Fiber-Optic Sensing Technology

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In this article we will offer a basic review of fiber-optic sensing technology, or more specifically, fiber-optic sensing technology as applied to the qualitative or quantitative identification of a chemical sample, and how it works. We will list references in which the various techniques we will mention have been applied. This list of references is by no means exhaustive, but is illustrative of the type of work that has been done.

What is fiber-optic sensing?

Light transmitted via optical fibers can be used to interrogate samples for the presence of target analytes either directly or indirectly. In the former case, the optical fiber is the probe, detection relies on the spectroscopic properties of the analyte, and there is no chemical-specific sensor element. In the latter case, modifications are made to the fiber optic, such as applying coatings that are sensitive to the presence of a particular chemical species. We shall return to these points after a discussion of spectroscopic techniques.

Spectroscopic techniques

Among the various spectroscopic techniques that may be used with fiber optic probes or sensors are: absorbance, fluorescence, Raman and diffuse reflectance. These are applied in one or more of the following spectral regions: ultraviolet (UV, 200-400 nm), visible (400-750 nm), near infrared (NIR, 750-2000 nm), and infrared (IR, 2000-25,000 nm or 5000-400 cm^{-1}). These techniques are illustrated schematically in Figure 1. The practical lengths of fiber that may be used before absorption losses become too large vary depending upon the wavelength of the light being carried. In the UV region, fiber runs of a few tens of meters are the maximum. In the visible and NIR regions, fiber runs of a few hundred meters are possible. In the IR, transmission has been severely limited, however, newly developed chalcogenide fibers may make fiber runs of a few tens of meters possible.

Absorbance

In absorbance (transmission) spectroscopy, light is transmitted to a sample where some of it is absorbed; the remaining light travels on through the sample to the detector. The wavelengths of light and amount of light absorbed at specific wavelengths is characteristic of a chemical and its concentration in the sample. Light sources may be deuterium lamps, arc lamps, or inexpensive tungsten-halogen light bulbs. Ordinary diode arrays serve as good detectors for this type of spectroscopy. This technique is typically sensitive to the low parts-per-million range, depending on the analyte and path length. It is used in all spectral regions: UV, visible, NIR and IR. In the former three, absorption features are broad and the technique is more useful as a quantitative tool for specific analytes in some known process or matrix. In the IR, qualitative information from the molecule's fundamental vibrational frequencies may be garnered. The UV spectrum of sodium nitrite in a process flow cell is shown in Figure 2.

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Fluorescence

Fluorescence is a process in which a molecule absorbs light of one wavelength (usually ultraviolet), and later emits light at a longer wavelength (ultraviolet or visible). This is a weak phenomenon compared to absorbance, though this is not necessarily a disadvantage. Light from the excitation source (usually a flash lamp or laser) must be excluded from the detector by some means. These include using a gated detector, off-axis detection (90°) of the fluorescence, or filtering. More sensitive detectors, typically CCDs, must be used for fluorescence. In fluorescence spectroscopy, analytes may be distinguished through temporal information from their decay lifetimes, as well as through the excitation and emission wavelength information. Fluorescence can actually be more sensitive (parts-per-billion levels) than absorbance spectroscopy because the signal photons come with a very low background (no source photons due to the time delay), whereas absorbance spectroscopy relies on the absorption by the sample of what is generally a small portion of the total light reaching the detector. Examples of fiber-optic fluorescence sensors include the use of laser fluorescence for detection of polyaromatic hydrocarbons in water by fiber optics,[1] fluorescent polymers for acid detection at 0.1-10 M concentrations,[2] and fluorescent CO_2 and pH indicators trapped inside a gas permeable polymer at the end of an optical fiber.[3]

Raman

The Raman effect is even weaker than fluorescence, typically occurring with only one out of every million photons that strike the sample. In this case, light is inelastically scattered from the sample, and the scattered light is shifted down in frequency from the source, which is usually a visible or near-infrared laser. Raman spectroscopy gives a "fingerprint" of the molecule's vibrations, complementary to the information obtained by infrared spectroscopy, but shifted to the visible region of the electromagnetic spectrum.[4] This makes it amenable to use with normal silica optical fibers. A sensitive detector is required, coupled with filtering to exclude the laser line and any fiber-generated Raman or fluorescence signal from the spectrometer.[5-7] Raman spectroscopy may be used on solids, liquids, or gases and gives good discrimination among different analytes. Raman spectroscopy also works on samples of high optical density for which absorbance spectroscopy does not. This condition could arise from the presence of particulates, high absorption cross-sections of the analytes, or long transmission path lengths. However, due to the weakness of Raman scattering, specially designed multifiber probes must be used.[8-11] The weak signal makes Raman useful only at higher concentrations (down to 0.1% typically) and fluorescence can cause significant interference. Use of an excitation source with longer wavelengths (red or near-infrared) can reduce fluorescence interference. Recent advances in diode lasers have lead to stable, high power sources at 780 nm.[12] Typical spectra of solids are shown in Figures 3 and 4.

Diffuse Reflectance

In this technique, light is absorbed by the sample, and the reflected light is picked up and returned to the detector. This is useful for samples that are too thick, or absorb too strongly for a transmission measurement to be made. A strong light source is required, due to scattering losses at the sample. The technique is typically applied in the

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NIR or visible spectral regions in a quantitative fashion and in the IR where qualitative information may be collected.

Direct Sensing

An optical fiber may be used as a direct probe in two ways. In distal mode, light travels down a fiber or fiber bundle and emerges from the end, interacts with the sample, and travels back to a detector. In evanescent mode, the evanescent field from the light traveling down the fiber enters the fiber cladding where it may interact with some absorbed analyte, causing changes in light intensity that are picked up by the detector. Both of these modes may or may not be chemical specific, depending on the composition of the matrix being interrogated. Detection of a particular analyte relies on the interaction of the particular wavelength of light being used with that analyte.

Evanescent Wave

A small portion of the light wave traveling down the optical axis of the optical fiber penetrates into the cladding that surrounds the light-carrying core of the fiber. This is known as the evanescent wave. The cladding is usually an organic polymer and many organic chemicals will be soluble in the cladding. If the fiber is stripped down to the cladding layer, and then placed in contact with a solution (liquid or gas) containing the organic analyte, the analyte will partition into the cladding and cause a change in the light intensity returned to the detector. This change is proportional to the amount of analyte penetrating into the cladding. A more in-depth overview of this technique may be found in reference 13. Evanescent wave sensing has been applied to not only fibers, but also to planar waveguides.[14]

Distal

In the distal mode, the fiber serves as a conduit for the light to the sample, and for the return of the light to the detector, once it has interacted with the sample. Either single fibers or fiber bundles may be used. Collimating lenses may be attached to the fiber to aid in light delivery and collection. Absorbance, reflectance, fluorescence or Raman spectra may be collected by this means. A rugged version of a multifiber probe that is designed to focus the excitation and collection to a spot near the probe tip is shown in Figures 5a and b. This is achieved without collimating lenses; the focused spot is just outside the covering window in order to make sample alignment as simple as placing the window in contact with the sample.

Indirect Sensing - Immobilization Methods

In the cases in which an analyte has no spectrum in the spectral region of interest, or if it does, its concentration is too low to be detected, then an indirect sensing method is required. Usually this means trapping or fixing an indicator in place and using it to detect the analyte of interest. An indicator is a molecule whose spectrum changes (usually in the ultraviolet or visible regions) upon interaction with a particular analyte or group of analytes. The indicator may give significantly different spectra with different analytes.

Thousands of indicators are known for such applications as pH, metal ions, temperature, moisture, and organic species.[15] Specificity is attained either through use of a selective indicator, or through multivariate analysis of the spectrum given by the more general indicator. Another means of differentiating among a suite of analytes is by using an array of sensing fibers with different indicators or coatings. Different analytes will give a different pattern of results from the sensor array, and can then be identified by a neural network.[16]

Trapping

The indicator and/or other needed reagents are held at the tip of the optical fiber and separated from the sample matrix by some means, typically a semi-permeable membrane. The analyte diffuses across the barrier and interacts with the indicator and this reaction is monitored by the optical fiber. This scheme has been used for sensors for NO_x gases,[17] CO_2,[3] organic solvents,[18] and pH.[3,19]

Direct Binding

In direct binding, the indicator is bound to the substrate through a series (usually) of chemical reactions. Typically the substrate is a lens, additional flat glass substrate, or the bare fiber itself (in both distal and evanescent modes). The techniques used to achieve this binding are similar to those used in the field of chromatography, in which the bound molecules are used in a column for separation of various analytes. However, coverage of the substrate which is "good" for chromatographic purposes, is usually poor by spectroscopic standards, though this is less so the case in recent years with the advent of more sensitive spectroscopic instrumentation. Direct binding has the advantage of rapid response times, because the indicator is in direct contact with the sample medium. Examples of this include work with pH and metal indicators on glass[20-22] and polymer[23-25] substrates.

Coatings

An alternative to direct binding that can lead to higher indicator loadings is to incorporate the indicator in matrix which is then in turn coated on the substrate. Such host matrices include polymers and sol-gel glasses. Sol-gel glasses are porous glasses formed at ambient or near-ambient temperatures from a metal alkoxide precursor. The organic substituents are removed during the condensation reaction, leaving a glass network of metal-oxygen bonds. A good source of further information on sol gels is the book by Brinker and Scherer.[26] Both pH and metals indicators have been trapped in sol-gel matrices.[27,28] Spectra showing the time response of an arsenazo III sol-gel sensor to uranium are given in Figure 6. The two main problems facing this type of sensor are indicator leaching and response time. The indicator is merely trapped, or physisorbed within the host matrix. The indicator can leach from the host over time depending on the conditions of the sample matrix. Silica sol-gel glasses, for instance, are dissolved in high pH (> 10) solutions in a relatively short time. Other sol gels, namely alumina and titania, are more resistant, though not impervious to attack at high pH.[26] Unlike the direct binding sensor, the analyte must travel into the coating in order to interact with the indicator molecule. Factors such as coating thickness and pore size can lengthen the response time

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of the sensor. Another stumbling block facing this type of sensor is hysteresis. In the sol-gel sensor, this can be caused by the indicator molecules existing in a range of slightly different microenvironments within the sol-gel glass coating. Indicator molecules in some environments may respond at different rates than those in other environments, leading to hysteresis. Polymer coatings without indicators have been used as acid sensors,[2,29] and with indicators as pH sensors.[30] Polymer coatings can be susceptible to swelling, and may not always return to their original states. The swelling of the polymer coating has itself been used as a sensor for salt concentration.[31]

Indicators may be absorbed into the cladding of a fiber and used in the evanescent mode. The analytes diffuse into the cladding and interact with the indicator, typically altering its fluorescence signature, which is then detected.

Conclusion

Fiber-optic sensing offers the flexibility to apply a wide range of spectroscopic techniques by themselves or in combination with a sensor element located at or near the fiber itself. These devices have applications to gases, liquids, and solids in laboratory, process, and environmental settings. The advantages afforded by fiber-optic sensing include remote location of instrumentation and personnel away from hazardous or undesirable environments, in-situ analysis and ease of alignment of the optical path.

Acknowledgements

Captions

Figure 1 - Types of interactions of light with a sample.

Figure 2 - UV spectra of sodium nitrite in 0.2 M sodium nitrate. The nitrite peak is located at about 350 nm.

Figure 3 - Fiber-optic Raman spectrum of sodium nitrate showing effects of various filtering schemes.

Figure 4 - Fiber-optic Raman spectrum of Tylenol™ collected with a 780-nm diode laser at 20 mW power and 60-second integration time.

Figure 5a - Side and top views of a multifiber probe.

Figure 5b - Side view of multifiber probe showing intersection of light cones.

Figure 6 - Time response of sol-gel uranium sensor to 118 ppm solution of uranyl ions.

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Biography

Lewis C. Baylor is a Senior Scientist A in the Analytical Development Section of the Westinghouse Savannah River Company, Savannah River Technology Center.

Dr. Baylor has a B.S. in chemistry from Juniata College (Huntingdon, PA) and an M.S. and Ph.D. in physical chemistry from Northwestern University (Evanston, IL). Since graduation, he has been in his current position with Westinghouse. His interests are in the area of spectroscopy, spanning the infrared, near-infrared, and ultraviolet-visible regions. At Westinghouse, his work has centered on applications of fiber optics, probes and sensors to process monitoring and environmental applications. In 1993, he received the Corporate George Westinghouse Signature Award of Excellence.

Lewis Baylor is a member of the American Chemical Society and Treasurer of the Savannah River Section of the Society.

Stanley Nave is a Principal Scientist in the Analytical Development Section of the Westinghouse Savannah River Company, Savannah River Technology Center.

Dr. Nave has a B.S. in physics and mathematics from East Tennessee State University (Johnson City, TN) and a M.S. and Ph.D. in solid state physics from the University of Tennessee (Knoxville, TN). He did post-doctoral work at Oak Ridge National Laboratory/University of Tennessee concerning basic magnetic properties of exotic transplutonium elements and compounds.

Since this time, he has worked at Westinghouse and his current interests are in the general areas of thin-film fiber-optic sensors and spectroscopy, with a special interest in the areas of Raman and laser induced breakdown spectroscopies. At Westinghouse, his work has involved developing fiber-optic probes and systems for Raman spectroscopy with the ultimate goal of remote chemical analysis for process control or real-time in-situ monitoring. He is also currently developing thin-film fiber-optic hydrogen sensors for process monitoring applications.

Note - ray angles are arbitrary

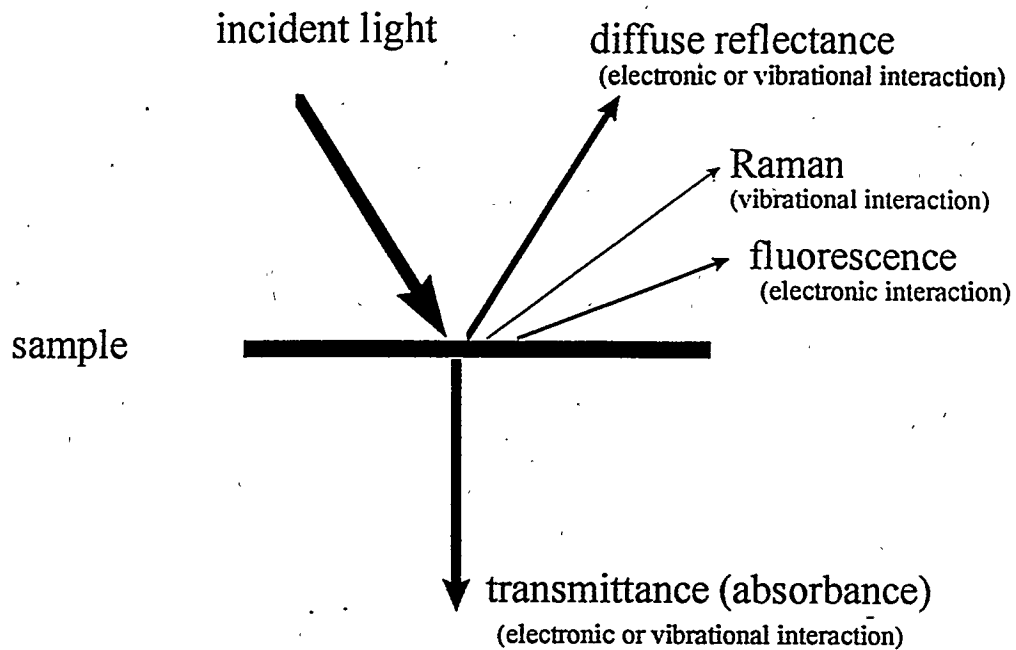Line thickness is representative of strength of signal

incident light   diffuse reflectance
(electronic or vibrational interaction)

Raman
(vibrational interaction)

fluorescence
(electronic interaction)

sample

transmittance (absorbance)
(electronic or vibrational interaction)

Figure 1 - Types of interactions of light with a sample.

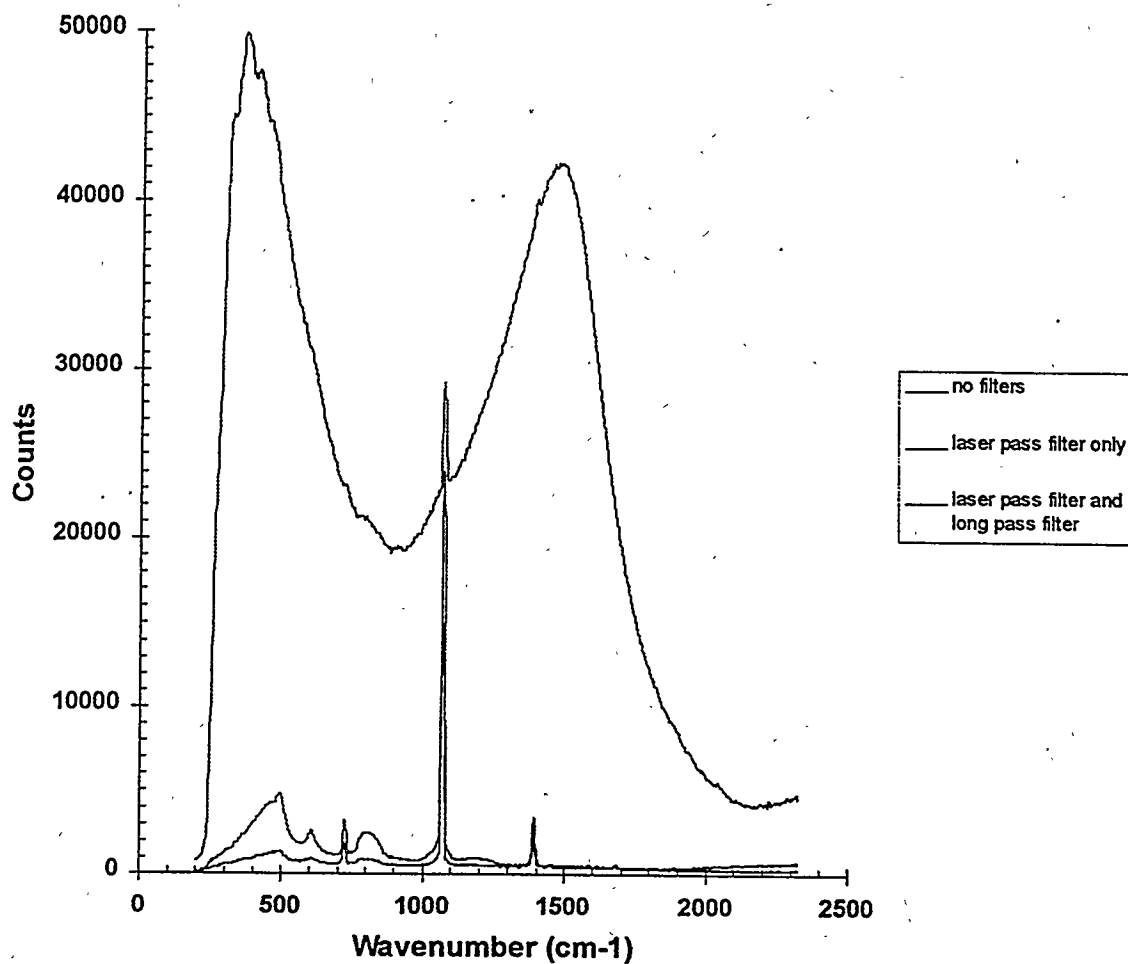Figure 2 - UV spectra of sodium nitrite in 0.2 M sodium nitrate. The nitrite peak is located at about 350 nm.

NaNO$_3$ Raman Spectra

Figure 3 - Fiber-optic Raman spectrum of sodium nitrate showing effects of various filtering schemes.
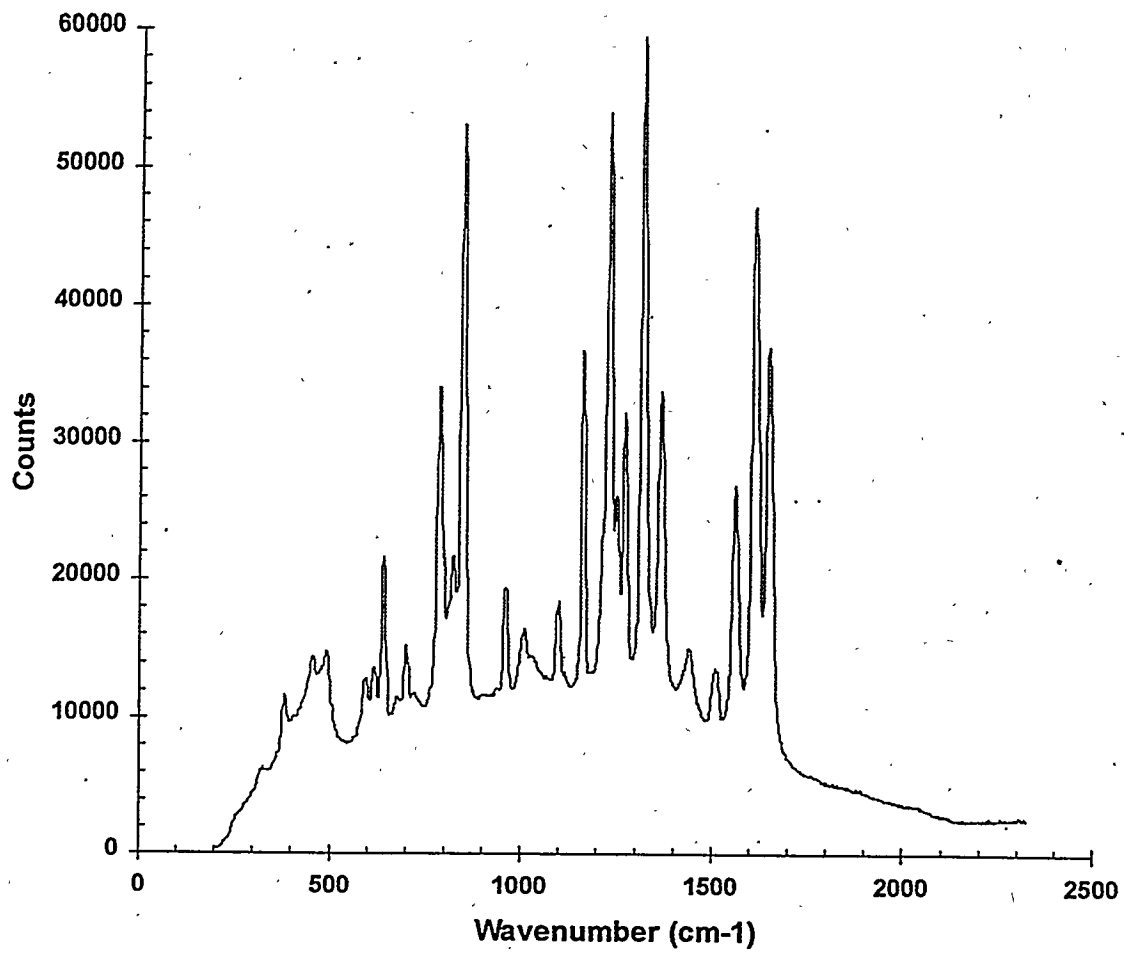
Tylenol Raman Spectrum

Figure 4 - Fiber-optic Raman spectrum of Tylenol™ collected with a 780-nm diode laser at 20 mW power and 60-second integration time.
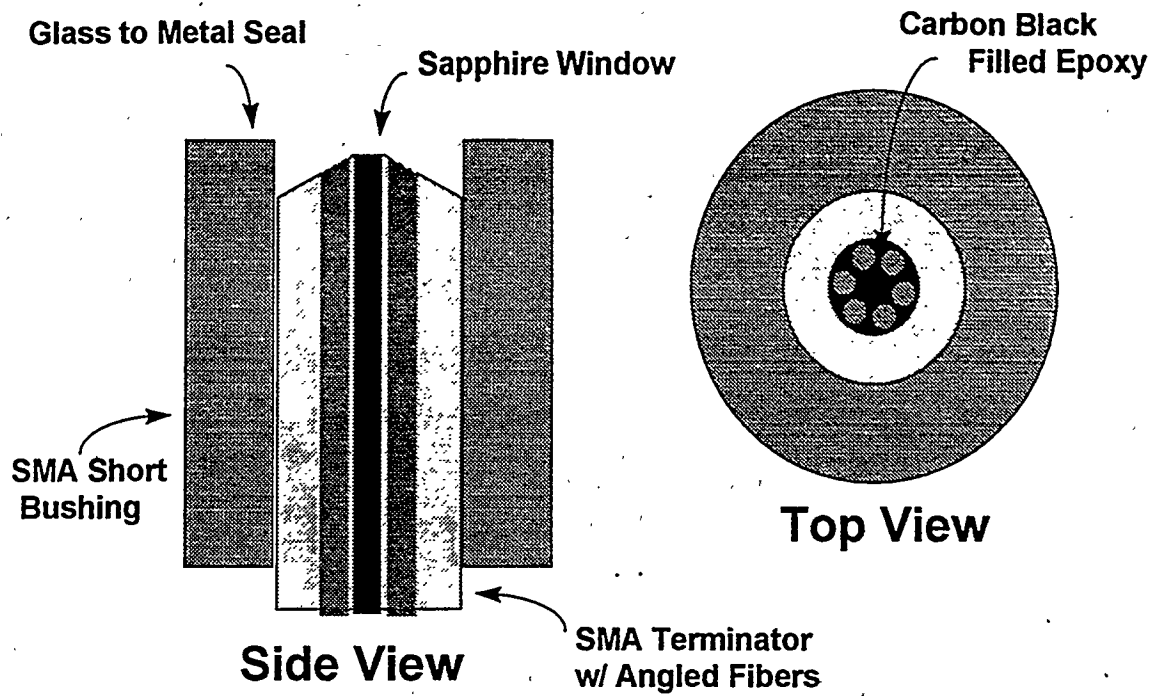
Figure 5a - Side and top views of a multifiber probe.
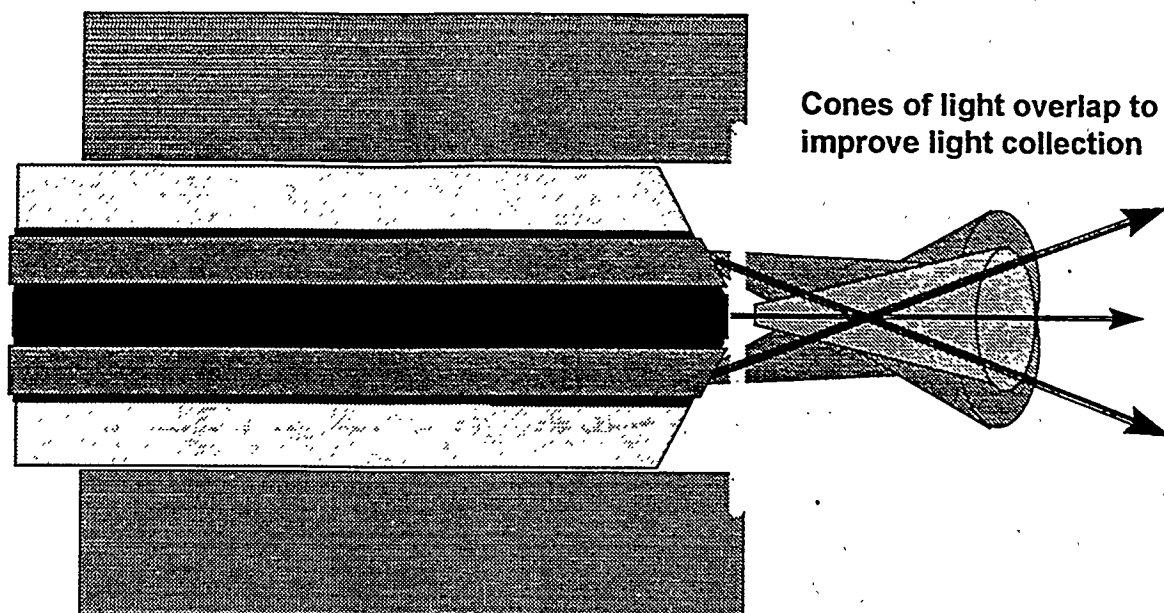
Cones of light overlap to improve light collection

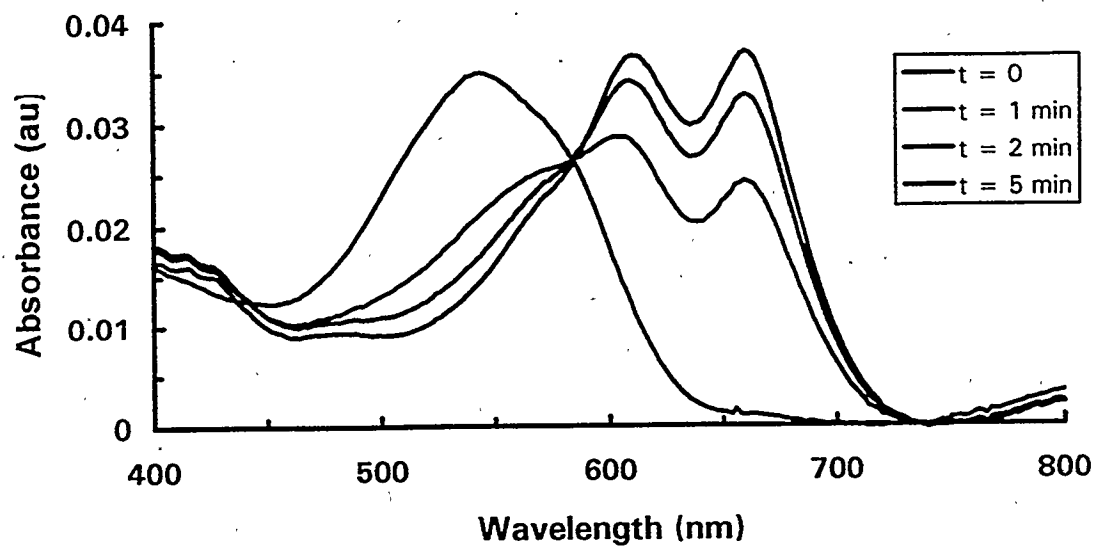Figure 5b - Side view of multifiber probe showing intersection of light cones.

Figure 6 - Time response of sol-gel uranium sensor to 118 ppm solution of uranyl ions.