Guest Forum

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Development of Spectroscopic Technique using Capillary Flow Cells

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Decreasing the diameter of the flow cell used for spectroscopic analysis allows for a smaller sample amount, faster response time, and higher sensitivity through a longer light path. Recently, a special type of optical fiber that traps light in gas or liquid, allowing efficient transmission of visible light or infrared light has been developed. A trend in spectroscopic measurement technology using such a capillary flow cell is introduced in this article.

Introduction

Spectroscopic analysis of fluid such as gas or liquid requires a cell that traps the fluid. Today, we'll discuss using capillary for that cell.

I was involved in the development of optical fiber for infrared light about 20 years ago at HORIBA. At that time, crystals such as alkali halide and metal halide, as well as glass-forming materials such as chalcogenide were used. A problem exists when light is transmitted through a material, because the material absorbs infrared light. After having moved to Tohoku University, I tried transmitting light through a capillary. The original intent was the transmission of laser, but we came upon the idea to use the capillary for spectroscope.

Cells in which liquid or gas flows generally have diameters ranging from 10 to 20 mm. The big advantage of thinning the cell tube down to a capillary of about 1 mm diameter is that the sample amount can be reduced significantly. By merely reducing the diameter from 10 mm to 1 mm, the sample amount can be reduced to 1/100 of the original. A small sample amount allows for fast sampling. Furthermore, if a tube is thin, then it can be wound to make a capillary as long as several meters, and absorption can be increased to allow higher sensitivity. Many have thought of this and many have tried, but it has never been put into practice. Light becomes attenuated when it is transmitted through a capillary. Problems exist in the inner wall of the capillary, but polishing the inner surface of the metals does not necessarily solve them. Here, we will discuss in detail, where the problems exist.

Spectroscopic Liquid Measurement Using Capillary Cell

Practical use of capillary cells for liquid has started earlier than those for gas, in which sample water was fed into a glass capillary for measurement. Typical optical fibers have higher refractive indices at the core and lower at the clad, so that light is totally reflected and trapped inside the core. However, since the internal water (refractive index 1.33) and glass (refractive index 1.5) are inversely arranged with respect to refractive index, total reflection does not occur at the boundary between water and glass. Light is totally reflected when it reaches to the boundary between glass and air, and transmission may somehow occur but with unfavorable sensitivity. If organic solvent is used in place of water, refractive indices become 1.5 for C_6H_6 and CCl_4 and 1.6 for CS_2, which are larger than 1.5 for quartz glass. This leads to total reflection occurring at the boundary between liquid and glass. Since this happens only with organic solvents, extractable components are limited. In addition, organic solvents will absorb infrared light, so there's a problem that configuration can only be used for visible light.

Capillary Made of Fluorocarbon Polymer

The refractive index of water is 1.33, which is less than refractive indices of materials that are found around us. As shown in Figure 1, the refractive index of fluorocarbon polymer is specifically low among others. If this material forms the clad, light can be transmitted by using water as the core. Such capillary cells are already commercially available, manufactured based on fluorocarbon polymer developed about 20 years ago. Fluorocarbon polymer is sold in liquid form, which is coated and then dried to form a thin film. It is a very convenient material, transparent in the spectral range from ultraviolet to infrared with 6 µm wavelengths. Transparent amorphous Teflon tubes are also available, whereas the conventional Teflon tubes are opaque.

Water can be measured using this Teflon tube, and there are several examples of spectroscopic measurement.

It is reported that Fe ion in water may be measured (as low as 2 nmol/m^3) with very high sensitivity using Teflon tube longer than 4 m (Figure 2).

Capillary Made of Fluorocarbon Polymer

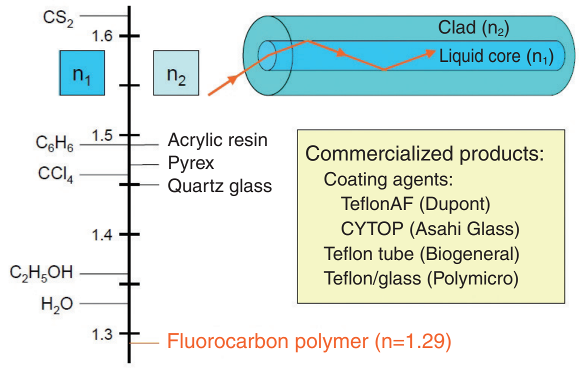
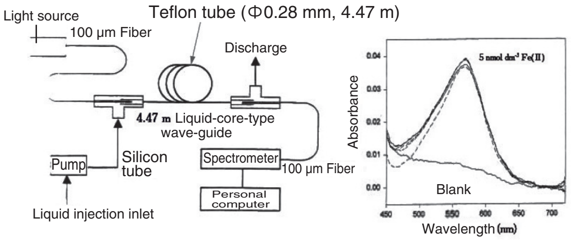


Figure 1 Capillary Made of Fluorocarbon Polymer

Detecting Fe Ion



This system may detect Fe ion in water as low as 2 nmol/m^3.

R. D. Waterbury, *Anal. Chim. Acta*, **357**, 99 (1997)[1]

Figure 2 Detecting Fe Ion
(Reprinted from [1] with permission from Elsevier)

Infrared Gas Measurement Using Capillary Cell

A paper on the application of capillary cells for gas measurements was presented in 1977. The capillary used was a glass tube 3 mm in diameter, with the inside coated with gold, relatively thick for a capillary. It had a transmittance of 30% at 0.5 m length, which was not necessarily sufficient data. Part of the light is absorbed when it reflects on the surface of gold, and the loss is substantial. Transmittance decreases as the diameter is reduced. Figure 3 shows theoretical calculations of transmittance of a glass tube inside coated with gold. If a polished metal tube is used, numbers will drop even lower, influenced by irregular surfaces.

A Capillary Cell for Gas Measurement

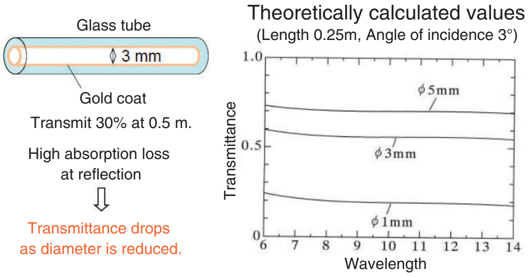


Figure 3 A Capillary Cell for Gas Measurement

Why is there significant loss when light is reflected on metal? Reflectance of metal appears to be high, but in fact drops substantially under certain conditions. As Figure 4 shows, reflectance is greatly influenced by polarization and the incident angle with respect to glass and metal. The reflectance of p-polarized light (linearly polarized light where the oscillation direction of the light electric field is on the plane of incidence) differs considerably from that of s-polarized light (linearly polarized light where the oscillation direction of the light electric field is perpendicular to the plane of incidence). For instance, it is the nature of s-polarized light that reflectance increases as the incident angle increases. With p-polarized light, reflectance decreases as the incident angle increases and reaches zero at a certain angle (the Brewster angle), where after reflectance increases rapidly. The difference between both types of polarized light becomes larger when the refractive index increases. It is a characteristic of metal that the extinction coefficient corresponding to absorption is larger than the refractive index, and in addition it changes significantly by wavelength. With metals, s-polarized light reflects well, but the reflectance of p-polarized light drops depending on the incident angle.

Reflectance will drop further when the wavelength is becomes longer and reaches an area where the refractive index and the extinction coefficient are high. With capillary cells, the system actually works at incident angles at which the reflectance drops rapidly, so metal capillary does not work well fundamentally.

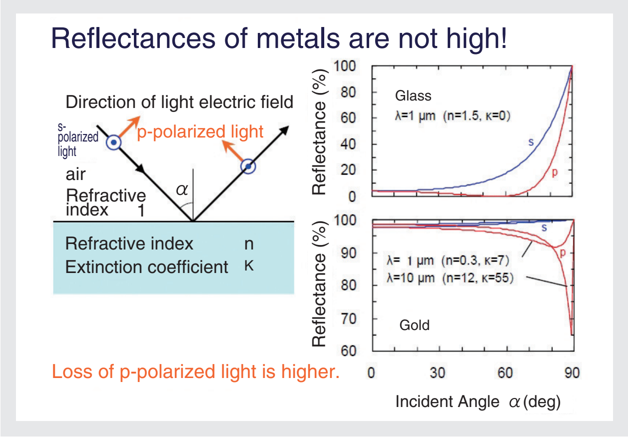


Figure 4 Reflectances of Glass and Metals

Using Total Reflection

If there is a material with refractive index less than that of air, the transmittance may get higher due to total reflection, as in optical fibers. Such materials are rather familiar; the refractive index of quartz glass may be less than that of air, which is 1, depending on the wavelength. The refractive index of glass is 1.4 to 1.5, which drops as the wavelength enters into infrared region. Every material has a characteristic that changes refractive index rapidly in the vicinity of the absorption band. Quartz glass has the absorption band in the vicinity of 9 μm wavelength, and its refractive index drops less than 1 in the region of 7 to 9 μm. Figure 5 shows the refractive index and the extinction coefficient of quartz glass, and the attenuation level of a quartz glass tube, in the infrared region, with the horizontal axis representing wavelengths.

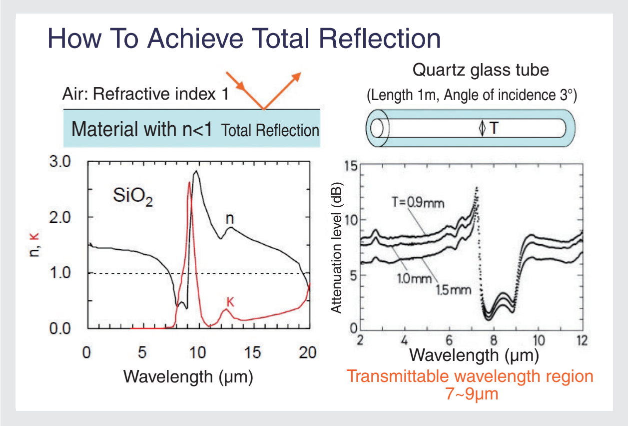


Figure 5 Refractive Index and Extinction Coefficient of Quartz Glass, and attenuation Level

While I was in Tohoku University, I tested about 100 different types of various glass materials, with help from a glass manufacturer, for example, adding Ta or Na to quartz glass, or adding Nb or K to Ge-based glass.
As the result of these tests, we found that the region where the refractive index drops is determined by the ratio of Si in the positive ions of glass. The region of low refractive indices shifts on the long-wavelength side as Si ratio declines (with increasing additives). If Ge is used, the region of low refractive indices lies in the range of more than 10 μm wavelength and shifts on the long-wavelength side with increasing additives. These phenomena are shown in Figure 6. Changing glass composition according to the required wavelength allows transmission of light with various kinds of wavelengths. In addition, since sapphire has refractive indices less than 1 in the wavelength range of 9 to 17 μm, hollow fibers made of sapphire allows transmission in a substantially wide range of wavelengths, from 9 to 17 μm. These are excellent in chemical resistance and high temperature resistance, but impractical because of their high costs.

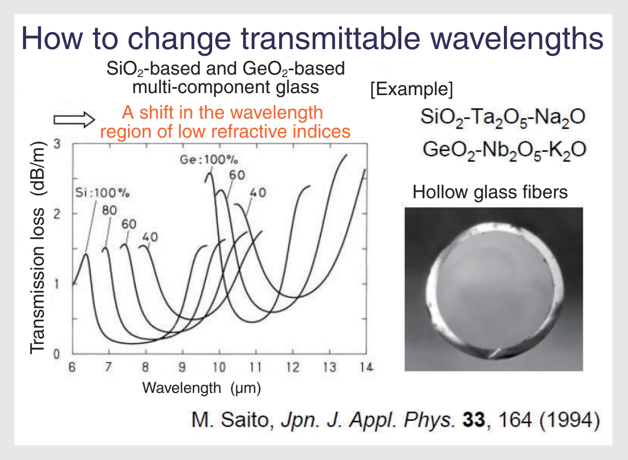
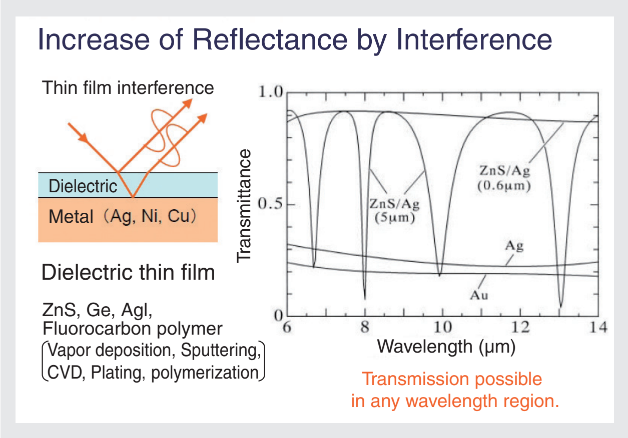


Figure 6 Glass Composition and Transmittable Wavelengths

Increase of Reflectance by Interference

Reflectance is improved by interference if the surface of metal is coated with a thin dielectric film with the comparable thickness as the wavelength of light. For instance, if the surface of Ag is coated with a thin film, the transmittance may increase. Figure 7 compares transmittances of Ag surfaces with thin ZnS films (5 μm and 0.6 μm thick), and uncoated Ag. The advantage of this approach is that altering the thickness can change the transmittable wavelength region.
With the thickness of 5 μm, high transmittance points and low transmittance points cycle, whereas with the thickness of 0.6 μm, the transmittance can be kept high

for a considerably wide region. In the case of capillary manufacturing, dielectric such as ZnS, Ge, AgI, and fluorocarbon polymer would be coated on to metals that can be plated.



Transmission possible in any wavelength region.

Figure 7 Increase of Reflectance by Interference

How can thin film be applied inside the capillary? In an approach developed at Tohoku University, a pipe is first made out of aluminum or polyimide to form a core, to which ZnS is coated by sputtering and then Ag is applied from the outside. On top of it, Ni is coated by electrolytic plating for mechanical reinforcement, before finally melting the core with a chemical agent. This way, a dielectric-coated hollow metal fiber with Ag inside Ni and a thin film of ZnS on the surface of Ag is made.

An alternative is an AgI/Ag-coated hollow glass fiber where an Ag solution is poured into a glass capillary, to coat Ag inside using the so-called silver mirror reaction. Next, a solution containing iodine (I) is poured in the capillary, Ag and I react to form an AgI layer on the surface. The thickness of the AgI film can be made uniform by controlling the flow rate and the temperature. Such products by Polymicro are already on the market at around 170,000 yen/m, based on an idea provided by an Israeli group.

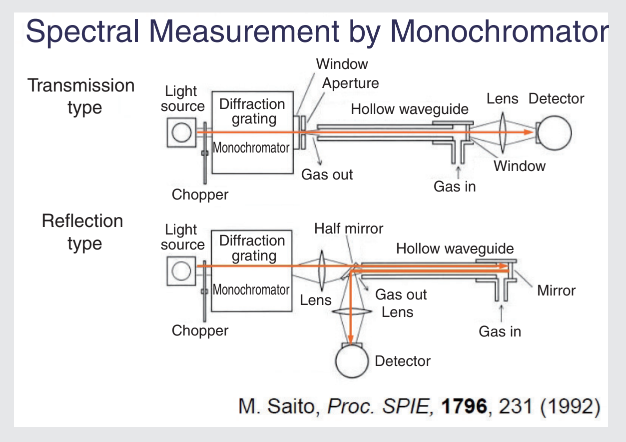
C_2H_4 Gas Detection by CO_2 Laser and Capillary Cells

Infrared gas measurement using capillary cells started over 10 years ago, and various gases have been measured. The first apparatuses used a GeO_2 glass tube that can guide CO_2 laser of 10.6 µm wavelength to measure C_2H_2 that absorbs that wavelength.

Use of laser was inevitable as the onset since ordinary light source provided insufficient light intensity to illuminate the narrow space.

Spectral Measurement by Monochromator

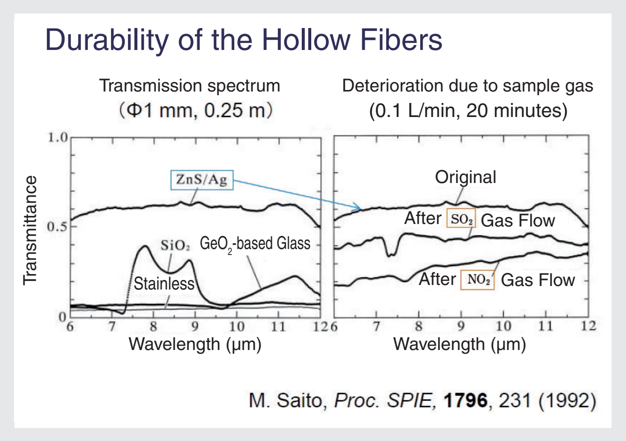
At that time, I conducted spectral measurements using a monochromator. Figure 8 shows the measuring system, transmission and reflection types. The spectral measurement was conducted using a Siliconit light source and a monochromator with diffraction grating, since spectrometers based on FTIR was not yet readily available at the time.



M. Saito, *Proc. SPIE,* **1796**, 231 (1992)

Figure 8 Spectral Measurement by Monochromator

Durability tests of the system were also conducted, and it was found that ZnS/Ag hollow fiber deteriorates when NO_2 or SO_2 flows (Figure 9). This led to the manufacturing of hollow fibers based on SiO_2 or GeO_2, as cited above.



M. Saito, *Proc. SPIE,* **1796**, 231 (1992)

Figure 9 Durability of the Hollow Fibers

Detecting Toxic Gas Using Chemical Reaction

The system we will introduce is not just a capillary, but also a highly functional system (Figure 10). The system has a glass tube with Ag coated on the internal surface. Therefore, it is basically a wave-guide because light is reflected on the Ag surface, but has added reactivity, with a monomolecular film on the Ag surface. Measurement utilizes changes in infrared light absorption levels, when the monomolecular film adsorbs gases that cause sick building syndromes.

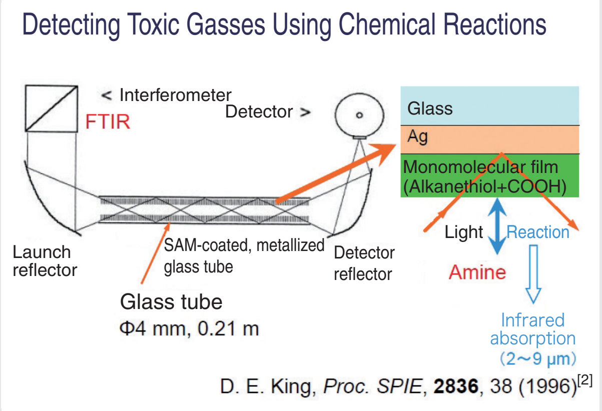


Figure 10 Detecting Toxic Gasses Using Chemical Reactions

Utilizing Quantum Cascade (QC) Lasers or Semiconductor Lasers

With recent developments in infrared light source, there are reports of quantum cascade (QC) lasers and of combining near-infrared light semiconductor laser used for optical communication with hollow fiber. Near-infrared light must have a longer pathlength than infrared because of the smaller absorption. Even though it is a capillary cell, a tube as long as several meters requires time for gas substitution to occur. Therefore, capillary cell is designed to have a number of gas inflow ports to facilitate gas substitution.

Reminders on Using Hollow Fibers

Figure 11 shows reminders when using hollow fibers. It is important to recognize that hollow fiber is not ordinary fiber. Although total reflection occurs when refractive index is less than 1, in adjacent areas where refractive index is less than 1, absorption definitely occurs. It is not total reflection since absorption does occur. For this reason, the angle of incidence and the core diameter is very important. When the angle of incidence becomes larger, the loss of reflection in the p-polarized light increases, and the number of reflection increases as well. Consequently, larger angle of incidence doubles the reduction of transmittance. Reducing the diameter or bending cause an increase in the number of reflection, leading to a reduction of transmittance.

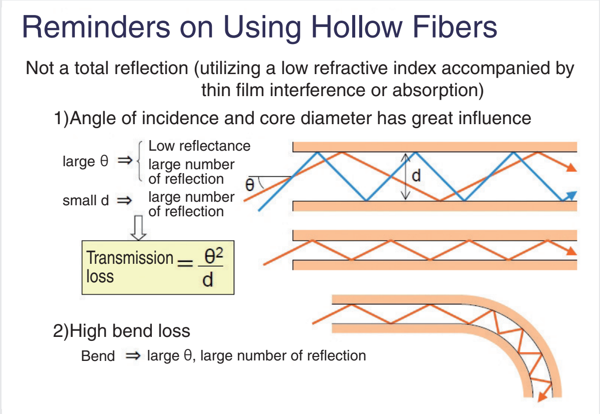
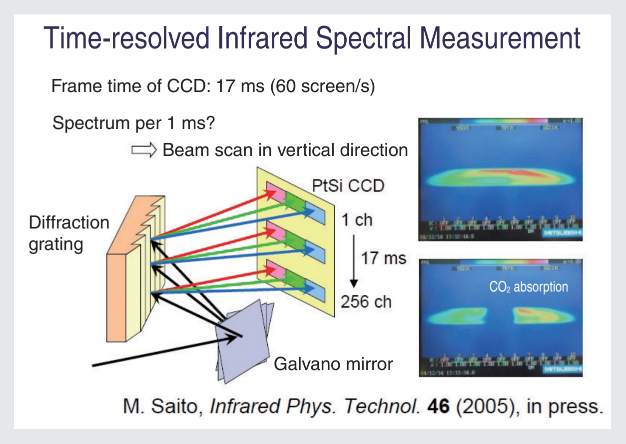


Figure 11 Reminders on Using Hollow Fibers

High Speed Spectral Measurement

At the moment, a spectroscope system featuring a high-speed sampling capability (less than 1 ms at a normal flow rate) of capillary flow cells is under development. Since the response time of the infrared spectrometer is long, the speed of the capillary flow cell is negated. In ultraviolet, visible, and near-infrared light regions, systems that combine a diffraction grating with a CCD, providing a measuring time of about 1 ms, are available in market. An ordinary CCD, however, is made from Si and is limited to 1 μm wavelength. Even recent systems with InGaAs are limited to 2.5 μm and cannot measure in the infrared light region with longer wavelengths. So efforts are under way to speed up the system using CCD made from PtSi, capable of measuring infrared with long wavelengths.
Such CCDs will take 17 ms to measure a screen. The goal is to cut measurement time to 17 ms divided by the number of channel, 256, (less than 0.1 ms), by scanning beams using a galvano mirror. Figure 12 shows screen images during such an experiment. The scan width is still narrow. Spectral information is shown in the horizontal direction and time in the vertical direction, in order from top to bottom. The screen images show the absorption appearing in the center, at around 4.3 μm, when CO_2 gas is flowing.


Time-resolved Infrared Spectral Measurement

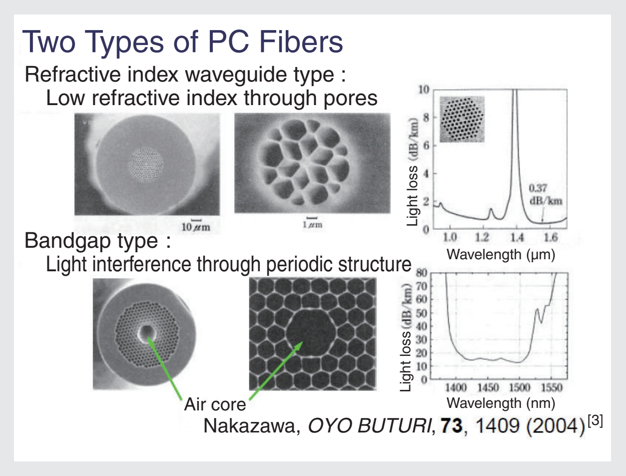
M. Saito, *Infrared Phys. Technol.* **46** (2005), in press.

Figure 12 Time-resolved Infrared Spectral Measurement

Photonic Crystal (PC) Fibers

Photonic crystals having structures finer than the wavelength of light has gained a lot of attention recently. Photonic crystal fibers can be made, by drawing a bundle of glass tubes. There are two types as shown in Figure 13: a refractive index waveguide type and a bandgap type, and are offered in various shapes. The refractive index waveguide type provides total reflection, with the air in pores formed around the glass (core) being the clad.

A product with losses as low as 0.37 dB/km, closer to numbers for communication optical fibers (0.2 dB/km), is also available. With the bandgap type, light transmits within an air core in the center. The air core has periodic structures in its periphery, which improves reflectance by interference and prevents light loss. They are gaining attention since properties of these fibers can be modified artificially.


Two Types of PC Fibers

Refractive index waveguide type :
Low refractive index through pores

Bandgap type :
Light interference through periodic structure

Nakazawa, *OYO BUTURI*, **73**, 1409 (2004)[3]

Figure 13 Two Types of PC Fibers

Conclusion

Capillary flow cells conserve sample amount, have a quick response and high sensitivity, and are effective for liquid measurement and gas analyses. Photonic crystal fibers cited at the end have shown interesting potential as research material for the future. Fibers with air cores that allow transmission in infrared region is a possibility. Integrating capillary flow cells with peripheral equipment, e.g. combining technologies of light sources, filters, and sensors may also bring interesting results.

<Excerpt from the Screening Committee Lecture for Masao Horiba Awards, June 9, 2005 (Publication members have responsibility for the translation)>

Reference

[1] Robert D. Waterbury, Wensheng Yao, Robert H. Byrne, Long pathlength absorbance spectroscopy: trace analysis of Fe(Ⅱ) using a 4.5 m liquid core waveguide, *ANALYTICA CHIMICA ACTA*, 357, 99-102(1997).

[2] David E. King, John D. Webb, “Infrared waveguide sensor with functionalized monolayer for detection of airborne pollutants” in Chemical, Biochemical, and Environmental Fiber Sensors VIII, *ProC. of SPIE*, 2836, 38-49 (1996).

[3] Masataka Nakazawa, Photonic crystal fibers and their applications, *OYO BUTURI* ,73, 1409-1417 (2004).