# A Raman cell based on hollow optical fibers for breath analysis

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## ABSTRACT

A compact Raman cell based on the hollow optical fiber for highly sensitive breath analysis is reported. A polycarbonate tube-based hollow optical fiber with inner coating of silver is used for both a gas cell and a Stokes collector. An excitation laser light at 532 nm is launched into the cell filled with analytes and the Stokes light collected in the cell is detected by the multichannel Raman spectrometer. A high-reflectivity mirror was placed at the output end of the cell for the effective excitation of trace gases. The Raman spectrum of major breath molecule (oxygen, carbon dioxide, and water) is obtained without a serious decrease of the signal-to-noise ratio even if the cell is coiled into a multiple loop with a 3.8 cm radius. Because the cell examined in this report needs very small volume of only 0.4 ml or less, it has great potential for gas analyses that need fast response such as in critical care and operating rooms.


**Keywords:** Raman spectroscopy, hollow optical fiber, gas analysis

## 1. INTRODUCTION

Quantitative analysis of trace gases in human breath for clinical diagnosis and therapeutic management is an exciting field with great potential [1, 2]. Since the breath analysis causes no pain to patients, it may be incorporated into routine clinical care as blood tests which are used today. Development of trace-gas sensor technologies is a key factor in the advancement of breath analysis. Small, easy-to-use, sensitive and accurate techniques are needed.

Mass spectrometry with or without prior separation by gas chromatography is the most commonly used method to quantify exhaled molecules [1]. Currently, atmospheric pressure ionization mass spectrometry (API-MS) and selected ion flow tube mass spectrometry (SIFT-MS) are the most frequently used methods for direct breath analysis. Mass spectrometry has advantages that it is accurate, highly sensitive, and can monitor many kinds of gases simultaneously with a single device on time scales of seconds [3]. The mass spectrometer is, however, complex and expensive, and thus is not suitable for clinical applications.

It has long been considered that Raman spectroscopy is a potential candidate for the quantitative analysis of gases in human breath [4, 5]. The commonly used Raman setup, which consists of a laser source, a spectrometer and a CCD detector, is simple and robust. The Raman spectroscopy, however, remains less employed in breath analysis mainly because the intensity of the Raman scattered light is so weak that it is difficult to detect signals of trace gasses with sufficient signal-to-noise ratio. Recently, to overcome this problem, Pearman and coauthors proposed a capillary cell for Raman measurements of gasses [6]. In order to enhance the Raman intensity, a capillary tube with Ag film on the inside is used for both a gas cell and a Stokes collector. In this case, the observed Raman intensity is proportional to an effective cell length $x_e$ defined as [7]

$$x_e = \frac{1 - e^{-2(\alpha_1+\alpha_2)l}}{2(\alpha_1+\alpha_2)}, \tag{1}$$

where $l$, $\alpha_1$, and $\alpha_2$ are the physical length of cell, the attenuation coefficient for excitation and Raman scatter lights, respectively. It is clearly found from Eq. (1) that long and low loss cell is necessary to observe strong Raman intensity.

The purpose of this report is to demonstrate the potential of capillary cell in the quantitative analysis of trace gasses in human breath. To improve the signal-to-noise ratio of the Raman spectra, we developed a hollow-optical-fiber based gas cell specially designed for Raman spectroscopy where fluorescence that causes Raman background noise is highly suppressed. We set up a Raman system based on the hollow optical fiber suitable for the analysis of exhaled gases. The effect of fiber bending is examined to verify the feasibility of coiled cell for compact and robust Raman system.

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## 2. EXPERIMENTAL SETUP

Figure 1 shows a schematic of our Raman-gas measurement setup. Linear polarized excitation light from a SHG-Nd:YAG laser is reflected by a long-pass filter (LF) with the 539 nm cut-off wavelength and then focused into the cell via a lens with the focal length of 70 mm. The returned light, which includes Raman scattered light, is collimated by a lens and the light passes through the long-pass filter (LF) and a 532-nm notch filter (NF). it is then focused by a lens with the focal length of 55 mm onto a slit of 100 μm width. The Raman spectra were recorded with a single polychromatic Raman spectrometer with f/4.9 optics and a cooled charge-coupled device (CCD) detector.

Gases are introduced from the input end of the cell that is covered with a metal sleeve. The sleeve covers the end surface of capillary cell not to generate unnecessary noise.

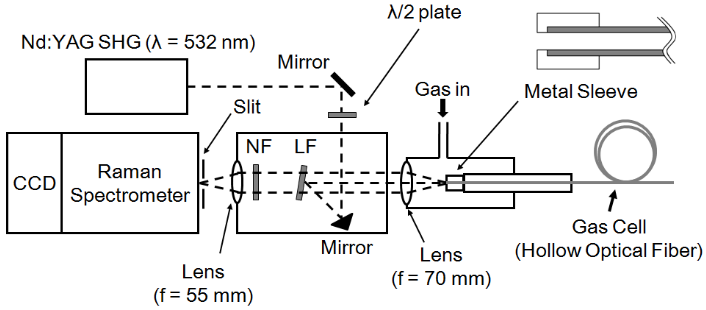


Figure 1. Schematic of the Raman gas measurement setup.

## 3. HOLLOW OPTICAL FIBER FOR RAMAN CELL

We first measured fluorescence background noises from hollow-optical fiber Raman cells. Figure 1 shows Raman spectra of $N_2$ gas measured with four different types of cells, i) silica-glass based hollow optical fiber without the metal sleeve, ii) silica-glass based hollow optical fiber with the metal sleeve, iii) polycarbonate based hollow optical fiber without the metal sleeve, and iv) polycarbonate based hollow optical fiber without the metal sleeve. Although a clear Raman band of $N_2$ at 2324 $cm^{-1}$ is observed for all the cells, it is found that, in the cell based on the glass hollow optical fiber without the metal sleeve, an intense fluorescence background is superposed on the original spectrum over the wide wavenumber region. The background is suppressed effectively by covering a fiber end face with the metal sleeve because the background is generated from the base silica-glass tube, especially in a thin polyimide protective layer on the glass. In a polycarbonate hollow optical fiber, there is little background noise even if the cell has no sleeve. We found, however, that it is better to put a metal sleeve to suppress Raman scattered light of polycarbonate at 1220 $cm^{-1}$ and 1600 $cm^{-1}$. The polycarbonate-tube based hollow optical fiber is useful for Raman gas cell because it has advantages not only in sensitivity, but also in flexibility.

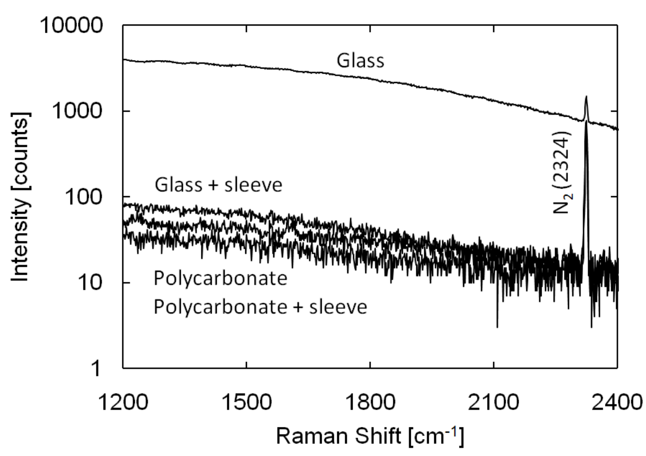


Figure 2. Background noise property of four types of Raman cells. (excitation wavelength: 785 nm)

## 4. PERFORMANCE OF RAMAN CELL

We examined effect of the mirror put at the output end of the gas cell. For the gas cell with the mirror at the end, the observed Raman intensity is calculated as [7],

$$x_e = \frac{1 - e^{-2(\alpha_1+\alpha_2)l}}{2(\alpha_1+\alpha_2)} + \frac{R(e^{-4\alpha_1 l} - e^{-4\alpha_2 l})}{2(\alpha_1-\alpha_2)} + \frac{R^2\left(e^{-2(\alpha_1+\alpha_2)l} - e^{-4(\alpha_1+\alpha_2)l}\right)}{2(\alpha_1+\alpha_2)}, \tag{2}$$

where R is a reflectance of the mirror for the excitation and scattered light.

Figure 3 shows Raman intensities of $N_2$ measured by using Raman cells with and without an aluminum mirror put on the output end of cells. The cells (inner diameter: 700 μm) are straight and the result is shown as a function of the cell length. . We found that the measured intensities coincide well with the theoretical curves, which is calculated by using the Eqs. (1) and (2), In the cells without the mirror, the Raman intensity increases and saturates when the cell length is extended. On the other hand, it is shown that, for the cells with the mirror, there is the optimum cell length at 0.8 m where we observe the maximum Raman intensity. When the cell length is longer than 0.8 m the Raman intensity gradually decreases and then converges to the same value with the cell without the mirror since the effect of the mirror is reduced by the loss of the long cell. The maximum intensity for the cell with the mirror is about 1.5 times larger than that for the cell without the mirror because of double excitation effect by the reflected laser light.

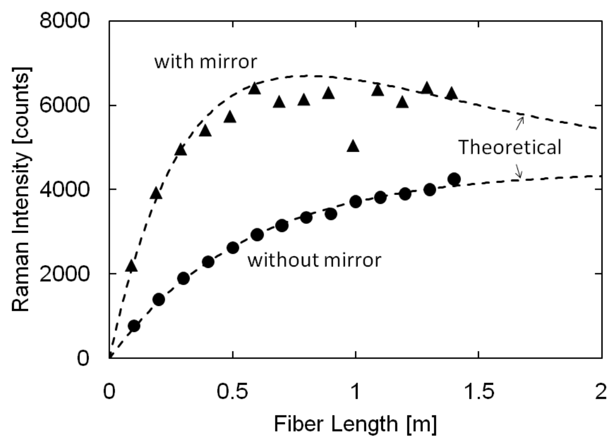


Figure 3. Measured and calculated Raman intensity as a function of cell length. (excitation wavelength: 532 nm)

We next examined the bending property of the Raman cell to check feasibility of compact Raman cells based on the coiled hollow optical fiber. Figure 4 shows the normalized Raman intensities of $N_2$ measured by using the coiled Raman cell as a function of the curvature of loops. The fiber-gas cell used in this measurement has an inner diameter of 700 μm and the length of 1.1 m. The input and output ends of the fiber are kept straight 13 cm and 5 cm in length, respectively. The rest of the fiber is coiled on a spool with a constant curvature. For comparison, the output power of the excitation laser light detected at the output end of the cell is also shown in the figure. These measurements were performed for both polarizations: electric field parallel to the axis of the spool (TE) and magnetic field parallel to the axis of the spool (TM).

In contrast to the output power, which is strongly attenuated by bending, the Raman intensity is kept at about 60% of that of the straight cell even when the curvature is 0.26 $cm^{-1}$, which means that the cell is coiled four times with the bending radius of 3.8 cm. This is because the collection efficiency of the Raman scattered light is higher in the input end of the cell. Note that, because the Raman scattered light collected by the first straight part of 13 cm can be estimated to be about 25 % from Fig. 3, the coiled parts still contribute to enhance the Raman intensity. Although it is known that the bending loss of an Ag hollow optical fiber depends on the polarization, we did not observe clear difference between the polarizations. This may be because the polarization is not maintained in the cell that is sharply bent.

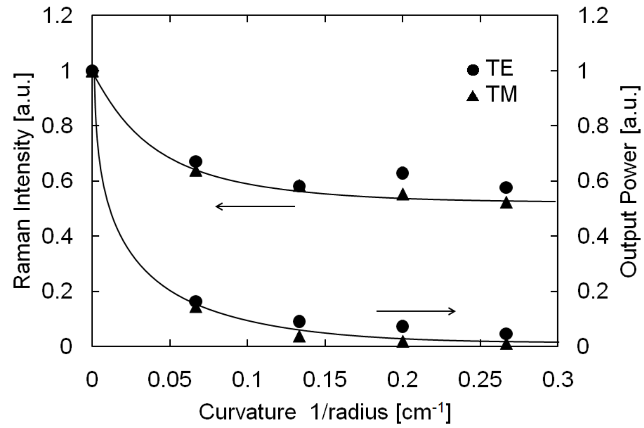


Figure 4. Bending property of the Raman cell. (excitation wavelength: 785 nm)

# 5. BREATH ANALYSIS

We finally measured Raman spectrum of exhaled gases. The result is shown in Fig. 5. In this measurement, we utilized a straight Raman cell with the inner diameter of 700 μm and the length of 1.1 m. The cell is kept straight, and the output end is opened. The typical concentrations of endogenous breath molecules are shown in Table 1. It is shown that the peaks corresponding to $CO_2$, $O_2$, and $H_2O$, which have concentrations of percent level, are clearly observed although bands of other trace gases, which have concentrations of ppm level, is not found in this measurement. Figure 6 shows the intensity of the peak at 1555 $cm^{-1}$ as a function of the concentration of $O_2$ gas. It is shown that the Raman intensity is proportional to the gas concentration in the cell. We roughly estimated the lower detection limit (S/N = 1) at 0.2 % by considering the measured noise level of 60 counts.

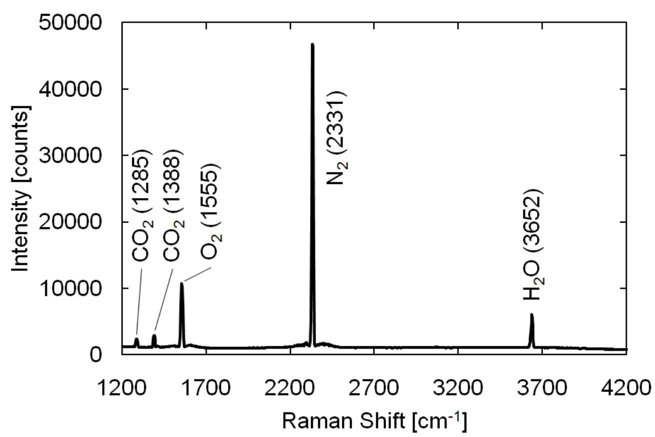


Figure 5. Raman spectrum of a human breath sample. (excitation wavelength: 532 nm)

Table 1. Typical concentrations of endogenous breath molecules [2].

| Concentration level | Molecule |
|---|---|
| percent (%) | oxygen, water, carbon dioxide |
| parts-per-million (ppm) | acetone, carbon monoxide, methane, hydrogen |

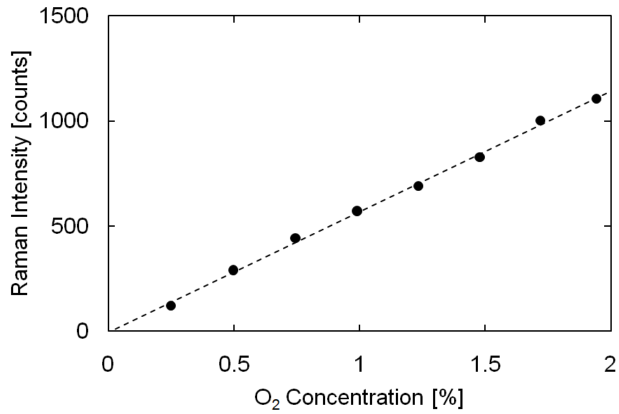


Figure 6. Raman intensity as a function of $O_2$ concentration. (excitation wavelength: 532 nm)

## 6. CONCLUTION

A Raman cell based on the hollow optical fiber for highly sensitive breath analysis was reported. A polycarbonate tube-based hollow optical fiber with inner coating of silver, which had a metal sleeve to minimize the background noise, was used for both a gas cell and a Stokes collector. A high-reflectivity mirror was placed at the output end of the cell for the effective excitation of trace gases. It was found that the Raman spectrum was obtained without a serious decrease of the signal-to-noise ratio even if the cell was coiled into a multiple loop with a 3.8 cm radius. Because the cell examined in this report needs very small volume of only 0.4 ml or less, it has great potential for gas analyses that need fast response such as in critical care and operating room.

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