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Absorption-based sensors☆

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Abstract

Many chemical sensors based on fiber optics and absorption spectroscopy have been reported in applications ranging from biomedical and environmental monitoring to industrial process control. In these diverse applications, the analyte can be probed directly, by measuring its intrinsic absorption, or by incorporating some transduction mechanism such as a reagent chemistry to enhance sensitivity and selectivity. Physical and performance requirements are placed on a device depending on its intended use. In applications such as chemical process monitoring, survivability and the assurance of the long-term quality of the analytical data are paramount. The above needs have resulted in devices that now employ multivariate data analysis, complex sampling interfaces, and reagent renewal mechanisms. The response from such systems can provide information not only about target analyte(s), but can also signal the presence of interferences, and may potentially be used to follow sensor degradation. Examples are given of devices currently being investigated along with a discussion of some of the remaining material, chemical, and optical challenges.

Keywords: Absorption; Chemical sensors

1. Introduction

Absorbance-based fiber-optic sensors were the very first type of fiber-based chemical sensor described in the literature [1]. This first sensor simply used the fibers as pipes to guide light to and from the region near the fiber tip where the intrinsic spectroscopic properties of the analyte matrix, in this case hemoglobin in blood, were probed. Many measurements are now routinely made in remote cells by means of fibers. The technique is excellent for applications where the measurement is to be made over a long period, with the major instrumental problems being window fouling and calibration. While the approach is very effective and potentially simple, it can also be limiting in the range of applications that can be addressed. The limitations arise from the somewhat restrictive spectral windows that can be effectively accessed using available low-cost fibers. Frequently, an analyte will not have an intrinsic spectral feature within a usable window or will simply be too weak an absorber in any optical path length that could reasonably be accommodated in the remote cell. Even when a measurement is possible, the ability to handle interfering species in the sample matrix that spectrally overlap with the target analyte can be a limiting factor.

In order to circumvent some of the problems associated with the use of the intrinsic spectral properties of the analyte alone, a reagent chemistry can be physically confined at, or near, the fiber end face, or within the fiber cladding. The reagent–analyte product is selected to absorb light in a spectral region within the fiber transmission window. In conjunction with a support phase or a membrane over-layer, the sensor may be designed to be reasonably selective for a given analyte, especially if the sample matrix is well characterized. For the purposes of sensor calibration, it is necessary that the reagent–analyte reaction be reversible and that the reagent concentration within the sensor remain constant. Therefore, the reagent cannot leak from the sensor or be readily photo degraded. For some applications, it can also be problematic if the reagent loading is not reproducible in the process of fabricating the sensor. Because a limited number of reagent systems can fulfil these requirements, developing a reagent-containing sensor for any given application can engender a significant challenge.

The use for which the sensor is intended places different economic, physical, and performance require-

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ments on the device and the approach that is taken in developing the technology. For example, the targeted application for many of the fiber-optic sensors reported in the literature has been in the area of biomedical sensing. A sensor for use in an in vivo biomedical application must be small and can utilize only a fairly restricted set of biocompatible materials. Since the sensor will be disposable, it must be inexpensive to fabricate and only needs to function reliably for a relatively short period of time. The development effect in both time and money that has gone into the in vivo blood-gas sensor can be examined to illustrate how difficult it can be to meet the requirements for this type of application.

In contrast, there is a need for sensors in a variety of industrial and environmental applications which have very different constraints. The variety of analytes and matrices in this arena is large compared to that for biomedical sensors. In many of these applications it is important that a sensor operate in situ and continually for months or even years with occasional servicing. Thus size and per point cost of the sensor are less of an issue. In these systems the quality of the long-term analytical data that the device can provide is the paramount feature. In applications where a sensor is to be deployed for long-term in situ measurements, designing for ruggedness and ensuring the reliability of the device present some interesting challenges. In general, developing sensors for industrial and environmental applications requires rethinking the approach and introduces some new challenges that will be the topic for the rest of the discussion.

2. Approach

So how does one approach developing devices for process and environmental sensing applications? The challenge is to incorporate into a sensor package a system that will function as an in situ chemical analyzer. This will require that the system be integrated into a package that can perform the functions that we normally associate with classical laboratory analysis: sampling, sample conditioning, analysis, data reduction, and reporting. Ideally, the system will be easily calibrated and be capable of detecting and perhaps adjusting for problems when they occur.

I would like to present one approach, using as an example the renewable-reagent optical-fiber-based sensors (flow probes) being investigated in our laboratory [2–4]. In one possible geometry for this sensor, shown in Fig. 1, a reagent chemistry is delivered in a continuous or stop-flow format to the sensor tip via a small-bore capillary of the same dimensions as the optical fiber. The tip is composed of a semipermeable membrane reservoir of porous polypropylene (Celenese X-20), surrounding the optical-fiber end face. The analyte is sampled by passage across the membrane into the reagent stream, where it forms a detectable product. Fibers contained within the reservoir are used to analyze the product spectroscopically. The dimensions of the probe tip are such that the diffusion distances are kept short while maintaining reasonably long paths for optical detection and keeping the total volume of reagent in the probe head to less than 1 μl.

The selectivity of the sensor for a particular analyte can be achieved at several levels, which include proper choice of semipermeable membrane and analyte-specific reagent chemistry. One very important feature of flowing the reagent into the probe head is that the reagent–analyte product may be cleared from the sensor by fresh reagent. The renewable format permits the use of reagent chemistries that have very high binding constants for the analyte and are, therefore, irreversible. In addition, the stability of the reagent phase to leaching or photo degradation becomes less of a problem. It is possible to alter the sensitivity and operating range of this type of device by changing the reagent composition or delivery rate while the probe remains in situ. A simple example is shown in Fig. 2, in which the sensitivity and dynamic range for the measurement of ammonia in an aqueous system may be altered by changing

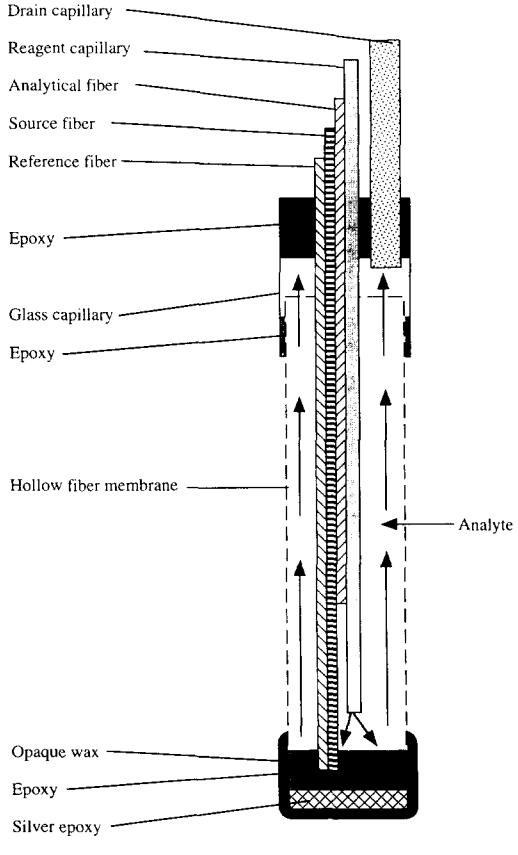

Fig. 1. Schematic of a fiber-optic probe with a flow-through reagent configuration.

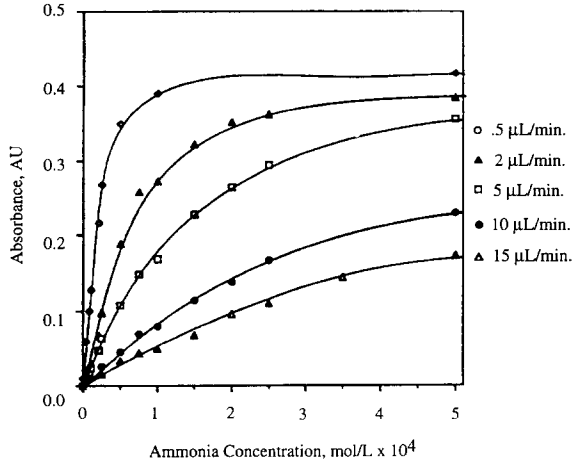

Fig. 2. The effect of reagent flow on the sensitivity and dynamic range for the measurement of ammonia.

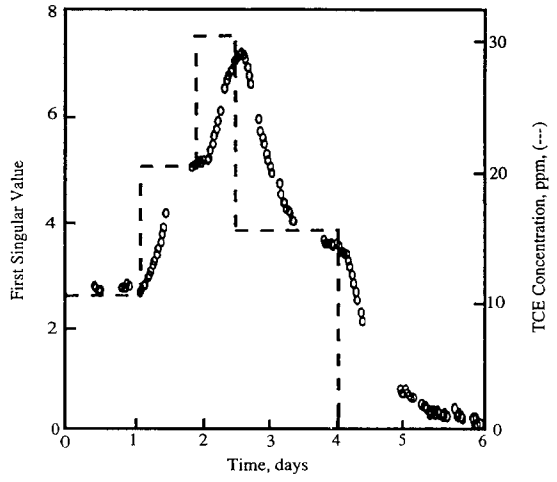

Fig. 4. Response from a thick-walled liquid-core probe to step changes in analyte (TCE) concentration.

the reagent delivery rate [2]. In this case, the reagent is an acid–base indicator being monitored at a single wavelength. The limit in sensitivity for a given reagent is reached in a stop-flow format, where it becomes a function of integration time.

Alternative geometries for a flow probe can be developed to take advantage of various membrane types. The membranes serve as the sensor–sample interface and can also be part of an optical lightguide in the reagent-core waveguide sensor shown schematically in Fig. 3. Light can be guided if the refractive index (RI) of the reagent within the tube is greater than the tubing RI, and if the tubing does not absorb or scatter the light excessively. The propagation of light in such a waveguide results in an effective pathlength for spectroscopic analysis within the core that is greater than the actual cell length due to a multipath effect [5]. A 10 cm long 380 µm i.d. piece of PTFE Teflon (RI $\approx$ 1.35) filled with a modified Fujiwara chemistry, a mixture of pyridine, organic base, and water [6], was investigated in our laboratory for the detection of chlorinated hydrocarbons in vapor [7]. In this example, it was important to have a very rugged device that could be used both to track changes in concentration for extended periods of time and exhibit a high degree of mechanical stability. The Teflon tubing has a 150 µm thick wall and thus transport of the analyte across this membrane reaches equilibrium very slowly. Each point in Fig. 4 represents the rate of color formation over a 40 min cycle, at the end of which the core is flushed and refilled with fresh reagent. The analyte concentration is varied in steps and is represented by the dashed line. Although the time to reach steady state is very long, the fact that a change has occurred is detectable within one cycle.

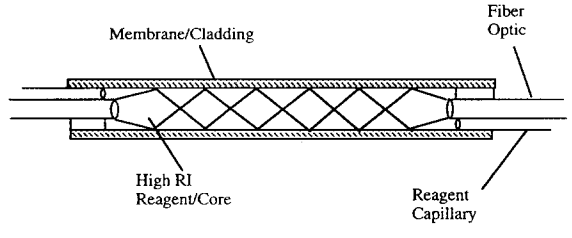

Fig. 3. Configuration of the liquid-core waveguide probe.

In this example, the sensor is operated only in stop-flow mode; however, this allows two additional levels of selectivity of the sensor to be added by including the reaction and diffusion kinetics and full spectroscopic analysis of the reaction product(s). A sensor can be made to detect multiple species by changing the reagent chemistry while the probe remains in place. In the case of the Fujiwara chemistry, the reagent is sensitive to a class of analytes. A mixture of analytes within this class may be discriminated by using multiwavelength detection and multivariate data analysis. The full spectral approach requires a more expensive and complicated detection system than the simple single- or dual-wavelength filter-detector geometry that is frequently used in fiber sensors, but it has many advantages. The spectrum is composed of multiple measurement channels that constitute a vector of responses. Statistical data-analysis techniques may be used to determine multiple analytes in a mixture provided that the pure spectra of the analytes are not severely overlapped. Even this constraint may be relaxed by temporal modulation, i.e., flushing the reagent–analyte product from the probe head and collecting a time course of responses. If at many intervals in time we collect a spectrum, the sensor response will be a matrix.

The rate of color formation in the sensor for a given analyte is a function of both the permeation rate through the membrane and the rate of reaction with the reagent. Each variable is affected by several physical and chemical parameters. Among these, the variability may be used to help discriminate between analytes in a

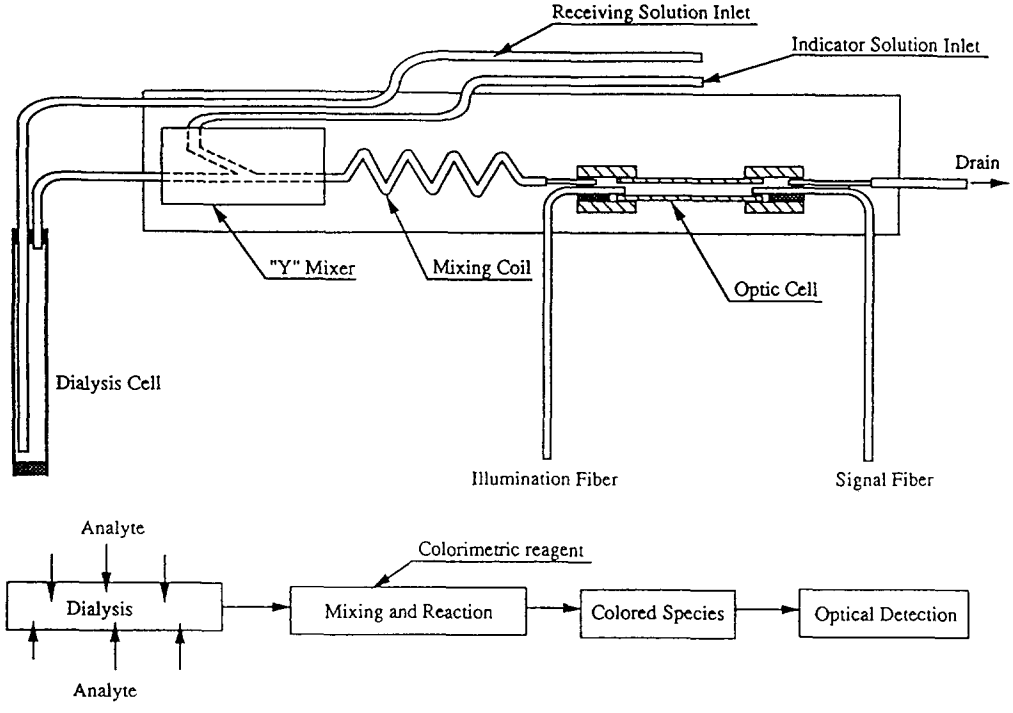

Fig. 5. Second-order heavy metals analysis system.

multicomponent system. Permeation of an analyte through the membrane is affected by the membrane composition, thickness, matrix temperature, and porosity. Factors affecting the formation of absorbing species in the sensor include reagent composition, reaction kinetics, temperature, secondary reaction pathways, and reagent and reaction-product stability. The net result is that we can take advantage of these factors to increase the information content in the response of the sensor to the chemical matrix that we wish to analyze. In addition to simultaneous multispecies determinations, there may be sufficient information to detect unanticipated interferences, signal sensor failure, or be able to quantitate a target analyte in the presence of unknown interferences.

We have tested some of the above concepts working closely with the Chemometrics Research Group under the direction of Dr Bruce Kowalski. We are examining both reaction-kinetics-limited and membrane-transport-limited systems on the temporal axis. One model, based on membrane-transport limitation, is a heavy metal sensor [8]. A schematic of this device is shown in Fig. 5. The probe tip consists of a Nafion™ ion-exchange membrane into which a receiving solution flows at a slow rate. The receiving solution contains a complexing reagent that facilitates transport of a selected subset of the metal ions found in the sample matrix. The receiving solution is then mixed with a competitive complexing reagent that forms colored complexes with a variety of metal ions. The second derivative spectra of several metals with the complexing reagent are shown in Fig. 6.

In operation, the probe is exposed to the sample for some fixed time period (membrane loading) and then withdrawn. The analysis begins at the time the probe is removed from the sample as the metal ions are eluted from the membrane. Neither the spectral nor temporal response are fully selective for a given species, but in combination they can be used to analyze a single species.

The sensor is calibrated by exposure to a solution of pure target analyte. The generalized rank annihilation method (GRAM) is used to process the response matrices as a generalized eigenvalue–eigenvector problem [9–11]. The ratio of the eigenvalues for sample and

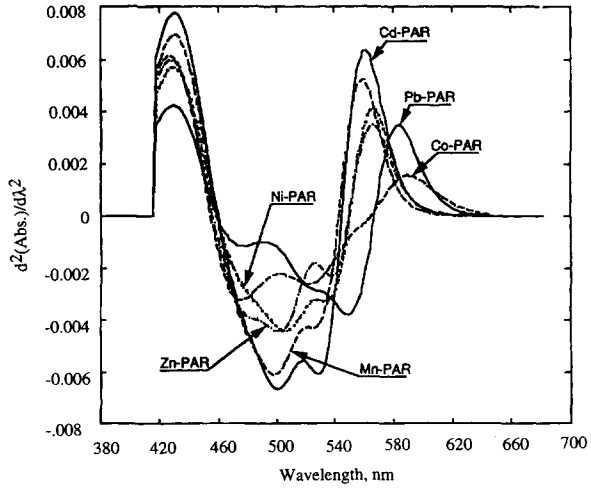

Fig. 6. Second derivative spectra of various metal–PAR complexes.

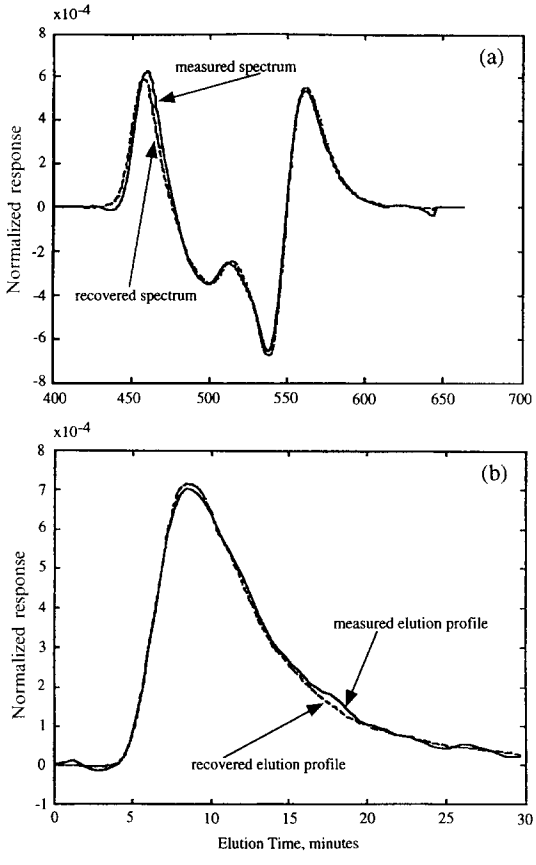

Fig. 7. GRAM profiles of (a) analyte standard and (b) that recovered from sample matrix.

calibrant gives the concentration of analyte. In addition, comparison of the recovered temporal and spectral response profiles of the sample with that of the pure target analyte can be used as an indication of how well the sensor functioned. Fig. 7(a, b) shows examples of GRAM profiles for a pure Pb^{2+} calibration solution and those recovered for the analysis of a lake water sample that contained approximately 10 ppb Pb as verified by graphic furnace atomic absorption, respectively. Failure to recover the proper profiles may be used to signal sensor degradation or other problems with the analysis. Unfortunately, this scheme does not detect all analysis errors. The sensor-measured concentration of lead in this case was 5.7 ppb due to organic complexation in the lake water matrix. In tap water experiments, the results agree very well with the standard method, indicating that more work is required to build a device that can be used for both free and complexed species.

3. Conclusions

The examples used above all represent reagent-containing absorbance-based sensors in which the chemistry can be renewed. A hugh storehouse of knowledge exists in automated wet chemical techniques for the laboratory. A subset of the concepts presented here can be applied in many different ways to construct devices that will meet industrial and environmental sensor needs.

Thin-film membrane materials that are stable and selective or to some degree variable to transport of chemical speceis serve as the basis for developing in situ analyzer technology. Materials research for sensor applications must address the response dynamics and degradation of materials designed to have specific properties during long-term exposure to complex chemical matrices.

It is obvious that a high degree of functionality needs to be economically combined into each device. We already have data-analysis and system-control electronics available to meet the needs. Currently we are seeing rapid technological advances in the areas of micromechanics and micro-optics. Much of this technology, especially efforts that are not restricted only to silicon machining, can be applied to fabricate sensors that will be cost effective. The development of the mathematical techniques to extract the maximum amount of chemical information is emerging in parallel with the sensor hardware technology.

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Biography

Lloyd W. Burgess is a senior research scientist at the Center for Process Analytical Chemistry, an Industry/University cooperative research center located at the University of Washington in Seattle. He directs the Optical Waveguide Sensor group, which is investigating new concepts in the development of integrated multicomponent analysis systems for use in industrial and environmental monitoring applications.