Effects of an X-ray absorber in Grazing Exit Micro X-ray Fluorescence Analysis of Arsenic Attached to an aqueous leaf of *Camellia hiemalis*

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Aqueous leaf of *Camellia hiemalis* [mm]

Grazing exit micro X-ray fluorescence analysis (GE-µ-XRF) using an X-ray absorber method was applied to an analysis of Pb attached to an aqueous leaf of *Camellia hiemalis*. As a result of the analysis, we found that X-rays emitted from the surface region of the leaf could be detected selectively and then X-rays of Pb could be detected with low background using this analytical method. In this research, an effect of the X-ray absorber was indicated by comparing between X-ray spectra gained with and without use of that. However, since Pb was not attached to a leaf analyzed for this comparison, peak/background ratios of the X-rays of Pb using the X-ray absorber were not compared with those without use of the X-ray absorber. Moreover, X-ray exit angles did not correspond with each other between with and without use of that. We, therefore, applied the GE-µ-XRF to an analysis of As attached to a leaf of *Camellia hiemalis*, and then investigated the effect of the X-ray absorber at identical X-ray exit angles with and without use of that. As a result of that, we found peak/background ratios of X-ray peaks of As with use of the X-ray absorber drastically increased at grazing exit angles as compared to those without use of that.

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I. INTRODUCTION

In order to monitor air pollution, an analysis of atmospheric suspended particles (aerosols) attached to a surface of a plant leaf is regarded as an important way. Though X-ray fluorescence analysis (XRF) can analyze an aqueous plant leaf in the atmosphere, it is difficult to detect only X-rays emitted from such particles attached to the leaf surface with low background due to X-rays emitted from the inside. Therefore, we developed grazing exit micro XRF (GE-µ-XRF), which was expected to analyze the localized surface of an aqueous plant leaf with a much faster and simpler treatment as compared to conventional analytical methods [1–3], to detect X-rays emitted from fine Pb particles artificially attached to a surface of an aqueous leaf of *Camellia hiemalis*. A micro X-ray beam for this analytical method was produced by using a polycapillary X-ray lens. GE-µ-XRF is a grazing exit X-ray analysis (GE-XA) methods in which X-rays emitted from only the near-surface region of a specimen can be detected under a grazing exit angle condition (extremely low exit angle near 0°). In any GE-XA method, X-rays emitted from inside the specimen must be absorbed inside the specimen and attenuated when X-rays pass through the specimen. However, we deduced that X-rays emitted from inside aqueous organic material such as a plant leaf is scarcely absorbed because X-ray absorption in any aqueous organic material is much smaller than that in most metallic and semiconductor materials, which was analyzed with GE-XA methods. Therefore, we have developed a novel GE-µ-XRF method “X-ray absorber method” in which a chip of a silicon wafer is placed between the analyzed leaf and an X-ray detector as an absorber of the X-rays emitted from inside the leaf. As a result of GE-µ-XRF analysis of the Pb particles attached to the aqueous leaf using the X-ray absorber, we have for the first time selectively detected X-rays emitted from the near-surface region of an aqueous plant leaf. Therefore, we have detected X-rays emitted from the Pb particles with much higher peak/background ratios (P/B ratios), as compared to those of conventional XRF analysis [4]. In this research, an effect of the X-ray absorber was indicated by comparing between X-ray spectra gained with and without use of that. However, since Pb was not attached to a leaf analyzed for this comparison, peak/background ratios of the X-rays of Pb using the X-ray absorber were not compared with those without use of the X-ray absorber. Moreover, X-ray exit angles did not correspond with each other between with and without use of that. In this research, we, therefore, applied the GE-µ-XRF to an analysis of As attached to a leaf of *Camellia hiemalis*, and then investigated the effect of the X-ray absorber method.

FIG. 1: Leaf of *Camellia hiemalis* and sections cut from it. (a) Analyzed section. (b) Section used for a height adjustment spacer for a chip of a silicon wafer as an X-ray absorber.
absorber at identical X-ray exit angles with and without use of the absorber.

II. EXPERIMENTAL

A. Sample

Figure 1 is a picture of a leaf of *Camellia hiemalis*, which was used as the sample in this research. The leaf was collected in a courtyard of Osaka City University. Two sections were cut from the leaf as shown in Fig. 1 so that one was used for measuring. The analyzed section was dipped in Arsenic standard solution (As2O3 and NaOH in water, PH 5.0 with HCL, ID No. 013-15481, Wako Pure Chemical Industries, Ltd) for 3 min. After dipping, it was dried naturally in the air at room temperature for several minutes.

B. XRF apparatus

In this research, the XRF analysis was performed by an XRF apparatus developed in our laboratory. The primary equipments were as follows: Target of an X-ray tube: molybdenum; Energy dispersive X-ray detector (EDX): X flash detector type1201 by Rontec, USA; X-ray collection device for an X-ray emitter: polycapillary X-ray lens [5, 6].

Figure 2 shows the geometry between the detector and the sample. The detector was a silicon drift detector (SDD). A beryllium window was located in the front of the detector and covered with an aluminum cylindrical collimator. A 0.03-mm wide tantalic slit was fit on the collimator to limit the angle ranges of the X-rays detected by the X-ray detector. The polycapillary X-ray Lens was used to focus the X-rays onto the sample. The diameter of the X-ray beam focused by the X-ray lens was approximately 30 μm on the sample surface. The positions of the specimen stage in the X-Y direction (the horizontal direction) and those of the X-ray detector in the Z direction (the vertical direction) can be shifted with electric motors. The exit angles of the X-rays were adjusted by shifting the position of the X-ray detector along the Z-axis. When the X-ray detector was shifted down, the exit angle decreased. We used geometry to calculate the exit angles of the X-rays.

C. Arrangement of sample for analyses with XRF

Figure 3(a) is a picture of the leaf section set on a sample holder. Figure 3(b) is a schematic diagram of the cross section of the arrangement for XRF analysis. A chip of a...
D. Investigation for an effect of the X-ray absorber on surface analysis of the leaf with GE-μ-XRF

At first, X-ray spectra were obtained with XRF using the X-ray absorber. The identical area on the leaf was irradiated by the primary X-ray at any exit angle. Next, the X-ray absorber was removed from the sample holder and the X-ray spectra were then obtained at the same exit angles as the case in which X-ray absorber was used. In case the X-ray absorber was used, the X-ray tube current was approximately 0.43 mA and the X-ray tube voltage was approximately 43.5 kV. In case it was not used, the X-ray tube current was approximately 0.43 mA and the X-ray tube voltage was approximately 44.4 kV. The X-ray collection time was 300 s in live time. The X-ray detector was cooled to $-20.3\,^\circ\mathrm{C}$ with Peltier cooling.

silicon wafer was placed next to the leaf section, as shown in Fig. 3(a). Figure 4 is a picture of the sample set in the XRF apparatus. As mentioned above, because the X-ray absorption rate of the leaf was low, we deduced that most X-rays emitted from inside the leaf would not be absorbed by the leaf and could reach the X-ray detector even at grazing exit angles. Therefore, we placed the silicon wafer chip, the width of which was approximately 2.2 mm, between the analyzed leaf and the X-ray detector as an X-ray absorber for the X-rays emitted from inside the leaf. Figure 5 shows the effect of the X-ray absorber under the grazing exit angle condition. A section cut from the same leaf as the one under analysis was placed below the X-ray absorber, as shown in Fig. 3(b). Since the sum of thicknesses of the silicon chip, the carbon adhesive sheets, and the leaf section in the $\alpha$ part of Fig. 3 (b) would be equal to that in the $\beta$ part, the position of the leaf surface in the vertical direction would also be equal to that of the X-ray absorber. Furthermore, both the analyzed leaf section and the X-ray absorber were covered with clean paper and the covered faces were softly pressed with a flat broad in order to make their height correspond with each other more closely (flattening process). In a previous research, we measured the working distances (WDs) of a leaf of *Cammelia hiemalis* treated with the flattening process at various points with the SEM. Then the differences in the working distances of the leaf were very small and were 0.2 mm at most. Thus, we found that the curvature of the leaf was slight because of the flattening process [4].

FIG. 4: A photograph of the sample set in an m-XRF apparatus.

FIG. 5: Difference of detections of X-rays between the conventional angle condition and the grazing exit angle condition when a chip of a silicon wafer is used as an X-ray absorber. (In XRF analysis, we defined an angle, which was formed by the sample surface and an X-ray beam entering into the X-ray detector, as an exit angle. Then we defined the angle at which X-rays of Ca emitted from the surface becomes undetectable as zero degree when the X-ray absorber is used.)

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
E. Elemental distribution of a cross section of a leaf of *Camellia hiemalis* and calculation of X-ray exit angles in the XRF analyses

In the previous research, we investigated elemental distribution of a cross section of a leaf of *Camellia hiemalis* with a SEM-EDX analysis. As a result of this investigation, we found that a Ca-rich layer 3.1-19.9 \( \mu m \) thick was observed near the surface. In contrast, no Mn was detected on this layer, but it was detected in deeper areas [4]. Based on this result, we defined the position in the Z-axis where Ca K\( \alpha \) emitted from the surface layer became undetectable as 0° by using the X-ray absorber in the following XRF analyses.

III. RESULTS AND DISCUSSION

A. Effect of the X-ray absorber on the surface analysis of the leaf with GE-XRF

X-ray spectra of the leaf that were obtained without use of the X-ray absorber are shown in Fig. 6. Peaks of Ar, Ca, Mn, and As K\( \alpha \) could be seen in the spectra gained from the exit angle of 2.73° to 0°. Ar peak was derived from gaseous argon in the atmosphere. Even though X-ray exit angles were reduced, X-rays of Mn passed through the inside of the leaf and reached the X-ray detector. A peak of the As K\( \beta \) could not be seen in these spectra of Fig. 6.

X-ray spectra of the leaf that were obtained with use of the X-ray absorber are shown in Fig. 7. Peaks of Ar, Ca, Mn, and As K\( \alpha \) could be seen at the exit angle of 2.73° and 0.4°, as shown in Figs. 7(a) and (b). On the other hand, peaks of Ar, Ca, and As K\( \alpha \) could be seen in the spectrum shown in Fig. 7(c), while no peak of Mn could be seen when the exit angle was reduced to 0.05°. Moreover, As K\( \alpha \) became undetectable at 0.05° in this spectrum. At 0°, As K\( \alpha \) and K\( \beta \) could be seen, while the X-rays of Ca became undetectable, as shown in Fig. 6(d). Thus, X-rays emitted from only the surface region of the leaf could be detected with GE-\( \mu \)-XRF using the X-ray absorber. Since background noise at 0.05° and 0° decreased as compared to 2.73° and 0.4°, the peak of As K\( \alpha \) became detectable.

Thus, it was found that most X-rays emitted from the inside was not absorbed by the leaf even though the exit angle became lower, as shown in Fig. 6. If width of a leaf could become extremely large, it could be an X-ray absorber for X-rays emitted from its inside. However, it is actually impossible because width of plant leaves are several tens millimeters at most. In contrast, a Si wafer chip of comparatively shorter width could perfectly absorb the X-rays emitted from the inside. For example, a width of an X-ray absorber made from Si where the peak intensity of As K\( \alpha \) in Fig. 6(a) (87 counts) becomes less than 1 count after it passes through the absorber was estimated to be 0.67 mm by calculating with the following equation (1) and (1').

\[
I/I_0 = \exp(-\mu \rho t). \tag{1}
\]

Equation (1) can be modified as follows:

\[
t = -\ln(I/I_0)/(\mu \rho), \tag{2}
\]

where \( I_0 \) is incident X-ray intensity, \( I \) is transmission X-ray intensity, \( \mu \) is mass absorption coefficient of As K\( \alpha \) for Si (=28.9 cm\(^2\)/g) [7], \( \rho \) is density of Si (=2.33 g/cm\(^3\)), \( t \) = width of the Si X-ray absorber (cm). Therefore, the silicon X-ray absorber of 2.2 mm in width could be enough...
FIG. 8: Peak intensities and background intensities of As Kα as functions of X-ray exit angles. (a) Without use of the X-ray absorber, and (b) with use of the X-ray absorber.

FIG. 9: Peak/Background ratios of As Kα as functions of X-ray exit angles.

to perfectly absorb the X-rays from the inside in this experiment.

The X-ray peaks of Ar became larger than the other X-ray peaks in Fig. 7(c) and Fig. 7(d) as compared to Figs. 7(a), 7(b), and 6. We have deduced the cause of the difference, as mentioned below. When the X-ray absorber was used, total amount of X-rays emitted from the sample decreased due to being absorbed by the X-ray absorber at the lower exit angle. On the other hand, intensities of X-rays emitted from gaseous Ar, which was uniformly distributed in atmosphere in the sample chamber, was constant at any X-ray exit angle. Therefore, X-rays of Ar could be larger than those emitted from the sample at the lower exit angle in Fig. 7.

B. Intensities of As Kα Peaks, their backgrounds, and peak/background ratio as functions of X-ray exit angles

Figure 8 (a) shows area intensities (energy range: 10.062-11.027 KeV) of As Kα peak and their backgrounds as a function of X-ray exit angles when the X-ray absorber was used and Fig. 8 (b) shows those when it was not used. When the X-ray absorber was not used, the intensities of both As Kα peak and their backgrounds were nearly constant even though the exit angle was reduced from 2.73° to 0°, as shown in Fig. 8(a). On the other hand, both the intensities decreased as exit angle was reduced, and the decrease rate of the peaks was smaller as compared to that of the backgrounds when the X-ray absorber was used, as shown in Fig. 8(b). Figure 9 shows the peak/background (P/B) ratio of As Kα as a function of X-ray exit angles. The P/B ratios gained without use of the X-ray absorber were nearly constant at any angle. In contrast, those gained using the X-ray absorber increased as the exit angles decreased, and reached the highest value at an exit angle of 0.05°.

IV. CONCLUSIONS

We placed a chip of a silicon wafer, the width of which was approximately 2.2 mm, between the analyzed leaf and an X-ray detector as an absorber of the X-rays emitted from inside the leaf in GE-XRF, as shown in Fig. 3(a). We
measured the X-rays emitted from the leaf section dipped in As standard solution using the XRF method with and without use of the X-ray absorber at identical X-ray exit angles and investigated the changes in the X-ray spectra depending on the exit angles. As a result of that, we found P/B ratios of X-ray peaks of As with use of the X-ray absorber drastically increased at grazing exit angles as compared to those without use of that, as shown in Fig. 9. From these result, we found that the X-ray absorber was effective to detect As attached to the aqueous leaf with high P/B ratio in the GE-µ-XRF analysis.

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