Distribution of Metal Elements in Wood Impregnated with Aqueous Solutions of Metal Salts as Determined by SEM-EDXA*1

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Abstract——Distribution and concentration of salts in the wood of three species, all treated with aqueous salt solutions of Cr, Cu or Zn to the longitudinal direction of the air-dried wood by capillary pressure, were determined using the SEM-EDXA technique. In the line analysis the X-ray intensities varied widely with positions analysed since the rough surface structure of wood caused incomplete detection of X-rays. However, when the scanning line was put along the intercellular layer between the regularly oriented radial files of tracheids, a smooth curve was obtained. In this case overall trends of curves obtained were coincident with the results of the point analysis. The line-scan curve took a peak on the initiatively penetrated cell and gradually lowered at its surrounding region. Deposition of the salt could be seen frequently on the inner surface of the cell wall of the penetrated cell. From the gentle gradient of metal concentration in the surrounding region it was shown that the metal-distribution in this region was attributed to the ionic diffusion through the cell wall, not to the lateral liquid-flow through the lumen-pit system. The smooth curves were drawn across the different cell types, the multiseriate rays and across the annual ring boundary. Hence, it was concluded that the ionic diffusion through the cell wall proceeded uniformly from the penetrated cells to their surrounding regions.

1. Introduction

In a previous paper,[1] Yata *et al.* reported on the morphological aspects of capillary liquid-flow of aqueous salt solutions into the air-dried wood and subsequent lateral ionic movement from the penetrated cells to their surrounding regions on the basis of light microscopic observation. The potential and limitations of the SEM-EDXA technique for qualitative localization and quantitative determination of wood-preservatives were investigated in the latest paper in this series.[2] Successively, this paper deals with the metal distribution in the wood penetrated with the aqueous salt solutions of Cr, Cu or Zn by the capillary pressure as determined using the SEM-EDXA technique based on the operating conditions reported in the latest paper.[2]

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2. Materials and Methods

Sapwood of Buna (*Fagus crenata* Blume) and Hōnoki (*Magnolia obovata* Thunb.), and heartwood of Ezomatsu (*Picea jezoensis* Carr.) were used in this study. The dimensions of specimens were $5_{(L)} \times 2_{(R)} \times 2_{(T)}$ (cm) and their moisture contents were in the range of 10 ~13 percent. The aqueous salt solutions used and their penetration method into wood were the same as the previous paper.[1] The penetration direction was the longitudinal alone. Immediately after penetration treatment the specimen were vacuum-dried by evacuating from the base of specimens using a rotary oil vacuum pump. The dried specimens were cross cut at the intervals of about 3 mm from their base successively. Apart from these cross sections, radial sections were split from the dry specimens. These cross and radial sections were surfaced with a knife blade, mounted on the carbon specimen holders and then coated with carbon in a vacuum evaporator. Examination and analysis were performed with a Hitachi S-500 scanning electron microscope coupled with a Kevex 700 energy dispersive spectrometer. Operating conditions such as the distance of the X-ray detector from the specimen, the accelerating voltage (20 keV), illuminating current (200 $\mu\mu$A), working distance (15 mm), tilting angle of specimen (0°) and X-ray acquisition time (180 seconds) were held constant throughout the entire study. Two methods were adopted for X-ray acquisition; line analysis and point analysis. Line analysis was practiced to determine the qualitative distribution pattern of metals in wood. The point analysis was made to test the accuracy of line analysis and to determine the concentration of metals in the various morphological regions in wood.

3. Results and Discussion

In line analysis, the X-ray intensities varied widely with positions analysed since the rough surface structure of wood caused incomplete detection of X-rays (Fig. 1-a). In the case of cross section of softwood, however, tracheids were regularly oriented in the radial direction. Hence, when the scanning line was put on the inter cellular layer between the radial files of tracheids, a relatively smooth curve was obtained because the scanning line passed on the surfaced cell walls alone (Fig. 1-b). Figure 2 shows the cross-sectional views of Ezomatsu heatwood which was penetrated with the $K_2Cr_2O_7$ solution. The salt solutions selectively penetrated into the latewood tracheids. Hence, the line scan curve attained to a peak on these latewood tracheids and gradually lowered in their surrounding region. It is considered that this gentle gradient of metal concentration is due to the ionic diffusion through the cell walls. Because, free water does not exist in the air-dried wood except for the lumina of the initiatively penetrated cells, but water vapour can diffuse into the

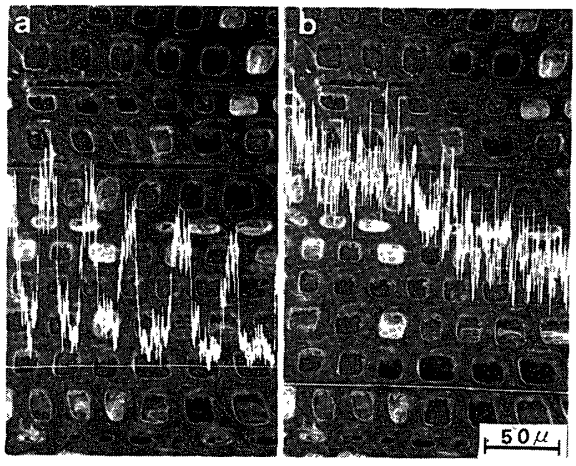

Fig. 1. Line analysis of Cr-K_α X-ray on the cross-sectional surface of Ezomatsu which was penetrated with the $K_2Cr_2O_7$ solution. *a*: Line scan along the center of a radial file of cells. *b*: Line scan on the double cell wall between the two radial files of tracheids.

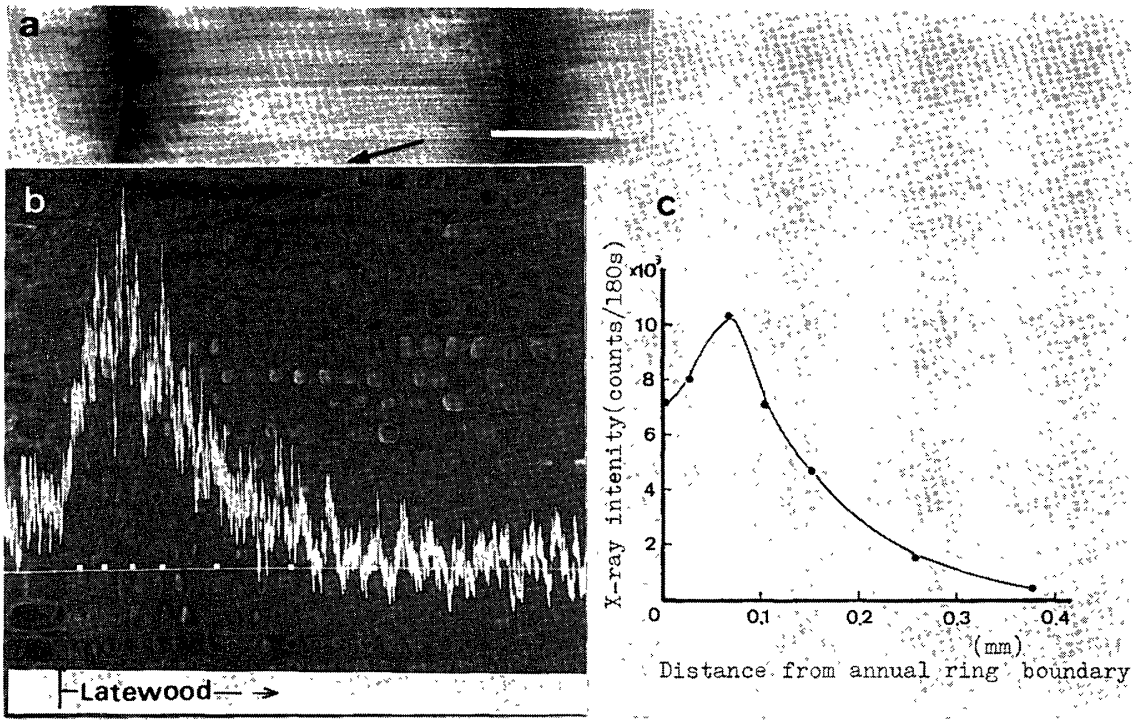

Fig. 2. Line and point analyses of Cr-K_α X-ray on the double cell walls along the radial file of cells of Ezomatsu which was penetrated with the $K_2Cr_2O_7$ solution for 4 hours. *a*: LM micrograph of cross section at the pentration height of 5.5 mm. *b*: Line scan on the white line in *a*. White points on the line show the position of point analysis. *c*; point analysis at the various positions on the line in *b*.

cell wall and provides diffusion paths for the subsequent ionic diffusion. If lateral movement is attributed to the liquid-flow of the solution alone, the curve ought to

draw an abrupt boundary at the perimeter of the liquid-flow region. This result supported the conclusion in the previous paper[1] which revealed that the lateral movement of the salt was mainly due to the ionic diffusion through the cell wall. When the results of point analysis are substituted to the equation of calibration line presented in the latest paper[2], the concentration are obtainable. The chromium concentrations in the cell wall were estimated at 2.65 w/w percent at the peak, about 0.93 percent at 0.1 mm distance from the peak and about 0.35 percent at 0.2 mm distance from the peak. Chromium was almost undetectable at 0.4 mm distance from the peak. This distance was approximately equal to the width of staining region in the light microscopic view (Fig. 2-a). When the scanning line was put on the intercellular layer between the radial files of tracheids, overall trends of the curve obtained were coincident with the results of the point analysis. From this result it is concluded that the line analysis is a useful technique for presenting the qualitative distribution of metallic elements across the specimen.

Figure 3 shows a gross distribution pattern of chromium in the cross section of Buna sapwood which was penetrated with the $K_2Cr_2O_7$ solution. From the point analysis it was shown that the solution penetrated selectively to a vessel, which was

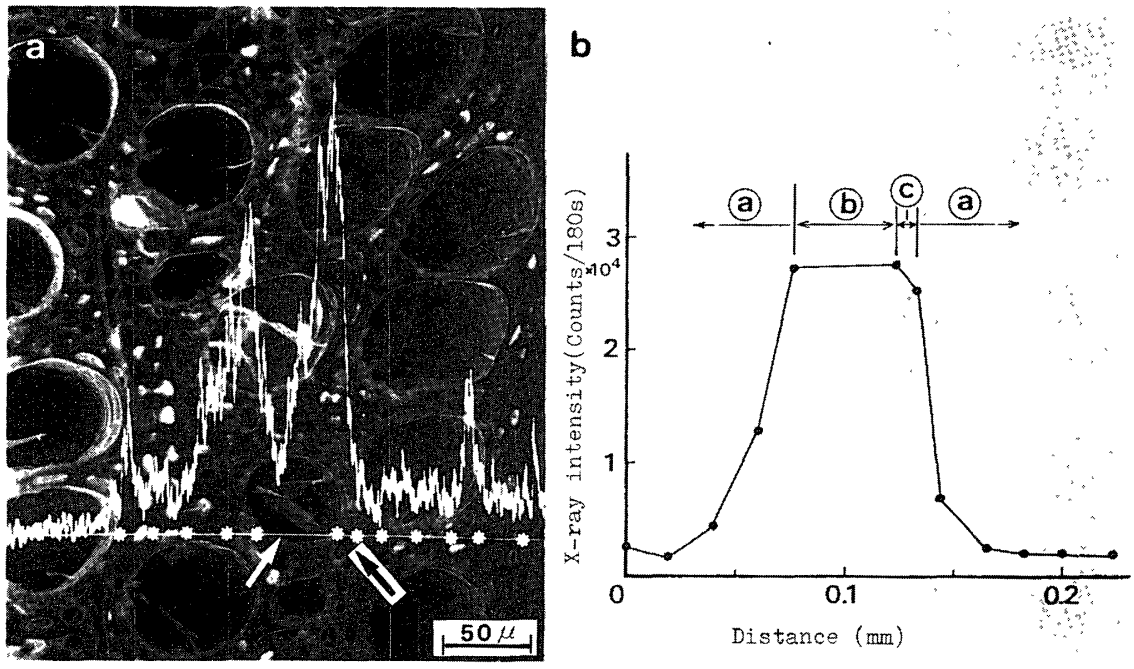

Fig. 3. SEM-EDXA of Cr-K_α X-ray of Buna which was penetrated with the $K_2Cr_2O_7$ solution. *a*: Cross-sectional view at the penetration height of 9.9 mm and line-scan to the tangential direction. *b*: Point analysis at the positions with white points on the line in *a*. ⓐ; Region of ionic diffusion through the cell wall. ⓑ; Initiatively penetrated vessel which was indicated with the white arrow in *a*. ⓒ; Lateral liquid-flow from the vessel to a adjacent cell which was indicated with the black in *a*.

shown with the white arrow, in latewood. The X-ray intensity of a tracheid, which was shown with the black arrow, adjacent to the vessel was as high as that of the vessel. It was assumed from this fact that the lateral flow of the solution occurred from the vessel into the tracheid. It could be seen from these point analyses that ionic diffusion through the cell wall also proceeded from the vessel to its surrounding cell walls. The chromium concentration obtained from the calibration line in the latest paper[2] was attained to 6.8 w/w percent at the peak. This value was higher than that of the equilibrium chromium concentration in the cell wall with the 0.5M-$K_2Cr_2O_7$ solution.[3] This excessive concentration in the vessel wall is presumably attributed to the deposition of the salt on the inner surface of the vessel wall. In fact, deposition of $K_2Cr_2O_7$ was observed frequently at the penetration front. The cell wall thickness of the vessel was only 1.2 μm whereas the size being analysed was 3.5 ~4.5 μm in diameter. Hence, the inner surface of the vessel wall was included within the analysis field when the electron probe was set on the I+P layer. In the case of hardwood, the line-scan curve was not necessarily correspondent with the results of the point analysis. This is probably due to the complicated cellular structure of hardwood. In cross section, cell size and its orientation are so irregular that the electron beam inevitably pass through the rough surface consisting of the lumen and the cell wall.

Figure 4 shows the line scans of Cr-K_α line at the three heights from the base of the specimen of Ezomatsu heartwood which was penetrated with the $K_2Cr_2O_7$ solution. Successive stages on the change of the chromium concentration to the

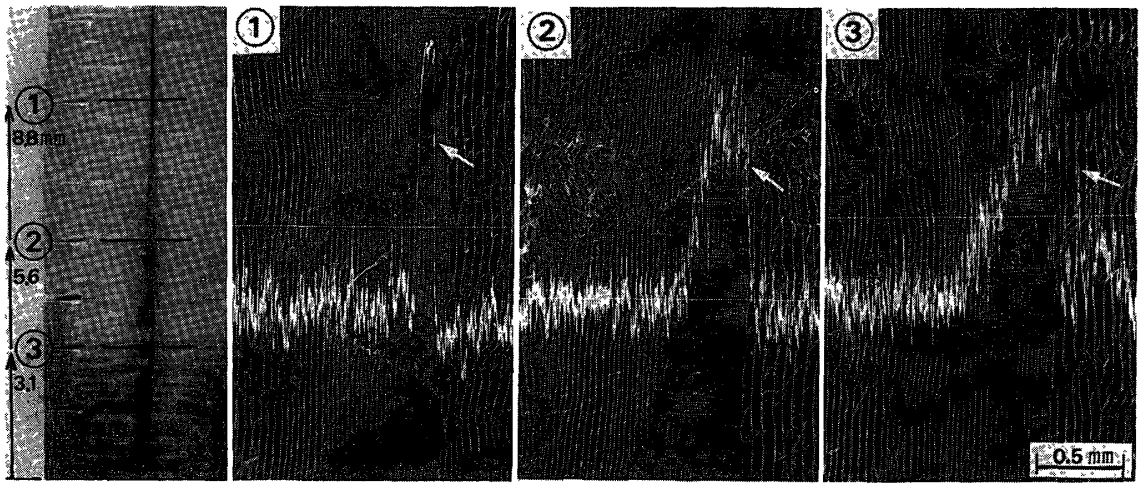

Fig. 4. Change of lateral distribution of chromium with the height from the base of the Ezomatsu specimen which was penetrated with the $K_2Cr_2O_7$ solution to the longitudinal direction for 4 hours. Note; a narrow and sharp curve (white arrow in ①) was drawn near the penetration front, but the slope of the curves gradually moderated and spreaded to the radial direction at the positions near the base (② and ③).

radial direction with the elapsed time after penetrating into the limited tracheids can be seen from these line-scan curves. In the position near the penetration front it seems that no ionic diffusion yet occurs to the surrounding region since a sharp peak is drawn on the penetrated tracheids (Figure 4-①). In the more advanced stages the concentration gradients were gradually moderated in the surrounding region by the proceeding of the ionic diffusion through the cell wall (Figures 4-② and -③).

Figure 5 shows the multiseriate ray and its neighbouring region of Buna sapwood and their SEM-EDX line scan. In this wood the salt solution penetrated selectively into the latewood vessels. Hence, a belt-like staining of latewood could be seen in cross-sectional view (Fig. 5-a). A relatively smooth curve of the X-ray intensities was drawn from the axial cells toward the ray cells (Fig. 5-b). From this fact it is evident that the ray cell walls never prevent the ionic diffusion through the cell walls. At annual ring boundary, a smooth curve was also drawn across the annual ring boundary from earlywood to latewood or latewood to earlywood. These findings supported the results obtained from the light microscopic observations in the previous paper[1] which revealed that ionic diffusion proceeded uniformly to all directions through the cell wall of all cell types. These findings also supported the conclusion of Stone and Green[4] who stated that diffusion was a much variable mechanism than penetration.

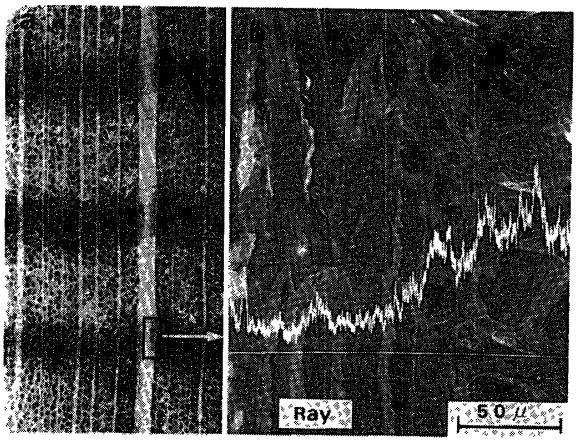

Fig. 5. Distribution of chromium across the multiseriate ray of Buna. *a*: LM image of cross-section at the penetration height of 9.9 mm in longitudinal capillary rise for 4 hours. *b*: Line scan of Cr-K_α X-ray across the ray tissue.

Figure 6 shows that the line analysis of Cr-K_α and K-K_α lines along the same line position on the Hōnoki sapwood which was penetrated with the $K_2Cr_2O_7$ solution. The salt solution penetrated into a vessel which was shown with a white arrow. De-

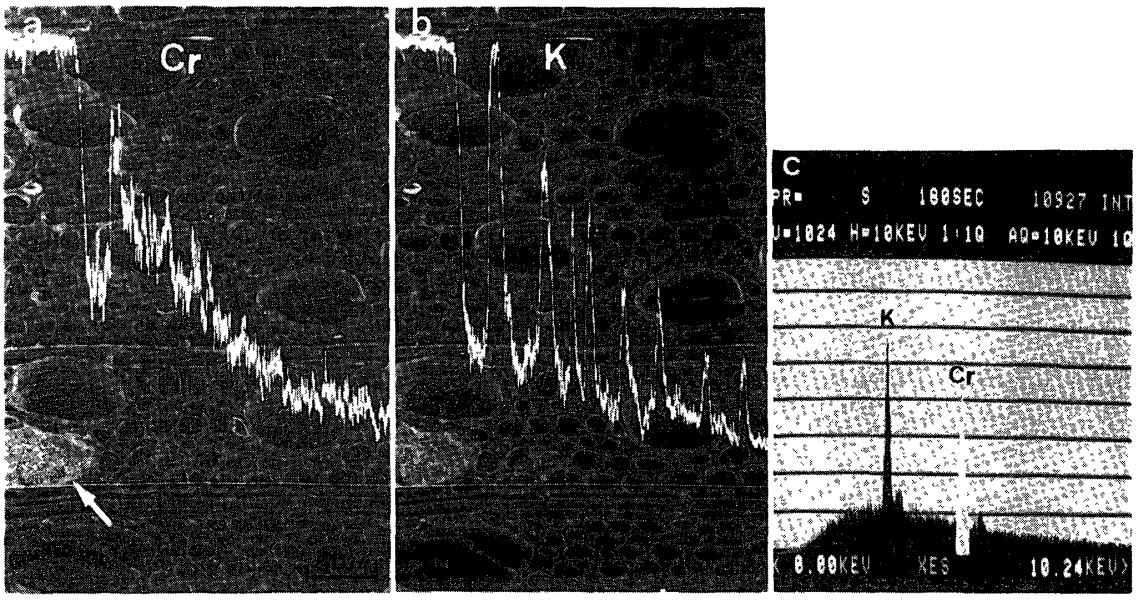

Fig. 6. Line scans of Cr-K_α and K-K_α X-ray and their X-ray spectrum of Hōnoki which was penetrated with the $K_2Cr_2O_7$ solution. *a*, *b*: Cross section at the height of 9.5 mm in longitudinal capillary rise for 4 hours. White arrow shows a deposition of $K_2Cr_2O_7$ in the vessel lumen. *c*: Energy disperive X-ray spectrum on the scanning line in *a*.

position of the salt can be seen in the lumen of the vessel. It could be seen from these two curves that diffusion of K^+ cations occurred simultaneously with that of $Cr_2O_7^{2-}$ anions because both curves had a similar tendency of gradual decrease of X-ray intensities. However, the difference of X-ray intensities between the cell wall and the lumen in the K-K_α line was more distinct than that in the Cr-K_α line. This might be caused by the difference of the size of analysis field available between chromium and pottasium. Because the energy of Cr-K_α line (5.41 keV) is higher than that of potassium (3.31 keV) as shown in the energy dispersive X-ray spectrum (Fig. 6-c), the size of analysis field of the former is larger than that of the latter.

Figure 7 shows a result of SEM-EDXA of Buna sapwood which was penetrated with the $CuSO_4$ solution. In this solution the penetration height into the dried wood was lower than that of the other salt solutions as already reported in the previous paper.[1] A cause of this poor penetration is presumably due to the obstruction of lumen by the deposition of the salt as shown with white arrow. The gross distribution patterns of copper in the treated wood was similar to that of chromium. However, when the specimen was examined in detail, the concentration gradient of copper at the surrounding region of the penetrated cell was steeper than that of chromium. From this fact it was considered that the ionic diffusion through the cell wall of copper was poorer than that of chromium. Figure 8 shows a cross-sectional view of Buna sapwood which was penetrated with the $ZnCl_2$ solution. A line-scan curve of Zn-K_α

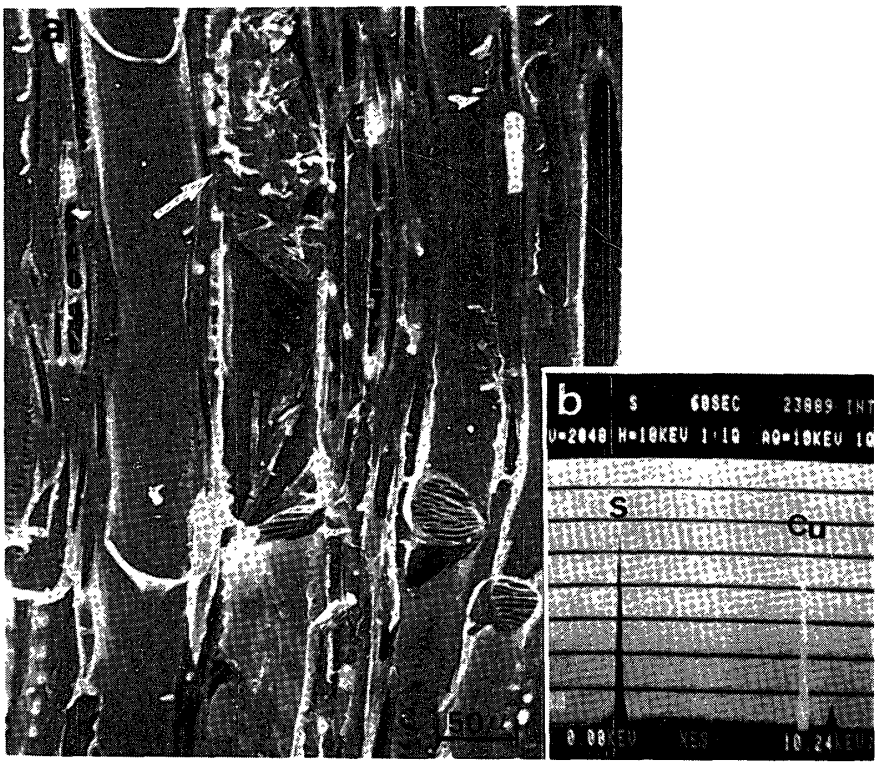

Fig. 7. A SEM micrograph of Buna showing the $CuSO_4$ precipitation in the vessel lumen (white arrow in *a*) and the X-ray spectrum of the precipitate (*b*).

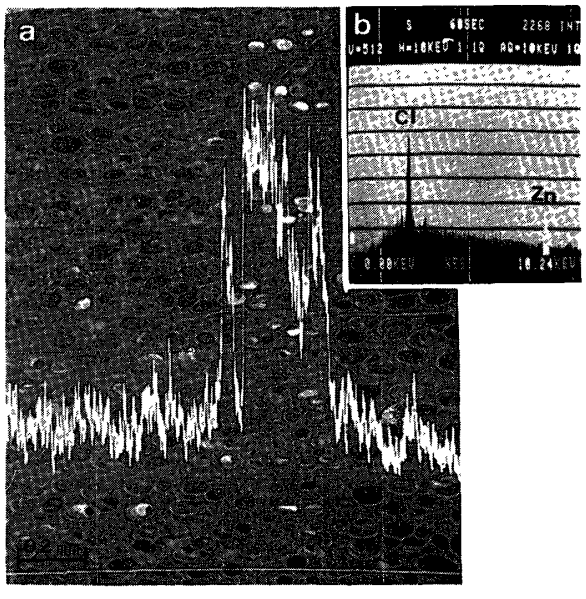

Fig. 8. Line scan of Zn-K_α X-ray of the cross section at the height of 18 mm from the base of Buna which was penetrated with the $ZnCl_2$ solution for 4 hours (*a*) and the X-ray spectrum on the scanning line in *a* (*b*).

X-ray and its X-ray spectrum was shown in this Figure. A peak of Cl-K_α line also can be seen in the X-ray spectrum. The overall trend of this line-scan curve coincided with that of chromium.

From the measurement of metal distribution in wood by the SEM-EDX in the current study it was clearly demonstrated that the lateral movement of ions such as $Cr_2O_7^{2-}$, Cu^{2+} and Zn^{2+} from the initiatively penetrated cells to their surrounding region was mainly performed by the ionic diffusion through the cell wall, not by the liquid-flow through the pit pairs. From the smooth line-scan curves of X-ray intensity through the different cell types, the multiseriate rays and through the annual ring boundary it was suggested that the ionic diffusion through the cell wall proceeded uniformly from the penetrated cells to their surrounding regions.

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References

1) S. YATA, J. MUKUDAI and H. KAJITA: Mokuzai Gakkaishi, submitted.
2) S. YATA and K. NISHIMOTO: WOOD RESEARCH, No. 69, 71–79 (1983).
3) S. YATA, J. MUKUDAI and H. KAJITA: Mokuzai Gakkaishi, **28**, 10–16 (1982).
4) J. E. STONE and H. V. GREEN: Tappi, **42**, 700–709 (1959).