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Abstract. We optimized the configuration of a hollow-fiber gas cell used in a Fourier-transform infrared spectroscopy system for quantitative analyses of low-concentration gas components with small sample volume. Numerical calculation shows that the signal-to-noise ratio (SNR) of this measurement system is maximized in a condition dependent on a fiber's bore size and length, transmission loss of the fiber, and absorption coefficient of the objective gas component. From the design calculation, a hollow optical fiber with a large diameter of 2 mm was chosen, and a measurement system was constructed with the fiber. In analyses of measured absorption spectra, evaluation of the total area of multiple peaks with different rotation levels enables precise evaluation of gas components with high SNR. Experimental results with sample gases containing nitric oxide showed that a minimum detection limit <1 ppm is obtained owing to gas-cell optimization and numerical procedures.
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Subject terms: infrared gas spectroscopy; hollow waveguides; infrared fibers.

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1 Introduction

Fourier-transform infrared (FTIR) spectroscopy has been widely applied to gas sensing in various areas such as environmental surveillance, industrial process monitoring, and medical diagnoses. For detection and quantitative analyses of specific gases, tunable infrared lasers represented by quantum cascade lasers (QCLs) have recently been used because of their compactness and ease of handling.[1,2] Since these lasers emit higher power than common infrared-broadband sources and can be modulated by an external controller, lock-in detection enables measurement with very high sensitivity by being combined with multiple-pass, long-path gas cells. For high-speed sensing and samples with very low volume, however, these multipass cells are not very suitable because of the relatively large volume.

Hollow-waveguide-based gas cells for infrared absorption spectroscopy have the advantages of small volume and simple structure. Hollow-core bandgap fibers[3,4] and common hollow-core waveguides with an internal silver reflection layer with silver-iodide overcoating[5–7] have been used as gas cells. To improve sensitivity of absorption spectral measurement, combinations of hollow-waveguide gas cells and QCLs have also been reported.[8,9]

By using theoretical simulations, we carefully optimized the configurations of hollow optical fibers, such as the fiber's length and diameter, to improve the signal-to-noise ratio (SNR) of the measurement with FTIR. As far as we know, this is the first trial to theoretically optimize hollow-waveguide–based gas cells. Due to the optimized parameters, highly sensitive measurement with a low minimum detection limit is possible, and the results are shown in this paper.

2 Design

Figure 1 shows a schematic view of the measurement setup for gas absorption using an FTIR spectrometer and a hollow-fiber gas cell. Infrared light emitted from the spectrometer (Vertex 70, Bruker Optics) is focused on the input end of a coupling hollow fiber by using a gold-coated, off-axis mirror with a focal length of 30 mm. The coupling fiber with a length of 10 cm reduces beam divergence, thus lowering the transmission loss in the connected long hollow fiber functioning as a gas cell. The input end of the hollow fiber is sealed with a ZnSe window, and sample gas is injected into the bore of the fiber. The output power is detected with a HgCdTe detector placed at the distal end of the fiber. Absorption spectra of the sample gas are calculated using a background power spectrum measured with pure nitrogen gas. Although the system is similar to that reported by Kim et al.,[7] the hollow waveguides used in our system are plastic tube–based, hollow optical fibers having an internal silver layer with polymer top-coating.[10] With this type of hollow fiber, inner diameters larger than 1 mm, which provide higher transmitted light power, are available for retaining a fiber's high flexibility.

We first discuss the optimum length of the hollow optical fiber, which results in the highest SNR during measurement, for the design of the hollow-fiber gas cell used in the setup shown in Fig. 1. When the power of the input light is defined as P_0, the power of the detected signal from the gas cell P_S is expressed as

$$P_S(\lambda) = P_0(\lambda)e^{-[2\alpha_L(\lambda)+2\alpha(\lambda)c]l} + N(\lambda). \quad (1)$$

We assume that a hollow optical fiber with length l has an attenuation constant of α_L and that the sample gas with concentration c has an absorption constant of α. From our preliminary experiments, it was found that the dominant source of noise is not a power-dependent shot noise but detector noise that is independent of detected power. In Eq. (1), therefore, the power of noise N overlaps the detected signal.

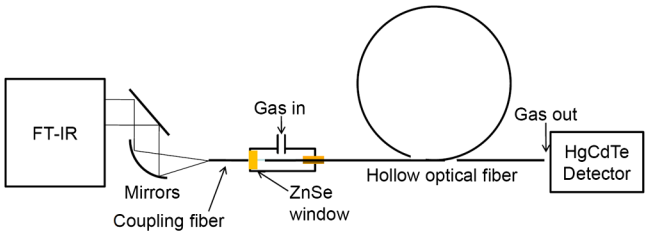

Fig. 1 Schematic view of measurement setup.

Because the output power P of the hollow fiber with nitrogen used as a background is expressed as

$$P(\lambda) = P_0(\lambda)e^{-2\alpha_L(\lambda)l}, \tag{2}$$

the absorption spectrum is calculated as

$$A(\lambda) = \frac{P_S(\lambda)}{P(\lambda)} = e^{-2\alpha(\lambda)cl} + \frac{N(\lambda)}{P_0 e^{-2\alpha_L(\lambda)l}}. \tag{3}$$

Note that noise N is only added to the signal due to randomness. It is apparent that the first term in Eq. (3) is the absorption signal of the sample gas and that the second term is the noise amplitude appearing in the absorption spectra. Therefore, the SNR of the measured spectrum is expressed as the ratio of these two terms as follows:

$$\mathrm{SNR}(\lambda) = \frac{P_0[1 - e^{-2\alpha(\lambda)cl}]e^{-2\alpha_L(\lambda)l}}{N(\lambda)}. \tag{4}$$

Because $P_0/N(\lambda)$ is inherent to the measurement system in Eq. (4), the SNR is dependent on the absorption of measured gas and the transmission loss of fiber. The optimum fiber length l_{opt} is derived by calculating the derivative with respect to length l and solving the zero crossing as follows:

$$l_{\mathrm{opt}} = \frac{1}{2\alpha c} * \ln\left[1 + \frac{\alpha c}{\alpha_L}\right]. \tag{5}$$

To calculate SNR by using Eq. (4), parameters that are inherent to specific measurement systems should be decided. Figure 2 shows input power P_0 and noise N measured for our system with hollow optical fibers of three different diameters. Here, P_0 and N are normalized by the input power to the hollow optical fiber with an inner diameter of 2 mm. In contrast to power P_0 that increases with the fiber diameter, noise N remains a constant value. This means that the detector noise is dominant in the system, as described above.

We calculated the SNR of our system by assigning the above parameters derived from the experiment. We used the constants, listed in Table 1, of a hollow optical fiber with three different diameters and sample gas of nitrogen monoxide (NO), which is frequently used in breath analysis and atmospheric monitoring. The wavelength was set to 5.3 μm, which coincides with an absorption peak of NO gas.

Figure 3 shows theoretical SNR derived with Eq. (4) for hollow fibers with three different diameters. The figure shows that the highest SNR was obtained at the optimum length of the hollow-fiber gas cell calculated by Eq. (5). This is a result of the tradeoff between sensitivity increasing with the optical length and transmission efficiency of the fiber that decreases with length. For fibers with larger diameters, the optimum length increases because of the smaller attenuation constants α_L in Eq. (5). The optimum lengths for the hollow fibers with inner diameters of 1, 2, and 3 mm are 1.25, 1.72, and 2.16 m, respectively. From this result, considering balance between high SNR and compactness of the measurement system, we decided to use the hollow optical fiber with an inner diameter of 2 mm as a gas cell in our system.

It is shown in Eq. (5) that the optimum fiber length l_{opt} is affected by gas concentration c; thus, the optimum condition may change with concentration. To investigate this effect, we calculated the optimum fiber length l_{opt} as a function of gas concentration c. Figure 4 shows the results for the fiber with an inner diameter of 2 mm. We confirmed that the optimum length remains constant with a concentration <10 ppm.

Table 1 Parameters used in calculation of SNR.

Inner diameter of hollow fiber (mm)	1	2	3
Attenuation constant of hollow fiber, $\alpha_L(\mathrm{m}^{-1})$	0.40	0.29	0.23
P_0/N at 5.3 μm	1010	2380	3160
Absorption constant of NO at 5.3 μm, α	5.68 cm^{-1}		
Concentration of NO sample gas, c	5 ppm		

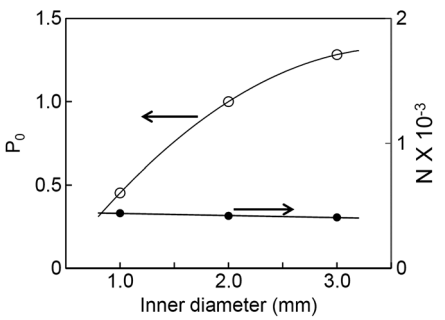

Fig. 2 Powers of input light P_0 and noise N measured using hollow optical fibers with three different diameters.

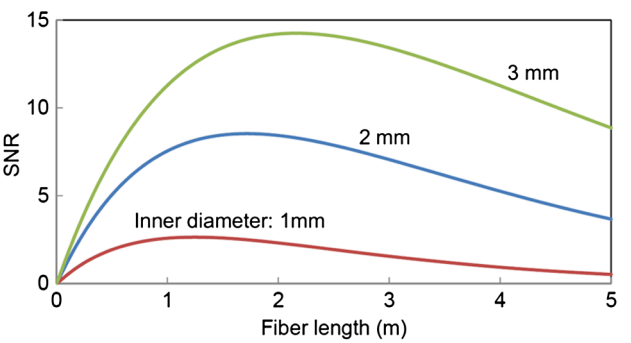

Fig. 3 Theoretical SNR of gas-sensing system with hollow-fiber gas cell as function of fiber length.

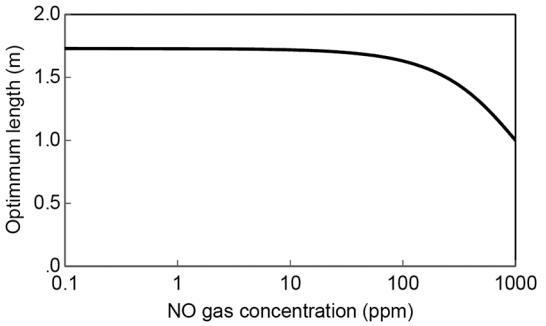

Fig. 4 Calculated optimum fiber length as function of NO gas concentration.

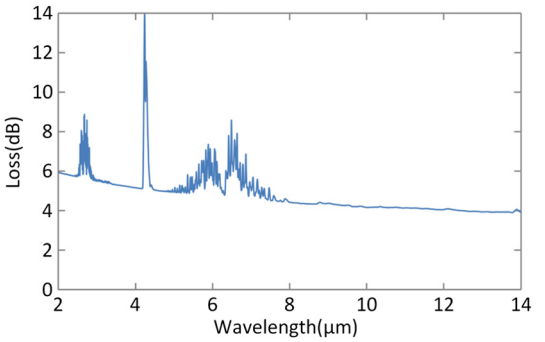

Fig. 6 Measured loss spectrum of hollow optical fiber with inner diameter of 2 mm and length of 2 m.

Therefore, for measuring low-concentration components, such as breath analysis, the effect of concentration on the optimum condition can be ignored.

To make the measurement system compact, coiling the hollow optical fiber is effective, as reported by Fetzer et al.[11] However, bending of hollow optical fiber induces additional losses, which affects the SNR of the measurement system. We investigated this effect. Figure 5 shows additional losses due to bending of the hollow fiber. In the measurement, a hollow optical fiber with an inner diameter of 2 mm and length of 1 m was used. The first 50 cm of the fiber was kept straight and the rest was bent into uniform radii. As previously reported,[12] the loss proportionally increases with the curvature, and at a curvature of 6.7, where the fiber is bent 180 deg, the additional loss was 2.55 dB/m. Figure 5 also shows the maximum SNRs as a function of curvature. These values are calculated from Eqs. (4) and (5) by using the values of the measured bending losses shown in Fig. 5. Bending of hollow optical fiber strongly affects the SNR of the system even with moderate curvatures. Therefore, we found that, from the viewpoint of SNR improvement, looping the fiber is not suitable for detecting low-concentration gases, although it is effective in increasing the optical pathlength of the hollow-fiber-based gas cells.

3 Experiment

Figure 6 shows the loss spectrum of a hollow-core fiber with an inner diameter of 2 mm and a length of 2 m, which results in a sample volume as small as 2 cc. The measurement was done with a spectral resolution of 4 cm^{-1} and an integration time of 64. The fiber is based on a flexible polycarbonate tube having an inner coating of thin silver film that acts as a reflection layer.[10] The fiber is flexible and can be bent into radii smaller than 10 cm and looped to make the gas-sensing system more compact. However, the fiber was kept straight for simplicity for our experiment. During the experiment, the bore of the fiber was filled with air, and absorption peaks of water were observed at wavelengths of around 3 and 6 μm, as shown in Fig. 6. Although strong absorption peaks of CO_2 were also observed at 4.2 μm, these peaks did not affect the wavelength of around 5.3 μm, where there were absorption peaks of NO.

Figure 7 shows the absorption spectrum of 5-ppm NO gas measured with the setup in Fig. 1. The spectral resolution in this measurement was 0.5 cm^{-1} and the integration time was 256. The measurement time was around 6 min. A standard gas with a concentration of 10 ppm (nitrogen balance) was diluted with nitrogen using mass flow meters. Many peaks corresponding to the rotational levels of NO molecules clearly appeared around the wave number of 1875 cm^{-1}. Figure 8 shows the SNR for the measurement of 5-ppm NO using hollow-fiber gas cells with different lengths. The SNRs coincided well with the estimated value shown in Fig. 3, and they saturated with lengths larger than 2 m.

For low concentrations, such as a few parts per million and <1 ppm, the SNR is not very large, as shown in Fig. 7, which makes precise quantitative analyses difficult. To improve repeatability, we simultaneously evaluated multiple peaks. Figure 9 shows an enlarged spectrum of four strong peaks around 1900 cm^{-1}. We calculated the total area of these four peaks using original software. The software first defines a baseline by filtering out noise, automatically detecting the peaks, and calculating the total area of the four

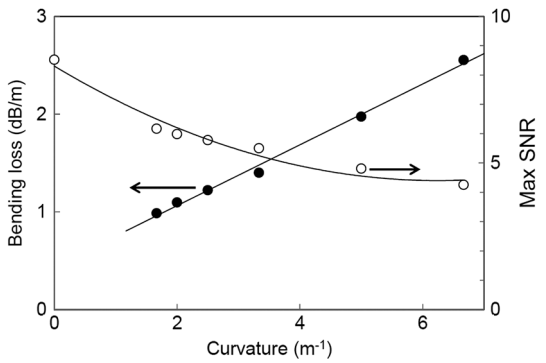

Fig. 5 Measured bending losses of hollow optical fiber and calculated maximum SNR as a function of curvature.

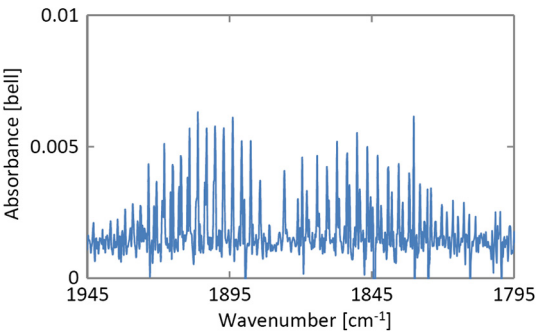

Fig. 7 Absorption spectrum of 5-ppm NO gas measured using hollow-fiber gas cell.

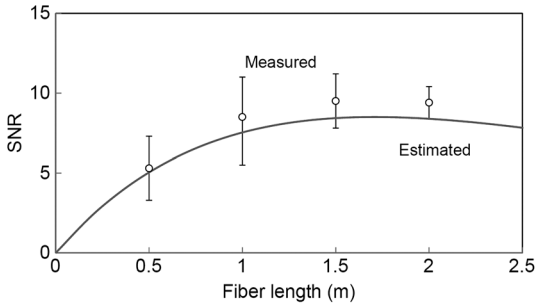

Fig. 8 Measured SNR compared to estimated values.

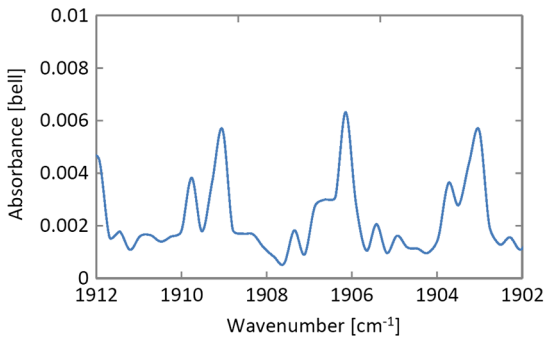

Fig. 9 Measured absorption peaks of 5-ppm NO gas.

peaks with a trapezoid formula. By using peak area instead of peak height, variation in measured peak height that is mainly caused by discrete point measurement can be suppressed.

Figure 10 shows the calculated values of peak height of a single peak [Fig. 10(a)] and total peak area of the four peaks [Fig. 10(b)]. The dots and bars show the averages and errors of the four measurements, respectively. Linear regression lines are also shown. The coefficients of determination R^2 are 0.80 for Fig. 10(a) and 0.99 for Fig. 10(b). By

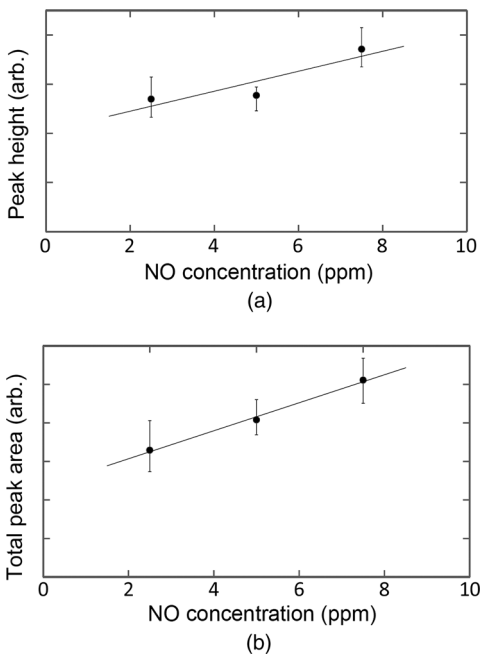

Fig. 10 Calculated values of peak height of single peak (a) and total peak area of four peaks (b) as a function of NO concentration.

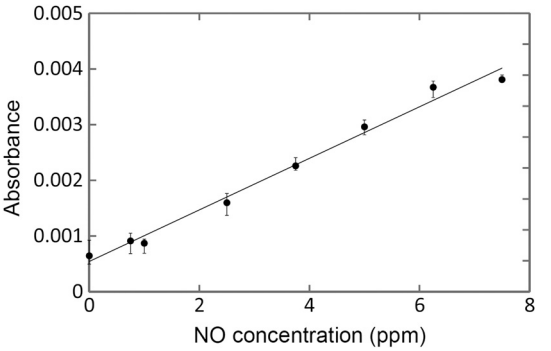

Fig. 11 Calibration curve between absorbance and NO concentration.

calculating the area of multiple peaks, error due to measurement uncertainty can be suppressed. Figure 11 shows a calibration curve between absorbance and NO concentration, which were calculated considering the total area of the four peaks, as shown above. The determination coefficient R^2 is 0.99 for the result in Fig. 11. This result suggests that the minimum detection limit is <1 ppm and that the gas-sensing system is suitable for quantitative measurement of a few parts-per-million concentrations of NO gas.

4 Conclusion

We optimized the configuration of a hollow-fiber gas cell used in an FTIR spectroscopy system for quantitative analyses of low-concentration gas components with small sample volume. Numerical calculation showed that the SNR of this measurement system is maximized in a condition dependent on a fiber's bore size and length, transmission loss of the fiber, and absorption coefficient of the objective gas component. From the design calculation, a hollow optical fiber with a large diameter of 2 mm was chosen, and a measurement system was constructed with a 2-m-long, flexible, plastic-tube-based hollow fiber. Because it was also shown that looping the fiber greatly affects the SNR of the measurement system, the fiber was kept straight in our system. In analyses of measured absorption spectra, evaluation of the total area of multiple peaks with different rotation levels enables precise analyses of gas components with high SNR. Experimental results with a sample gas of NO showed that the minimum detection limit <1 ppm was obtained due to gas-cell optimization and numerical procedures. Although the capability of multiple component analyses is one of the largest advantages of an FTIR spectroscopy system, sensitivity will be greatly improved by using light sources with higher radiation energy, such as quantum cascase laser (QCL), when target components are fixed in advance. By simple estimation, a light source with 100 times higher energy than that of an FTIR system may enable detection of parts-per-billion levels of NO, which will allow the diagnosis of asthma and other respiratory diseases. We are working on the evaluation of a QCL-based gas measurement system and will report the results.

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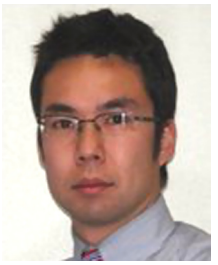

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