

Application of SEM-EDXA Technique to the Study of Metal Distribution in Preservative-Treated Wood*¹

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Abstract—The potential and limitations of the SEM-EDXA technique for determination of the metal concentration and its distribution in the preservative-treated wood were investigated. Operating conditions such as the accelerating voltage (20 keV), the working distance (15 mm), the illuminating current (200 μA) and the distance of the X-ray detector from the specimen were held constant throughout the entire study. Results obtained were as follows. (1) The smallest size which it was practicable to analyse in the bulk specimen was in the range of 3.5–4.5 μm in diameter. Hence the different cell wall layers were not analysed as separate entities in the point analysis. (2) Acquisition time of X-rays at one point on the cell wall at most should be restricted within 200 seconds for the prevention of the heat-damage of the specimen by electron bombardment. (3) Tilting angle of the specimen affected greatly the X-ray emission. Hence, for quantitative analysis, the comparison of X-ray intensities should be restricted within the portion which take the same tilting angle. (4) The X-ray intensity increased linearly in proportion to the metal concentration in the cell wall although there was a considerable variation in analysis. (5) Minimum detection limit of Cr, Cu and Zn in the cell wall was about 0.1 w/w percent in every case.

1. Introduction

In preservative treatment of wood, various toxic substances are impregnated into wood. It is known that the gross loading of preservative alone is not enough to afford total protection of wood against decay; the uniform distribution of preservative in wood is a necessary condition for total protection.^{1,2)} There is a considerable interest in defining the final distribution of the preservative in wood. In recent years energy-dispersive X-ray analysis (EDXA) in scanning electron microscopy (SEM) has been applied to wood as a means of simultaneous morphological examination of surface with qualitative element distribution.^{1~5)} The quantitative potential of this technique is not necessarily clear yet. The purpose of this study is to clarify the potential and limitations of the SEM-EDXA technique in application to the bulk wood samples by the examination of following items: (1) the size of the specimen

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which is being analysed; (2) variation of X-ray intensities with the acquisition time of X-rays; (3) effect of the tilting angle of the specimen; (4) relationship between the X-ray intensity and the metal concentrations in the cell wall, and (5) minimum detection limits of metals in the cell wall. Ionic distribution in wood tissues penetrated with the salt solutions by the capillary pressure will be dealt with the next paper.

2. Materials and Methods

Small samples of Hinoki (*Chamaecyparis obtusa* Endl.) specimens ($2_{(L)} \times 15_{(R)} \times 15_{(T)}$ mm, $r_0=0.34$) were embedded by vacuum/immersion process with epoxy resin. After polymerization, the end surface of each specimen was trimmed with a sand paper so as to expose the cut ends of the cell wall and then its thickness was measured. These specimens were immersed in aqueous solutions of various concentration of $K_2Cr_2O_7$, $CuSO_4$ or $ZnCl_2$ for ten days at $30^\circ C$. A part of the specimen was examined with the SEM-EDXA. The rest was decomposed with sulphuric-nitric acid mixture by heating and the metal concentration in the cell wall was determined by spectrophotometry as described in the previous papers.⁶⁻⁸⁾ For SEM-EDXA the specimen was surfaced with a glass knife to expose a smooth cross-sectional view of wood. The surfaced blocks were mounted on a carbon specimen holder and coated with carbon in a vacuum evaporator. In addition, the non-embedded samples of Buna (*Fagus crenata* Blume) were also mounted on a specimen holder and coated with carbon. Examination and analysis were performed with a Hitachi S-500 scanning microscope and a Kevex 7000 energy-dispersive X-ray spectrometer. It has been reported that the most efficient production of characteristic X-rays generally occurred when the energy of bombarding electrons had about three times of the characteristic X-ray energy.⁹⁾ Energy of K_α line of Cr, Cu and Zn are 5.41 8.05 and 8.64 keV, respectively. Hence in this study the system was operated at 20 keV. The illuminating current was adjusted to $200 \mu A$ using a Faraday cup prior to analysing of any samples. Working distance of the apparatus was always set to 15 mm. Except for the measurement of the size of the specimen which is being analysed, all acquisition of X-rays were taken by the point analysis.

3. Results and Discussion

3.1 Size within a specimen from which X-rays are emitted.

In the SEM, the incident electron-beam spot can be adjusted to about 100 \AA in diameter. However, in bulk specimens the electrons are scattered within the specimens and hence the X-ray emission fields are greatly enlarged. It was considered of importance to define the smallest size which it is practicable to analyse in wood by the SEM under the usual operating conditions. Scattering range of

electrons is variable with the density and the elemental composition of the specimen, and X-ray energy of the element even if the operating conditions are identical. A specific gravity of 1.26 was determined for the cured epoxy resin alone whereas the specific gravity of the dry cell wall has been reported to be 1.04–1.32 by the optical measurements¹⁰⁾ or 1.39–1.47 by mercury porosimetry.¹¹⁾ Hence, it might be regarded that the specific gravity of epoxy resin was not so different from the cell wall. Elemental composition of the resin also resembled to that of wood. From these facts it was assumed that the scattering range of electron beam was not so different between the epoxy resin and the cell wall of wood. Figure 1 shows a line scan of K_{α} X-ray of chromium on the surfaced cross-section of the embedded sample.

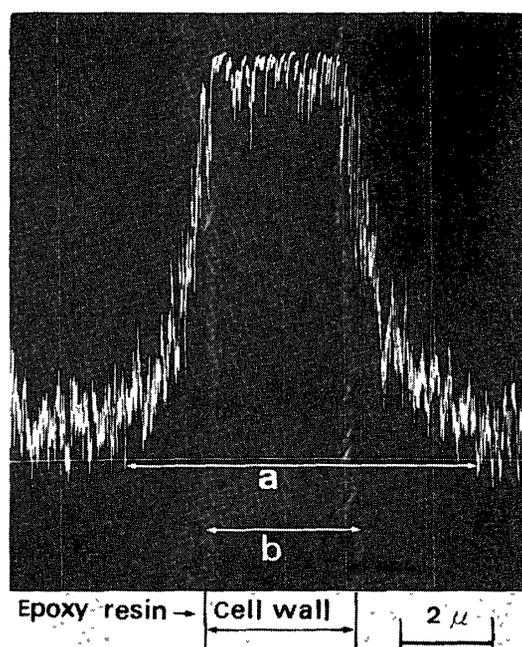


Fig. 1. Line analysis of Cr- K_{α} X-ray across the double cell wall of Hinoki tracheid (chromium concentration: 2.57%) which was embedded with epoxy resin. The size being analysed: $c=a-b$.

Emission of Cr- K_{α} X-ray was clearly detected in the epoxy resin, not including chromium, distant from the cell wall. The size analysed was estimated from the $(a-b)$ value in Figure 1. The size was in the range of 3.4~4.5 μm in diameter in the case of chromium. In the case of copper and zinc, it may well be that the size will further enlarged because the X-ray energies of K_{α} -line in copper and zinc are higher than that of chromium. Hence, it was concluded that the different cell wall layers were not analysis as separate entities in the SEM-EDXA using the bulk specimen, that is, the emission field of X-ray was extended to about overall width of the cell wall when the electron beam was positioned on the I+P layer.

3.2 Variation of X-ray intensity with the acquisition time.

Point analysis is the most useful method for the quantitative analysis because of its greater precision. Since X-rays are emitted at random intervals, not at a constant rate, it is necessary to take longer acquisition time for better statistical precision. However, it is probable that the X-ray emission rate is changed with the elapsed time because the specimen may be damaged by the heat generation due to the bombardment of electrons. Figure 2 shows some stages of damage of the embedded sample and the

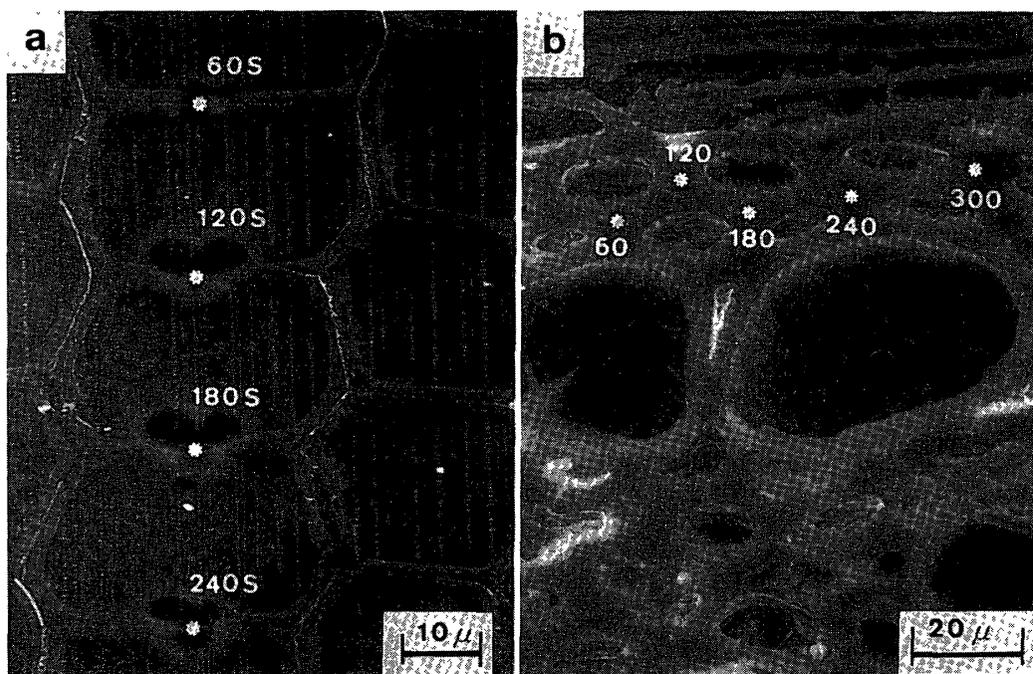


Fig. 2. Time-lapse damage of the specimen by the electron bombardment. *a*; embedded sample of the Hinoki, *b*: non-embedded sample of Buna. Note: *; the irradiated position of electron probe, numerical values; irradiating time (seconds).

non-embedded sample by the electron bombardment. While the non-embedded sample was apparently not damaged, the embedded sample suffered the appreciable damage which was probably due to the heat-damage of the epoxy resin. Figure 3 shows a result of plotting the X-ray intensity of Cr- K_{α} line of the embedded sample as a function of the acquisition time. The X-ray intensity increased linearly in proportion to the time in the range of 10~200 seconds. But in further prolonged acquisition time, the emission rate of the X-ray shows a tendency of a little decrease. From these facts it is evident that the excessive acquisition time is never profitable for the precise analysis. Hereafter, in this study, the spectrometer was operated at 180 seconds of the acquisition time.

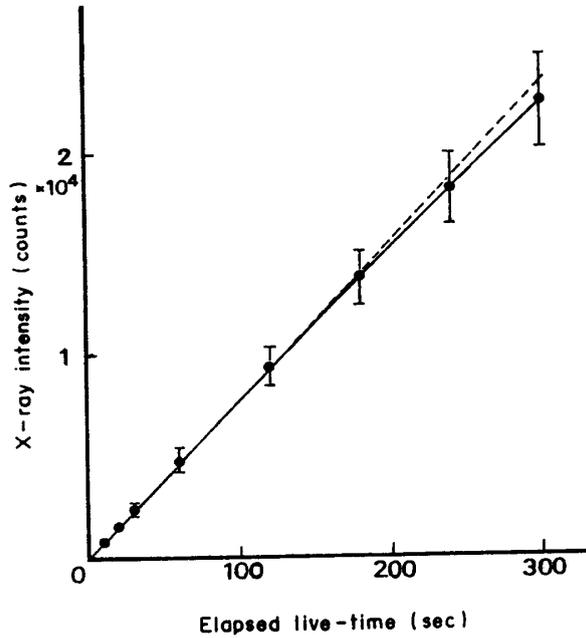


Fig. 3. Relationship between X-ray intensity of Cr-K_α line and the elapsed live-time. The vertical line through the data points shows the standard deviation. The broken line shows an extension of the line through the data points of the early stages of the elapse time (0~120 second).

3.3 Effect of tilting angle of specimen.

Relationship between the X-ray intensity of the cell wall and tilting angle of the specimen was examined at a certain point on the cell wall of surfaced specimen (Fig. 4). The X-ray intensity was greatly affected by the tilting angle of the surface even though other electron-exciting parameters were identical. It is impossible to regulate the tilting angle of all positions on the wood surface to the constant value,

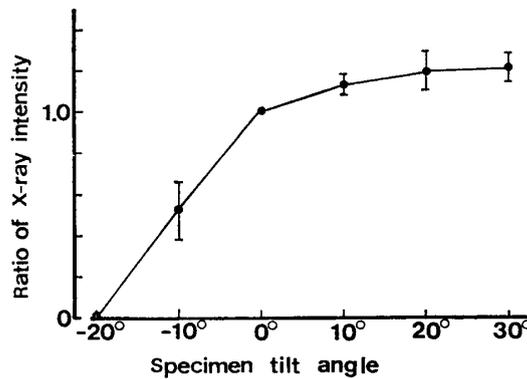


Fig. 4. Effect of tilting angle of specimen on the X-ray intensity of Cr-K_α line (Cr-concentration: 2.57%). The vertical line through the data points shows the standard deviation.

because wood is originally a porous material and hence it has more or less rough surface when it is examined under the SEM. Greaves⁵⁾ stated that at best only semiquantitative analysis could be performed since the rough surface structure of wood would cause absorption of X-rays and hence incomplete detection. The result of our study also demonstrated clearly that the comparison of X-ray intensities should be made at the portions which were regarded as the same tilting angle. In other parts of this study, tilting angle of specimen was strictly held to the zero degree.

3.4 Relationship between the X-ray intensity and the metal concentration in the cell wall.

Preliminarily, variations of the X-ray intensity with the four different positions on the cell wall were investigated (Table 1). The X-ray intensity on the I+P layer of earlywood tracheid was poorer than that of the three others. This might be caused by the difference in the thickness of the cell wall available to analysis, because the thickness of double cell wall of Hinoki was in the range of 2.5–3.5 μm in earlywood and 4–7 μm in latewood while the smallest size of specimen analysed attained to 3.5–4.5 μm in diameter as described previously. Hence it is necessary that the comparison of the X-ray intensity was restricted to the portions with the same size of analysis field.

Table 1. Variations in X-ray intensities of Cr-K α line in various positions of tracheid wall of Hinoki (Cr-concentration; 4.14 w/w %).

Illuminating point		X-ray intensity (counts/180s)		
		Mean	Std. dev.	Number
Earlywood	I+P	11,850	750	5
	I*	15,300	1,720	5
Latewood	I+P	14,080	1,560	5
	I*	16,100	2,170	6

*Intercellular layer of the cell corners.

Figure 5 shows the relationship between the metal concentration and the X-ray intensities in the cell walls which were irradiated the electron probe on the center of the intercellular layer at the cell corners. The X-ray intensity increased linearly in proportion to the metal concentrations of the cell wall which were determined by spectrophotometry as described in the previous papers.⁶⁻⁸⁾ However, there was a considerable variation in analyses owing to the many factors which influence X-ray emission from the specimens and detection by the Kevex system. The correlation coefficients of the regression lines were in the range of 0.976–0.992. In the case of chromium, the slope of regression line and its 95 percent confidential limit were

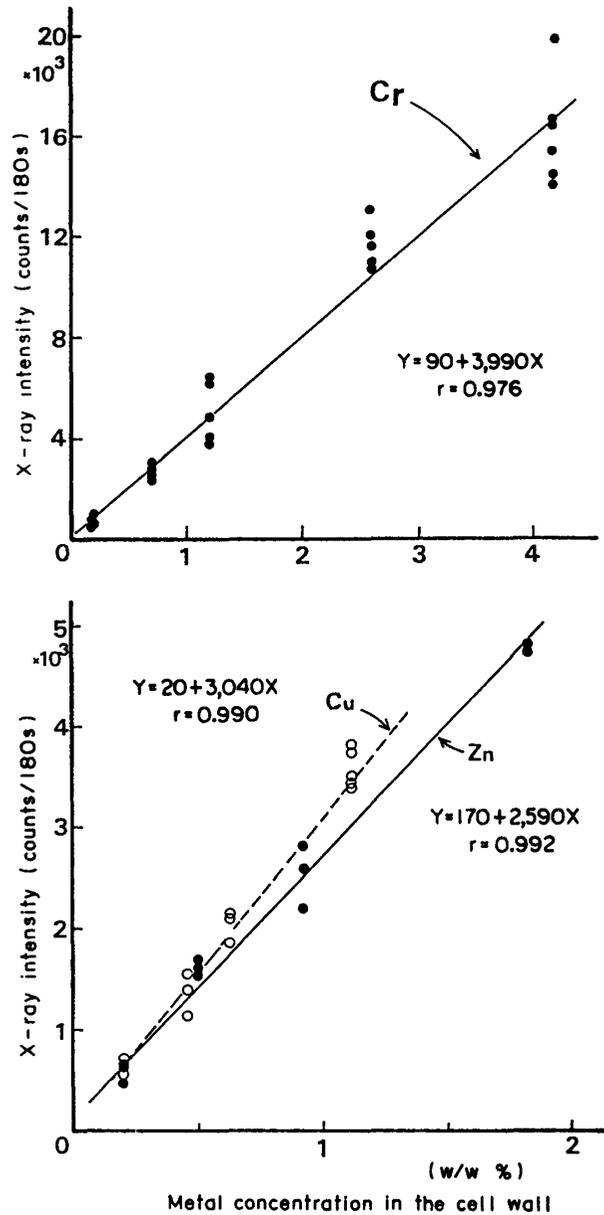


Fig. 5. Relationship between X-ray intensities and the metal concentrations in the cell wall.

$3,990 \pm 340$ and hence the error of about ± 10 percent occurred inevitably in the estimation of the slope of regression line even if operating conditions are carefully controlled. Slopes of the regression lines varied considerably from element to element because the emission efficiencies of X-rays differed with energies of K_{α} -line of each element.

3.5 Minimum detection limits of metals in the cell wall.

It is important to define the minimum detection limits of elements in the cell

wall for quantitative analysis and moreover for qualitative analysis. This limit is especially important in the analysis of the preservative-treated wood in which the metal concentration may be only a few percent at most. Minimum detection limit (MDL) is obtained from the following equations¹²⁾:

$$\text{MDL} = 3 \cdot \frac{\sqrt{b}}{A} \cdot \sqrt{\frac{2}{t}}$$

where **b** is the X-ray intensity of background, **A** is the X-ray intensity of the element per unit concentration of element in the sample and **t** is the counting (acquisition) time. MDL of the metals in the cell wall was 0.07, 0.08 and 0.09 w/w percent in Cr, Cu and Zn, respectively. Examples of energy-dispersive X-ray spectra of the cell wall which contained chromium at the concentration near the minimum detection limit were shown in Figure 6. At the concentration of chromium less than 0.095 w/w percent, it became almost impossible to distinguish the peak of Cr-K_α line from the background. From these results it was concluded that the minimum detection limit of these elements in the cell wall were about 0.1 percent.

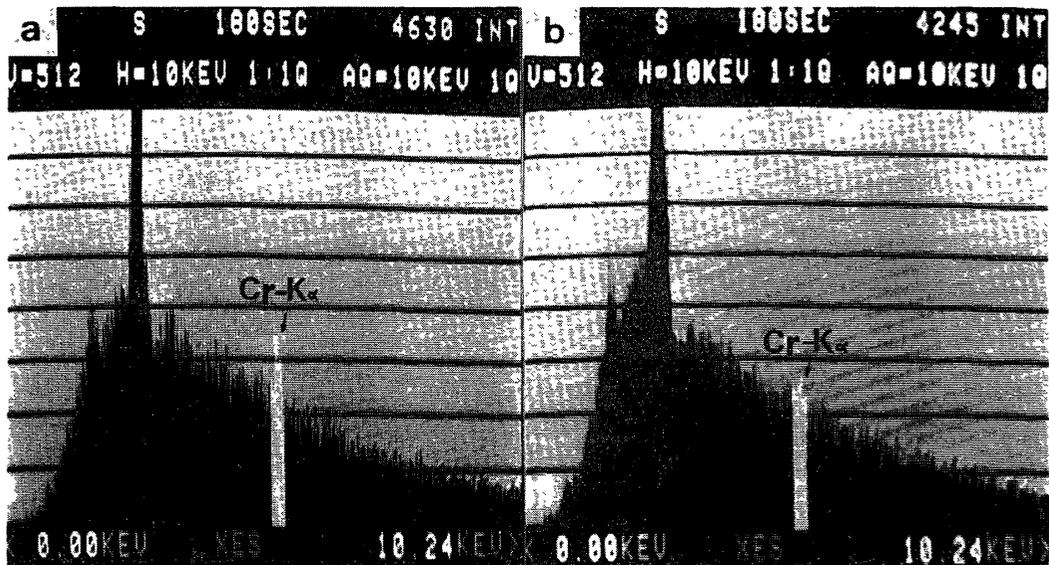


Fig. 6. Energy-dispersive X-ray spectra showing the minimum detection limit of chromium in the cell wall.
Cr-concentration: a-0.18%. b-0.095%.

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