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In the Classroom

A Tutorial on Fiber-Optic Chemical Sensors

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…because of the small size and flexibility of the fibers, the acquisition of data could be performed in situ in environments not easily accessible by conventional methods of analysis.

The development of low-loss optical fibers in the early 1970s not only started a dramatic change in the approach to modern communications but it also triggered the imagination of chemists and physicists, who realized the power of guiding radiation in which a chemical or physical response could be encoded. This chemical or physical information could be transmitted over fairly long distances without complicated optical systems. In addition, because of the small size and flexibility of the fibers, the acquisition of data could be performed in situ in environments not easily accessible by conventional methods of analysis. The range of sensor designs and applications is so very wide and fascinating that it would be quite difficult to describe it all in the limited space of this tutorial.

In the past 20 years, the number of instrumental techniques available to the chemist has grown exponentially. In order to help our readers keep up with this rapidly growing field, tutorial articles on chemical instrumentation will be a regular feature of The Chemical Educator. The articles are designed to serve as a brief introduction to emerging instrumental techniques, with an outline of the underlying principles and major applications.

—Martin Schimpf, Series Editor

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To summarize the key features of fiber-optic chemical sensors and their applications to chemical analysis, a series of questions and answers follows.

What Is an Optical Fiber and How Does It Work?

An optical fiber is a cylindrical cable whose diameter can range from less than one μm to several hundred μm. The materials most commonly used in the fabrication of the fibers are plastics, glasses, and quartz. The choice of material depends on the spectral range of the radiation to be transmitted along the fiber. For example, if visible radiation is to be transmitted, glass or plastic fibers work well, whereas for guiding UV radiation, the more expensive quartz or fused silica fibers can be used. As shown in Figure 1, the fiber consists of an inner shaft, known as the core, of a given refractive index, surrounded by a second material of slightly lower refractive index, known as cladding. To give mechanical strength and flexibility to the fiber, a jacket or buffer, generally made of a polymeric and flexible material, is used.

The principle of transmission of light along optical fibers is that of *total internal reflection*, which can be described using different rays as illustrated in Figure 2. In order for a ray to be effectively "trapped" within the fiber core, it must strike the core/cladding interface at an angle α_2 greater than the critical angle α_c. This critical angle is related to the refractive indices of the core η_1 and the cladding η_2 by Snell's law and can be calculated as

$$\alpha_c = \arcsin (\eta_2 / \eta_1) \quad (1)$$

This requirement means that any ray entering the fiber with an incidence angle α between 0 and $\pm\ \theta$ will be internally reflected along the fiber core. This angle θ is known as the *semiaperture angle* or *acceptance angle* and is related to the *numerical aperture* (NA), a typical parameter used in the characterization of an optical fiber, as follows

$$\mathrm{NA} = \eta_0 \sin \theta = (\eta_1^2 - \eta_2^2) \quad (2)$$

where η_0 is the refractive index of the medium surrounding the fiber. The radiation cone trapped within the core will exit the fiber with an aperture angle of $\pm\theta$. The greater the value for the NA, the wider the angle θ and thus the larger the cone of radiation accepted.

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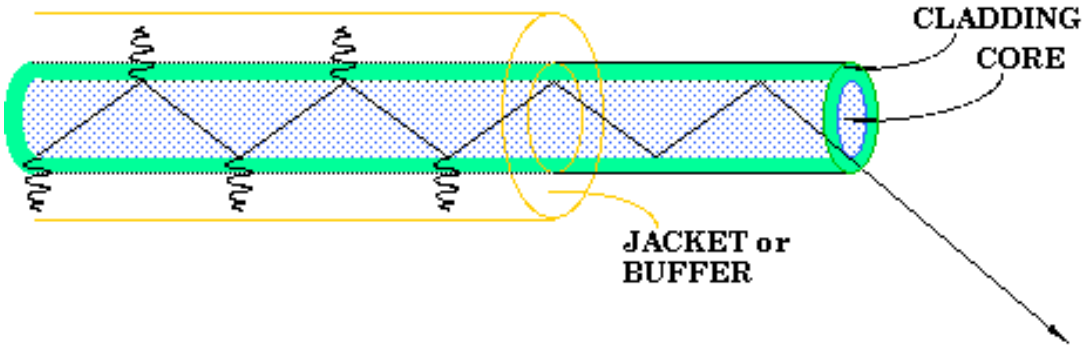

FIGURE 1. OPTICAL FIBER COMPONENTS AND SCHEMATIC REPRESENTATION OF LIGHT TRANSMISSION.

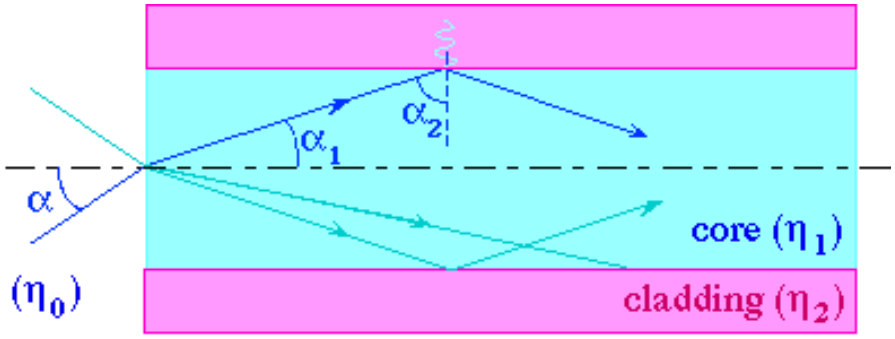

FIGURE 2. PRINCIPLE OF PROPAGATION OF LIGHT IN AN OPTICAL FIBER.

A relevant aspect in the transmission of the radiation needs to be mentioned at this point as it will be considered later in this tutorial: the electromagnetic field does not fall abruptly to zero at the core/cladding interface. Instead, the overlap of the incoming beam and the internally reflected beam leads to a field that penetrates into the medium next to the core. This electromagnetic field, which tails but does not propagate into the second medium, is called the *evanescent field*; its intensity $I(z)$ decays exponentially with the distance z perpendicular to the interface as follows

$$I(z) = I_0 \exp(-z/d_p) \quad (3)$$

where I_0 if the intensity of the incident radiation. The depth of penetration d_p of the evanescent field is related to the angle of incidence α_2 at the interface and the wavelength of the radiation λ_0 as follows:

$$d_p = (\lambda_0/4\pi)\,(\eta_1^2 \sin^2 \alpha_2 - \eta_2^2)^{-1/2} \quad (4)$$

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The short depth (a few μm) of penetration of the evanescent field and the dependence of d_p on experimentally controllable parameters have been used in rather ingenious ways to probe interfacial physicochemical properties.

How Can Optical Fibers Be Used As Chemical Sensors?

One of the definitions of sensing invokes the ability to monitor a given property of the system in a continuous and immediate fashion. The coupling of the light-transmitting properties of optical fibers with optical spectroscopic methods of analysis has resulted in the development of *fiber-optic chemical sensors (FOCSs)*, which are rapidly becoming conventional tools in chemical analysis.

To describe the wide range of sensor designs and detection schemes, we can first distinguish between *intrinsic* and *extrinsic* sensors. The detection process of intrinsic sensors is based on the alteration of the light-transmission characteristics of the fibers as a result of some change in a fiber property (e.g., refractive index or length) upon interaction with the system being sensed. This type of sensor has been applied mainly to the measurement of physical or physicochemical parameters, such as pressure, temperature, or enthalpy of reactions.

Extrinsic sensors, on the other hand, make use of the optical fibers as a means of guiding the radiation from the source to the sample or from the sample to the detection system. The radiation traveling along the fibers carries the sought after chemical information. This is the most prevalent type of FOCS.

Among extrinsic sensors, a further classification can be made based on the nature of the sensing process and the illumination mode. The simplest sensing approach is based on the direct spectroscopic detection of the analytical signal. In this type of sensor, known as *conventional* or *plain-fiber* sensor or as a *passive optode*, the spectral information is specific enough to sense the analyte. When the analyte cannot be sensed directly by its own spectroscopic properties, or when the selectivity of the analysis must be enhanced, a chemical speciation/separation/ recognition phase must be included in the FOCS. This chemical phase interacts with the analyte to generate a detectable spectral signal or a spectral response specific to a given analyte in a complex matrix.

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If the classification criterion is based on the illumination mode, extrinsic sensors can be subdivided into *distal* and *lateral* types. In a distal sensor, the sample is placed at the distal end of the fiber(s). The radiation exiting the sensor interacts with the sample to generate a spectral signal that can be guided along the fiber(s) to its proximal end so that it can be finally detected. In a lateral sensor, the evanescent field interacts with sample coated onto the fiber core.

Which Spectrochemical Methods of Analysis Can Be Used with FOCSs?

Spectroscopic methods for which the spectral range of the radiation can be transmitted without losses along the optical fibers are suitable. Spectral methods that utilize FOCSs include UV-Vis, mid and near infrared spectrophotometry, spectrofluorimetry, spectrophosphorimetry, conventional and resonance Raman scattering, and chemiluminescence. The vast majority of FOCS applications, however, involve the detection of molecular fluorescence, particularly laser-excited fluorescence. In addition to the tremendous sensitivity that can be achieved with this technique, the small size of the laser beam makes it easy to couple the radiation onto optical fibers with high efficiency. As a result, chemical information can be obtained from very minute samples even when the analyte concentration is very low (nM to μM).

In the last three to five years there has also been a significant increase in the development and applications of Raman-scattering-spectroscopy-based FOCSs. The challenge in the successful design and application of these sensors lies in the inherent weakness of conventional Raman scattering signals, yet the richness of compositional and structural information available in a single Raman spectrum justifies the efforts. One of the most significant problems encountered in these sensors is the intense background interference caused by Raman scattering of the fiber material itself.

Driven by the need for fast, reliable, online, qualitative and quantitative analysis in industrial settings, FOCSs are being coupled to NIR spectroscopy with increasing frequency for in situ analysis. The technique requires that radiation traverse a known pathlength of sample and that the transmitted radiation is detected. One of the most common configurations for such a measurement in situ with FOCSs involves the addition of a mirror at distance $b/2$ from the distal end of the fiber. Thus, the radiation exits the fiber, traverses the sample, is reflected, and traverses back through the sample for a total pathlength b that is twice the sample thickness.

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Chemiluminescence is the simplest methodology to couple with FOCSs. In this technique there is no external source of radiation; the optical fiber(s) is only used to guide the radiation generated by the chemical reaction to the detection system. Since chemiluminescence is a very selective technique and lacks a background signal, chemiluminescence-based FOCSs offer great selectivity and detectability.

What Are the Main Features of the Instrumentation for FOCSs?

Figure 3 illustrates the basic instrumentation needed to acquire spectrochemical signals with a FOCS. Radiation from a source is focused onto the proximal end of the sensor. When high sensitivity is required (e.g., in fluorescence, phosphorescence, and Raman Scattering), the use of lasers is highly desirable, due to the limited amount of light from a conventional source that can enter the fiber. For spectrophotometric analysis, however, the radiant intensity of the source is not as critical. In this case, polychromatic sources such as a tungsten or high-pressure Xenon arc lamps are common because they more readily yield an absorbance spectrum.

Except for chemiluminescence applications, in which only the emitted radiation is guided along the fiber(s), most other spectrochemical techniques require the transmission of both excitation and emission radiation along the sensor. The method used to separate the two types of radiation depends on the number of fibers used in the sensor. The *single-fiber sensor*, which is illustrated in Figure 3a, offers the greatest collection efficiency because the excitation and collection cones overlap completely; however, detection of the emitted energy requires spectral or spatial separation from the excitation energy. If the wavelengths of excitation and emission are different enough, dichroic filters can be used to transmit only the excitation energy while reflecting the emitted radiation. When greater resolution is required to separate the excitation and emission wavelengths, a perforated mirror can be used, however, this reduces the detection efficiency because the central part of the excitation/collection cone is not intercepted by the detector. In *dual-* or *multiple-fiber sensors* (see Figure 3b), one fiber carries the excitation energy to the sample while the emitted or scattered radiation is collected by one or more additional fibers, which guide the radiation to the detector. In most designs the fibers are parallel to each other; however, because the collection efficiency is related to the overlap of the excitation and collection cones, V-type configurations, in which the collection and excitation fibers form an angle (10 to 20°), provide greater collection efficiency and, therefore, higher

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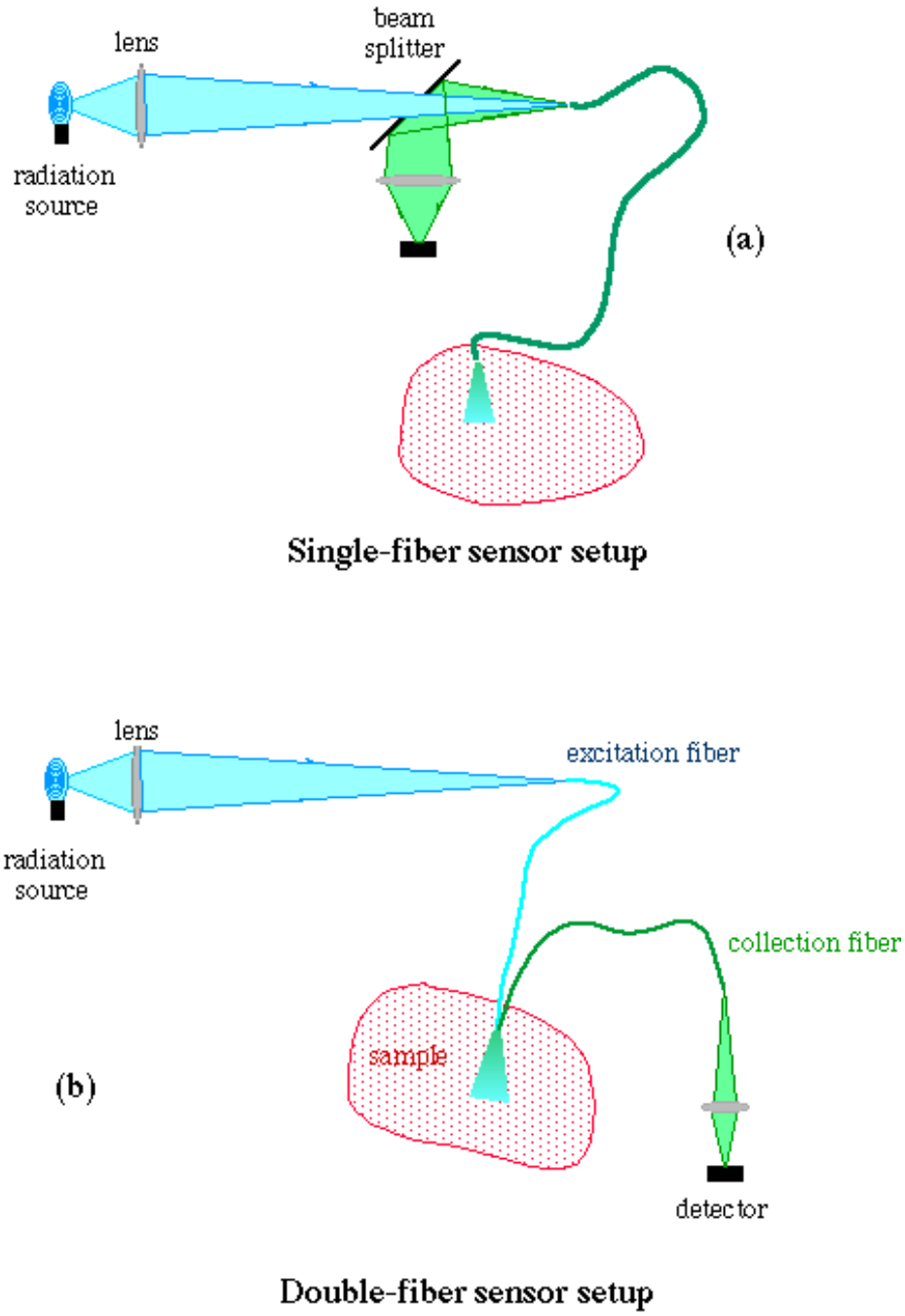

FIGURE 3. TYPICAL INSTRUMENTAL SETUPS USED FOR THE ACQUISITION OF LUMINESCENCE SIGNALS WITH A) A SINGLE-FIBER SENSOR AND B) A DOUBLE-FIBER SENSOR.

sensitivity. Although multiple-fiber sensors are more difficult to fabricate than single-fiber sensors, they reduce the difficulties in resolving the excitation from the emission

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radiation because the cones of excitation and collection are overlapped only partially. As a result, there is less interferences from background scattering.

The collected radiation is typically analyzed spectrally with the use of a scanning monochromator or a polychromator. The detector most frequently is a photomultiplier tube (PMT). The use of *intensified diode arrays* (IDAs) and *charge-coupled devices* (CCDs) in conjunction with polychromators allows for very sensitive and fast acquisition of spectral traces. CCD cameras are most beneficial for the detection of weak signals, which require prolonged exposure. This is because CCDs have a very small dark signal, that is the signal accumulated when no radiation strikes the detector.

What Are Some of the Most Interesting Applications of FOCSs?

The number of reports on applications of FOCSs continues to increase year after year. Current research efforts are focused on improving the selectivity of the analysis so that complex matrices can be probed in situ or even in vivo. In addition, papers on new, more sensitive sensor configurations and on the factors that control sensitivity continue to be published.

The review papers listed at the end of this tutorial contain more specific comments on a great variety of applications. Some of the most interesting ones are related to bioanalysis. For example, FOCSs have been designed for the in vivo detection of O_2 and pH by monitoring spectral changes (e.g., quenching of fluorescence and changes in the absorbance spectrum of a dye) associated with the interaction of an analyte with a chemical-recognition phase. Sensors based on the competitive binding of the analyte or ligand with the binding site of a reagent phase have also been developed. Provided that an optical signal of the ligand changes significantly upon binding to the reagent, the detection of optically inactive analytes can be pursued successfully. High specificity can be achieved with sensors that utilize an antibody as the chemical recognition phase.

Environmental analysis has benefited by the development of FOCSs that allow access to waterways without the difficulties associated with sample collection and treatment. Waste-water contaminants can be sensed directly in the water stream at different depths without immersion of the bulk of the instrumentation. Sensors have also been developed to detect high levels of acidity or basicity. The advantage in this case is that

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the analysis can be performed without exposure of personnel to hostile chemical environments.

In summary, the aspects of FOCSs that are most efficiently exploited today are: (1) the small size of the fibers, which allows for *in vivo* sensing; (2) the ability to transmit radiation over long distances without significant losses, which allows for *remote* sensing; and the ingenuity in the design of the chemical recognition phase, which leads to *highly sensitive* and *selective* analyses.

What Are the Unique Advantages and Current Limitations of FOCSs?

The small size and flexibility of the sensors makes them ideal tools for in situ and in vivo analysis**.** The ability of FOCSs to transmit chemically-encoded radiation between the spectrometer and a remote sample, in environments that are either hostile or not easily accessible, is the driving force behind FOCS development. Furthermore, because optical fibers are relatively insensitive to sources of noise, such as radioactivity and electric fields, signals acquired with optical fibers are much less prone to environmental interferences than those transmitted along electrical wires.

Optical fibers are able to channel a high density of information, such as wavelength, polarization, and phase. The ability to analyze each of these parameters enhances both the quality and quantity of chemical information obtained by FOCSs.

Perhaps the largest difficulty that faces FOCSs is the development of chemical separation phases with both long term stability and fast response times. As mentioned earlier, a true sensor output must respond instantaneously to a change in input. If, however, the chemical reactions involved in the sensing process are slow or nonreversible, the sensor cannot provide a continuous and accurate response. Conventional sensors without a chemical separation phase are indeed true sensors; however, they may not always provide the selectivity required. These drawbacks are exciting challenges to chemists and biochemists today and provide unending themes of interdisciplinary research in both academic and industrial settings.

FURTHER READING

1. Arnold, M. A. *Anal. Chem.* **1992**, *64*, 1015 A.

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http://journals.springer-ny.com/chedr
S 1430-4171 (97) 06071-8

2. Dessy, R. E. *Anal. Chem.* **1989**, *61*, 1079A.

3. Seitz, W. R. *CRC Crit. Rev. Anal. Chem.* **1988**, *19*, 135.

4. Borman, S. A. *Anal. Chem.* **1982**, *54*, 1071 A.

5. *Fiber Optics*; Daly, J. C. , Ed.; CRC Press: Boca Raton, 1991.

6. Wolfbeis, O. S. *Fiber Optic Chemical Sensors and Biosensors*; CRC Press: Boca Raton, 1991.

7. Kapany, N. S. *Fiber Optics: Principles and Applications*; Academic Press: New York, 1967.