Development of a solid-state scintillator using a porous glass for detecting tritium in water

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Abstract

We have developed a solid-state scintillator by impregnating a porous glass with benzoic acid (BA), 2,5-diphenyloxazole (PPO), and 1,4-bis(5-phenyl-2-oxazolyl) benzene (POPOP). The developed scintillator does not have high absorption at 470 nm, which is the fluorescence wavelength of POPOP, suggesting that emissions can be detected from the surface as well as from the inside of the scintillator. Therefore, we propose a measurement method, whereby the developed scintillator is immersed in tritium water, and we could measure the tritium water of 83 Bq/µL using the developed scintillator. It was found that BA impregnated in a porous glass was not stable less than PPO and POPOP. The emission efficiency of the scintillator after impregnated in water and then dried was found to be 1/10 due to the decrease in BA. In addition, we examined H_2O adsorption behavior on the scintillator by measuring the substitution rate from D_2O to H_2O. We found that D_2O in the developed scintillator was replaced by H_2O in 210 mins, suggesting that any tritium water adsorbed onto the scintillator would be desorbed within several hours.

1. Introduction

Tritium (³H, T) is a radioactive isotope of hydrogen which has a half-life of 12.3 years, emits β-rays, and decays to ³He. The energy of the emitted β-rays is very low, with an average of 5.7 keV and a maximum of 18.6 keV. Consequently, β-rays have a very short penetration range of 0.9 µm in water.[1] Tritium can be generated naturally or artificially. It is naturally produced when cosmic rays from space collides with nitrogen atoms and oxygen atoms in the atmosphere, and is artificially produced by nuclear weapons tests and the operation of nuclear power plants. After the accidents at the Fukushima daiichi nuclear power plant caused by the Great East Japan Earthquake, the amount of tritium-bearing contaminated water stored in tanks has become a serious problem. A treatment method for this contaminated water has been proposed, whereby diluted contaminated water is discharged into the ocean. However, it is necessary to monitor seawater, tap water, and groundwater, etc. after treated water is discharged. Presently, the measurement of tritium water is generally conducted using a liquid scintillator (LS) combined with a low-background liquid scintillation counter (LSC).[2,3,4] This method is highly efficient for detecting β-rays in treated water but generates a large amount of radioactive organic waste liquid after the measurement. The treatment of radioactive organic waste liquid is time-consuming and expensive. Therefore, a plastic scintillator (PS) is commonly used as an alternative to the LS. [5,6] The efficiency of PS is lower than that of LS, because PS is not transparent and the fluorescence from its

surface could be measured. The previous studies have shown that the hydrophilization of PS [7,8] and vial material and size [8] are important factors affecting the efficiency of measurement with PS. In addition, a pellet-shaped solid scintillator, which uses both an organic scintillator and a fine silica scintillator powder, has been studied.[9] However, the efficiency of such a system remains low. To increase the efficiency of the solid-state scintillator, we aimed to develop a transparent scintillator, comprising a porous glass as the substrate and impregnated with organic fluorescent. In addition, to reduce the amount of radioactive waste, we have examined the reusability of this newly developed solid-state scintillator using D_2O.

2.   Proposed measurement method

To measure tritium content with greater efficiency and less radioactive waste, we developed a solid-state scintillator by impregnating porous glass with benzoic acid (BA), 2,5-diphenyloxazole (PPO), and 1,4-bis(5-phenyl-2-oxazolyl) benzene (POPOP). We proposed a measurement procedure using this scintillator as follows:

(1) The solid-state scintillator is immersed in tritium water in a glass vial container, and the emitted light is then measured using a commercially available LSC equipment.

(2) After the measurement, the scintillator is removed from the tritium water, and dried in the atmosphere to evaporate any tritium water in the pores.

(3) After drying, the scintillator is immersed into the next water sample to measure the tritium content.

Using this procedure, we could use the scintillator repeatedly, reducing the amount of radioactive waste. To realize the proposed measurement method, we evaluated the transparency of the developed scintillator, the stability of BA, PPO, and POPOP in the pores, and the evaporation rate of H_2O from the pores. After this evaluation, we conducted a trial tritium measurement using the developed scintillator.

3.   Experimental

3.1   Preparation of a solid-state scintillator using a porous glass and its properties

Porous glass (Gikenkagaku, Japan) had the size of 8 mm × 8 mm × 1 mm, an average pore size of 4 nm, and specific surface area of 200 m^2/g. We prepared toluene solvent solution of BA, PPO, and POPOP with five different concentration ratios as shown in Table 1. A porous glass was washed with ethanol solution and immersed into 25 mL of the mixed solution for 24 h. The porous glass was then dried in a dry nitrogen atmosphere for approximately 20 – 24 h, and the UV-vis-near-IR and FT-IR (ATR) spectra of the prepared scintillator was measured using V-770 (JASCO Co., Japan) and Nicolet iS10 (Thermo Fisher Scientific, USA) spectrometers, respectively. In addition, the fluorescence emission spectrum was measured using an F-7000 fluorescence spectrophotometer (HITACHI, Japan) using excitation light at 260 nm.

Table 1   The concentration ratios of the three substances in the prepared solution

Type	BA (mmol/L)	PPO (mmol/L)	POPOP (mmol/L)
A	0.11	0.05	0.02
B	9.71	19.0	0.26
C	1.67	0.91	0.06
D	16.3	8.95	0.54
E	0.08	0.03	0.01

3.2   Stability of impregnated substances in a porous glass

The stability of the three impregnated substances in the pores of the porous glass was evaluated by repeated immersion in a water solution and drying in a nitrogen atmosphere. In particular, the prepared scintillator was immersed into 50 mL of water for 2 h, removed,

and then dried in a nitrogen atmosphere for 24 h. We measured the absorption in the UV-vis-near-IR and FT-IR (ATR) spectra. The cycle of immersing for 2 h, drying in a nitrogen atmosphere, and measuring the scintillator was repeated 5 times. We also impregnated a porous glass with only PPO or POPOP using solutions of 35.8 μmol/L and 6.71 μmol/L, respectively, and evaluated the stability of each reagent in the pores using the same method.

3.3　Tritium water measurement experiment

The tritium water measurement was carried out in three different methods;

(i) The tritium water was measured using the four scintillators prepared with different compositions (Type A to D in Table 1). Each prepared scintillator was placed in a glass vial and 200 μL of the tritium water (910 Bq/μL) was delivered by dropper onto the scintillator in the vial. The emission spectrum was measured for 1 min using the LSC (Tri-Carb 2100TR, PerkinElmer, USA).

(ii) The tritium water was measured using the four scintillators A to D (Table 1). We added 2 mL of the water to the vial described in (i). The scintillator was immersed into the tritium water (83 Bq/μL) and the emission spectrum was measured for 1 min using the LSC.

(iii) The tritium water was measured using the two scintillators B and D (Table 1), after three treatments comprising H_2O immersion followed by drying. A PS with the size of 8 mm × 8 mm was also used for comparison. The prepared scintillator or the PS was placed in a glass vial and 100 μL of the tritium water (445 Bq/μL) was delivered by dropper onto it. The emission spectrum was then measured for 1 min using the LSC.

3.4　H_2O evaporation from a pore surfaces

We used D_2O to evaluate water evaporation from the pore surfaces. The prepared scintillator was immersed in 100 μL of D_2O for 30 minutes, then removed and dried in air at room temperature. The near-IR spectrum was measured every 20 to 30 minutes using a spectrometer (U-4100, HITACHI, Japan).

4.　Results and Discussion

4.1　Properties of a solid-state scintillator

The photographic images of the prepared scintillator (Type D) are shown in Fig.1 (a). When the prepared scintillator (Type D) was irradiated with UV at 254 nm, the light emission was confirmed as shown in Fig.1 (b). The UV-vis absorption spectrum of the prepared scintillator (Type A, B, C, and D) is shown in Fig.2 (a). The prepared scintillator had no absorption from 500 nm to 800 nm and high absorption below 450 nm. The spectrum indicated 91 % transmittance at 470 nm, the fluorescence wavelength of POPOP. The absorption spectra of the three substances (BA, PPO, and POPOP) in the porous glass are shown in Fig.2 (b). PPO and POPOP had an absorption peak at 310 nm and 355 nm respectively, and the amount of PPO and POPOP in the prepared scintillator could be evaluated by the absorbance at 310 nm and 355 nm. Therefore, the enrichment rate of PPO and POPOP was calculated using Lambert-Beer's law (Abs = εCℓ), the molar absorption coefficient of PPO (310 nm) and POPOP (355 nm) in the toluene solution, and its absorbance at 310 nm and 355 nm. The enrichment rate is shown below as Eq. (1).

$$\text{The enrichment rate} = \frac{\text{The concentration in a porous glass (μmol/L)}}{\text{The concentration of impregnation solution (μmol/L)}}$$

(1)

The calculated PPO concentration in the porous glass was 544.5 μmol/L when the absorbance at 310 nm (Abs_{310}) = 2.25, the molar extinction coefficient at 310 nm (ε_{310}) = 41290, and the thickness (ℓ) = 0.1 cm. When the impregnation solution had a PPO concentration of 35.8 μmol/L,
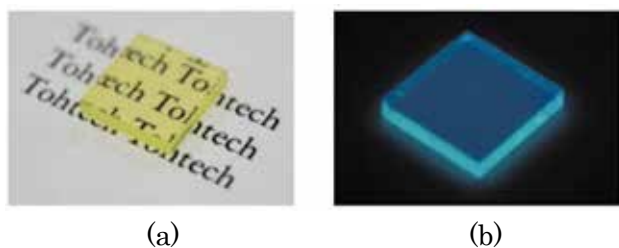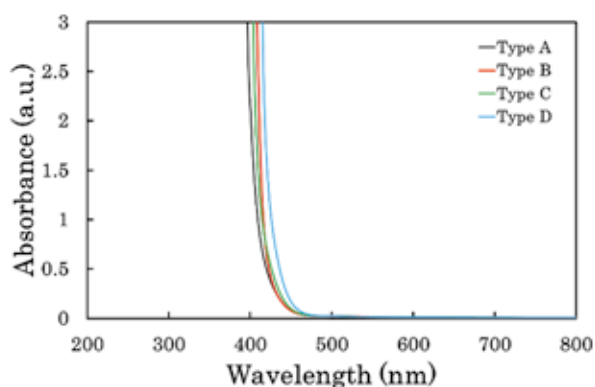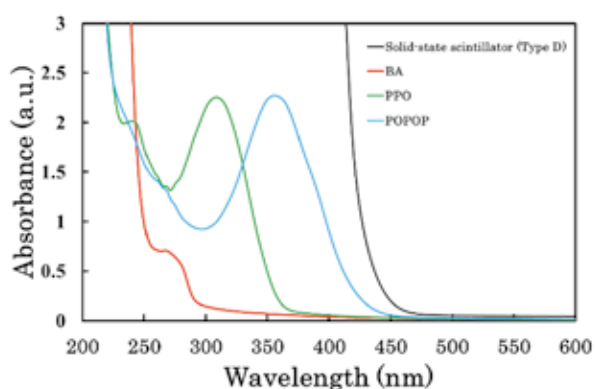
Fig.1　The photographic images of the solid-state scintillator (Type D)：(a) Before UV irradiation, (b) Under UV irradiation

Fig.2　UV-vis spectra of (a) the solid-state scintillators (Type A, B, C, and D) and (b) three substances (BA, PPO, and POPOP) in the porous glass and solid-state scintillator (Type D)

the enrichment rate of PPO was calculated to be 15.2 times greater. The calculated POPOP concentration in the porous glass was 468.7 μmol/L when the absorbance at 355 nm (Abs_{355}) = 2.27, the molar extinction coefficient at 355 nm (ε_{355}) = 48420, and the thickness (ℓ) = 0.1 cm. When the impregnation solution had a POPOP

concentration of 6.71 μmol/L, the enrichment rate of POPOP was calculated to be 69.9 times greater.

The FT-IR ATR spectra of the prepared scintillator (Type D) and a porous glass are shown in Fig.3. The left-axis of Fig.3 shows the relative absorbance with 1800 cm^{-1} as zero. The difference between the prepared scintillator and the porous glass was measured at around 1700 cm^{-1}. Since the absorption at 1700 cm^{-1} was attributed to the C=O bond of BA, the amount of BA in the pores could be evaluated from the absorption at 1700 cm^{-1} in the FT-IR ATR spectrum.
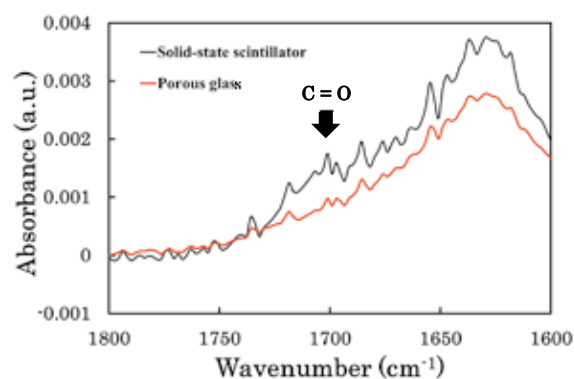

Fig.3　The FT-IR ATR spectra of the solid-state scintillator (Type D) and a porous glass

The fluorescence emission spectra of the four types of prepared scintillator (Type A, B, C, and D) are shown in Fig.4. Emissions from all four scintillators maximized at 470 nm and 360 nm,
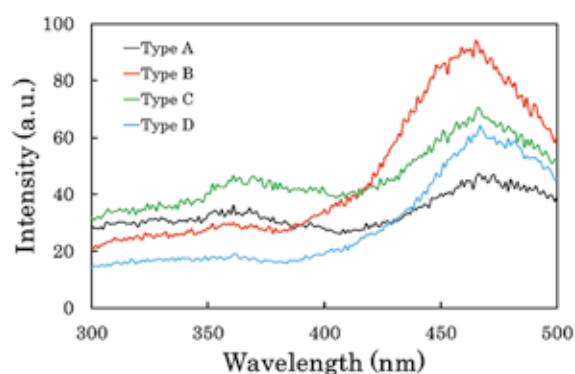

Fig.4　The fluorescence emission spectrum of the four types of solid-state scintillator

attributed to POPOP and PPO, respectively. The Type B scintillator had the highest intensity at 470 nm, and is considered to have the highest fluorescence emission efficiency of the four.

4.2　Stability of impregnated substance in pores of porous glass

Changes in absorption spectra of the sample after repeated H_2O impregnation and drying are shown in Fig.5. The spectrum of porous glass containing PPO, POPOP, PPO&POPOP is shown in Fig.5 (a), (b), and (c), respectively. The spectrum of prepared scintillator (Type E) is shown in Fig.5 (d). The absorbance at 310 nm decreased by approximately 5 %, 4 %, and 4 % for the PPO, the PPO&POPOP and the Type E samples, respectively. The absorbance at 355 nm decreases by approximately 0.6 %, 0.9 %, and 1.3 % for the POPOP, the PPO&POPOP and the Type E samples, respectively. Based on these results, the POPOP would be more stable in the pores than PPO. The absorbance at 240 nm in Fig.5 (d) was attributed to BA, and significantly decreased absorbance at 240 nm was likely caused by the elution of BA. The rate of absorbance decrease at 240 nm was 29.1 %, 23.6 %, 9.1 %, 4.7 %, and 3.8 % at each H_2O impregnation time.

Changes in FT-IR spectra of the prepared scintillator (Type D) after repeated H_2O impregnation and drying are shown in Fig.6. The absorbance at 1700 cm^{-1}, which was attributed to the C=O bond of BA, decreased as the H_2O impregnation time increased, and was
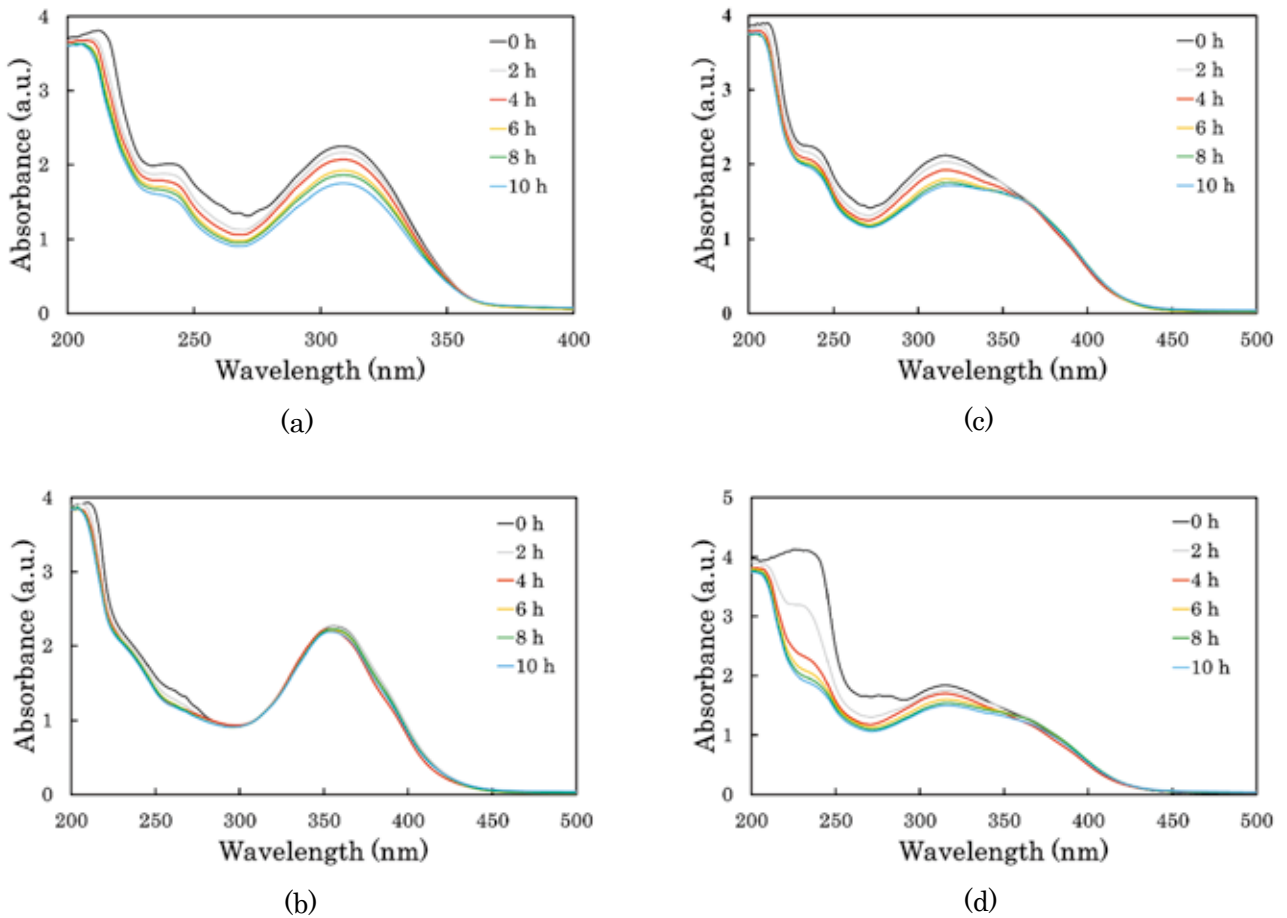

(a)

(c)

(b)

(d)

Fig.5　Changes in absorption spectra of the porous glass after repeated H_2O impregnation and drying: (a) porous glass containing PPO, (b) porous glass containing POPOP, (c) porous glass containing both PPO&POPOP. (d) Changes in absorption spectra of the solid-state scintillator after repeated H_2O impregnation and drying

not observed finally, suggesting that BA was not stable in the pores and was eluted.
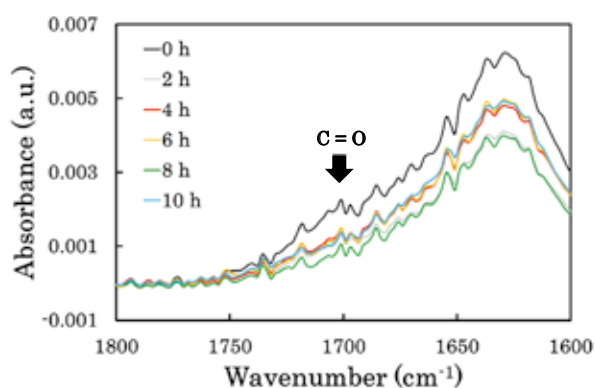

Fig.6   Changes in FT-IR spectra of solid-state scintillator (Type D) after repeated H_2O impregnation and drying

4.3   Measurement of tritium water

The results of tritium water measurement are shown in Table 2. The Type C and Type D have about 10 times difference in the concentration of the impregnation solution, and in both Method (i) and (ii), the intensity of Type D was 1.1 times larger than that of Type C. Based on the enrichment rate calculated in section 4.1, the fixed amounts of PPO and POPOP in Type C scintillator were calculated to be 0.89 μmol and 0.27 μmol respectively, and the fixed amounts of PPO and POPOP in Type D were calculated to be 8.7 μmol and 2.4 μmol respectively. Although the difference of the calculated fixed amounts of PPO and POPOP in Type D were approximately 10 times higher than those in Type C, the measured CPM of Type D was only 1.1 times higher than that of

Type C. This results that the impregnated substance was only adsorbed onto the first layer of pores, and the fixed amount remained fairly constant even if the concentration of the impregnated solution was increased.

The intensity of Type C was 5.2 times larger in Method (i) and 4.5 times larger in Method (ii) than that of Type A. Considering the enrichment rate, the fixed amounts of PPO and POPOP in Type A were calculated to be 0.05 μmol and 0.09 μmol respectively, and the fixed amounts of PPO and POPOP in Type C were 17 times larger and 3 times larger, respectively, than in Type A. The increase in intensity was attributed to the increase in the fixed amount of PPO and POPOP in a porous glass, which was not saturated below 1.0 μmol.

The intensity of Type C in Method (i) was 1.2 times larger than that of Type B and the intensity of Type B in Method (ii) was 1.2 times larger than that of Type C. Since the porosity of the porous glass is 28 %, the inside volume of the pores was calculated to be 17.9 μL. Although the tritium water volume in Method (i) was sufficient to fill the pores, it is unlikely that all pores in the porous glass are filled with tritium water. Surface tension prevents the tritium water from easily entering the 4 nm pores, resulting in greater variation of the measured values in the Method (i).

We defined measurement efficiency as the ratio of intensity to the radioactivity of tritium in water and examined the measurement efficiency of Method (i) and Method (ii). The measurement efficiency was calculated using Eq. (2). Although the measurement efficiency

Table 2   Tritium water measurement results

Type	BA (mmol/L)	PPO (mmol/L)	POPOP (mmol/L)	method (i) (counts/min)	method (ii) (counts/min)	method (iii) (counts/min)	method (i) (I)	method (ii) (I)	method (iii) (I)
A	0.11(5.5)	0.05(2.5)	0.02(1)	324	193	–	0.36	2.33	–
B	9.71(37)	19.0(73)	0.26(1)	1421	999	309	1.56	12.04	0.69
C	1.67(28)	0.91(15)	0.06(1)	1669	864	–	1.83	10.41	–
D	16.3(30)	8.95(17)	0.54(1)	1868	948	87	2.05	11.42	0.20
PS	–	–	–	–	–	344	–	–	0.77

※ I = counts min^{-1}/BqμL^{-1}

calculated by Eq. (2) is different from the general counting efficiency obtained by Eq. (3), we used the value in Eq. (2) for comparison of the measurement methods.

The measurement efficiency =

$$\frac{\text{The measured value (counts/min)}}{\text{The concentration of tritium water (Bq/μL)}} \quad (2)$$

The counting efficiency =

$$\frac{\text{The measured value (counts/min)}}{\text{The radioactivity of tritium water (disintegration/min)}} \quad (3)$$

The calculated measurement efficiency of Method (ii) was several times larger than that of Method (i) with all four scintillators. This result was attributed to the pores not being filled with the tritium water in Method (i), while the pores were filled sufficiently in Method (ii), which reduced the measurement loss.
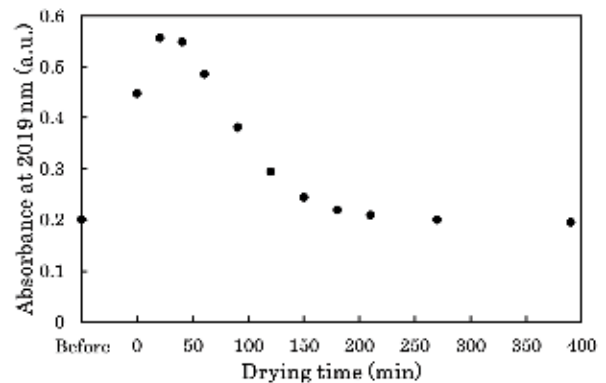
The measurement efficiency with Type B and Type D scintillators was 2.2 times and 10.5 times lower in Method (iii) than in Method (i). This was attributed to the elution of BA in pores, due to the immersion in H_2O, because BA is an essential material for higher measurement efficiency.
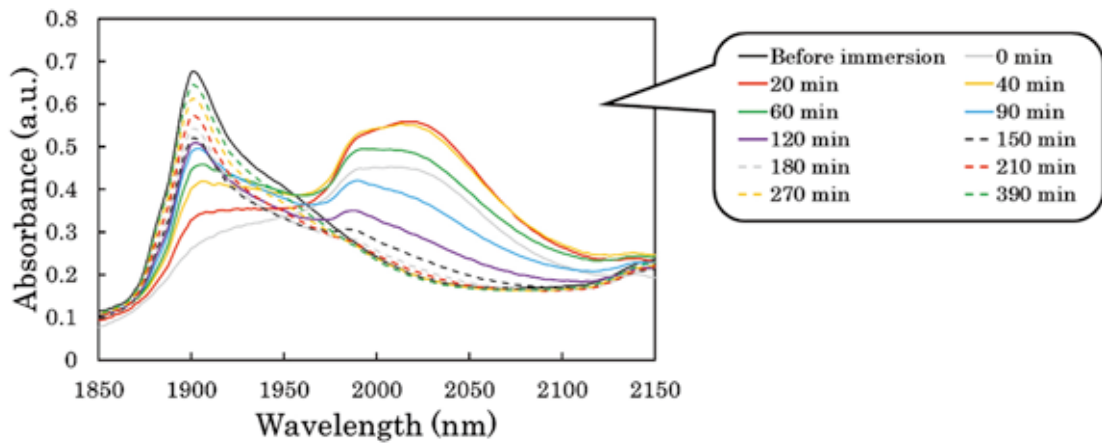
(a)
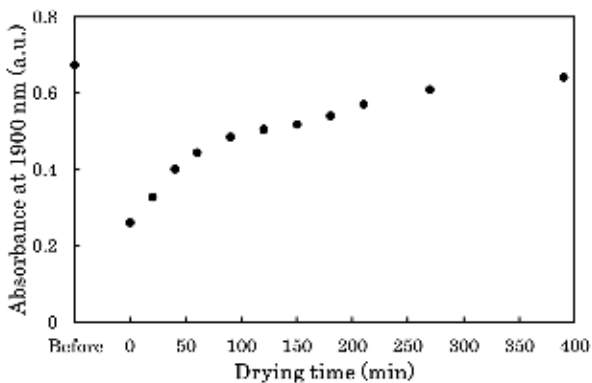
(b)

(c)

Fig.7 (a) Changes in absorption spectrum of solid-state scintillator in D_2O, (b) Relationship between Abs_{1900} and drying time, (c) Relationship between Abs_{2019} and drying time

4.4　D_2O desorption and H_2O adsorption behavior in the solid-state scintillator

The near-IR absorption spectrum of the prepared scintillator (Type D) is shown in Fig.7 (a). The absorption at 1900 nm is assumed to originate from H_2O [10], and the absorption at 2019 nm is assumed to originate from D_2O. The absorbance at 1900 nm and 2019 nm defines Abs_{1900} and Abs_{2019}, respectively. Abs_{1900} and Abs_{2019} variations with drying time are shown in Fig.7 (b) and Fig.7 (c). Abs_{1900} increased and Abs_{2019} decreased as the drying time increased, suggesting that D_2O in the prepared scintillator was desorbed and replaced with H_2O when the scintillator was dried in the atmosphere for 210 mins. This indicates the possibility of tritium desorption in the developed scintillator, because D_2O is an isotope of the tritium water and is thought to have similar chemical properties.

5.　Conclusion

We developed a solid-state scintillator which comprises porous glass impregnated with fluorescent substances (BA, PPO, and POPOP). We evaluated the properties of this scintillator and examined the possibility of using it to measure tritium in water. The transmittance of the developed scintillator was 91 % at 470 nm, suggesting that the emission from the surface, as well as from the inside of the developed scintillator can be detected. We used this scintillator to measure the tritium content of water of 83 Bq/μL. In addition, approximately 4 % of PPO and 1.3 % of POPOP in the developed scintillator were eluted for every 2 h of immersion, and BA in the developed scintillator was less stable in the pores than PPO and POPOP. When BA is not supported in the pores, the measurement efficiency was reduced by a factor of 10, due to the decrease in energy propagation efficiency. We also evaluated the evaporation rate of the water in the developed scintillator and found that D_2O in pores was replaced by H_2O in 210 mins.

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