Development and applications of grazing exit micro X-ray fluorescence instrument using a polycapillary X-ray lens

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Abstract

A polycapillary X-ray lens is an effective optics to obtain a μm-size X-ray beam for micro-X-ray fluorescence spectrometry (μ-XRF). We developed a μ-XRF instrument using a polycapillary X-ray lens, which also enabled us to perform Grazing Exit μ-XRF (GE-μ-XRF). The evaluated diameter of the primary X-ray beam was 48 μm at the focal distance of the X-ray lens. Use of this instrument enabled two-dimensional mapping of the elemental distributions during growth of the plant “Quinoa”. The results of the mapping revealed elemental transition during growth. In addition, a small region of thin film was analyzed by GE-μ-XRF. We expect that GE-μ-XRF will become an effective method of estimating the film thickness of a small region.

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1. Introduction

X-ray fluorescence spectrometry (XRF) has unique advantages over other analytical methods in that it enables non-destructive, multi-elemental analysis and does not damage the sample. In addition, XRF analysis can be performed at ambient air pressure. These analytical characteristics are effective in the field of material research, especially for biomaterials. XRF has been applied to micrometer-scale analysis (μ-XRF) by using various X-ray optics to focus its μm-size X-ray beam [1,2]. It had been difficult to focus a hard X-ray for excitation in XRF. Recently, however, it was possible to obtain an intense and small X-ray beam in the laboratory by using a polycapillary X-ray lens [3–5]. This X-ray lens consists of several hundred thousand glass capillaries. Currently, analytical methods using electrons and ions, such as EPMA and SIMS, are used for analysis on a micrometer-scale. However, μ-XRF is superior to such methods because they require the sample to be placed in a vacuum, and the electron or ion bombardment damages the sample. In addition, μ-XRF, as well as some other micrometer-scale analytical methods, produces two-dimensional elemental mapping by scanning the primary X-ray beam [6].

In XRF, at grazing exit (GE) angles, the X-rays emitted from deep inside a sample are not detected by the detector. Therefore, this analytical method (GE-XRF) enables surface sensitive analysis. [7–9]. In addition, the angle of incidence is not important in GE-XRF. Therefore, surface analysis of a small region can be performed with a combination of GE-XRF and μ-XRF (GE-μ-XRF) [7–9].

2. Experimental

The experimental setup is schematically shown in Fig. 1. An X-ray tube with a Mo anode (spot size: 1.0 × 10 mm²) was used in point focus mode. It was operated at a tube voltage of 30 kV and a tube current of 20 mA (or at a tube voltage of 40 kV and a tube current of 30 mA).

The geometrical parameters of the polycapillary X-ray lens are as follows. In regard to focal distance, the distance from the X-ray source to the lens input was 60.5 mm and the distance from the lens output to the focal spot was 15.0 mm.
The lens was 67.7 mm long. The coefficient of power density amplification was 2650. The transmission efficiency was 2.08%. The lens captured X-rays that were emitted at a take-off angle of 5° from the X-ray tube.

This setup has two types of EDX-detectors. A silicon drift detector (SDD) [X Flash Detector Type 1201, RÖNTEC, Germany] (sensitive area: 10 mm², <150 eV FWHM at 5.9 keV) was used for μ-XRF analysis, while a Si(Li) detector [EMAX S-209, HORIBA, Japan] (sensitive area: 5 mm², 156.6 eV FWHM at 5.9 keV) was used for GE-μ-XRF analysis. The SDD was fixed at a large take-off angle of 40°. The distance from the detector to the sample was about 90 mm. The Si(Li) detector was placed at the grazing exit angle and equipped with a 60 μm slit. The distance from the detector to the sample was about 100 mm. Therefore, the broadness of solid angle for the detection was 0.035°. This detector was moved perpendicularly to the sample surface using a one-axis directional stage to change the take-off angle for X-ray detection in GE-μ-XRF analysis. The minimum step size of this stage was 8 μm. Therefore, the minimum angle of adjustment was 0.005°.

The sample position was controlled very precisely (±1 μm) in three directions using a three-axis linear positioning stage. Both stages were automated and controlled by a PC, which also stored the X-ray spectra.

3. Results and discussion

3.1. Evaluation of the beam diameter

The diameter of the X-ray beam was evaluated by a tungsten (W) wire with a diameter of 10 μm. The W wire was scanned perpendicularly through the X-ray beam. The X-ray tube was operated at a tube voltage of 30 kV and a tube current of 20 mA. As can be seen from Fig. 2a, a Full Width Half Maximum (FWHM) value of 48 μm was obtained at the focal distance of the polycapillary X-ray lens. This X-ray lens was designed and fabricated at Beijing Normal University, where the diameter was evaluated at less than 25 μm using a microfocus X-ray tube. However, since we used a commercial X-ray tube having a large focal dimension for electrons of 1.0 × 10 mm² in point focus mode (the effective size of the X-ray source was 1.0 × 1.0 mm², which is still large), the diameter of the primary X-ray beam actually obtained was not as small.

As can be seen from Fig. 2b, the diameter of the primary X-ray beam is sensitive to the distance between the sample and the X-ray lens, and it becomes wide if the sample position is far from the focal point. This tendency is also seen in Fig. 3, which shows the primary X-ray beam images (2D-image and 3D-image) obtained at different distances between the lens and the wire. In addition, it was confirmed that the maximum intensity of the beam becomes weak if the position of the sample is far from the focal point.
A Ni film deposited on a Si substrate was measured by GE-μ-XRF analysis. The Ni thin film, which was approximately 50 nm thick, was prepared by magnetron sputtering. The X-ray tube was operated at a tube voltage of 30 kV and a tube current of 20 mA. The sample was fixed, and the Si(Li) detector was moved perpendicularly to the sample at a take-off angle between 0.0° and 1.0° (minimum step size: 0.004°). The X-ray intensities of Ni Kα from the sample were recorded automatically as a function of the grazing exit angles. In addition, the X-ray intensities of Ni Kα were calculated according to a multilayer model [10]. In this calculation, the film thickness was included as one of the calculation parameters. The experimental and calculated X-ray intensities of Ni Kα as a function of the exit angle are shown in Fig. 4. As can be seen in this figure, the experimental and calculated results agreed well. Therefore, we can conclude that the film thickness is 50 nm. As mentioned above, this method would be effective for estimating the film thickness of a small region.

In addition, an oscillation structure was observed in the calculation curve of Fig. 4. This is considered to be the results of interference between the refracted X-rays at the Ni surface and the reflected X-rays at the Ni–Si interface. However, this oscillation was not observed clearly in the experimental plots because of the weakness of the observed intensities or the poor angle resolution in our instrument. Therefore, if a primary X-ray beam of a higher intensity, the better angle resolution by narrowing the slit width, and the longer measuring time could be applied, the thickness of the Ni film would be determined precisely.

3.3. In vivo X-ray mapping of a seed (Quinoa)

Elemental mapping of the seed of the Quinoa plant was performed. Quinoa has a high adaptability to cold regions, dry weather, and barren soil. The seed is rich in minerals and its size is about 2 mm. The photograph of the seed is shown in Fig. 5a and the seed with a sample holder is also shown in Fig. 5b. The seed was put on damp cotton, one end of which had been soaked in water, and attached to the sample holder perpendicularly. This arrangement enabled measurement of the seed while the plant was growing. The sample was scanned perpendicularly to the X-ray beam using a two-axis linear stage at the focal distance of the
X-ray lens. The X-ray tube was operated at a tube voltage of 40 kV and a tube current of 30 mA.

Fig. 6 shows the elemental mapping for the individual elements in the seed “Before growth” and the seed after the growth 1 day “After 1 day”. In “Before growth,” K and Ca are distributed over the pericarp. Fe is distributed over the embryo and its circumference, and Cu is distributed throughout a wider range. Previously, SEM-EDX analysis had been performed for the cross-section of the seed, and similar results had been obtained as for K and Ca [11]. In that experiment, the measurement for Mg and P had also been performed. In our experiment, however, these light elements could not be detected because of the absorption by the atmosphere. In addition, elemental distribution was concentrated on the left in every mapping as shown in Fig. 6. We think that it is because the detector was fixed on the left of the seed and X-ray fluorescence was hardly detected by the influence of the self-absorption on the right of the seed.

In “After 1 day,” a comparison between the mapping results “Before growth” and “After 1 day”, confirms the transition of the elemental distributions (K, Ca) during growth of the seed. Throughout growth, the K signal was strong at the stem (the cotyledon and the hypocotyl), while the Ca signal was strong at some specific parts of the seed. As far as we know, this is the first time that the transition of elemental distribution during growth has been demonstrated.

As mentioned above, we expect that elemental mapping will become an effective research method for the transition of elements during plant growth.

4. Conclusion

In this research, we developed an instrument for conducting μ-XRF and GE-μ-XRF analysis. A polycapillary X-ray lens was used for obtaining a μm-size primary X-ray beam with this instrument; the beam diameter was 48 μm at the focal distance of the X-ray lens. Elemental mapping by μ-XRF and surface analysis of a small region by GE-μ-XRF was performed by using this instrument. As an application for elemental mapping, we expect that this instrument will be effective in the research of the elemental transition during plant growth. Moreover, as an application for the surface analysis of a small region, we expect that the instrument will be effective in measuring thin film thickness.

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