THE DEVELOPMENT OF A LARGE-AREA CHEMICAL SENSOR:
A NEW PLATFORM FOR SELECTIVE COATINGS

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The Development of a Large-Area Chemical Sensor: A New Platform for Selective Coatings^(a)

Introduction

The Large-Area Chemical Sensor (LACS) concept for chemical detection is based on a combination of three techniques. Specifically, it uses: 1) optical waveguides as the sensor substrate, 2) selectively adsorbing or absorbing materials to concentrate the target materials, and 3) spectroscopic interrogation (absorption or Raman spectroscopy) for verification and quantification. This approach combines the effectiveness of selective coatings with the precision of spectroscopic analysis, thereby avoiding interference and calibration problems associated with many chemical sensors. A schematic of the LACS is shown in Fig. 1.

A fiber waveguide consists of a core and a cladding layer. When the core refractive index is greater than that of the cladding, total internal reflection can occur at the interface, confining light to the waveguide core. In any waveguide, the confined light penetrates into the cladding slightly. This is the evanescent field. This field drops off exponentially over distances of a few micrometers from the core/cladding interface. The evanescent field can interact with molecules in the cladding, making absorption or Raman scattering possible. Because the entire length of the fiber is part of the active sensor, large detector areas are feasible.

Fig. 1. The target compound is preferentially sorbed and concentrated in the polymer cladding of a multimode waveguide. The presence of the target compound is verified and quantified by through-the-fiber spectroscopy.

Silicone polymers 1) have a small refractive index and 2) are very permeable to both gas- and liquid-phase materials. The small refractive index means that these can serve as an optical cladding. The permeability means that when the selective material is incorporated into a silicone cladding, the analyte passes freely through the cladding material until a selectively sorbing unit is encountered.

The optical interrogation method can include two spectroscopies: visible-near infrared absorption spectroscopy or visible-near infrared Raman spectroscopy. Visible-near infrared spectroscopy takes full advantage of the wavelength transparency of silica waveguide cores. These energy shifts are the characteristic vibrational frequencies of the material. Raman scattering occurs when the absorbed photon is re-emitted at a slightly different energy. These characteristic vibrations interact with light, resulting in IR-absorption or Raman scattering. From the absorbed wavelengths or the Raman-shift wavelengths, the molecular species can be identified and quantified. This approach is widely used for analyzing bulk materials.

The same thing can happen for photons in a waveguide. The guided photon can simply be absorbed by the molecule in the evanescent-field region. This results in an attenuation of the trapped signal and is referred to as evanescent-field absorption or attenuated total reflection. In this case, only the characteristic molecular absorption wavelengths (and a baseline wavelength) need to be monitored.

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Raman scattering also can occur in the same way via interaction between the evanescent field and the molecule. It happens over a wavelength regime centered on the laser used, and so the sensor system can collect data where the fibers are most transparent. Raman frequency shifts are mass-sensitive and so help to sort out interferences from different compounds with similar chemistry.

The primary added value from the LACS concept is applying multiple phenomena to identify and measure the concentration of selectively sorbed molecules in an optical-fiber cladding. In addition, once the selective material is incorporated into the cladding monomer, manufacturing and calibrating the sensor is straightforward. A typical fiber sensor will involve, at most, a few meters of fiber. The sensitive fiber can be manufactured at the rate of several thousand meters per hour. A few meters of fiber can be used for calibration and testing, leaving thousands of meters of calibrated sensor ready for use.

Relationship to Other Types of Chemical Sensors

The LACS is distinctly different from other chemical sensors, although it does have some similarities with some. These other chemical sensors are briefly described here to emphasize their differences from the LACS concept. The related sensors fall into the categories 1) selective coating-based sensors and 2) fiber-optic sensors.

Selective coating-based sensors. The most common selective coating-based sensor designs are the Chemical Field Emission Transistor (Chem-FET), mass-loading devices, and optical probes.

Chem-FETs have a selective coating applied to the gate of a field-emission transistor (FET). The target analyte reacts with the coating and, via electron exchange in the reaction, changes the electron density in the FET. This, in turn, modifies the conductance of the transistor.

Mass-loading devices come in two forms, microbalances and surface acoustic wave (SAW) sensors. In each of these, the selective coating is applied to the surface of a piezoelectric crystal. When the selective medium absorbs the analyte, in the microbalance, the increase in mass of the coating changes the resonant frequency of the oscillator; in a SAW device, the mass change results in a change in the velocity of a surface acoustic wave.

Optical probes using selective coatings fall into two types. First, fiber-tip probes rely on the fiber strictly as a signal-carrying device. In these, the fiber carries the light to a chemically sensitive coating on the fiber tip. Sorbed analytes can be analyzed by 'through-transmission' or 'back-reflection'. The second type of optical probe uses a planar waveguide with a single selective-coating surface. Light is launched into the planar waveguide using a prism or a grating; the interaction with the selective coating is colorimetric via an attenuated total reflection.

Both Chem-FETs and mass-loading devices are small-area sensors because their sensitivity decreases as the area increases. The area of the optical fiber-tip probe is limited by the area of the fiber tip. The active area of these sensors is on the order of 10^{-4} cm² as compared to the LACS for which the active area can be several cm². It is extremely difficult to launch the light into planar waveguide sensors and, by their nature, these are basically monochromatic probes. The use of multimode fibers (as in LACS) means that broadband radiation can easily be launched and propagated; this permits true spectroscopic measurements.

In addition to these device-specific difficulties, the principal problems with selective-coating devices are identifying the appropriate selective materials and interferences from other species. In addition, for irreversible selective coatings, any calibration is destructive of the sensor. The LACS incorporates selective chemical species to preconcentrate the target species. In this case, the

problem of interferences is addressed by the spectroscopic interrogation. In the LACS, a single fiber run can easily prepare 3 kilometers of sensor; using a few meters for calibration destroys only a small portion of the available fiber.

Fiber-optic sensors. Existing fiber-optic schemes for chemical detection work by evanescent-field absorption in porous claddings or on infrared transmitting fibers. In sensors based on absorption in porous claddings, the optical cladding on a short section of fiber is made porous so that a solution to be analyzed can be absorbed. Then the fiber transmission is measured. The intensity of the light absorption indicates the concentration of target species in the cladding.

The utility of porous coated fibers is limited by the wavelength restrictions imposed by the optical properties of silica or plastic fibers. A relatively small fraction of all interesting compounds has significant and uniquely identifying absorptions in that part of the UV-vis-near IR for which these fiber optics are transmitting. Alternatively, infrared transmitting fibers which can measure in this region of the spectrum are brittle, difficult to handle, and sensitive to corrosion.

Status of Development of the LACS

Some of the analyses required in support of a full picture of the underlying principles of the LACS have been performed and demonstrated for short lengths of fiber. A conceptual design of a prototype sensor is shown in Fig. 2. In the case of a colorimetric selective material, light of the appropriate wavelengths is launched into the fiber and the transmitted light intensities recorded as a function of time. For the probes using other selective materials, the molecular absorption lines or Raman lines can be monitored.

Fig. 2. Conceptual design of prototype LACS. The fiber sensor is wound around a form and exposed to air (in this case containing iodine whose concentration is varying with time). Light is passed through the fiber and the spectrum analyzed to give the target compound concentration.

Chemically specific compounds have been identified for two important classes of compounds: organic phosphates and iodine. The choice of selective compounds sensitive to iodine and tributyl phosphate was based on these being contributors to a nuclear-weapons-proliferation signature. Methods for incorporating these selective materials into the cladding of optical fibers are being developed.

The iodine-specific coating is a metal phthalocyanine. It is incorporated into the cladding via a sol-gel process. This selective coating has been tested on a planar waveguide. Sensitivity at the ppb level appears possible. Figure 3 shows an absorption spectrum of a metal phthalocyanine sol-gel film and the same film after exposure to iodine vapor. Figure 4 shows the response to 10 ppm of iodine vapor of a planar waveguide coated with this sol-gel film (at 514 nm).

Tributyl phosphate-sensitive compounds have been identified and synthesized; these are to be incorporated into the cladding by grafting onto a silicone polymer backbone. The interaction between the phosphate and the selective polymer is via a hydrogen bonding. This is a strong interaction and consequently results in a large preferential sorption of the target phosphate.

Incorporating other selective materials into the cladding can extend the technology to other chemical species. Possibilities include chemical species indicative of chemical weapons or environmental pollutants.

Fig. 3. Spectra of an iodine-selective film before and during exposure to 10 ppm concentration of iodine vapor. Structure in unexposed spectrum are interference fringes.

Fig. 4. Response of iodine selective sol-gel planar waveguide to 10 ppm iodine vapor. The iodine was transported in a nitrogen carrier gas.

Pacific Northwest Laboratory has a full-service fiber-optic facility capable of custom drawing optical waveguides and of applying custom coatings to these fibers. In addition, a laboratory for performing the optical interrogation of such fibers has been assembled and is in operation.

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