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## Direct Detection of Aqueous CO<sub>2</sub> by Infrared Waveguide Spectroscopy with an Amorphous Fluoropolymer Coating Rod

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Infrared waveguide spectroscopy using a sapphire rod coated with an amorphous fluoropolymer (Cytop, Asahi Glass Co., Ltd, Japan) has been developed in order to directly observe CO<sub>2</sub> in aqueous solutions. Since the amorphous fluoropolymer has a relatively high gas-permeability and hydrophobic feature, the aqueous CO<sub>2</sub> transmits into the amorphous fluoropolymer coating film, but water cannot penetrate into the film. Good linearity of calibration curves for CO<sub>2</sub> in the gas and the aqueous solution were obtained.

**Keywords** FT-IR waveguide spectroscopy, amorphous fluoropolymer, aqueous CO<sub>2</sub>

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### Introduction

The CO<sub>2</sub> concentration in the atmosphere is emphasized when discussing global environment conservation, including global warming. Because CO<sub>2</sub> in the atmosphere is constantly exchanged, especially between the oceans, lakes, and river water, the measurement of CO<sub>2</sub> dissolved in these locations is a very important issue for researchers in analytical chemistry. Generally, dissolved CO<sub>2</sub> is measured by quantifying the CO<sub>2</sub> that is distributed in the gas phase by gas-exchange equilibrium.<sup>1-3</sup> This method requires a relatively large device, and it takes a long time to achieve equilibrium for its distribution to the gas phase. Also the CO<sub>2</sub> concentration at the ocean surface can only be measured by this method. pH measurements using a pH indicator have also been reported for measuring dissolved CO<sub>2</sub>.<sup>4,6</sup> Changes in the equilibrium due to the addition of indicators must be paid sufficient attention concerning this method. It is necessary to measure another parameter for an equilibrium calculation. In these assays, dissolved CO<sub>2</sub> is indirectly measured using the chemical equivalent calculation. Thus, faster and more accurate direct quantitation of the aqueous CO<sub>2</sub> is expected to be realized. Electrochemical CO<sub>2</sub> detection using a carbonate selective electrode in seawater has also been reported.<sup>7</sup> An electrochemical assay is convenient and highly sensitive; thus, further development is expected. On the other hand, we have examined a direct determination of dissolved CO<sub>2</sub> by infrared waveguide spectroscopy. The optical waveguide technique has often been used in CO<sub>2</sub> detection using visible light.<sup>6</sup> However, there has been no reported example of CO<sub>2</sub>

detection using infrared light. This is because water is a major interference in infrared spectroscopy. In this study, we have developed an infrared waveguide spectroscopy technique with an amorphous fluoropolymer (Cytop) as a cladding material in order to detect aqueous CO<sub>2</sub>. The material has a low refractive index, and a relatively high gas permeability. It is possible to detect only the gas component, without passing water through the material in the aqueous sample solution.

### Experimental

#### *Reagents and chemicals*

CO<sub>2</sub> standard gas (99.9%) was obtained from GL Sciences Inc. Tokyo, Japan. Each concentration of CO<sub>2</sub> gas was obtained from dilution by N<sub>2</sub> gas in a tightly sealed bag (150 × 250 mm, 1 L of internal volume). Sodium hydrogen carbonate was purchased from Wako Pure Chemicals Co. Ltd (Osaka, Japan).

#### *Apparatus*

The experimental setup is shown in Fig. 1 (a photograph of the device is shown in Fig. S1 in Supporting Information). FT-IR spectra were recorded using a FT-IR spectrometer (FS9550, Jasco Corp., Tokyo, Japan). A sapphire rod (4 mmφ, 155 mm long) coated by an amorphous fluoropolymer (Cytop, Asahi Glass Co., Ltd, Japan, which was coated by a small factory, 1 μm thickness) was used as a core material of the waveguide. The rod was fixed in the center of the PTFE tubing (i.d., 6 mm; o.d., 8 mm). The internal volume of the cell was 2.4 mL. Infrared light from the FT-IR spectrometer was introduced from an edge of the rod at 35° with respect to the reflection surface. Because the light source was not collimated it showed a central angle of the incident light. The light was transmitted through the rod by multiple total reflection. The rod acted as an optical waveguide. The output light from the

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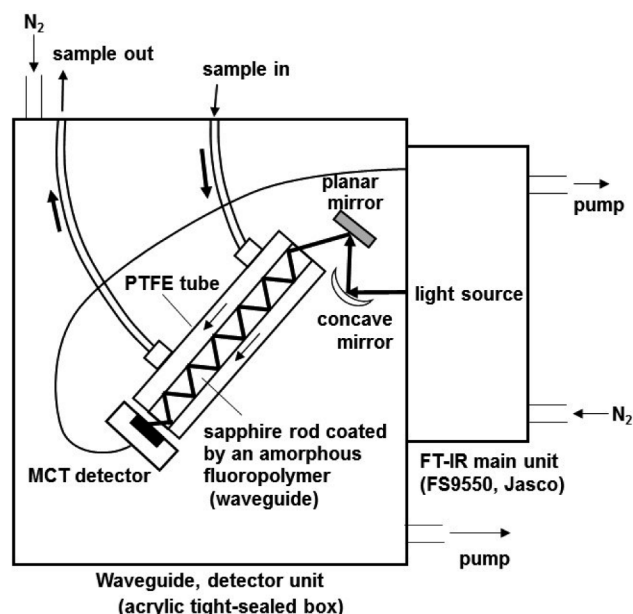


Fig. 1 Experimental setup.

opposite edge of the waveguide was detected by a HgCdTe (MCT) detector. The flow cell and the detector were set in an acrylic tight-sealed box (35 cm (W)  $\times$  45 cm (D)  $\times$  15 cm (H)), and the sample gas/solution was injected from outside of the box. To prevent interference by water vapor and CO<sub>2</sub> in the air, inside the box and the light source unit of the FT-IR spectrometer were replaced with N<sub>2</sub>. The detailed procedure of the N<sub>2</sub> substitution was as follows:

(1) The light source unit of the FT-IR spectrometer was vacuumed by a diaphragm pump (FTP-20A; Iwaki Co. Ltd., Japan) for 30 s with a pressure difference from the atmosphere of 0.06 MPa. Then, N<sub>2</sub> gas was flowed into the unit until the pressure difference to the atmosphere became 0 MPa. These procedures were repeated 4 times.

(2) The acrylic box and the inside of the optical waveguide cell were also vacuumed by the diaphragm pump with the pressure difference from the atmosphere of over 0.02 MPa; shortly after that, N<sub>2</sub> gas was supplied into the box and the cell. This was continued for over 10 min.

(3) Before sample injection, N<sub>2</sub> gas, or N<sub>2</sub> bubbled water (purified by Milli-Q system) was flowed into the cell for 3 min at 0.7 L/min for the gaseous sample or with 2.5 mL/min for the aqueous sample, respectively. Then, the transmitted light intensity was measured for a spectral reference.

(4) During the measurement, N<sub>2</sub> gas was flowed at 0.7 L/min into the acrylic box in order to prevent the mixing of air into the box.

In preliminary experiments, this procedure was optimized. The details are described in Supporting Information.

## Results and Discussion

### Detection of gaseous CO<sub>2</sub>

Figure 2A shows the absorption spectra of standard CO<sub>2</sub> gas with (a) and without (b) an amorphous fluoropolymer coating. Sample gas of 15 mL was injected at first by a plastic syringe, and was then continuously flowed into the cell at 150 mL/h by a syringe pump (KDS100, Kd Scientific Inc., MA, USA).

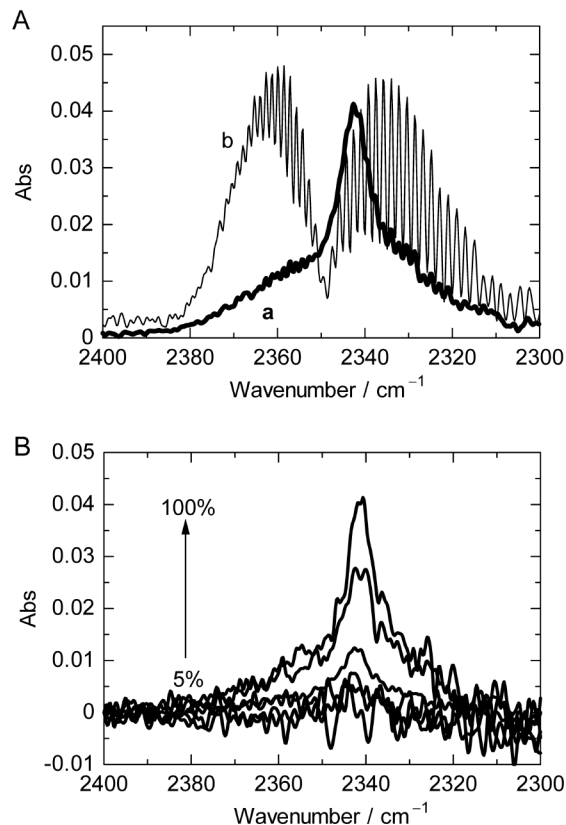


Fig. 2 (A) FT-IR absorption spectra of CO<sub>2</sub> (100%) measured with the amorphous fluoropolymer coating sapphire rod (a) or with the bare sapphire rod (b). (B) FT-IR absorption spectral change for CO<sub>2</sub> concentrations of 5, 10, 25, 50, 75, 100 vol%. N<sub>2</sub> gas was used as the diluent medium.

When a bare sapphire rod was used as a core of the waveguide (line b), fine structures with two major peaks at around 2330 and 2360 cm<sup>-1</sup> were observed. These absorption bands correspond to the antisymmetric stretching mode of CO<sub>2</sub>. This spectrum shows that CO<sub>2</sub> molecules that are rotating freely in the sample gas are detected. On the other hand, there was only one peak in the spectrum that was measured by an amorphous fluoropolymer coating sapphire rod as a core of the waveguide (line a). This shows that CO<sub>2</sub> molecules were bound in the amorphous fluoropolymer film, and these molecular movements were prevented.<sup>8-10</sup> Also, the transmitted light was two-times greater than that without the amorphous fluoropolymer coating. The incident infrared light was passed through inside the sapphire rod with multiple reflections at a sapphire/gas or a sapphire/amorphous fluoropolymer interface. Because the CO<sub>2</sub> molecules present near the interface absorbed evanescent light generated at the reflection surface, the absorption spectrum was observed. Since the amorphous fluoropolymer has a high gas-permeability, CO<sub>2</sub> in the sample gas will be transmitted into the amorphous fluoropolymer coating film. These absorption spectra remained constant within 1 min after sample injection. Further, no change in the spectra were observed after 1 h. CO<sub>2</sub> molecules bounded in the film were certainly to the outside of the film within 3 min by flowing N<sub>2</sub> gas into the cell at 0.7 L/min. Figure 2B shows the absorption spectral change upon the CO<sub>2</sub> concentration (5 to 100 vol%). From the peak absorbance at 2343 cm<sup>-1</sup> of these spectra, a liner calibration curve was obtained as  $\text{Abs} = 4.0 \times 10^{-4}[\text{CO}_2(\text{vol}\%)] - 2.6 \times 10^{-3}$  ( $R^2 = 0.963$ ).

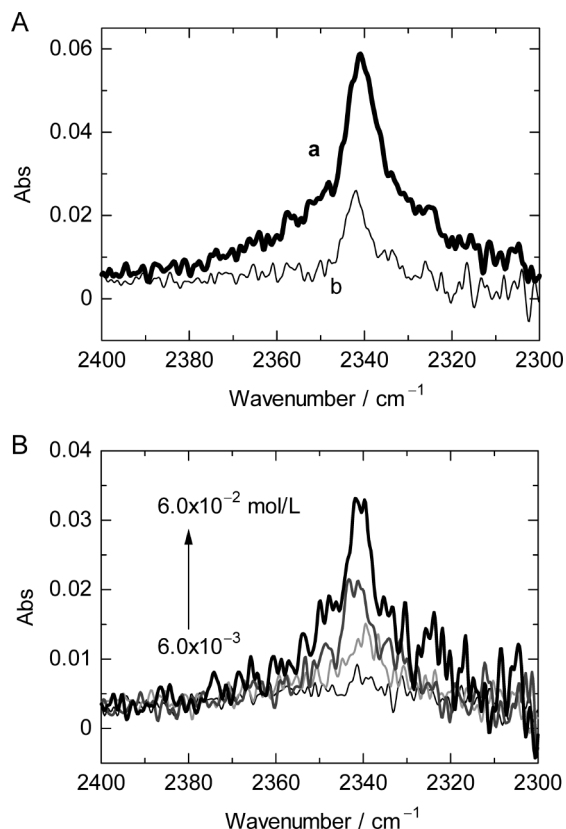


Fig. 3 (A) FT-IR absorption spectra of the NaHCO<sub>3</sub> aqueous solution at a sapphire rod waveguide with (a) or without (b) an amorphous fluoropolymer coating. (B) FT-IR absorption spectral change against the NaHCO<sub>3</sub> concentration;  $6.0 \times 10^{-3}$ ,  $1.2 \times 10^{-2}$ ,  $3.6 \times 10^{-2}$ ,  $6.0 \times 10^{-2}$  mol/L. These solution pH (pH 1.9) values were adjusted by adding H<sub>3</sub>PO<sub>4</sub>.

#### Detection of aqueous CO<sub>2</sub>

Figure 3A shows a comparison of the absorption spectra for commercial soda water with (a) and without (b) the amorphous fluoropolymer coating. Since the amorphous fluoropolymer has a hydrophobic feature as well as a relatively high gas-permeability, the aqueous CO<sub>2</sub> would be transmitted into the amorphous fluoropolymer coating film; however, water cannot penetrate into the film. Since these spectra showed only one peak, even when there was no amorphous fluoropolymer coating, it is considered that the detected CO<sub>2</sub> molecules were slightly adsorbed on the bare sapphire rod. However, the sensitivity, *i.e.* the transmitted light intensity, improved about three-times more intensely due to the amorphous fluoropolymer coatings. This means that the CO<sub>2</sub> in the aqueous phase was strongly distributed into the amorphous fluoropolymer film. Then, a NaHCO<sub>3</sub> aqueous solution, whose pH was adjusted at pH 1.8–1.9 by the addition of phosphoric acid, was prepared and was flowed into the waveguide cell as a sample. The sample solution was continuously flowed into the cell at 150 mL/min by a syringe pump after rapid manual injection of the sample solution. Figure 3B shows the absorption spectra of 6 to 60 mM of NaHCO<sub>3</sub>. The peak absorption at 2342 cm<sup>-1</sup> increased with the NaHCO<sub>3</sub> concentration. The calibration curve of  $\text{Abs} = 0.440[\text{CO}_2] + 0.0033$ ,  $R^2 = 0.9698$ , and a limit of detection of  $1.6 \times 10^{-2}$  mol/L ( $3\sigma$ ) were obtained. These spectra measured for the aqueous samples also remained constant within 1 min

after the sample injections. And, no changes in the spectra were observed after 30 min. The CO<sub>2</sub> molecules bounded in the film certainly moved to the outside of the film within 3 min by flowing N<sub>2</sub> bubbled water into the cell at 2.5 mL/min. The stable repeatability and the high durability of the measurement system were also confirmed from the series of measurements.

Furthermore, the incident angle was changed up to 45°, which is the upper limit of the present apparatus. The change of the transmission intensity due to the incident angle from 10 to 45 degrees is shown in Fig. S3. As a consequence, the transmission intensity decreased to 1/3 of that measured at incident angle of 35°, but the detection sensitivity was improved by about 4.5 times. The absorption spectra are shown in Fig. S4 against 1.2 to 36 mM of NaHCO<sub>3</sub>. Under this condition, the calibration curve was  $\text{Abs} = 2.02[\text{CO}_2] + 0.0045$ ,  $R^2 = 0.9827$ , and the limit of detection was  $4.4 \times 10^{-3}$  mol/L. This value indicates that it is possible to detect carbon dioxide in the ocean.<sup>11</sup>

## Conclusions

Aqueous CO<sub>2</sub> was directly detected by the FT-IR optical waveguide method. When a bare sapphire rod (4 mmφ, 155 mm long) was used as a core material, its sensitivity was relatively low, since only a little CO<sub>2</sub> adsorbed on the rod surface was detected. On the other hand, the sensitivity was improved by coating of an amorphous fluoropolymer of 1 μm thickness on the sapphire rod.

## Supporting Information

A photograph of the experimental setup, the details of the results concerning the optimization of the N<sub>2</sub> substitution procedures, the change of transmission intensity due to the incident angle and the results obtained at an incident angle of 45° are given in the Supporting Information. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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