Multi-Analyte Sensing: From Site-Selective Deposition to Randomly-Ordered Addressable Optical Fiber Sensors

Frank J. Steemers and David R. Walt*

The Max Tishler Laboratory for Organic Chemistry, Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, Massachusetts 02155, USA

Abstract. In this report we review the progress in the development of imaging fiber chemical sensors. Emphasis is placed on the chemical sensor component and the fabrication of architectures appropriate for multi-analyte sensing, such as optical fiber sensors. Two main approaches in the fabrication of such sensors will be highlighted: first, sensors made with spatially-resolved sensing sites by site-selective polymerization, second, sensors prepared by random distribution of microsphere sensors on an optical imaging fiber containing thousands of μm-scale wells. Examples of each are given.

Key words: fiber optics; optical sensors; fluorescence; luminescence; array sensors.

Introduction

There is continuing interest in developing new sensing technologies, motivated by the wide potential applications of sensors in such important areas as medical diagnostics and environmental monitoring [1–5]. Sensors typically have two components; a receptor site that selectively binds an analyte, and a readout or transduction mechanism that signals binding [6]. Signal transduction has been accomplished with electrochemical, field-effect transistor, optical adsorption, fluorescence, interferometric, piezoelectric, and other devices [7]. Sensors based on an optical transduction mechanism coupled to fiber-optics are the subject of the present discussion. The heart of an optical fiber sensor is a filament of light-guiding dielectric material that operates by total internal reflection. An optical fiber is comprised of an inner region of a higher refractive index material (the core), and an outer region of lower refractive index (the cladding). This configuration enables light to travel from one end of the fiber to the other with relatively low loss in intensity. Long-range transmission capability (for remote-sensing applications), extremely high sensitivities, imaging capability, rapid response times, high bandwidth (for information-carrying capacity) and small sizes are characteristics of optical fibers that allow them to be made into sensors for detecting analytes in very small sample volumes [8–15]. Moreover, because signals of many different wavelengths can be propagated in either direction through an optical fiber, the fiber is capable of carrying multiple sensing signals. The principle of a typical optical fiber sensor is depicted in Fig. 1.

Monochromatic light is focused through coupling optics into an optical fiber core, passes through it and interacts with the sensing layer immobilized at the tip of the fiber. The sensing layer responds to the concentration of the analyte and modifies the light signal, which returns through the fiber and coupling optics to the detector. The optical fiber sensing component, of which an enlargement is shown in Fig. 1, can be divided into three parts: 1) the optical fiber surface, 2) polymer deposited on
the fiber, 3) sensing chemistry in the polymer (indicating chemistry).

**Fiber-Optic Sensing**

**Optical Fiber Surface**

The optical fiber serves merely as a conduit to transport light to and from the sensing element, and the sensing chemistry is immobilized on the distal end surface of the optical fiber. The optical fiber surface must first be modified to allow attachment of the sensing chemistry. This modification is done by silanizing the glass, and then introducing photopolymerizable or amino groups (Fig. 2), or various other functional groups.

**Polymer Deposited on the Fiber**

The second critical aspect of sensor fabrication is the polymerization and immobilization of indicating chemistries on the optical fiber. Fiber-optic sensors are usually based on thin indicator-loaded polymer films or membranes in contact with the optical fiber surface. In this respect, photopolymerization and sol–gel chemistry are often used to immobilize or confine indicators at the distal end of the fiber [16, 17]. In addition to holding the indicator in place, membranes can be used to exclude substances from interfering with the indicator. It is essential that the thickness of the sensing layer be minimized to improve the temporal response of the sensor.

**Sensing Chemistry in the Polymer**

The indicator’s optical properties in the polymer are monitored as they are modulated by the presence of analyte. A variety of optical transduction schemes have been used such as absorbance, fluorescence, reflectance, and polarization. While optical sensing schemes and instrumentation are well documented, the development of novel active sites tailored to specific sensing functions is relatively unexplored. Most optical sensors reported to date employ traditional indicators as the sensing chemistry. In some cases, these indicators are coupled to enzymes or antibodies to expand their sensitivity [18–20]. Fluorescence quenching and enhancement schemes are commonly employed in this respect [21]. Other methods are based on analyte-induced spectral wavelength shifts or emission lifetime changes rather than steady-state intensity measurements. Lifetime measurements have the important advantage that “autofluorescence” and light scattering (background noise) can be eliminated for most samples, by time-resolved detection of the fluorescence signal from the sensor. Lifetime measurements are not subject to instrumentation drift and are not affected by changes in the optical properties of the sensing chemistry (photobleaching or leaking of dye). Recently, an interesting application of this approach has been achieved in sensors comprising lanthanide luminesphores (millisecond luminescent lifetimes, large Stokes shifts, and line-like emissions) as photoinduced electron transfer sensor components [22] for use with analytes stimulating time-resolved lanthanide emission [23].