualitative
analysis of trace elements and the quantitative analysis of toxic element arsenic in actual food sample was evaluated.

5.2 Experimental

5.2.1 Portable total reflection X-ray fluorescence spectrometer

The schematic view and detailed information of the portable TXRF spectrometer were reported elsewhere by Kunimura et al.\textsuperscript{1,2}. The spectrometer (less than 5 kg) mainly consisted of a low-power X-ray tube, a collimator, a detector, and a sample stage. The present portable TXRF spectrometer used a 4 W X-ray tube with a Rh target (40 kV Magnum, Moxtek, Orem, UT). A waveguide slit was placed in front of the X-ray tube to restrict the incident radiation to a parallel beam of 10 mm in width and 10 μm in height. X-ray fluorescence signals were recorded by a Si-PIN photodiode detector with an effective area of 7 mm\textsuperscript{2} (X-123, Amptek, Bedford, MA). A quartz optical flat (Sigma Koki, Tokyo, Japan. \(\lambda/10\) of surface flatness, \(\lambda = 632.8\) nm) was used as a sample holder. All measurements were performed in air. Incident angle was adjusted via a goniometer.

5.2.2 Sample preparation and measurements

Four commercially available hijiki seaweed products in Japanese market were analyzed. The four hijiki seaweed samples' origins, certified mineral nutrition contents, and categories are shown in Table 1. Their photos are shown in Fig. 1. Dried hijiki of 0.0015 g was weighed and then was soaked in 20 mL ultrapure water for LC/MS (Wako Pure Chemical Industries). After 1-hour or 3-hour soaking, a 1-μL aliquot of the leaching solution was pipetted onto the quartz optical flat and subsequently dried on a
Table 1 Origin, mineral nutrition content (certified on the package), and category of the four *hijiki* seaweed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>Mineral Nutrition Content (mg / 10 g)</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Na</td>
<td>Ca</td>
</tr>
<tr>
<td><em>me-hijiki</em>-1</td>
<td>Japan</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td><em>me-hijiki</em>-2</td>
<td>South Korea</td>
<td>13</td>
<td>—</td>
</tr>
<tr>
<td><em>naga-hijiki</em>-1</td>
<td>Japan</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td><em>naga-hijiki</em>-2</td>
<td>Japan</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

heating plate. Four independent replicate measurements were carried out for each sample by the portable TXRF. Blank samples of ultrapure water were also prepared and analyzed under the same measurement conditions as the *hijiki* samples. Measurement time was 600 seconds. X-ray tube was operated at 25 kV and 100 µA. Glancing angle was set to 0.04°. Arsenic standard solutions of 0, 0.5, 1.0, 5.0 and 10.0 ppm were prepared by diluting a 1000 ppm arsenic standard solution for atomic absorption (Nacalai Tesque) with ultrapure water. Calibration curve method was used for arsenic quantification. In order to evaluate the accuracy of the arsenic quantification analysis by the portable TXRF, the results were compared to those obtained by ICP-AES (SPS 3520 UV, SII NanoTechnology).

5.3 Results and Discussion

Fig. 2 shows TXRF spectra of the leaching solutions of *hijiki* samples after 1-hour and 3-hour soaking in ultrapure water. Table 2 lists detected elements in the leaching solution of each *hijiki* sample. TXRF spectra of the blank samples are shown in Fig. 3. Ar and Si were detected due of air containing 0.93% Ar and the quartz optical
flat. As shown in Table 2, chlorine, potassium, calcium, iron, arsenic and bromine were detected in all hijiki samples. In addition, sulfur in me-hijiki-1, sulfur, titanium and nickel in me-hijiki-2, nickel in naga-hijiki-1, nickel and sulfur in naga-hijiki-2 were detected. Previous studies\textsuperscript{13-16} reported that dried hijiki contains sulfur, chlorine, potassium, calcium, iron, arsenic, bromine and nickel. Titanium was only detected in the dried hijiki made in South Korea. There was no difference in the elemental composition between me-hijiki and naga-hijiki. Compare to the certified mineral nutrition contents shown on the packages of dried hijiki seaweed products (Table 1),
Table 2 Detected elements in the leaching solution of each hijiki seaweed sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Detected elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>me-hijiki-1</td>
<td>S, Cl, K, Ca, Fe, As, Br</td>
</tr>
<tr>
<td>me-hijiki-2</td>
<td>S, Cl, K, Ca, Ti, Fe, Ni, As, Br</td>
</tr>
<tr>
<td>naga-hijiki-1</td>
<td>Cl, K, Ca, Fe, Ni, As, Br</td>
</tr>
<tr>
<td>naga-hijiki-2</td>
<td>S, Cl, K, Ca, Fe, Ni, As, Br</td>
</tr>
</tbody>
</table>

Magnesium and sodium were not detected by the portable TXRF. This might be due to the following reasons: (1) the detection efficiency of an energy-dispersive spectrometer strongly diminishes for X-ray photons below 2 keV energy; (2) solubility of magnesium and sodium in water is smaller than that of iron and calcium; (3) interferences of escape peaks of the Ar- and Cl-Kα lines. The TXRF measurements found the presence of potassium, sulfur and chlorine in the dried hijiki seaweeds. The three elements were not certified on the packages of the hijiki products.

Fig. 2 shows TXRF spectra of the leaching solutions of the four hijiki samples after 1-hour (A, C, E, G) and 3-hour (B, D, F, H) soaking in ultrapure water. It is seen from Fig. 2 that the amount of dissolved nutrition elements potassium and iron in ultrapure water increased with soaking time. Areas of potassium Kα peaks (counts/600 s) were increased to 20582 from 15125 (me-hijiki-1), 15107 from 13399 (me-hijiki-2), 3392 from 3124 (naga-hijiki-1), and 16741 from 15672 (naga-hijiki-2). In case of Fe Kα peak areas, the values were increased to 213 from 119 (me-hijiki-1), 1984 from 704 (me-hijiki-2), 252 from 236 (naga-hijiki-1), and 139 from 135 (naga-hijiki-2). The amount of dissolved potassium after 3-hour soaking in ultrapure water was increased by 36% and 13% for two me-hijiki samples, 9% and 7% for two naga-hijiki samples. The
Fig. 2 TXRF spectra of the leaching solutions of *me-hijiki*-1 (A and B), *me-hijiki*-2 (C and D), *naga-hijiki*-1 (E and F), and *naga-hijiki*-2 (G and H) after 1-hour (A, C, E, G) and 3-hour (B, D, F, H) soaking in ultrapure water.
values for iron were 78\% and 182\% for two me-hijiki samples, 7\% and 3\% for two naga-hijiki samples. Therefore, compared to naga-hijiki, me-hijiki seaweed was more strongly influenced by soaking time with regard to potassium and iron dissolution.

Table 3 shows the results of arsenic quantification by TXRF and ICP-AES analysis. Two-way analysis of variance (ANOVA) method was applied to test the significance of the results obtained by the two methods. From the ANOVA analysis results shown in Table 4, it is found that the TXRF quantification results of arsenic were not significantly different from those of ICP-AES ($F_A = 0.0243 < F_{0.05} (1, 3) = 10.13$), whereas arsenic concentrations in the leaching solutions of four hijiki samples were significantly different ($F_B = 68.441 > F_{0.05} (3, 3) = 9.28$). Concentrations of arsenic
Table 3 Concentrations (ppm) of arsenic from TXRF and ICP-AES analysis in the leaching solutions after 1-hour soaking in the ultrapure water.

<table>
<thead>
<tr>
<th>Method</th>
<th>me-hijiki-1</th>
<th>me-hijiki-2</th>
<th>naga-hijiki-1</th>
<th>naga-hijiki-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TXRF</td>
<td>2.32</td>
<td>2.20</td>
<td>0.97</td>
<td>1.19</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>2.42</td>
<td>1.95</td>
<td>1.01</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 4 Two-way analysis of variance (ANOVA) table.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Degree of Freedom</th>
<th>Mean Square</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method (Factor A)</td>
<td>0.0003</td>
<td>1</td>
<td>0.0003</td>
<td>0.0243</td>
<td>0.8860</td>
<td>10.13</td>
</tr>
<tr>
<td>Hijiki Sample (Factor B)</td>
<td>2.638</td>
<td>3</td>
<td>0.879</td>
<td>68.441</td>
<td>0.003</td>
<td>9.28</td>
</tr>
<tr>
<td>Error</td>
<td>0.039</td>
<td>3</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2.6764</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

were higher in the leaching solutions of *me-hijiki* seaweeds than those of *naga-hijiki* seaweeds. Kunimura *et al.*\(^1\) applied a portable TXRF with an “50 kV Magnum” X-ray tube (W target, Moxtek) to the analysis of arsenic in urine. When the X-ray tube was operated at 25 kV and 200 \(\mu\)A (5 W), arsenic of 1 ng in the urine could be detected. In this study, X-ray tube was operated at 25 kV and 100 \(\mu\)A (2.5 W). Although the X-ray tube power was reduced by 1/2, arsenic in nanogram range could also be detected. Based on the calibration curve of arsenic in Figure 4 and the following equation, detection limit for arsenic achieved by the present portable TXRF was calculated to be 210 ppb.

\[
C_{LLD} = 3 \times \frac{\sigma}{a}
\]  

(1)
where $C_{LLD}$ is the detection limit (ppm); $\sigma$ is the standard deviation of six time measurements of a blank sample; $a$ is slope of the calibration curve.

### 5.4 Conclusions

A portable TXRF was used to analyze leaching solutions of four commercial *hijiki* seaweed products. The portable TXRF not only could detect the nutrition elements (calcium and iron) listed on the packages of the dried *hijiki* seaweed products, but also could detect the elements that are not listed on the packages, such as nutrition elements of potassium, sulfur, chlorine, and toxic elements of arsenic and bromine. The TXRF quantification results of arsenic (ppm order) were not significantly different from those of ICP-AES. In TXRF analysis, the dry residue of a small amount of liquid sample can be assumed to be a thin film. Therefore, matrix effects during TXRF measurements can be neglected, and then it is possible to simultaneously quantify multi-elements by
adding an internal standard with known concentration into the sample. By comparison, quantification analysis of ICP-AES relies on calibration curves; therefore, simultaneous multi-element quantification by ICP-AES is impossible. As an alternative to ICP-AES, this kind of small and high sensitive TXRF spectrometer can be used for trace elemental and/or toxic elemental determination such as arsenic in the investigation of food quality, environmental pollution, and children’s toys.

Acknowledgements

The authors would like to thank Kengo Ohira (Department of Materials Science and Engineering, Kyoto University) for his Japanese correction.

References


Chapter 6

Low Power Total Reflection X-ray Fluorescence Spectrometer using Diffractometer Guide Rail*

Abstract

An X-ray diffractometer (XRD) was modified to a low power total reflection X-ray fluorescence (TXRF) spectrometer. This was realized by reducing the XRD tube power (3 kW) down to 10 watts by a Spellman power supply. The present spectrometer consisted of a waveguide slit, a Si-PIN detector, a goniometer and two Z-axis stages that were set on a diffractometer guide rail. This unit was small and easy in assembly. The first measurements with this spectrometer were presented. The minimum detection limit for Cr was estimated to be a few nanograms or at the level of $10^{13}$ atoms/cm$^2$.

Key words: Low power TXRF, High power XRD tube, Power supply, Diffractometer guide rail

*This chapter is based on a paper submitted to the journal “Powder Diffraction” in June, 2014. This topic was orally presented at “The 15th International Conference on Total Reflection X-Ray Fluorescence Analysis and Related Methods, Osaka, Japan, Sep. 23-27, 2013.” by Y. Liu, S. Imashuku, and J. Kawai.
6.1 Introduction

In total reflection X-ray fluorescence (TXRF) spectrometry, monochromatic X-rays from high power X-ray sources (kW X-ray tube or synchrotron radiation) are generally used for the detection of trace and ultra-trace elements (Klockenkämper, 1997; Wobrauschek, 2007; Streli et al., 2008). Using monochromatized synchrotron radiation (SR) for TXRF analysis has made it possible to detect elements in the femtogram ($10^{-15}$ g) range. However, such low detections limits were only achieved for several elements in Si wafer analysis (Wobrauschek et al., 1997; Sakurai et al., 2002; Streli et al., 2006). In addition, the limited access to SR facility restricts its practical applications in semiconductor industry. On the other hand, Kunimura and Kawai (2007) have developed a portable TXRF spectrometer with a 1 W X-ray tube, and found that when low power X-ray tube was used, non-monochromatic TXRF was more sensitive than monochromatic TXRF. The lowest detection limit of 10 picogram achieved by the portable TXRF (Kunimura and Kawai, 2010a) was only four orders of magnitude higher compared to that obtained by an SR-TXRF spectrometer. The portable TXRF spectrometer has been proved a versatile tool by which many analytical problems could be satisfied (Kunimura and Kawai, 2010a; Liu et al., 2013). Accordingly, low power TXRF technique without incident beam monochromatization is rapidly becoming an alternative method in TXRF spectrometry to efficiently perform rapid multi-elemental determination at low cost. At the same time, the realization of the low power TXRF analysis is severely limited to the laboratory that has an appropriate X-ray source – a specially designed X-ray tube for low power load (<10 watts). While this limitation might be reduced if a high power X-ray source existing in a widely used laboratory instrument, such as X-ray diffractometer (XRD), could be switched its use to low power.
TXRF analysis. The application of XRD tube in high power TXRF analysis has been reported previously (Wobrauschek and Kregsamer, 1989; Greaves et al., 1995; Wobrauschek et al., 2008). For instance, Wobrauschek and Kregsamer (1989) developed a compact unit carrying all necessary components for high power TXRF analysis that can be attached to the tube housing for XRD tube. In contrast to the application of XRD tube in high power TXRF analysis, in the present report, with the aim to explore the suitability of high power XRD tube to low power TXRF analysis, we modified an XRD to a low power TXRF spectrometer by reducing the XRD tube power (3 kW) down to 10 watts by a power supply.

6.2 Experimental

Schematic of the low power TXRF spectrometer setup is presented in Fig. 1. The set-up comprised of an XRD tube, a power supply, a water cooling unit, a waveguide slit, a goniometer, two Z-axis stages, a diffractometer guide rail and an X-ray detector. Apart from the power supply and water cooling unit, all the other elements were contained in a box with the size of 40 cm (height) × 40 cm (width) × 45 cm (length). A Mo-target X-ray tube (PW2275/20, Philips, Netherland) that originally used in an XRD (XD-3A, Shimadzu, Japan) was employed as an excitation source. Four Be windows (300 μm) allowed simple changeover from line to point focus and vice versa in this tube. In this set-up one Be window through which the X-rays emerged with a line focus of 0.4 × 12 mm was used. The anode design of the XRD tube was capable to power loads up to 3 kW (60 kV max. and 50 mA max.). However, the tube was reduced its power down to 10 watts by a Spellman power supply (30 kV max. and 10 mA max., Model: DXM30*300, Spellman, USA). A standard shielded RS-232 cable was used to
connect the power supply to the serial port on a standard personal computer. Remote programming and monitoring the output voltage and current was allowed via RS 232 interface of the power supply. A simple water cooling unit consisting of a magnetic drive centrifugal pump (MD-6, Iwaki, Japan) was made for the tube cooling. The maximum operating pressure of this pump is 0.02 MPa. At zero discharge head, the pump can provide the maximum flow of 8/9 L/min. A waveguide slit proposed by Egorov and Egorov (2004) was placed in front of the X-ray exit window of the tube housing (Fig. 2). This slit was capable to restrict the continuum X-rays from the tube to
a parallel beam of 10 mm in width, 10 μm or 20 μm in height. Goniometer as well as two Z-axis stages were set on a diffractometer guide rail (Rigaku-Denki, Japan). In experiments, sample holder was put on top of the goniometer. The angle between the incident beam and the surface of the sample holder was manually adjusted via the goniometer. Vertical position of the sample carrier was manually adjusted via the Z-axis stages. The supporting plane of the guide rail was made to tilt by an angle of 6° with respect to the horizontal plane, with the aim of permitting the sample stage parallel to the primary beam at a take-off angle of 6°. The detector in use is Peltier-cooled Si-PIN photodiode detector (X-123, Amptek, USA) with an effective detection area of 7 mm² and silicon thickness of 300 μm. This detector unit contained a preamplifier and a digital signal processor in the detector housing and was directly connected to a computer via a USB cable.

Fig. 2 Photograph of the waveguide slit.
6.3 Results and Discussion

Fig. 3 shows two TXRF spectra of a blank quartz glass optical flat ($λ/20$ of surface flatness, $λ=632.8$ nm, Sigma Koki, Japan) measured at 20 kV, 0.5 mA and 10 kV, 1.0 mA, respectively. The scattered X-ray spectra were measured with the aim to estimate the spectral distribution of the primary X-rays. In both spectra, Si K-line, Mo Lα and Lβ lines, and Ar K-line were detected. Ar and Si were detected due of air containing 0.93% Ar and the quartz optical flat. At the voltage of 20 kV, the Si peak was higher than that at 10 kV. This is due to the fact that a thicker layer in the optical flat was passed through when the X-ray tube was operated at 20 kV since the penetration depth of the beam into the optical flat increased with X-ray photon energy increment. Mo L-characteristic X-rays were detected because of the anode material of the X-ray tube. Mo Lγ lines could not be seen in the spectra because they were overlapped with the strong Ar K-lines. Bremsstrahlung edge energy in each spectrum agreed well with the maximum energy of the X-ray photons at the corresponding accelerated voltage.

Fig. 4 shows the TXRF spectrum of a dry residue containing 2 $μg$ Mn measured at 10 kV and 1.0 mA. This sample was prepared by dropping a 2-$μL$ portion of a 1000 ppm Mn standard solution (Wako Pure Chemical Industries, Japan) onto the quartz optical flat and then dried on a heater. Si, Mo, and Ar peaks were detected because of the same reasons as those explained above. Both Mn Kα and Kβ lines from the sample residue were detected. The ratio of Mn Kα/Kβ intensity was 150:17, which agreed well with the theoretical value (Kortright and Thompson, 2009). The minimum detection limit (MDL) for Mn evaluated from the following equation was 35 ng.
Fig. 3 TXRF spectra for a blank quartz glass optical flat measured at the X-ray generator power of 10 watts. The dashed and dotted line was measured at 20 kV and 0.5 mA, the solid line was measured at 10 kV and 1.0 mA.

\[ Detection \ limit = 3m \sqrt{\frac{I_B}{I}} \]

where \( m \) is the sample amount (nanogram), \( I_N \) and \( I_B \) are the net and background intensity (counts/s), respectively, and \( t \) is the measurement time (s).

Fig. 5 shows the TXRF spectra for a dry residue containing 1 \( \mu \)g Cr measured at the glancing angles of 0.1° and 0.3°. The applied voltage was 10 kV and the electron current was 1.0 mA. Chromium was detected in both spectra. The potassium peaks were also detected because the Cr dry residue was obtained by pipetting 1-\( \mu \)L portion of a
Fig. 4 TXRF spectrum for a dry residue containing 2 µg Mn. X-ray tube was operated at 10 kV and 1.0 mA.

1000 ppm Cr standard solution for atomic absorption (K₂Cr₂O₇ in 0.015 mol/L HNO₃) (Nacalai Tesque, Japan) onto the quartz optical flat. Argon peaks were strongly overlapped with the potassium peaks. The signal-to-background ratios of the Cr Kα and Kβ peaks at the glancing angle of 0.1° were two times higher than those at 0.3°. At the angle of 0.1°, the net and background intensity of the Cr Kα peak were 263 and 60 counts/s, respectively. The MDL for Cr was estimated to be 5 ng. This was equivalent to 200 ppb Cr in 25 µL of solution, or the level of 10¹³ atoms/cm² if the irradiated area on the optical flat was assumed to be 1 cm². The MDL for Cr (5 ng) was 1/7 of that for Mn (35 ng), this might be attributed to the following reasons: (1) a waveguide slit with the height of 20 µm was used for Cr measurement, compared to the 10 µm in Mn measurement. Due to the fact that the incident beam intensity formed by the waveguide
Fig. 5 TXRF spectra for a dry residue containing 1 $\mu$g Cr measured at the glancing angles of 0.1° (solid) and 0.3° (dashed and dotted). X-ray tube was operated at 10 kV and 1.0 mA.

Slit increased as the increase of the slit height if slit height exceeds 3 $\mu$m (Egorov and Egorov, 2004), when the waveguide slit with the height of 20 $\mu$m was used more X-ray photons excited the Cr-containing dry residue; (2) the fluorescent X-rays of Cr were fully recorded since a smaller size dry residue was formed on the optical flat in Cr analysis (sample volume used in Cr analysis was 1/2 of that of Mn). The MDL for Cr (5 ng) was comparable to that obtained by the portable TXRF spectrometer with a commercial low power X-ray tube of 1 watt (Kunimura and Kawai, 2007), while it was two orders of magnitude higher than that obtained by the portable TXRF spectrometer with a commercial low power X-ray tube of 5 watts (Kunimura and Kawai, 2010b).
should be noted that the 5 ng MDL for Cr was achieved by the basic setting of this spectrometer without optimization with respect to the geometry and the experimental conditions. The detection sensitivity of the spectrometer would be increased via the optimization.

6.4 Conclusions

A low power TXRF spectrometer modified from an XRD was presented. The XRD tube was reduced its power (3 kW) down to 10 watts by a power supply. The suitability of high power XRD tube in low power TXRF analysis has been proven. The present TXRF spectrometer was easy in arrangement. The MDL for Cr was a few nanograms or at the level of $10^{13}$ atoms/cm$^2$. The initial results obtained by the present spectrometer are promising. Optimization of the geometry and experimental conditions should be conducted to enhance the performance of the spectrometer.
References


Chapter 7

Conclusions

7.1 Summary of this thesis

This thesis has presented the capability of low power portable TXRF technique in multi-element determination and its new applications in the fields of environment and food investigations. In Chapter 2, the experimental condition dependencies of a portable TXRF spectrometer in the analysis of multi-element solutions were studied. It is found that under the optimal excitation parameters (glancing angle of 0.04°, X-ray tube acceleration voltage of 25 kV, current of 100 μA) and the optimal sample amount of 1 μL, detection limits down to sub-nanograms were achieved for nearly all detected elements in a single TXRF run. This portable TXRF has been proved to be a suitable tool for simultaneously providing multi-elemental profiles of a wide range of elements with high sensitivity in a short time. In Chapter 3, the experimental condition dependency of the portable TXRF with regard to the substrate direction was further studied, and it is found that TXRF analysis was also affected by the substrate direction if a square shape optical flat was used as a sample holder, as the TXRF spectra measured in four substrate directions were significantly different. This is possibly due to a heterogeneous dry residue on the substrate after the drying process. In Chapter 4, the portable TXRF technique was applied to an urgent analytical requirement regarding unknown laboratory hazard identification. Based on the comparison among the qualitative results from TXRF, EDXRF, WDXRF, SEM-EDX, XRD, XPS and ICP-AES, it demonstrates that although TXRF is an easy and high sensitive technique to
analyze almost all the elements at a glance, the detection sensitivity may still not be enough in a real unknown sample analysis. At least two analytical techniques should be considered for real unknown sample identification. In Chapter 5, the elemental compositions of leaching solutions of *Hijiki* sea weeds were investigated by the portable TXRF. Both nutrition elements (some of them are not listed on the packages) and toxic elements (arsenic and bromine) were detected. Detection limit for arsenic was down to 210 ppb. It is demonstrated that the low power portable TXRF technique is suitable to trace elemental and toxic elemental determination such as arsenic in the food quality control.

Moreover, a newly developed low power TXRF spectrometer using a diffractometer guide rail has been reported in Chapter 6. The spectrometer with compact design proved the suitability of high power XRD tube (kW) in low power TXRF analysis, providing that a power supply reduces the X-ray tube's operational power down to 10 watts. The initial results obtained by the spectrometer are promising. Optimization of the geometry and measurement conditions should be conducted in the future to enhance the performance of the spectrometer.

### 7.2 Supplementary discussion

Several issues that were not addressed in the main text of this thesis are worthy to discuss here.

(1) *Divergence of the incident X-ray beam*

An Egorovs' waveguide slit was applied in the non-monochromatic and low-
power analytical technique as an X-ray collimator. Divergence of the X-ray beam formed by the waveguide depends on the slit size $S$ (distance between the two reflectors in the waveguide). The waveguide with a small slit size of $S \leq 0.2 \, \mu m$ is distinguished by the resonance (or quasi-resonance) manner of X-ray transportation, and the output angular aperture of the waveguide is the same as the input one ($< 2\theta_c$, $\theta_c$ is the critical angle for total reflection of the X-ray beam on the reflectors in the waveguide). The interval of the slit size of $0.2 \, \mu m \leq S \leq 3 \, \mu m$ is described by two independent components of direct and quasi-resonance propagating beams, and the output and input angular apertures are still the same ($< 2\theta_c$). Slit size that exceeds $3 \, \mu m$ is characterized by free passing and the multiple consequences of total reflection mechanisms of X-ray propagation through the slit. In this case, the output angular aperture is independent of the input one, and the value equals to $2\theta_c$.\textsuperscript{1-3}

The slit size of the waveguide used in this thesis was 10 $\mu m$ or 20 $\mu m$. Accordingly, divergence of the waveguide emergent beam (the incident beam in TXRF analysis) should depend on the critical angle $\theta_c$ for total reflection of the propagating X-rays on the reflectors in the waveguide. In addition, attenuation of the propagating radiation in the air core of the waveguide slit should be considered. The definitions of the critical angle and X-ray attenuation were not clear for non-monochromatic X-rays. Therefore, when non-monochromatic X-rays were used in the low power TXRF technique, divergence of the incident beam in TXRF analysis could not be
precisely determined.

(2) Formation of inhomogeneous dry residues on the sample carrier

The formation of an inhomogeneous dry residue after drying a drop on the sample carrier could be explained by the theory proposed by Deegan et.al\(^4,5\) and Popov.\(^6\) According to their theory, a contact line (the border where the surface of the drop contacts the surface of the sample carrier) is pinned in a drying drop when the surface irregularities (surface roughness or chemical heterogeneity) exist. In this case, an outward flow is produced so that the liquid removed by evaporation from the edge of the drop must be refilled by a flow of liquid from the interior.

The sample carrier used in this thesis is an optical flat with the surface flatness of \(\lambda/20\) or \(\lambda/10\) (\(\lambda = 632.8\) nm), which means the maximum peak to valley height difference across the clear aperture would be 31.64 nm (632.8/20) or 63.28 nm (632.8/10). The existence of the surface irregularities could anchor the contact line of the drop at one or more points. With the evaporation of the liquid, the outward flow is capable of transferring the solute particles to these points and then the contact line pinning is increased.\(^7\) Therefore, an inhomogeneous deposit could be produced on the sample carrier.

(3) Effect of surface flatness/roughness of the sample carrier on TXRF analysis

X-ray total reflection only appears when the medium is flat and smooth. For a rough surface, total reflection disappears. In the trace analysis of granular
residues, a sample carrier is necessary as it serves as both a sample support and a totally reflecting mirror. This carrier should highly reflect the X-rays that fall upon its surface as the spectral background in TXRF analysis is reduced in proportion to 1-R (R is the reflectivity). The high reflectivity could be ensured by using an optically flat carrier. Generally, the surface roughness should be less than 5 nm within an area of about 1 mm² (Ref. 8). The fact that the background scattering from the optical flat is dependent on its surface defects is due to the anomalous surface reflection (the secondary specular reflection of the small angle X-ray scattering from surface defects).\textsuperscript{9-10} The X-ray specular reflectivity considering the surface roughness is theoretically tractable.\textsuperscript{11-14} The web page (accessed 9th June, 2014) of The Center for X-Ray Optics at Lawrence Berkeley National Laboratory (http://henke.lbl.gov/optical_constants/mirror2.html) provides an on-line application for this calculation.

The effect of surface roughness of the substrate on angle dependent TXRF analysis has been previously studied.\textsuperscript{15, 16} However, few studies were found about the effect of the roughness/flatness on the detection sensitivity in TXRF analysis. In addition, the question as to why total reflection of X-rays happens on an optical flat with the flatness in the range of nanometer (typically > 25 nm) is open.

(4) \textit{Determination of toxic elements Cd and Pb by the portable TXRF}

As demonstrated in Chapter 4, detection sensitivity for Cd and Pb may not be enough in a real unknown sample analysis when a portable TXRF with a
Rh target was employed. There are several ways to solve this problem; however, the easiest one should be placing a foil filter in front of the X-ray tube to increase the signal-to-background ratio of the element of interest, since a filter can produce a quasi-monochromatic X-ray excitation beam by which the spectral background would be reduced. For example, Ag, Mo and Cu filters were employed in the Cd analysis by the portable TXRF, it is found that when the X-ray tube was operated at 30 kV and 80 µA, at the glancing angle of 2° the detection limit for Cd could be reduced by 1/2 after using a Cu filter with the thickness of 40 µm.
References

Academic Performance

List of published papers related to the present thesis


List of published papers not related to the present thesis


4. Liqiang Luo, Binbin Chu, Yingchun Li, Tao Xu, Xiaofang Wang, Jing Yuan, Jianling Sun, Ying Liu, Ying Bo, Xiuchun Zhan, Shuxian Wang, and Lijun Tang, Determination of Pb, As, Cd and trace elements in polluted soils near a lead–zinc mine using polarized X-ray fluorescence spectrometry and the characteristics of the elemental distribution in the area. *X-Ray Spectrometry*, 41(3), 133 (2012).


Oral and poster presentations at conferences


5. Ying Liu, Shinsuke Kunimura, Imashuku Susumu, Deh Ping Tee, and Jun Kawai: *High-Sensitivity Portable Total Reflection X-Ray Fluorescence Spectrometer (TXRF)*. The 10th Chinese X-Ray Spectrometry Conference, Chengdu, China, Jul. 31-Aug. 5, 2013. (Oral presentation)

Conference on Solution Chemistry (33ICSC), Kyoto, Japan, Jul. 7-12, 2013. (Poster presentation)


**Other academic activities**

1. Awarded financial support from International Atomic Energy Agency (IAEA) to participate in the 34th Berlin School on Neutron Scattering (Berlin, Germany, Mar. 13-21, 2014)

2. Selected as a representative (a total of four representatives) of Kyoto University to attend “The 2nd Global Young Scientists Summit @ one-north” in Singapore, Jan. 19-24, 2014.