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Analysis of boron in wood treated with boric acid solutions using Doppler broadening method of prompt gamma-rays

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Introduction

Wood preservatives such as boric acid and/or borate have been expected to emerge as effective substitutes for chromated copper arsenate (CCA) because of their lower toxicity. However, such preservatives have not been commercially available in Japan because these boron compounds are easily eluted from wood by rainwater. We have applied a multipronged approach to the problem of preventing the easy elution of boron. To obtain knowledge of the chemical species and distribution of boron in wood, we have explored wood treated with aqueous^{1,2} and methanolic³ boric acid solutions by using Raman spectroscopy.

The methods of analyzing boron in the solid state are restricted to Raman spectroscopy and only a few other techniques. Regarding the analysis of boron contained in

wood, there has so far been only an electron probe microanalysis (EPMA) study⁴ of boron distribution other than our Raman studies.¹⁻³ The Raman technique enables us to identify boron species in wood, because boric acid and most borates show several characteristic Raman bands. However, Raman spectroscopy is not sensitive enough to detect low concentrations of boron species in wood and is not suitable for quantitative analysis of solid samples.

In general, there are few analytical techniques that can determine the boron content in solids. However, the recent development of neutron-induced prompt gamma-ray analysis (PGA) has allowed us to obtain a powerful tool for the detection of trace amounts of boron in various samples,^{5,6} which is basically in a category of neutron-activation analysis although on-line measurement is absolutely necessary. Boron is one of the elements for which PGA has an ultimate sensitivity by using 478-keV prompt gamma-rays emitted from ⁷Li produced in the ¹⁰B (n, α) ⁷Li reaction. ⁷Li represents the ⁷Li atomic nucleus in an excited state. The cross section of the nuclear reaction is 3838 barn for the thermal-neutron capture. Such a large cross section should lead to high analytical sensitivity.

The PGA analysis of boron provides us not only the information on boron contents but also on boron states by probing the Doppler broadened line shape of 478-keV gamma-ray.⁷⁻¹⁰ The initial recoil energy imparted to a ⁷Li ion by the nuclear reaction is 840 keV, corresponding to an initial velocity ($4.8 \times 10^6 \text{ ms}^{-1}$) of a ⁷Li nucleus. A ⁷Li nucleus with a lifetime of $1.05 \times 10^{-13} \text{ s}$ emits a 478-keV gamma-ray in flight, which leads to Doppler energy shift. Because the direction of the ⁷Li recoil is isotropic, the spectral line shape is observed with Doppler broadening. An energetic ⁷Li ion loses kinetic energy through interaction with atoms that the moving ion encounters in medium. It was proved experimentally and theoretically that the velocity $v(t)$ decreases with time t as follows:

$$v(t) = v_0 \exp(-Dt) \quad (1)$$

where v_0 is the initial velocity ($4.8 \times 10^6 \text{ ms}^{-1}$) and D is known as the “degradation constant,” which primarily depends on the elemental constituent and density. The flight

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distance of the ${}^7\text{Li}$ ion is less than ca. $0.5\ \mu\text{m}$ in condensed phase.

In this study, we recorded the spectra of 478-keV prompt gamma-rays in Japanese cedar (*Cryptomeria japonica* D. Don) wood containing boron. Herein reported are the boron contents and D values obtained by curve fitting of the PGA data.

Materials and methods

Sapwood blocks, $15\ (\text{T}) \times 15\ (\text{R}) \times 50\ (\text{L})\ \text{mm}$, were cut from an 80-year-old Japanese cedar planted in Akita Prefecture, and used as specimen for boron-impregnation treatment. Details of the treatment procedures have been published previously.¹⁻³ Samples for PGA were cut as a disk, 5–10 mm in diameter and about 1 mm in thickness, from the center or end grain part of the treated wood block. These disk samples did not contain any part within 1 mm from the surfaces of the wood blocks because microcrystalline boric acid was concentrated at the surfaces.^{2,3}

PGA of the wood samples was performed using the prompt gamma-ray analyzing system installed at the thermal-neutron beam guide of JRR-3M at the Japan Atomic Energy Agency.^{5,6} The thermal neutron flux was $6.5 \times 10^7\ \text{cm}^{-2}\text{s}^{-1}$. Measuring time varied from 10 min to 2 h depending on the boron content of the wood samples. Boron content and degradation constant (D) were determined from our line shape analysis procedure.⁸

In order to determine boron contents, a PGA measurement of the reference standard was carried out under conditions that were identical to those used for the wood samples. The reference sample was prepared by adding aqueous solution containing a known amount of boron to a piece of filter paper. For comparison of D values, polycrystalline (solid) boric acid and aqueous solution of boric acid ($0.8\ \text{mol dm}^{-3}$) were also submitted to PGA measurement.

According to Yonezawa,⁵ the detection limit of boron in the PGA system was $0.0097\ \mu\text{g}$. The accuracy was found to be about 99.5% for a measurement of 0.05 mg of boron with a measurement time of 30 min in our PGA system, which was estimated from the statistic counting error and the fitting error.

Results and discussion

Figure 1 depicts a typical spectral line shape of 478-keV prompt gamma-ray, which is for a wood sample cut from a Japanese cedar sapwood block treated with $1.9 \times 10^{-2}\ \text{mol dm}^{-3}$ aqueous boric acid solution. The abscissa refers to energy shift from 478 keV. The Doppler broadened line width was seen to be about 13 keV as shown in Fig. 1, although the full width at half maximum was obtained as 1.3 keV for gamma-rays emitted from stationary ${}^7\text{Li}$ produced by neutron capture of ${}^6\text{Li}$. The solid curve in Fig. 1 is the fitted result, giving a D value of $1.33 \times 10^{12}\ \text{s}^{-1}$.

Table 1 shows the local boron contents and D values of wood blocks treated with boric acid solutions. For the sample treated with $7.3 \times 10^{-1}\ \text{mol dm}^{-3}$ methanolic boric acid solution, the boron content near the end grain was approximately ten times larger than that at the center of the wood block. This large difference in boron content between

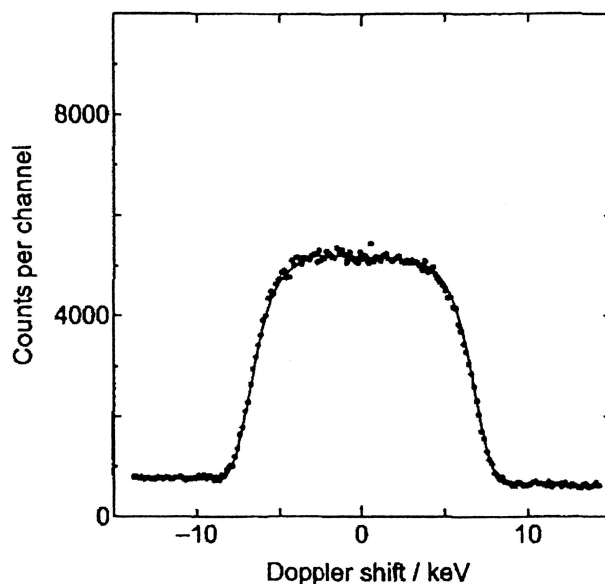


Fig. 1. Prompt gamma-ray spectrum of boron in sample cut from the center part of wood block treated with $1.9 \times 10^{-2}\ \text{mol dm}^{-3}$ aqueous boric acid solution

Table 1. Boron content and degradation constant of wood sample treated with boric acid solution

Location of Japanese cedar sample in wood block	Initial boric acid concentration in treatment solution (mol dm^{-3})	Solvent	Boron content (wt%)	Degradation constant ($10^{12}\ \text{s}^{-1}$)
Center of block, control	No treatment		0.0098 ± 0.0006	1.37 ± 0.03
Center of block	0.019	Water	0.0261 ± 0.001	1.33 ± 0.01
Center of block	0.20	Water	0.422 ± 0.002	1.36 ± 0.02
Center of block	0.73	Water	1.029 ± 0.009	1.33 ± 0.02
Center of block	0.020	Methanol	0.0245 ± 0.004	1.35 ± 0.05
Center of block	0.18	Methanol	0.161 ± 0.001	1.32 ± 0.02
Center of block	0.73	Methanol	0.854 ± 0.009	1.40 ± 0.02
Vicinity of end grain	0.73	Methanol	9.19 ± 0.10	1.36 ± 0.02
Solid boric acid				1.39 ± 0.01
Aqueous boric acid solution ($0.8\ \text{mol dm}^{-3}$)				1.10 ± 0.01

Errors were estimated from fitting results

the parts had been expected from our previous Raman studies¹⁻³ and was further confirmed by PGA.

There was no significant difference in boron content at the center between wood samples treated with $1.9 \times 10^{-2} \text{ mol dm}^{-3}$ aqueous and methanolic boric acid solutions. However, the boron contents of the samples treated with $2.0 \times 10^{-1} \text{ mol dm}^{-3}$ aqueous solution and with $1.8 \times 10^{-1} \text{ mol dm}^{-3}$ methanolic solution were 0.422% and 0.161%, respectively. Moreover, in the case of $7.3 \times 10^{-1} \text{ mol dm}^{-3}$ solutions, it was apparent that the boron content of the sample treated with aqueous solution was larger than that of the sample treated with methanolic solution. Thus, the PGA results indicate that the boron content at the center of the wood block treated with the aqueous solution is higher than that treated with methanolic solution when the initial boric acid concentration increases to some degree. A possible explanation for the differences in boron content is the swelling power of the solvent. Although the solvent effect is not obvious in low concentration solutions, water molecules probably pull a greater amount of the boron species into the cell wall than methanol molecules in intermediate or high concentration solutions because water has a more powerful swelling property than methanol.

Line shape of the prompt gamma-ray spectrum reflects physicochemical environments around boron.^{9,10} Therefore, we can obtain information on the chemical state of boron in the sample by determining the D value depending on the spectral line shape. It is revealed in Table 1 that D values of boron in wood are equal to or slightly lower than that of solid boric acid ($1.39 \times 10^{12} \text{ s}^{-1}$).

We also developed the calculation procedure for the D value in material according to the Lindhard-Scharff-Schiott (LSS) theory¹¹ for energy loss of charged particles with high kinetic energy.^{7,9,10} The elemental composition of wood should be estimated to be $\text{C}_{32.4}\text{H}_{46.7}\text{O}_{20.9}$ when trace elements with a sum weight percentage of 1% are neglected. The apparent specific gravity in oven-dry Japanese cedar wood used in the present work was 0.34. Thus, if this value is adopted, the degradation constant D for Japanese cedar

wood is $0.41 \times 10^{12} \text{ s}^{-1}$. In the case of using specific gravity of wood substance (1.50), we calculated that the D value is $1.81 \times 10^{12} \text{ s}^{-1}$. Both the D values calculated from LSS theory are quite inconsistent with the D values for the wood samples shown in Table 1, suggesting that micro air space and water in the cell wall should be taken into account for ^7Li degradation processes. The results for D values are currently under further investigation.

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