CHEMICAL SENSORS

Chemical sensors are devices that allow for the detection and measurement of individual chemical components, usually from a complex mixture. In practice, the sensor is always part of a larger system designed for the purpose of providing process or product information. This information might be needed for a control loop or quality assurance procedure. The mixture is typically a liquid or gas, but may also be a solid or semisolid substrate. For example, the pH of aqueous solutions in the presence of dissolved salts can be monitored by an electrochemical device called a glass pH electrode or pH sensor. This chemical sensor responds specifically to hydrogen ions over a concentration range spanning approximately 10 or more decades. The pH reading can then be used to regulate the pH level by the addition of acid or base to the process stream. As another example, gas sensors are available that use optical properties to track oxygen concentration over a wide range of temperatures and pressures. In automobile engines, this might be employed to adjust the fuel–air mixture for better engine performance. Many other examples can be cited since there are potentially as many different types of chemical sensors as there are different molecules. However, a few common sensing strategies and operating principles can be formulated that tie them neatly together. It is logical, therefore, to focus on these strategies and use a few well-developed chemical sensors to illustrate the approaches.

IDEAL CHEMICAL SENSORS

It is convenient to define an ideal chemical sensor as one that operates in an instantaneous, reversible, and absolutely selec-

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tive fashion without disturbing the composition or other properties of the sensing fluid. In the end, it provides an electrical signal that is precisely calibrated to the composition information. In practice, few of these characteristics are actually achieved; nevertheless, commercial chemical sensors are available with 1994 worldwide market values approximating $500 million (1). A similar market exists for biosensors (see BIOMEDICAL SENSORS), which we distinguish here from the term *chemical* sensors simply by the method in which the sensing is carried out. If no biological components are used to carry out the sensing, it will be called a chemical sensor regardless of its intended use. The relative importance of the various attributes found in an ideal sensor are dependent on the application in which the sensor will function. Unfortunately, this also tends to cloud the picture of what is meant by a sensor. Two simple examples are given to better highlight the definition.

First, consider a simple device that monitors pH (a measure of the acidity) of a sample using a paper "test strip," also called pH paper. The person carrying out the measurement would wet the paper by immersing it in a sample of fluid and then examine the color of the strip after a short time period, usually by placing it next to a calibrated color scale supplied with the container that held the test strip. The device gives the pH with a certain degree of accuracy, but it is not a chemical sensor since it lacks features that are important for its utility in a process or product monitoring environment. Its biggest failing is that the sensor provides no direct signal in the absence of the operator. It also has a single-use feature that is not reversible, and it would be more appropriately called a pH measurement device. Therefore, a better definition should include the point that chemical sensors are measuring devices that provide signal output in a continuous or nearly continuous fashion.

In a second example, consider a fluid where we extract a sample and pass it to a sophisticated gas chromatograph (GC) coupled with a mass spectrometer (MS). The gas chromatograph, for our illustrative purpose here, is capable of exquisite chemical separation, and the mass spectrometer is capable of equally exquisite identification of the separated components. The resulting signal could be used to provide detailed composition information of the fluid and can be subsequently coupled to a control system to better regulate the process being monitored; and, in fact, many chemical production facilities operate with GC/MS devices, as they are popularly known. This is also not what we intend to call a chemical sensor, however, since it is quite simply too "big." More precisely, the need for sampling the fluid stream and then characterizing it using bench-top analytical instrumentation is usually an undesirable step for process control. The lag times introduced between sampling and subsequent control action, the cost of the equipment, and the inability to position an arbitrary number of such devices at or near the process line severely limit the utility of such otherwise sophisticated approaches. In fact, such steps are often considered for replacement whenever a more practical device, like a chemical sensor, is introduced. Therefore, we amend our definition again by saying that the sensor should provide rapid output of the signal to the process in a cost-effective manner.

A somewhat cumbersome, but inclusive, working definition can now be stated: a chemical sensor is a device that provides quantitative information on the composition of a fluid mixture in a reversible, minimally invasive, selective, rapid, continuous, and cost-effective manner.

In examining different examples of chemical sensors, we will see that many of the designs are refinements and adaptations of strategies that have been known to work effectively in the analytical laboratory. For example, a pH sensor could be developed by placing pH indicators, originally present in the pH paper just considered, on the end of an optical fiber integrated with a compact light source and detector arrangement to overcome the previously cited limitations. Additionally, gas separation steps employing membranes instead of chromatographic operations could be used together with selective electrochemical electrodes to eliminate the unfavorable attributes of the gas chromatograph setup. Nowadays, even miniaturized GC/MS devices operating on a millimeter-scale device (like an analytical lab on a chip) are being envisioned to function as future chemical sensors. The many advantages of microfabrication techniques are being increasingly exploited to produce sophisticated, reproducible, and inexpensive sensing systems. Some of these sensors have no equivalence to any laboratory protocol, and they function as truly unique devices.

GENERAL FEATURES OF CHEMICAL SENSORS

Three general features can be identified that make up a chemical sensor. These include a selective surface, a transducer, and a processor as depicted in Fig. 1, along with some examples of different materials and techniques that can be used for each component. The selective surface allows for a specific interaction with the target analyte, where analyte refers to the compound whose composition or presence is being sought. The surface can be modified by addition of ligands or

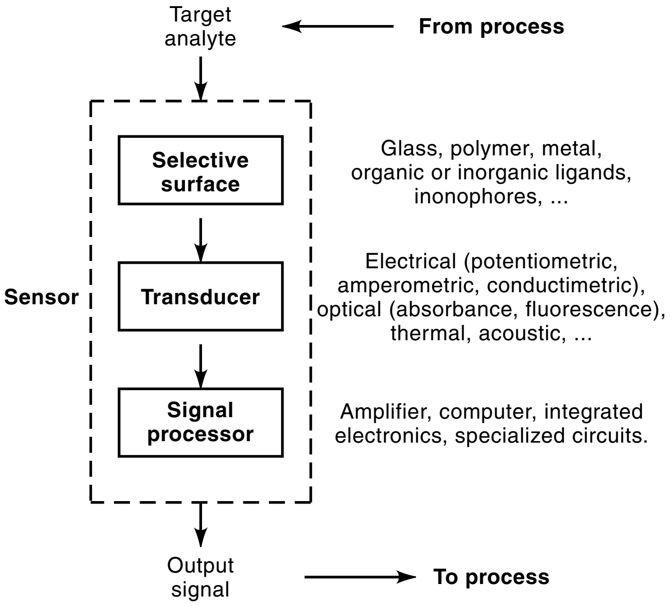

Figure 1. The basic features of a chemical sensor and its interaction with a process system. Representative examples of the three basic components found in any sensor are listed. The target analyte refers to the particular chemical species whose composition information is being sought.

catalysts that provide specific recognition features. The transducer tracks the association of the surface with the analyte. For example, the transducer may be a polymeric material that changes its electrical resistance with the incorporation of the analyte. Alternatively, the transducer may change color or modify the transmittance of light passing through it. Some signal detection, processing, and amplification are subsequently carried out to generate a practical output signal used by the process controller. The final signal coming from the sensor is invariably electronic so that it can be conveniently interfaced to standard controllers or data loggers.

The chief limitations of many chemical sensors are associated with the selectivity of the response to the target analyte compared with the response seen for potential background or contaminating compounds. In a constant background there is little need for selectivity, but in a more typical sensing situation the background concentration changes in unknown ways due to the presence of similar chemical components or "active" species as well as temperature and pressure fluctuations. A typical interferent in many gas-sensing situations is the background moisture or humidity level that is constantly undergoing variations.

The main types of chemical sensors developed to date rely primarily on electrical or optical transduction technologies. To a lesser degree, physical transduction processes such as displacement tracking, due primarily to pressure- or temperature-mediated effects, may also be used, but it is often the case that the operation of such devices rely, again, on electrical or optical signal modulation. Within the electrical transducers, it is convenient to divide them into amperometric, potentiometric, or conductimetric sensors depending on whether the measured signal is the current, voltage, or conductance, respectively. Optical sensors include those that monitor the light absorption, refractive index, polarization, or fluorescence of a transducer, perhaps at many different wavelengths and using continuous or variable light input schemes. The class of electrochemical sensors dominates the worldwide chemical sensors market and, for example, accounted for 88% of the sales share in Japan for all chemical sensors in 1989 (2).

SENSOR TYPES

Electrochemical sensors include the familiar wired electrodes as well as metal oxide semiconducting devices, fuel cells, ion-selective field effect transistors (ISFETs), interdigitated electrodes, high-temperature solid-electrolyte systems, and chemiresistors. Optical sensors include so-called optodes and surface plasmon resonance systems that operate as fiber or planar structured devices. A current trend in many chemical sensors is toward miniaturization and microfabrication that can impart novel properties to sensors, thereby affecting their selectivity, sensitivity, and stability. This introduction does not explore all the latest research variations and innovations but focuses on devices that are commercial or near commercial. Recent research results can be found in specialized journals devoted to chemical sensing and analytical chemistry.

Electrochemical Sensors

Table 1 lists the three main types of electrochemical sensors. They are explored in separate sections below, with specific examples that illustrate the important features. Not all sensors can be exactly categorized in this way since they represent only limiting behaviors. Nevertheless, such distinctions are routinely used and widely adopted in the chemical sensor literature.

Amperometric Sensing. An amperometric chemical sensor is composed, at a minimum, of two metal electrodes maintained at a constant potential (voltage) difference. The current flowing in a closed circuit (which is established and monitored by suitable electronics) through the two electrodes is measured and indicates the presence of "electroactive" species. The relationship between the moles, N, of electroactive species reacted (either oxidized or reduced) and the charge passed through the sensor, Q, is known as Faraday's law:

$$N = Q/nF \tag{1}$$

where n is the number of electrons transferred per mole and F is the Faraday constant (F = 96487 C/mol). By monitoring the charge over time, which is the current, the amount of electroactive compounds can be deduced. To operate as a true sensor, however, some selectivity is required, and this can be achieved by the choice of a suitable electrical potential, by the introduction of a catalytic reaction step, and/or through permselective membranes. For example, a common method for the detection of dissolved oxygen in liquids is through the use of a so-called polarographic or Clark electrode. In this chemical sensor, the reduction of oxygen is followed at constant potential by monitoring the current passing between a working Pt (platinum) electrode and a Ag/AgCl (silver/silver chloride) reference electrode. At steady state, the current is proportional to the dissolved oxygen concentration. This is often reported as an equivalent partial pressure corresponding

Table 1. Electrochemical Sensor Transduction Mechanisms

Transducer	Mechanism	Signal	Example Sensors
Amperometric	Electron charge transfer reaction (Faraday's law)	Current; due to production or consumption of electroactive species	Oxygen (Clark electrode), some hydrocarbons, hydrogen peroxide, fuel cells, high-temperature limiting-current sensors
Potentiometric	Multiphase equilibrium (Nernst equation)	Potential; due to distribution of ionic species across phases	Glass pH electrode, ion selective electrodes, gas sensors (Severinghaus CO_2 electrode), some high-temperature solid-state sensors
Conductimetric	Variation of resistance with composition	Conductance or resistance; due to changes in resistive elements with absorption–adsorption events	Metal-oxide-semiconductor gas and humidity sensors, tin oxide gas sensors, conducting polymer humidity and gas sensors, broad specificity sensors

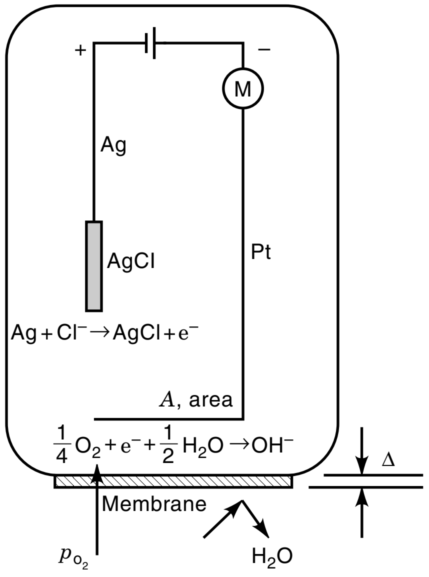

Figure 2. Features of an amperometric sensor for detecting oxygen (Clark electrode). The reactions occurring at the two electrodes are separated from the bulk fluid by an oxygen-permeable, nonporous membrane.

to the oxygen concentration in a gas phase that would be in equilibrium with the actual liquid-phase concentration.

Polarographic Sensors. In order to see how this chemical sensor functions and to draw analogies with many other equivalent systems, we examine the individual components of the device in greater detail. Figure 2 shows the salient features of a Clark electrode. First, in order to achieve some specificity to oxygen, a catalytic reaction is carried out at the cathode. The cathode is typically made of platinum, coated onto a wire or some other underlying support, that catalyzes the following electrochemical reaction,

$$\tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O + e^- \rightarrow OH^- \qquad E^0 = +0.40\,V$$

where E^0 is the standard electrode potential at 25°C for the reaction as written measured against the standard hydrogen electrode. The hydrogen electrode is further described in the next section on potentiometric sensing. The actual reference electrode often used in a Clark oxygen sensor, however, is not the hydrogen electrode, but rather a Ag/AgCl electrode at which the matching reaction occurs:

$$Ag + Cl^- \rightarrow AgCl + e^- \qquad E^0 = -0.22\,V$$

The net effect is the reduction of oxygen accompanied by the transfer of electrons at a standard electrode potential difference of about 600 mV. Second, the cathode is separated from the sensing fluid by the presence of an oxygen permeable membrane, usually made of a thin silicone polymer. This allows for oxygen transfer, but it eliminates many other electroactive polar and nonlipophilic compounds that would interfere if they were to be reduced at the cathode surface. The membrane also protects the sensor from fouling due to nonreactive adsorption that can severely degrade its performance. Finally, the anode is maintained at fixed reference conditions by establishing a constant chloride ion concentration. In practice, this is achieved by immersing the reference anode in a fixed KCl salt solution that is separated from the sampling fluid. The actual potential created between the reference and platinum electrodes confers further selectivity to the sensor in that it favors the reduction of oxygen.

The cathode in this example is often called the working electrode and has a surface area much smaller than the anode, or reference (also called the auxiliary) electrode. This ensures that the working electrode limits the current flow in the circuit and, hence, that the current measurements will only reflect reaction steps at the cathode (i.e., reactions with oxygen). The actual working potential is often greater than 600 mV to drive the oxygen reduction as much as possible. If the voltage is too high, however, undesirable electrolysis and corrosion steps can also take place that interfere with the measurement and limit the life of the sensor. A usual choice for the polarographic oxygen sensor (Clark electrode) is around 600 mV to 900 mV, where the working Pt electrode is made negative with respect to the auxiliary electrode. The two electrodes are often housed in an integrated package that provides a compact arrangement of all the necessary parts and allows the electric circuit to be completed on the sensing side of the permeable membrane.

Variations on this strategy for oxygen sensing have been developed that illustrate some alternative detection and sensing schemes. For instance, if a third electrode is introduced, called a "counter electrode," the current measurement can be carried out through a low-impedance circuit path that avoids driving large currents through the high impedance reference electrode (3). This has the advantage of maintaining long-term sensor calibration as well as prolonging the life of the sensor by avoiding corrosion reactions. The typical electric configurations for working with two- and three-electrode designs are shown in Fig. 3.

Galvanic Sensors. Alternatively, the reference electrode can be replaced by a base metal such as lead or zinc. The reaction at the anode (in the case of a lead auxiliary electrode) is now summarized as

$$\tfrac{1}{2}Pb \rightarrow \tfrac{1}{2}Pb^{2+} + e^- \qquad E^0 = +0.13\,V$$

This oxidation reaction obviously consumes the electrode over time, but nevertheless maintains a fixed potential that is sufficient to drive the reduction of oxygen. Usually, a silver cathode is used in combination with the base metal anode. Some simplification is introduced since no external potential is re-

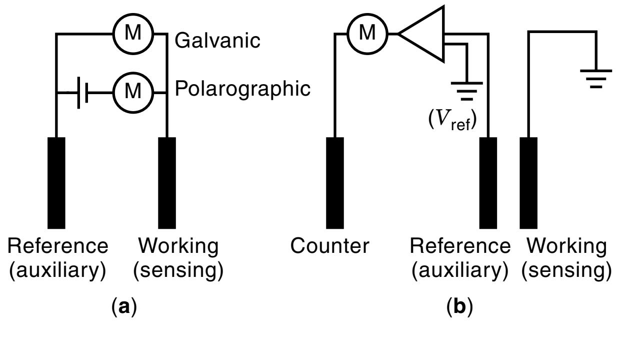

Figure 3. Electrochemical sensor configuration for amperometric sensors in two-electrode (a) and three-electrode (b) designs.

quired and a direct measurement of the current is proportional to the oxygen consumed. Such a design is referred to as a galvanic oxygen sensor, and a two-electrode configuration is shown in Fig. 3. In general, polarographic chemical sensors impose a fixed potential between the reference and sensing electrodes while galvanic chemical sensors do not. In both cases, however, the current is measured, and they are collectively referred to as amperometric sensors.

Fuel Cell Sensors. Finally, a "fuel cell" oxygen sensor can be constructed that contains the lead and working electrodes immersed in a basic electrolyte. Here, the anode generates a potential due to the following reaction:

$$\tfrac{1}{2}\mathrm{Pb} + \mathrm{OH}^- \rightarrow \tfrac{1}{2}\mathrm{PbO(s, red)} + \tfrac{1}{2}\mathrm{H_2O} + \mathrm{e}^- \qquad E = -0.58\,\mathrm{V}\ (\text{in } 0.2\ \mathrm{M\ Ba(OH)_2})$$

In combination with the cathodic reaction, a net overall stoichiometry can be written as

$$\mathrm{Pb} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{PbO}$$

which does not involve any of the electrolyte species. This is one reason it is often called a fuel cell sensor even though the generation of electricity is used only to obtain an appropriate signal. Again, a direct measurement of the current can be calibrated with the oxygen concentration.

Diffusion-Limited Current. Referring back to the polarographic oxygen electrode, it is instructive to consider the limiting case where the cathodic reaction is sufficiently fast that the oxygen concentration at the cathode surface goes to zero. As depicted in Fig. 2, the membrane will now generally limit the transport of oxygen from the measurement fluid to the electrode surface. Sensors that function under such conditions exhibit the maximum possible signal, all other things being equal, and are said to operate under diffusion-limited conditions. Such an operating protocol also allows for less stringent control over the applied potential. In fact, the potential can be allowed to fluctuate over small ranges without any dramatic effects on the sensor response since the applied potential is already sufficient to reduce all the oxygen at the electrode surface.

The mass transfer through the membrane satisfies Fick's second law:

$$\frac{\partial p}{\partial t} = D_{\mathrm{O_2}} \frac{\partial^2 p}{\partial x^2} \tag{2}$$

where p is the (equivalent) oxygen partial pressure in the membrane and $D_{\mathrm{O_2}}$ is the oxygen diffusion coefficient in the membrane. If we consider a step change in the bulk oxygen concentration from 0 to a value $p_{\mathrm{O_2}}$, the measured current at the cathode surface can be found by integrating the above equation. The solution is

$$i(t) = \frac{4FAP_{\mathrm{m}}}{\Delta} p_{\mathrm{O_2}} \left[1 + 2\sum_{n=1}^{\infty} (-1)^n e^{-n^2\pi^2 D_{\mathrm{O_2}} t/\Delta^2} \right] \tag{3}$$

The factor 4 in Eq. (3) reflects the transfer of four electrons per mole of oxygen reduced and A is the cathode surface area, as shown in Fig. 2. The other parameters include the membrane permeability, $P_{\mathrm{m}} = D_{\mathrm{O_2}} S_{\mathrm{m}}$, where S_{m} is the solubility of oxygen in the membrane. The membrane thickness is Δ and the oxygen diffusivity is $D_{\mathrm{O_2}}$. At sufficiently long times, the current is seen to be directly proportional to the oxygen partial pressure. This is the reading that would be measured at steady state, and the linearity of the steady-state current response with the oxygen partial pressure is a direct consequence of the diffusion-limited nature of the sensor. Furthermore, the time constant for the sensor can be characterized by the dominant exponential term and is conveniently represented as

$$\tau = \frac{\Delta^2}{\pi^2 D_{\mathrm{O_2}}} \tag{4}$$

For a 0.1 mm thick membrane with an oxygen diffusivity of 10^{-6} cm^2/s, the time constant will be approximately 10 s. Other factors such as poor mixing in the electrolyte solution as well as slow mixing in the external sensing fluid will cause the actual sensor response to be longer. If it is necessary to track oxygen concentration on a much shorter time scale, thinner and more permeable membranes would be needed, or mixing in the external as well as internal regions should be introduced.

Selectivity. Other species besides oxygen can also be detected by analogous procedures. In some cases, a preliminary reaction step is introduced that converts the target compound into oxygen or consumes oxygen at a rate proportional to the concentration of the intended analyte. This allows the sensor just described to be used directly. Many biosensors (see BIOMEDICAL SENSORS) have been developed with this strategy in mind where an enzymatic reaction generates or consumes oxygen. In other cases, appropriate selection of the electrode potential can provide some selectivity. For instance, an amperometric sensor for ethylene ($\mathrm{C_2H_4}$) has been reported (4) that oxidizes ethylene on a gold working electrode (anode). In this case, the gold was deposited on a membrane in order to generate high surface areas, rather than using a membrane to cover a typical wire electrode. The electrochemical sensor configuration was operated with an $\mathrm{Hg/Hg_2SO_4}$ reference electrode (cathode) as well as a gold counterelectrode, and a linear current was observed for gas-phase ethylene concentrations between 0 ppm and 500 ppm (1 ppm = 1 "part per million" = 1 molecule or mole per million molecules or moles of gas). However, this sensor exhibits some cross-sensitivity to other electroactive species as shown in Table 2. This indicates that the selectivity of the sensor is such that other compounds can simultaneously contribute to the amperometric response. In this case, the response is evaluated at 10 ppm (or higher)

Table 2. Selectivity Profile of Ethylene Sensor

Gas Measured (concentration is 10 ppm, unless indicated)	Relative Response (ethylene = 1; 10 ppm)
Acetaldehyde (100 ppm)	0
Acetylene	7.4
CO (100 ppm)	0
Ethanol (100 ppm)	0
NO	1.8
$\mathrm{NO_2}$	0.3
$\mathrm{SO_2}$	2.5

for a variety of gases and is normalized to the response seen for 10 ppm ethylene. Such a ratio is a convenient measure of the selectivity. The sensor was found to be more selective for some compounds when the response was compared with that seen for ethylene. This implies that it would, in fact, be a better sensor if the target compound had been chosen to be, in this case, acetylene or sulfur dioxide. The consequence of this on the usefulness of the sensor for ethylene detection, however, depends on the intended application. In general, selectivity considerations must always be considered from the point of view of known interferents and expected interferent levels. These factors are prone to change when the application environment changes, and sensors that function well in one situation may turn out to be completely unacceptable in other applications. If it is not likely that known interferents will be present in the sampling stream, the response to those components may be of little consequence.

Potentiometric Sensing. A potentiometric chemical sensor is composed of many of the same parts as an amperometric sensor, except that voltage is measured under conditions of a small, often negligible, current. The most important feature in a potentiometric measurement is that equilibrium conditions are established between electroactive species in solution and at the electrode. This is in contrast to the diffusion-limited condition just discussed for amperometric measurements and leads to relations between voltage and concentration that are logarithmic rather than linear.

Nernstian (Equilibrium) Behavior. The general way to describe the performance of an ideal potentiometric chemical sensor is to refer to it as Nernstian. The derivation of the Nernst equation can be found in many introductory chemistry texts, so we will only outline the important features here for a particular system (see Electrochemical electrodes). In particular, consider the silver–(porous) silver chloride (Ag/AgCl) electrochemical reaction described previously, but now as a reversible “half-cell” reaction:

$$\mathrm{Ag} + \mathrm{Cl}^- \leftrightarrow \mathrm{AgCl} + \mathrm{e}^-$$

The equality of electrochemical potentials for all reactants and products defines the equilibrium state of the system. Under ideal conditions, the electrochemical potential, μ_A^*, of a particular species in solution at a concentration $[A]$ is found from the thermodynamic relation (5)

$$\mu_A^* = \mu_A^0 + RT\ln[A] + zF\phi_A \tag{5}$$

where the brackets denote concentrations, R is the gas constant, T is the absolute temperature, z is the electric charge associated with the ion A, and ϕ_A is the electrode potential. For any phase consisting of only a pure component, such as the metallic silver wire or the porous silver chloride coating, the electrochemical potential will be a constant at a specified temperature. Thereby, the Ag/AgCl equilibria (referred to also as a “couple”) can be expressed in terms of the chemical and electrical potentials as

$$\mu_{\mathrm{Ag}}^0 + (\mu_{\mathrm{Cl}^-}^0 + RT\ln[\mathrm{Cl}^-] - F\phi_{\mathrm{Cl}^-}) = \mu_{\mathrm{AgCl}}^0 + (\mu_{e^-} - F\phi_{\mathrm{e}^-}) \tag{6}$$

If we rearrange this equation, collect all terms that are at most a function of the temperature, and introduce $\Delta\phi = \phi_{\mathrm{Cl}^-} - \phi_{\mathrm{e}^-} = \phi_{\mathrm{S}} - \phi_{\mathrm{M}}$ to emphasize that the potential is determined as the difference between the solution and the metal, we obtain

$$\Delta\phi = E^0 - \frac{RT}{F}\ln[\mathrm{Cl}^-] \tag{7}$$

The standard electrode potential is tabulated in many reference books (6) and was used previously in discussing amperometric reactions. It is seen that the potential at a fixed temperature will be a function of only the chloride ion concentration. In a saturated solution containing salt crystals, this is easily maintained at a fixed value and explains why this type of electrode is often used as a reference. The generalization of this expression to any number of soluble species participating in a half-cell reaction can be done using the same sequence of steps. The reaction, of course, must be properly balanced with respect to the stoichiometry as well as the charge.

If an experiment is set up to actually measure the potential predicted by the above equation, it will always be necessary to introduce a second wire (electrode) into the solution to complete the measurement circuit. This second wire is problematic since it can now establish its own potential difference in the solution under investigation and it will generally be impossible to isolate the individual contributions. For this reason, the $\mathrm{H}^+/\mathrm{H}_2$ couple has been arbitrarily chosen as a particular half-cell reaction to have a potential of zero (at 25°C). As a result, all measurements comprising a closed circuit with this electrode, called the standard hydrogen electrode (SHE), can be assigned unique values of the standard electrode potential.

For any two electrodes, the net resulting electrical potential will be found from the differences in their half-cell potentials. A cell made of any two half-cells that is balanced with respect to the production and utilization of electrons is called a “formal” cell, and the net reaction is called the formal cell reaction. The production of PbO from metallic lead and oxygen in a fuel cell oxygen sensor is a formal cell reaction, although it is not at equilibrium. It is convenient to summarize the components as well as the physical arrangement of a formal cell by using the following type of cell diagram:

$$\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl}^-|\mathrm{Hg}_2\mathrm{Cl}_2|\mathrm{Hg}$$

This indicates that the potential difference, for this example, between a mercury electrode (commonly called a calomel electrode) and the silver electrode will be measured. The single vertical bars indicate a different solid or liquid phase that participates in the equilibria. In this case, both electrodes share the same aqueous phase, but this is not usually possible when sensing is to be carried out—since we would already need to know the composition in order to predict the reference potential. For liquids, porous barriers are often introduced that allow for ion migration, but otherwise limit the bulk flow of aqueous solutions.

From the equation developed previously, we can write the electrode potentials for each half-cell and simply sum them. This eliminates the solution potential from the equations and leads to the Nernst equation, which in general will be expressed as

$$\Delta\phi = \Delta E^0 + \frac{RT}{F}\ln\frac{\prod a_{R_i}^{\nu_i}}{\prod a_{P_j}^{\nu_j}} \tag{8}$$

Here we have also introduced the activities in place of the concentrations to make the result applicable to nonideal solutions as well. The exponents ν_i and ν_j are the stoichiometric coefficients (always positive numbers) for those reactants and products, respectively, that participate as solution- or gas-phase species. The activity, a_i, is related to the concentration by the so-called activity coefficient,

$$a_i = \gamma_i[i] \tag{9}$$

Correlations for the activity coefficient are expressed in terms of the Debye–Hückel limiting law or its extension (7). Components that participate in the reaction as pure phases (like solids) or in great excess (like water) do not explicitly show up on the right hand side of Eq. (8). Experimentally, the measurement of electric potential together with the Nernst equation is often used to determine the activity coefficients of salt solutions.

Glass Electrode and the pH Sensor. By clever choice of electrode reactions and salt solutions, it is possible to construct chemical sensors for various ions that operate on the principles just described. However, poor sensor selectivity often limits such devices to a few specialized situations where the background interferents are fixed. Membranes, however, can offer a means to impart selectivity to potentiometric sensors in much the same way they were used for constructing the Clark electrode. One of the most widely used potentiometric sensors is the glass electrode, or pH sensor, which incorporates a glass membrane to limit the response to being dependent only on the hydrogen ion concentration or, more exactly, on the hydrogen ion activity. Figure 4 shows the construction of a pH sensor. With a suitable reference electrode, say a calomel electrode, the components of the cell can be summarized as

$$\mathrm{Ag|AgCl|H_i^+,\ Cl_i^+}\left|\underbrace{\mathrm{Na^+,\ -SiO^-}}_{\text{glass membrane}}\right|\mathrm{H^+\|K^+,\ Cl^-|Hg_2Cl_2|Hg}$$

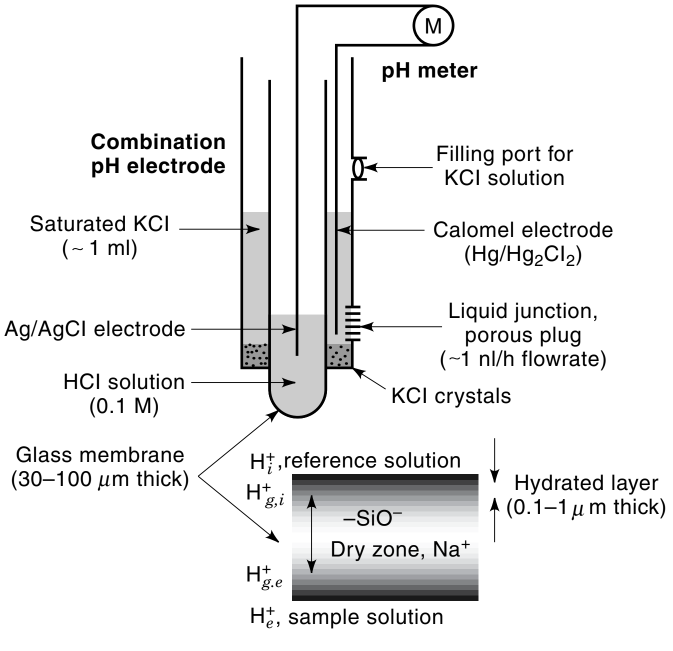

Figure 4. The glass electrode (pH sensor). A combination electrode is shown. The glass membrane region is expanded at the bottom of the figure to highlight the notation used in the text.

In fact, both the silver/silver chloride and the calomel electrodes can be considered as reference electrodes, and the potential-determining reactions are all confined to the glass membrane. The equilibration of hydrogen ions on the external side (surface) of the glass membrane and the external solution (this is the solution whose pH is sought) is due to an ion exchange with sodium ions in the special sodium/calcium-silicate glasses used. The anionic binding sites are fixed, and at high concentration of sodium ions this leads to the relation

$$\phi_e - \phi_{g,e} = -\frac{RT}{F}\ln\frac{H_e^+}{H_{g,e}^+} \tag{10}$$

where the notation $H_e^+ = a_{\mathrm{H}^+}$ is used to indicate the (external) solution activity. The subscript g denotes activities evaluated at the glass surface. At the inside surface of the glass membrane, an exactly analogous relation holds,

$$\phi_i - \phi_{g,i} = -\frac{RT}{F}\ln\frac{H_i^+}{H_{g,i}^+} \tag{11}$$

and, by adding the equations and rearranging, one obtains

$$-\frac{RT}{F}\ln\frac{H_e^+}{H_i^+} = \left[\frac{RT}{F}\ln\frac{H_{g,e}^+}{H_{g,i}^+} + (\phi_{g,e} - \phi_{g,i})\right] + (\phi_e - \phi_i) \tag{12}$$

The term in square brackets reflects equilibria occurring within the glass membrane but confined to a small region on each surface. It has been estimated that the exchange surface consists of a hydrated layer on the order of 0.1 μm to 1 μm thick, whereas the overall thickness of the glass is typically about 100 μm. Only sodium ions transport charge through the dry glass membrane (no hydrogen ions are transferred through the glass), and they also participate in the surface equilibria. Although not readily apparent, this leads to conditions such that the term in brackets is essentially constant.

The two reference electrodes monitor the internal and external potentials. The last step in developing a sensor is to maintain a constant internal hydrogen ion concentration. This is easily done by filling the inside of the glass bulb shown in Fig. 4 with a solution of, say, 0.1 M HCl since neither hydrogen ions nor chloride ions permeate the glass. Collecting all the constant terms as ϕ' and using activities, we obtain

$$(\phi_e - \phi_i) + \phi' = -\frac{RT}{F}\ln a_{H^+} = \frac{2.303RT}{F}\,\mathrm{pH} \tag{13}$$

The standard definition of the pH has been used:

$$\mathrm{pH} \equiv -\log_{10} a_{\mathrm{H}^+} \tag{14}$$

At 25°C, the equation above shows that for every unit change in pH the recorded potential should change by 59 mV (R = 8.313 J/K mol, T = 293 K). The selectivity, measured at equal concentrations, of the ion-exchange reaction is always greatly in favor of the hydrogen ion over other competing cations. At low pH and high sodium concentrations, however, the nature of the cation exchange mechanism shows that it will also be a function of the external sodium ion concentration. This usually limits pH sensors to values less than pH = 11. Special "high-pH" glass made of Li_2O (in place of Na_2O/SiO_2) can extend the range a few units higher, however.

In practice, the pH sensor is often designed as a "combination electrode" in which the calomel electrode is placed around the internal Ag/AgCl electrode as shown in Fig. 4. The calomel electrode must be exposed to a constant (usually saturated) chloride ion concentration, but it must also have continuous ionic contact with the analyte solution in order to allow for a complete electric circuit. A small porous plug or capillary channel, referred to as a liquid junction and indicated in a cell diagram by a vertical double bar, is used with a very small leakage flow rate to accomplish this. Furthermore, by choosing KCl as the salt, the anion and cation molar conductivities are such that very little additional potential is generated at the liquid junction.

A commercial pH meter includes the glass electrode, a high-impedance voltmeter, and some form of temperature compensation and calibration functions. Temperature compensation is usually built-in according to the predictions of the Nernst equation, and calibration protocols with buffers of known pH are established to account for asymmetry potentials in the glass membrane, reference electrode drift, and nonzero liquid junction potentials. The asymmetry potential arises from surface defects and strain due to production or aging of the glass bulb as well as surface adsorption phenomena. With proper care and operation, a pH meter is almost unmatched among all chemical sensors in its sensitivity, selectivity, dynamic range, and ease of operation.

Gas Sensors. The extension of this sensor to other chemical species or ions can be accomplished in two ways. On the one hand, a reversible reaction can be introduced that selectively generates or consumes hydrogen ions in proportion to the target analyte. On the other hand, membranes with selective permeability to other ions can be used. For the former situation, gas-sensing electrodes have been fabricated that rely on establishing an acid–base equilibrium in a solution exposed to the gas and also contacting a pH-sensing electrode. For example, if CO_2 is allowed to equilibrate in an aqueous solution, the following equilibria will be established:

$$\begin{aligned} CO_2(g) &\leftrightarrow CO_2(aq) & \\ CO_2(aq) + H_2O(l) &\leftrightarrow H_2CO_3(aq) & K_1 \\ H_2CO_3(aq) &\leftrightarrow H^+(aq) + HCO_3^-(aq) & K_2 \end{aligned}$$

This leads to the relation

$$p_{CO_2} = K a_{H^+} a_{HCO_3^-} \approx \kappa a_{H^+} \tag{15}$$

where the second equality depends on a constant concentration (activity) of HCO_3^- ion. This is readily achieved by using a 10 mM solution of sodium bicarbonate ($NaHCO_3$) in the aqueous phase. In practice, the bicarbonate ion is often integrated into the reference electrode that further communicates with the external solution through a gas-permeable membrane. It is also possible to wrap the membrane around the bulb of regular combination pH electrode so that the space between the membrane and the electrode sequesters a carbonate buffer solution. A combination pH electrode is often used in either of these situations since the entire sensing circuit can be placed behind the membrane. Levels as low as 10^{-5} M CO_2 can be detected. One of the most popular uses of this type of electrode is in biomedical applications to monitor arterial blood gases, and in such situations it is often referred to as a Severinghaus electrode.

The gas-sensing principle can be readily adapted to other gases such as ammonia (NH_3). In this case, a 0.1 M solution of ammonium chloride (NH_4Cl) is used in place of the bicarbonate salt. Through a series of equilibrium reactions, the ammonia gas solubility is directly related to the solution pH, and levels of NH_3 down to 1 μM can be detected. Table 3 lists some additional gas-sensing strategies for other species that can be coupled to the pH electrode. Other ion electrodes, mentioned below, have also been coupled to gas sensing in analogous fashion. Many enzyme electrodes work by further coupling enzymatic reaction steps in the membrane to eventual production or depletion of hydrogen ion, carbon dioxide, or ammonia. This allows for the detection of species that are not directly amenable to potentiometric analysis.

Ion-Selective Electrodes. As mentioned above, the alternative strategy for extending the concept of the glass electrode to other species is to develop membranes that are selective to the species of interest. Glasses have been developed for cations other than hydrogen, although the selectivity is generally much poorer. It is also possible to use (supported) liquid membranes or polymer films for ion sensing by incorporating ion-exchange sites that selectivity bind different target ions. Such ion-selective electrodes (ISEs) are widely used and commercially available. An instructive example is the sensing of potassium cations (K^+) carried out with a diphenylether film containing the ionophore valinomycin. Valinomycin is a cyclic peptide that binds to potassium with strength three to four orders of magnitude greater than that of competing cations such as sodium or ammonium. If the solution containing HCl in the pH sensor design is replaced by KCl and the glass membrane is replaced by the valinomycin membrane, the potential measured with a suitable reference electrode will be, again, 59 mV per decade change in the potassium ion activity. Such sensors have been used as potassium-selective microelectrodes to probe the ion concentration inside single living cells.

When the selective properties of the membrane are not sufficient to reject competing chemical species, the response often deviates from Nernstian behavior as shown in Fig. 5. At low target analyte concentrations, background ions can contribute to the signal through the generation of additional potentials. The exact analysis of such situations is complex and often approximated by the Nikolskij–Eisenman equation:

$$E = \Delta\phi = \phi_{\text{constant}} + \frac{2.303RT}{z_x F} \log\left(a_x + \sum_i K_{x,i} a_i^{z_x/z_i}\right) \tag{16}$$

The selectivity coefficient, $K_{x,i}$, is defined to represent the contribution to the sensor response for each interfering ion and

Table 3. Gas Sensors Based on pH Electrodes

Gas Analyte	Equilibria, (pK_a; 25°C)	Lower Limit (μM)	Reference Solution, Sample Condition
Ammonia, NH_3	$NH_4^+ \leftrightarrow NH_3^+ H^+$ (9.40)	1	0.01 M NH_4Cl, pH > 11
Acetate, HOAc (Ac = CH_3CO–)	HOAc ↔ H^+ + OAc^- (4.76)	1000	0.1 M NaOAc, pH < 2
Carbon dioxide, CO_2	$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$ (6.38; using ($CO_2 + H_2CO_3$) in denominator)	10	0.01 M $NaHCO_3$, pH < 4
Chlorine, Cl_2	$Cl_2 + H_2O = 2H^+ + ClO^- + Cl^-$ (multiple equilibria)	5000	H_2SO_4, pH < 2
Ethanol amine, Et_2NH (ET = $CH_3CH_2O^-$)	$Et_2NH_2^+ \leftrightarrow Et_2NH + H^+$ (9.01)	1	0.01 M Et_2NH_2Cl, pH > 11
Nitrogen dioxide, NO_2	$2NO_2 + H_2O \leftrightarrow NO_3^- + NO_2^- + 2H^+$ (1.4–3.2; multiple equilibria)	0.5	Citrate buffer, no SO_2
Sulfur dioxide, SO_2	$SO_2 + H_2O \leftrightarrow H^+ + HSO_3^-$ (1.89; includes dehydration)	1	0.01 M $NaHSO_3$

Adapted from J. Janata, *Principles of Chemical Sensors,* New York: Plenum Press, 1989, pp. 150–151.

can be evaluated independently. Note that this equation shows the correct limiting behavior when the solution contains only a single ion, whether that ion is the target compound or an interfering one. Nonlinear calibrations can be used if the background is constant. Figure 5 also shows how the limit of detection is defined for ISEs.

Conductimetric Sensing. The electrical resistance change that accompanies the interaction of a target analyte with a conductive layer (typically a polymer or ceramic) held between two electrodes can also be used to construct a sensor. Such devices are generally known as conductimetric or resistive sensors. They are one of the simplest types of sensor to construct and have been widely used for the past 30 years, predominantly in gas-sensing applications. At the same time, however, they are among the least understood in terms of their selectivity properties. For this reason, many of the applications have been discovered by empirical modifications to various selective layers and to electrode physical design. The result is that conductimetric sensors often require detailed calibration with a variety of potential interferents in order to carefully define the selectivity and be commercially useful. Nevertheless, these sensors are generally inexpensive, and the perceived disadvantages are easily outweighed.

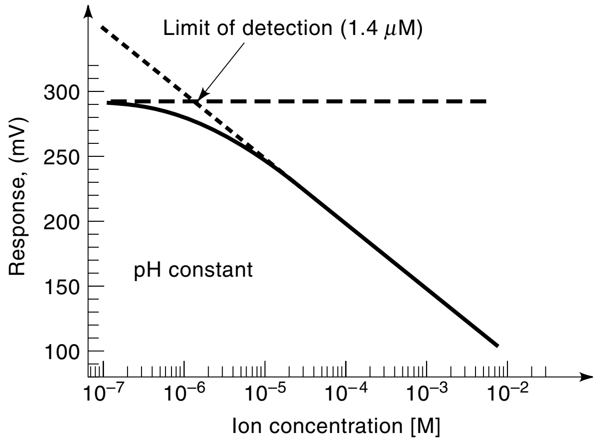

Figure 5. Deviation of ISEs from Nernstian behavior at low analyte concentrations. The deviation is due to presence of interfering ions. The IUPAC definition of the limit of detection (LOD) for ISEs is indicated by the intersection of the two straight-line extrapolations.

The electrodes in a conductimetric sensing circuit contact the resistive element in such a way that direct-current (dc) or alternating-current (ac) measurements can be taken with the resistive layer exposed to the sensing fluid. Adsorption of the analyte occurs both at the surface and within the bulk of the material, which leads to changes in the electrical resistance. Such measurements can usually be done very accurately. Two particular types of materials have found the widest application in their use as selective layers: metal oxide semiconductors (MOSs) and conducting polymers (CPs).

Metal Oxide Semiconductors. At elevated temperatures (200°C to 600°C) in an oxygen atmosphere, oxygen ions (O_2^-) are present on the surface of various metal oxides. These ions are formed by extraction of electrons from the oxide material. This electron depletion along with the surface morphology and microstructure will modulate the conductivity. If tin dioxide (SnO_2) is used, for example, the adsorbed oxygen ions will react with a variety of reducing gases to decrease the material resistance. The metal oxide functions as an n-type semiconductor in this case, and the underlying solid-state physics has been extensively investigated. The change in resistance can be quite dramatic, and linear responses have been observed over several decades of reducing gas concentration.

The requirement for high temperatures and oxygen (or other donor molecules such as water) leads to their predominance as gas sensors. The high temperature requirement could be met by the environment in which the sensor operates, but is often satisfied by integrating compact electrical heating elements into the design so they can function at room temperature conditions. The heating requirement necessitates a power consumption that is typically on the order of 10 mW. The tin oxide gas sensor (TGS) is the most popular MOS sensor and is produced by a variety of manufacturers. Some representative performance data are shown in Fig. 6 for Scimarec (Tokyo, Japan) gas sensors where the resistance is plotted as a function of gas concentration. Gases with resistance ratios much less than 1 will be easily sensed in a background of clean air.

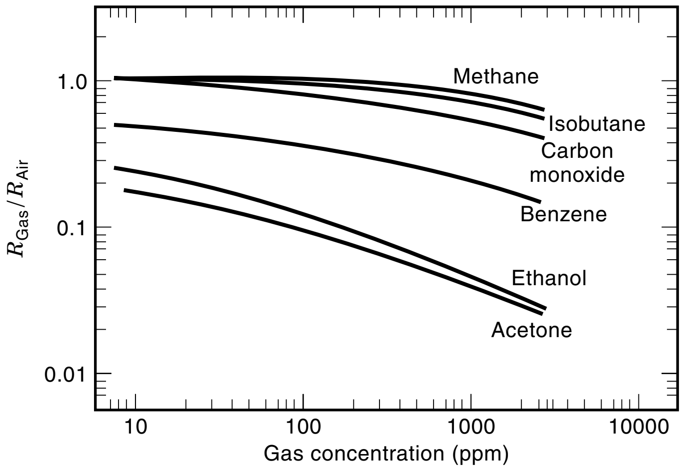

Figure 6. MOS sensor resistance ratios for target gases and for clean air as a function of the target gas concentration. [From Scimarec Co., Ltd. (Tokyo, Japan) specifications sheet (AF-63 sensor), with permission.]

The range of concentrations from 1 ppm to 1000 ppm is typical of the performance of MOS sensors. It is also seen that different sensor types have differing selectivities. The mechanism for imparting selectivity to the sensor is often not understood at a level to allow for rational design. Nevertheless, selectivity is known to depend on the addition of dopants that promote catalytic reaction steps and affect the semiconductor charge layer. The fabrication method can also change the MOS film thickness as well as the grain boundary profile that results in variable resistance changes. The particular choice of metal oxide (SnO_2, In_2O_3) or the use of mixed metal oxides (SnO_2 + Fe_2O_3) will change the selectivity. The heating cycle can also be adjusted in some cases to dynamically manipulate selectivity. In general, proprietary fabrication and processing steps distinguish one manufacturer from another. A basic dc circuit diagram that shows how an ethanol MOS sensor (Scimarec AF63) can be integrated with signal processing steps is seen in Fig. 7. The absolute ethanol level is replaced by readings corresponding to ethanol ranges such as low, medium, and high. Some additional features include ready, reset, power, and low battery indicators that make for a practical device.

Conducting Polymers. The use of a conducting polymer in place of a MOS has been recently investigated for many liquid and gas phase applications. The CP films can be made of polymers formed from acetylene, thiophene, pyrrole, furan, phenylene, quinoline, and aniline monomers, as well their substituted analogs. The key to producing usable sensors is to formulate conditions such that films are easy to process and manipulate. Polypyrrole, polythiophene, and polyaniline, as well as their derivatives, are generally easier to process into thin films than other CPs. Manipulation of polymer properties is done by addition of plasticizers and other constituents either before or after the polymerization process. The films are usually placed between two Pt or Au (gold) electrodes arranged as an interdigitated structure over an inert substrate such as silica. The sorption of vapors or liquid phase components causes swelling of the polymer films and/or modification of the charge-carrier complexes along the polymer backbone that results in either decreases or increases in the resistance. As with MOS devices, extensive calibrations are usually required.

The chemical specificity of CPs is manipulated to a certain extent through the additives used. It is also possible to covalently couple high-affinity ligands to the polymer, and this has been demonstrated with antibodies. Antibodies are biological molecules that have a strong affinity for other proteins, and specific antibodies can be generated for specific proteins. For small target molecules, antibodies are more difficult to obtain, but some success has been demonstrated. Some ul-

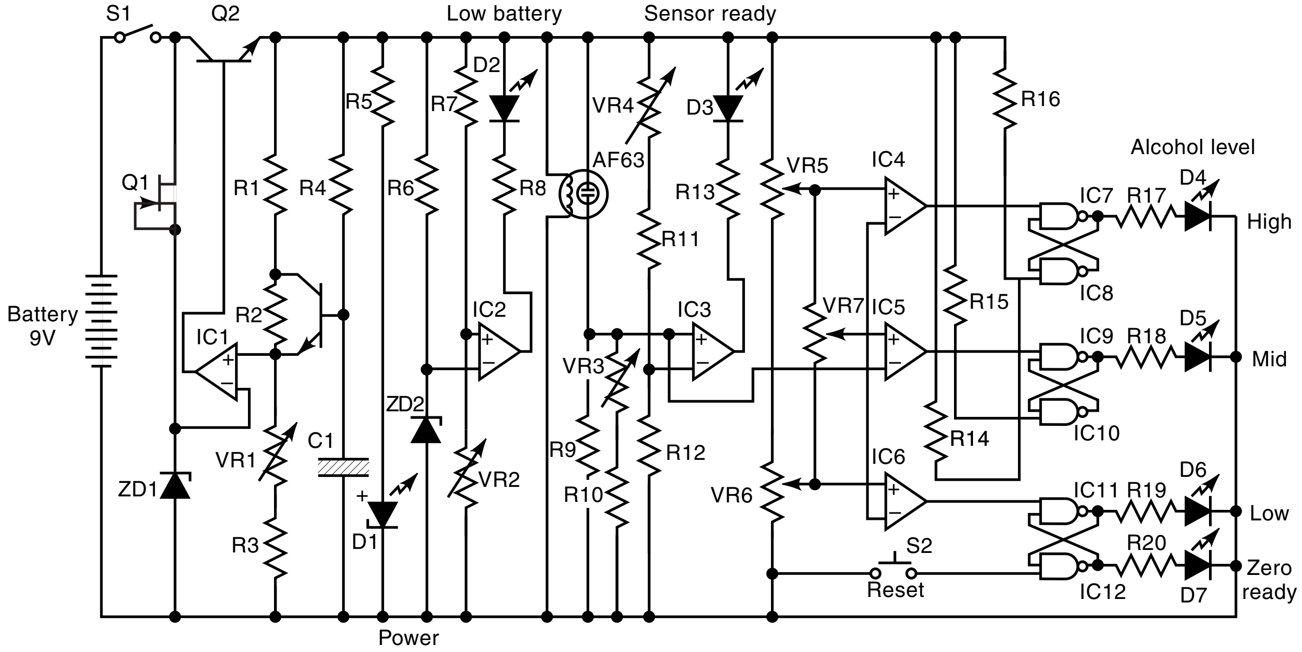

Figure 7. A circuit for utilizing a MOS sensor in the detection of gas-phase ethanol (alcohol).

trasensitive applications have been reported (8) for the conducting polymer poly(3-hexylthiophene) when it was used to detect hydrazine vapor. This sensor, however, operated as an irreversible device and depended on the cumulative changes in resistance to measure hydrazine vapor concentrations. When operated in such a manner, these devices are often referred to as dosimeters.

Optical Sensors

Optical chemical sensors use interactions with light as the transducer component of the sensor. The current market for optical chemical sensors is smaller than the electrochemical sensor market, but it is a rapidly growing segment. Many of the optical measurements employed in the design of sensors have their basis in analytical spectroscopy and employ optical waveguides to transmit light to and from a suitable detection region. The availability of high-quality optical fiber (cylindrical) waveguides, high-power light sources at a variety of wavelengths, and sophisticated detectors, due primarily to advances in communications technology, has been a primary impetus for, and has greatly accelerated the use of, optical chemical sensors. It is also possible to use planar waveguides as components of optical sensors and these devices have, in fact, been among the first of the optical sensors to be commercialized. Applications that rely strictly on spectroscopic measurements without fiber or planar waveguides are also widespread, but they are not discussed in this overview. The general field of analytical spectroscopy for composition analysis of gases, liquids, and solids is covered in many other textbooks, handbooks, and encyclopedias that are devoted exclusively to the topic.

An optical waveguide is simply a medium through which light is transmitted in such a way that there are distinct light input and output regions. The transmission of light from the input to the output region is done with minimal loss, or the loss is designed to correspond to the sensing capabilities of the waveguide. In the case of a fiber configuration, the waveguide consists of a solid cylindrical “wire” (core) typically made of “clear” glass that is surrounded by a coating (clad) of another material with a different refractive index. Light is transmitted through the fiber by internal reflections as demonstrated in Fig. 8, where the core–clad interface is shown along with the position of a light source and detector. According to Snell’s law, the geometric relationship between refractive index and refraction angle (corresponding to a bend in the light path) is

$$n_1 \sin \Theta_1 = n_2 \sin \Theta_2 \tag{17}$$

If $n_1 > n_2$, the refracted angle (measured for the light ray passing into the medium of lower refractive index) can go to 90°, and essentially all of the light will be reflected. Therefore, a critical angle exists that depends on the ratio of refractive indices above which the light will be totally internally reflected. For a borosilicate glass with a refractive index of 1.52 and a quartz clad of refractive index 1.46 [so-called hard-clad silica (HCS) fiber], the critical angle is

$$\Theta_{1,c} = \sin^{-1} \frac{n_2 \sin 90^\circ}{n_1} = 74^\circ \tag{18}$$

Fiber waveguides are made of different types of glasses or plastics, and the variety of possible core–clad combinations lead to different critical angles. Snell’s law can also be applied to the light entrance region of a fiber, and the maximum angle of light that can be directed into the fiber and still undergo total internal reflection can be found. This “acceptance” angle is summarized in terms of the numerical aperture of the fiber, NA:

$$\mathrm{NA} = \sin \Theta_0 = \frac{\sqrt{n_1^2 - n_2^2}}{n_0} \tag{19}$$

The numerical aperture is a convenient number to summarize the light collection efficiency of optical fibers and varies between 0 and 1. An NA of 0.5, for instance, corresponds to a 30° angle, which in three dimensions defines an acceptance cone. At the input to a fiber, therefore, NA gives a measure of the light-collecting ability of the fiber, and high NA is preferred. At the output of a fiber, NA describes the cone of light exiting the fiber. Fibers with high NA, however, direct light less well and present problems for coupling to detectors or other fibers where collimated beams are usually desired. Therefore, a compromise may often be needed.

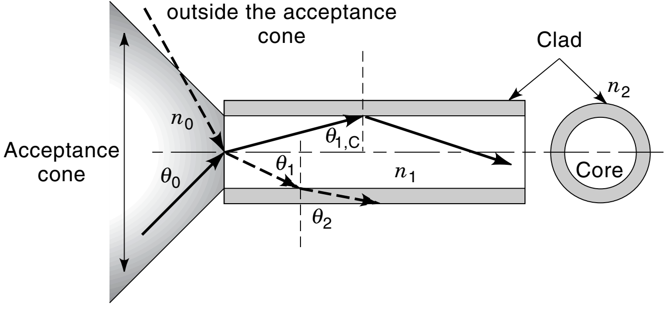

Figure 8. Refraction of light at an optical waveguide interface and at the entrance of a fiber waveguide. Light entering (or exiting) the fiber within the acceptance cone will be totally internally reflected. Additional sensor components often include specific choices for a light source and detector, various lenses, gratings, and/or filters.

Absorption Sensors. The light passing through an optical waveguide can interact with chemical species present within the acceptance cone of the fiber through absorption phenomena. At different wavelengths, the light is attenuated due to interactions with the electronic, vibrational, and/or rotational energy levels of the molecules. In the visible region (400 nm to 800 nm), electronic interactions dominate while at higher wavelengths (lower energy), vibrational and rotational energy transitions cause light absorption. As light of intensity P passes through an absorbing medium, the rate at which the intensity changes with distance penetrated, P, is directly proportional to both the local light intensity (Lambert’s law) and to the concentration of the absorber, c (Beer’s law). This can be expressed as

$$\frac{dP}{dl} = -kcP \tag{20}$$

This expression is an approximation (despite the use of the word *law*) that becomes more exact for dilute solutions and in the absence of secondary reflection, refraction, or re-emission effects. For a uniform concentration distribution, the integrated form of this equation yields the expression

$$\frac{P}{P_0} = e^{-kcl} = 10^{-kcl/2.303} \tag{21}$$

where the initial (input) light intensity is denoted by P_0. The ratio of light intensities is commonly called the transmittance (or percent transmittance when multiplied by 100) and the logarithm (base 10) of the transmittance is known as the absorbance, Abs. Thereby, an absorbance value of 2, for example, corresponds to absorption of 99% of the light entering the sample. From this, the Beer-Lambert relation can be found, which conveniently summarizes the absorption of light as

$$\text{Abs} = \epsilon cl \tag{22}$$

The parameter $\epsilon = k/2.303$ is known as the extinction coefficient or molar absorptivity. Different compounds will have characteristic absorption spectra due to the wavelength dependence of the molar absorptivity and this is used for identification as well as quantification. The linear dependence between the absorbance and the concentration can lead to simple quantitative assays for measuring the composition of unknown samples.

Sensor selectivity can be achieved, in principle, by using the inherent spectral features of the target molecule. In most cases, however, additional steps are needed since the spectral features are highly overlapping and it is impossible to account for unknown interferents. As with electrochemical sensors, target specific reactions and membranes have been developed.

pH Optodes. In particular, pH optical sensors (referred to also as pH optodes or pH optrodes) utilize an otherwise transparent membrane film that contains an entrapped pH indicator. In the simplest case, the absorbance properties of the film will then vary as a result of the acid-dissociation equilibrium taking place with the indicator molecules distributed throughout the film. The reaction scheme is

$$\text{HI} \leftrightarrow \text{H}^+ + \text{I}^- \qquad (K_\text{a})$$

The absorption spectra of the protonated indicator, HI, is different from the absorption spectra of the unprotonated indicator, I^-. Since the equilibrium shifts with increasing or decreasing hydrogen ions, by monitoring the change in the spectra, a calibration can be developed between the absorbance at a particular wavelength and the local pH in the vicinity of the film. The range over which the pH is measured depends on the $\text{p}K_\text{a}$ ($= -\log K_\text{a}$) value of the indicator and is usually restricted to one pH unit above and below the $\text{p}K_\text{a}$ value. Therefore, the pH optode has a much more limited dynamic range than the glass electrode. Nevertheless, it is of interest in applications where small size and electromagnetic immunity are important.

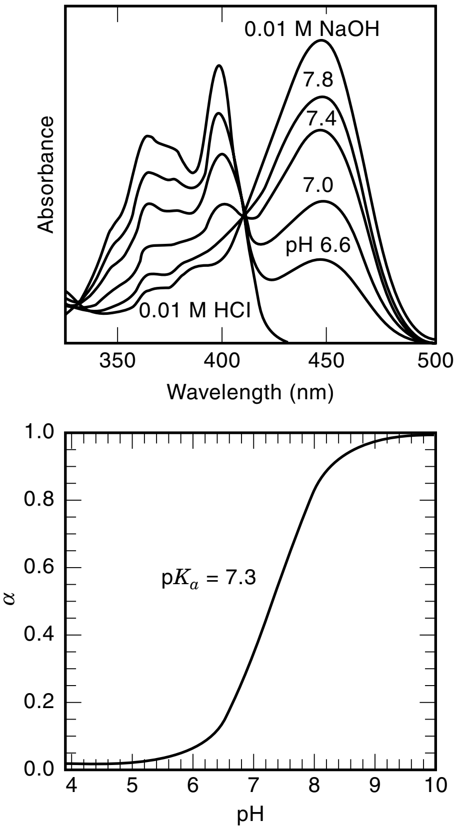

Figure 9. (a) The change in absorption spectra of HPTS (aqueous solution) at different pH values. (From R. P. Haugland, *Handbook of Fluorescent Probes and Research Chemicals,* 6th ed., Eugene, OR: Molecular Probes, 1996, p. 557, with permission.) (b) The absorption maxima at 450 nm can be plotted as a function of the pH to generate a calibration curve. The overlap of different curves at 405 nm is seen to be independent of the pH and defines a useful calibration wavelength.

As an example, consider the (aqueous solution phase) absorption spectra of the pH-sensitive dye 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS) which is shown in Fig. 9(a) as a function of different solution pH values. By tracking the absorbance at 450 nm, a calibration curve relating pH to absorbance can be easily developed, and this is demonstrated in Fig. 9(b). The absorbance values are conveniently normalized according to the relationship

$$\alpha = \frac{\text{Abs} - \text{Abs}_\text{prot}}{\text{Abs}_\text{unprot} - \text{Abs}_\text{prot}} = \frac{I^-}{I_\text{tot}} \tag{23}$$

where Abs is the experimentally measured absorbance at the appropriate wavelength. The subscripts refer to protonated and unprotonated species. An analytical expression can be derived from the definition of the acid dissociation equilibrium constant and a mass balance on the total indicator concentration, $\text{I}_\text{tot} = \text{HI} + \text{I}^-$:

$$(a_{\text{H}^+})K_\text{a}^{-1} = \frac{1-\alpha}{\alpha} \tag{24}$$

This equation can also be written as

$$-\text{pH} + \text{p}K_\text{a} = \log_{10}\frac{1-\alpha}{\alpha} \tag{25}$$

and emphasizes that when $\alpha = 0.5$, pH = pK_a. A membrane containing the HPTS dye at the face of an optical fiber could function in this way as a suitable pH optode. However, its high water solubility and “blue” (low visible wavelength) absorption spectra make it less desirable for such applications than other dyes that better match the light output available from cheap light-emitting diode (LED) sources and matching detectors. Fortunately, many other dyes are known with a wide range of pK_a values and absorption spectra. This allows for a broad range of optical as well as chemical characteristics to be designed into a pH sensor. The other feature in Fig. 9, which is seen for many indicators, is the so-called isosbestic point or pH-independent absorption wavelength at 405 nm. By ratioing measurements at 450 nm and 405 nm, a self-calibrating pH sensor can be designed that accounts for fluctuations in light source intensity as well as degradation or loss of the dye from the membrane phase.

Ion-Sensitive Optodes. The pH optode can also be adapted to the measurement of other cations and anions. The mechanism by which this takes place has been summarized for a wide variety of ion-exchange mechanisms (9). Briefly, if a membrane is designed that contains a pH indicator as well as an adsorption site for other ions (mediated by the incorporation of an ionophore into the membrane), the requirement for electroneutrality causes charged species to move in pairs. If a positively charged cation is adsorbed on the surface, for instance, a proton is exchanged in the opposite direction to preserve electroneutrality. For anionic sensors, a negatively charged anion brings with it the positively charged proton to the surface. In either case, the affinity sites for the ions act together with the absorption spectra of the particular pH indicator to generate a color change. Such optical ion sensors will suffer from selectivity problems, however, in much the same way as the corresponding ion-selective electrochemical electrodes. The selectivity of the pH-sensitive dye for hydrogen ions is usually absolute, but the ionophores chosen for other ions are more flexible in their capacity to bind different chemical species. It is also necessary to independently monitor or fix the pH of the solution to ensure that the measured spectral changes are associated with ions other than hydrogen.

The selectivity for the sensor can be evaluated from a consideration of the following mechanism, which is an expansion of the simpler acid-dissociation scheme written earlier (see pH Optodes):

$$\mathrm{I_f^-} + \mathrm{H^+} + \mathrm{S_f^+} + \mathrm{X}_i^- \leftrightarrow \mathrm{HI_f} + \mathrm{SX_f} \qquad (K_{\mathrm{X}_i})$$

The subscript f denotes film-associated components, and S refers to the ionophore. This equation is written for an anion exchanger with a stoichiometric binding ratio of 1 : 1. The indicator, $\mathrm{I_f}$, and the anionic binding site, $\mathrm{S_f}$, are both confined to the film while the hydrogen ion and target anion, X_i^-, can freely exchange with the bulk solution. A similar equation exists for each anion, X_i^-. In this equation, the exchange coefficient, K_{X_i}, plays the same role as the previously described acid dissociation constant to summarize the reaction equilibrium. We also consider only an anion with a single charge of valence $= -1$ for illustrative purposes. Using an electroneutrality balance together with mass balances on the indicator and ionophore, the relation equivalent to Eq. (24) is

$$(a_{\mathrm{X}^-})(a_{\mathrm{H}^+})K_{\mathrm{X}_i} = \frac{1-\alpha}{\alpha}\,\frac{\omega_i}{\alpha\beta} \tag{26}$$

where the a_i are the activities and β is the (molar) ratio of indicator to ionophore loaded into the membrane. The fraction of ionophore that is complexed with the target anion is ω_i and $\sum \omega_i = 1 - \alpha\beta$.

For a solution containing only an individual anion ($i = 1$), a calibration curve can be developed from these equations and, in particular, the exchange coefficient can be found. A single-ion response function is then defined by

$$a^0_{\mathrm{X}_1} = \frac{1}{K_{\mathrm{X}_1} a_{\mathrm{H}^+}}\,\frac{1-\alpha}{\alpha}\,\frac{1-\alpha\beta}{\alpha\beta} \equiv f_1(\alpha) \tag{27}$$

where the superscript on the anion activity is used to emphasize that the response function is measured in the absence of interferents. If the equations are now expanded to consider a solution of competing (interfering) anions with activities a_{X_j}, the result can be compactly expressed as

$$a_{\mathrm{X}_1} = f_1(\alpha) - \sum K_{1j} a_{\mathrm{X}_j} \tag{28}$$

The selectivity coefficient $K_{1j} = K_{\mathrm{X}_1}/K_{\mathrm{X}_j}$ is found from experiments with pure component data. This relation is the optical analogue to the Nikolskij–Eisenman equation, Eq. (16), introduced previously for ISEs. It summarizes how the presence of interferents will lead to an overprediction of the target ion concentration if the single-ion response function is blindly used. Similar equations can be developed for solutions of ions with mixed valences as well as for the analogous cation sensor (9).

Gas-Sensing Optodes. It is also apparent that pH optodes can be used for the measurement of gases such as CO_2 and NH_3 in a manner exactly analogous to that described for gas-sensing electrodes. Many patents have been issued, and several commercial designs of optical sensors have been put forward that detail exactly how the light from a fiber waveguide will pass through the measuring sample.

Evanescent Sensors. Light passing through an optical fiber can also interact with the surrounding medium at the core–cladding interface through the so-called evanescent field. This electromagnetic field extends from the interface into the medium surrounding the fiber (or any reflection surface) only a short distance—typically 0.1 μm. Nevertheless, this makes it possible to carry out optical measurements using a fiber in a “closed-loop” configuration. It also allows for the use of membranes that impart selective advantages toward different target analytes while at the same time function as an integral part of the optical waveguide. The light intensity penetrating into the evanescent field is much lower than the intensity found in the acceptance cone region. This is compensated for by using long pathlengths, which are introduced by exposing correspondingly long sections of the fiber to the analyte fluid.

In environmental sensing applications that deal with the measurement of volatile organic compounds in water, hy-

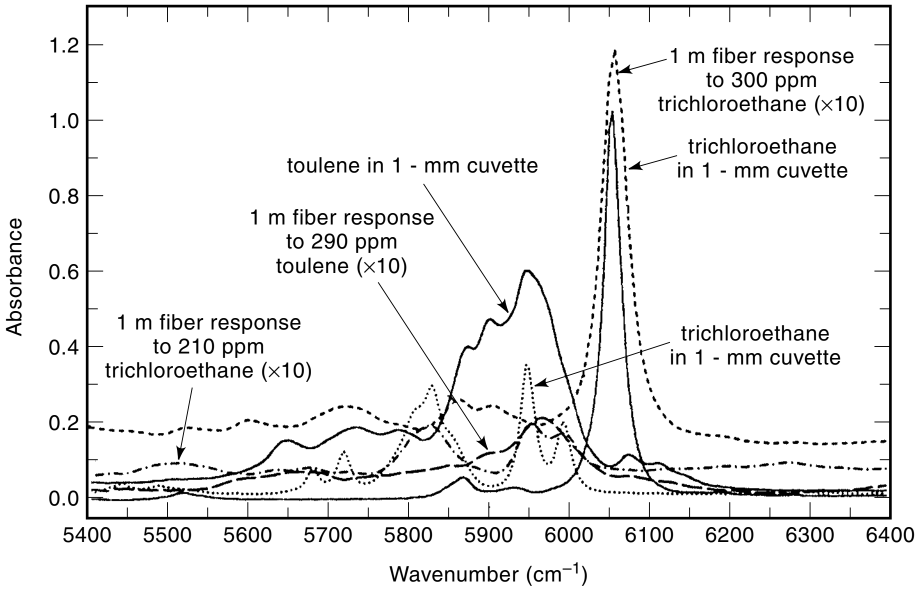

Figure 10. Equilibrium EFOCS responses at specified analyte concentration (magnified ×10) and transmission spectroscopy spectra of the pure components measured in a conventional instrument. (From Ref. 10, with permission. Copyright 1997 American Chemical Society.)

drophobic membranes can effectively separate and concentrate target analytes from the dilute aqueous background. In fact, the plastic-clad (silicon) silica fibers that are readily available from many commercial sources have been demonstrated to function quite well as "evanescent fiber-optic chemical sensors" (EFOCS) for the analysis of chlorinated hydrocarbons in water (10). Organic species absorbed into the silicon clad interact with the evanescent light field leading to wavelength-dependent light absorption that is characteristic of the composition of the surrounding solution. Figure 10 shows a comparison of the absorbance spectra measured with an EFOCS and with a conventional spectrometer for toluene, trichloroethylene, and trichloroethane. It is seen that long lengths of fiber are needed to generate even small absorbances (note also the 10× scale change) compared with conventional transmission spectroscopy. The spectra are plotted as a function of the wavenumber, ν, which is related to the wavelength, λ:

$$\nu\,(\mathrm{cm}^{-1}) = \frac{10^7}{\lambda\,(\mathrm{nm})} \tag{29}$$

Fluorescence Sensors. Absorption of light can also lead to reemission at lower energies (longer wavelengths). This can take place from an excited, singlet state to the ground level and leads to what is referred to as fluorescence. Applications of fluorescence to chemical sensing using optical waveguides are very similar in terms of the target compounds and mode of operation to those seen for absorbance sensors. One important additional feature, however, distinguishes this type of spectroscopy: The detection of emitted light often takes place against a zero (dark) background. As a result, fluorescence measurements are often done at a high signal-to-noise ratio. In combination with pulsed light sources and phase-resolved signal analysis, very accurate measurements can be taken of very small numbers of molecules. In this way, small changes can be monitored, and fluorescence assays are usually many orders of magnitude more sensitive than competing absorbance-based assays. The previously cited HPTS molecule, for example, emits light via fluorescence when excited at the absorbance wavelengths shown in Fig. 9. Such molecules are referred to as fluorophores and display a separate emission spectrum for each absorbance wavelength. The membrane-based design described earlier can now be used in a fluorescence-sensing mode by separating the incident excitation light from the emitted light using optical filters, gratings, and/or tunable light sources. In fact, by alternately exciting at 405 nm and at 450 nm, a ratioing scheme can also be devised for this type of fluorescent sensor that allows for internal calibration. Fluorescent optical sensors have found widespread application in many biosensing schemes where coupling of enzymatic reactions with fluoresence detection leads to extraordinary selectivity and sensitivity combinations.

Fluorescence quenching is another phenomenon that leads to reduction of the emitted light due to the presence of so-called quenching molecules. Optical sensors have also been designed around quenching effects, and oxygen, in particular, is a well-known quencher molecule. The relation between fluorescence intensity and oxygen concentration, for a constant excitation intensity, is often summarized by the Stern–Volmer equation:

$$\frac{F_0}{F} = 1 + K_{\mathrm{SV}}[\mathrm{O_2}] \tag{30}$$

This equation predicts a linear relation between the inverse of the fluorescence intensity, F, and the oxygen concentration, $[\mathrm{O_2}]$. Such quantitative behavior is often seen in practice, but sensors are also empirically adapted to a modified form of the Stern–Volmer equation in order to generate useful calibration functions. The temperature dependence of the Stern–Volmer constant, K_{SV}, is significant, and simultaneous temperature measurement or temperature control is often needed in interpreting results. This is true of any fluorescence-based chemical sensor, and the fluorescence is typically decreasing with increasing temperature. In contrast, the absorbance-based detection schemes are more immune to temperature fluctuations.

As with absorbance-based sensors, evanescent interactions can also be exploited and many of the designs proposed for fluorescence-based assays utilize fluorophores that are immobilized on a short segment of optical fiber at the core–clad interface. The fibers are often tapered to allow for better interaction of the fluorophore with the excitation light and better capture of the fluorescence emission. The thin interfaces that are used in evanescent detection can also lead to faster response times for the sensor compared with situations observed for thick clads.

Refractive-Index Sensors. Optical chemical sensors have been developed that are based on measurements related directly or indirectly to changes in the refractive index. The cladding can be used as a selective adsorbent (typically a polymer) which changes its bulk refractive index due to absorption of target molecules (11). Such a sensor functions as a refractometer, although absolute values of the refractive index are rarely obtained. Measurements of changes in the light intensity are related to the changes in the critical angle for total internal reflection described previously. Light can essentially "leak" from the fiber if the refractive index of the clad increases from its nominal level. The refractive index of the clad also affects the NA value of the fiber that can be observed in the exit light intensity measured for a fixed solid spherical angle. Such refractive index sensors, for example, have been introduced for monitoring aromatic hydrocarbons in groundwater.

Absolute refractive index changes can also be monitored through so-called surface plasmon resonance (SPR) effects. Surface plasmon resonance occurs when polarized light is reflected off a thin metal film covering a high refractive index material, such as glass, at particular incidence angle and wavelength combinations. Gold is often used to produce the thin film. The resonance effect is observed by rapid attenuation of the light intensity when either the angle or the wavelength of light is scanned across critical values. The critical values will change with the local refractive index at the interface; thus, molecules that adsorb to the gold surface and modulate the refractive index can be detected. A refractive index SPR sensor is most often fabricated on planar (flat) waveguides, but it has also been demonstrated on an optical fiber. Selectivity can be achieved by modification of the surface with specific affinity ligands for the target compound of interest. For example, in biosensing applications, antibodies have often been used for this purpose. One company, Biacore International AB (Uppsala, Sweden), markets instruments based on SPR technology for a variety of biosensor applications. Other designs have also been introduced (12) that utilize compact, integrated electrooptic features.

Sensor Arrays

Selectivity is one of the most important parameters in developing useful sensors (see Fig. 1). This is true for electrochemical as well as optical designs, and much effort has been devoted to fabrication and discovery of specialized surfaces. An alternative approach is to forgo absolute specificity and rely, instead, on simultaneous measurements over many incrementally selective surfaces. These sensor arrays can provide for versatile operation without highly specific interactions taking place. In the detection of volatile compounds and in odor-sensing applications, they are often referred to as "electronic noses." They have been used in analysis of food processing operations, perfumes and cosmetic production, environmental sensing and a variety of other application areas where odor is a recognizable quality indicator. Some companies that produce electronic noses commercially include Alpha M.O.S. America (Belle Mead, NJ), AromaScan (Hollis, NH), and Neotronics Scientific (Essex, UK).

Sensor arrays have been most often developed with conductimetric sensors such MOS and CP devices. They can also include chemical sensors based on surface acoustic wave (SAW) transduction schemes [see SURFACE ACOUSTIC WAVE DEVICES], and often a mixture of sensing elements is used to impart the greatest degree of flexibility. The interpretation of signals from such arrays requires extensive calibrations with pure components and/or known mixtures. The signal analysis often uses statistical methods, including principal component and partial least-squares analysis, or artificial neural networks to recover compositional information on unknown samples. Many times, it is sufficient to categorize the mixture in terms of "good" or "bad" or other loosely defined quality descriptors.

For example, a 14-element CP array has been developed that was shown to be capable of discriminating 8 different solvents (13). The CP array was fabricated from the conducting polymer poly(pyrrole), which was blended with 12 different plasticizers and two different combinations of oxidant. The polymers were dip-coated onto interdigitated electrodes, and resistance measurements were simultaneously performed on all elements of the array after exposing the array to an air–vapor gas phase of fixed composition. The data were analyzed for each array element by a simple binary criteria related to whether an individual sensor element was responding within a given range or not. The (saturated) pure components in air could be distinguished from each other and, with arrays of 19 elements, individual saturation levels as well as binary mixtures in air could also be quantified. The presentation of the data is often done with respect to the principal components, and in this case it was found that three components were sufficient in this particular experiment.

Arrayed sensors represent a rapidly emerging area of chemical sensor development. New coatings and structures as well as new methods for signal analysis greatly expand the role for chemical sensors into applications that were once deemed too complex. The ability to multiplex diverse sensors will continually expand their application to new areas of use. Together with miniaturization and efficient fabrication techniques, it is expected that chemical sensors will, in the near future, become pervasive in industry, medicine, the environment, and indeed everyday use.

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