Multi-Element Analysis by Portable Total Reflection X-ray Fluorescence Spectrometer

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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.

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, 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 Kα and Kβ 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

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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.

**Experimental**

**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, 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 H₂SO₄ and CuSO₄, 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 (λ/10 of surface flatness, λ = 632.8 nm). 1-μL aliquot of the 50 mg L⁻¹ solution, and 1, 5, 10 and 20 μL aliquots of the 1 mg L⁻¹ solution were pipetted and dried separately on the optical flat. Cleanliness of the optical flat before each use was checked by the same portable spectrometer.

**Apparatus**
A series of portable TXRF spectrometers with low power X-ray tubes were designed and developed by Kunimura and Kawai 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 photodiode detector (X-123, Amptek, Bedford, MA) that was cooled by a Peltier device and contained a preamplifier and a photodiode detector (X-123, Amptek, Bedford, MA). The detected signal was transmitted to 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.²

**Results and Discussion**

**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 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° for the SiO₂ substrate. This indicates that the critical angles for the X-rays with energies less than 25 keV were greater than 0.07° because the critical angle becomes larger as X-ray energy decreases. Thus, when glancing angles smaller than 0.07° were used, X-rays with energies lower than 25 keV could be totally reflected. Therefore, at glancing angles of 0.02° and 0.04°, the continuous incident beam was totally reflected. At 0.02°, 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°. At 0.14°, 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° in thickness.² The glancing angle dependence of a portable TXRF spectrometer was also investigated in previous research,²¹ in which a 1.5 W X-ray tube with a tungsten target was operated at 9.5 kV and 150 μA, 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°, 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° when the 4 W X-ray tube was operated at 25 kV and 50 μA.

Figure 2 shows the glancing angle dependence of fluorescence intensities of Sc, V, Mn, Co and Cu. At angles above 0.07°, 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.

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 × 10⁷ photons/μA s. The maximum count rate of a Si-drift detector is up to 10⁶ 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. 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.

Excitation parameter dependencies of background contributed by the optical flat

In the TXRF analysis, the Si fluorescence peak was generated by the SiO₂ optical flat. The excitation parameter dependencies of the Si fluorescence signal are shown in Fig. 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. This indicates that a thinner layer in the substrate was passed through with decreasing glancing angle, and consequently less fluorescence signal was produced. The 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.

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...
1.5 – 25 keV, and decreases outside this range. In Fig. 5(d), the glancing angle of 0.04°, the efficiency of the detector is above 25% for the X-rays from the Kα peaks of potassium strongly overlapped with the Ar peaks, so the detection limit for K was not considered here.

was used to calculate the detection limits:

\[
\text{Detection limit} = 3m \frac{\sqrt{I_{\text{BG}}I_t}}{I_{\text{Bkg}}}
\]

where \( m \) is the amount of a studied element (nanogram) in the sample, \( I_{\text{Bkg}} \) and \( I_{\text{Bkg}} \) 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 μA, and sample amount of 1 μL. 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 μL 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/cm² if we assume that the irradiated area is 1 cm². 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. The Kα peaks of potassium strongly overlapped with the Ar peaks, so the detection limit for K was not considered here.

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.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.

Acknowledgements

The authors acknowledge Dr. Shinsuke Kunimura for his helpful discussions and suggestions. The authors would also like to thank Deh Ping Tee for her cooperation at the early stage of the present research.

Table 1 Detection limits obtained at the glancing angle of 0.04°, voltage of 25 kV, current of 100 μA, and sample amount of 1 μL.

<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>
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<tr>
<td>Detection limit/ng</td>
<td>1.77</td>
<td>0.87</td>
<td>0.53</td>
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<td>0.23</td>
<td>0.43</td>
<td>0.27</td>
<td>0.50</td>
<td>0.47</td>
<td>0.37</td>
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References


