

7.7 Chemical Sensors

Learning objectives

- To introduce the needs for, and basic principles of, chemical sensors
- To understand the principles of electrochemical and micro-electronic, optical, thermal, and mass-sensitive sensors
- To understand the performance of sensor arrays in compensating for the limited selectivity of sensors

7.7.1 Introduction

The development of chemical sensors is important with respect to several objectives. A first aim is the substitution of classical analytical methods by sensor measurements. A typical example here is the systematic replacement of flame photometers for determination of blood electrolytes, such as lithium, sodium, potassium, and calcium, by ion-selective electrodes.

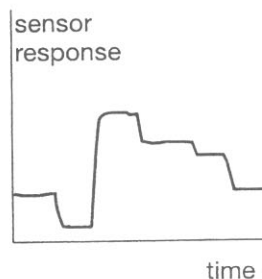
A second objective results from the increasing requirements for automation of industrial processes. Measurement of chemical parameters is needed for monitoring and controlling a process. Thus, in process analytical chemistry (Chap. 16) the methods for on-line analysis are based on the availability of chemical sensors. Special requirements in industry are robustness, long-term stability, or temperature insensitivity of the sensors. Additional needs arise in connection with biotechnological processes where multifunctional, biocompatible sensors are required.

Monitoring chemical quantities is also important in the environment, in industrial plants, in safety techniques and in medicine. Monitoring of pH and turbidity of water is a relatively easy task. pH can be measured by a glass electrode, and turbidity by means of an optical sensor. Conceivably, the pollution of water by heavy metals and organic compounds may be monitored continuously by sensors rather than by off-line methods in the laboratory. Chemical sensors will be needed not only for individual analytes but also for measurements of sum parameters.

The control of the emission of flue gases or the monitoring of air contaminants and emissions of SO_2 are important requirements in the *environmental field*. Gas sensors based on optical or microelectronic principles are already available. Continuous monitoring of contaminants in soils or solid waste is more difficult. For this purpose, sensors are needed that provide chemical information by remote measurements.

For monitoring of exposure to hazardous substances, inexpensive sensors are needed that can be mass-produced. This kind of sensor is expected to detect long-term exposition or maximum loads. In the mining industry, explosive or hazardous gases need to be determined, while for air-conditioning, the humidity and CO are important.

Another area is *in-situ* monitoring. For example, during a heart operation, the ratio of potassium to sodium needs to be measured since it is an important indicator for the patient's condition. The time-dependent monitoring of drugs, anesthetics, and metabolites in the body during the course of an operation is another active field of sensor application in medicine. There is a growing demand for sensors that can be used as noninvasive devices, e.g., for determination of glucose in blood by recording the NIR spectrum through the finger nail or skin.



7.7.2 Characteristics and basic principles

Chemical sensors are defined as follows:

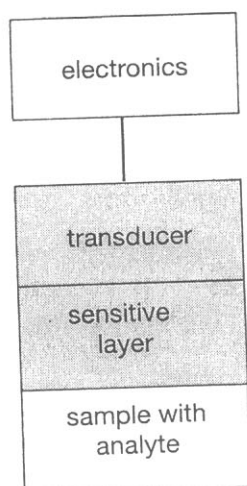
Chemical sensors are (small) devices capable of continuously recognizing concentrations of chemical constituents in liquids or gases and converting this information in real-time to an electrical or optical signal.

Table 7.7-1. Typical parameters for chemical sensors

Requirement
detection limit
working range
selectivity/specificity
drift
reproducibility
miniaturization
mechanical stability
response time
long-term stability
compatibility to pressure, temperature, explosiveness, radioactivity, biological conditions, sterilization

Table 7.7-2. Overview of sensing schemes and types of sensors

Sensing scheme	Sensor type
Conductivity change	Metal oxide semiconductors Organic semiconductors
Potential change	Ion-selective electrodes Solid-state gas sensors Field-effect transistors
Current change	Amperometric sensors (oxygen and enzyme electrodes, immunosensors, solid state gas probes)
Change of resonance frequency	Piezoelectric crystal resonators Surface acoustic wave sensors
Change of optical properties	Transmission/absorption, scatter, reflectance, fluorescence, refraction, decay time, polarization
Thermal effects	Thermal/calorimetric sensors Pellistors



Schematic sensor

In principle, a sensor consists of a chemically sensitive layer – the recognition system – a transducer for converting the chemical information into an electrical or optical signal, and data evaluation electronics, usually integrated into the sensor. As an example, for an ion-selective electrode (Sec. 7.3.1) the chemical-sensitive layer is a solid-state or liquid membrane and the transducer is based on the electrical potential, evaluated by means of a voltmeter.

The performance characteristics of a sensor are derived from general analytical criteria as well as from specific requirements, such as long-term stability. Table 7.7-1 lists typical parameters that characterize a sensor.

No universal basic principle exists for sensor development. Every practical task requires a specific adaption of the measuring principle, so that sensors are known which are based on electrical, optical, gravimetric, or thermal principles.

An overview of basic principles for developing chemical sensors is given in Table 7.7-2. Many of these principles are introduced elsewhere in this volume. This section concentrates on specific aspects of sensor construction, and new principles, such as microelectronic or fiber optical sensors are explained in more detail.

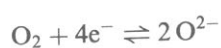
7.7.3 Electrochemical and microelectronic sensors

Potentiometric sensors

Sensors based on potentiometry are best represented by the pH glass electrode and ion-selective electrodes (ISEs) as discussed in Sec. 7.3.1. Potentiometric measurements can also be used to develop sensors for determination of gases, e.g., carbon monoxide or ammonia, and of organic compounds, such as urea.

Solid state gas sensors

Solids show conductivity at elevated temperatures due to the presence of ions. This effect can be used to construct a gas sensor. Solid state electrodes with oxide ion conductivity are especially important. These electrodes are redox electrodes. A typical material is ZrO_2 doped with CaO or Yb_2O_3 , giving a crystalline structure with cationic vacancies in the lattice which account for ion conductivity. Solid state electrolyte sensors based on ZrO_2 are suitable for determination of oxygen in combustion gases or for monitoring metallurgical processes, where oxygen is to be determined in molten iron at temperatures of about 1000°C . The redox equilibrium is:



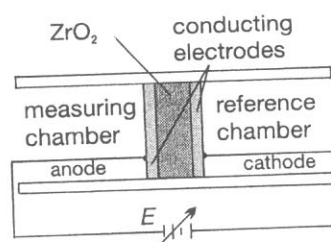
(7.7-1)

The O^{2-} ions tend to migrate into the vacancies causing the vacancy to be displaced. For measurements in molten iron, the solid state electrolyte is contacted by a platinum electrode and the resulting potential is measured with a second metal electrode in the molten iron. When measuring O_2 in gases, the solid state electrolyte is implanted in a porous platinum electrode and the electrode potential is measured relative to a reference signal. Usually, air is used as the reference medium.

According to the Nernst equation the relationship between the electrode potential E and the partial oxygen pressure in the reference $p_{\text{reference}}$ and sample chamber p_{sample} is:

$$E = \frac{RT}{4F} \ln \frac{p_{\text{reference}}}{p_{\text{sample}}} \quad (7.7-2)$$

The so-called λ -probe is commonly used for measuring automobile exhaust gases. This probe is based on the fact that for a value of $\lambda = 1$, at which the exact stoichiometric ratio of fuel to air is valid, a large jump in the oxygen partial pressure occurs. This change can be used to control the fuel to air mixture.



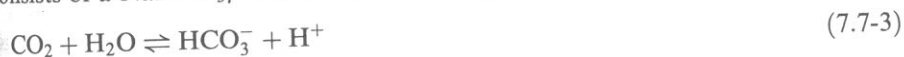
Solid state oxygen sensor for hot gases

Gas-permeable membrane sensors

Gas-sensitive potentiometric sensors incorporate an electrochemical cell with an ion-selective electrode and a reference electrode. Both are immersed in an internal electrolyte solution. The internal electrolyte is separated from the measuring solution by a gas permeable membrane (cf. Fig. 7.7-1). The microporous or homogeneous membrane is typically 0.1 mm thick. Microporous membranes are manufactured from hydrophobic polymers, e.g., polytetrafluoroethylene (PTFE) or polypropylene. Such membranes consist of 70% of pores with pore diameters of less than 1 μm , so that gases can permeate by effusion, while water or ions are rejected by the hydrophobic membrane.

Homogeneous membranes are prepared from silicon rubber. The gas dissolves in the membrane and diffuses through it. In order to warrant fast gas transfer, the membranes are often much thinner than porous membranes, i.e., about 0.02 mm thick.

Let us consider the mode of operation of a potentiometric gas sensor for CO_2 . The gas penetrates the membrane and dissolves in the internal electrolyte that consists of a $NaHCO_3/NaCl$ solution. Protolysis of CO_2 occurs according to:



A relatively high concentration of HCO_3^- ions in the internal solution guarantees a direct relationship between the CO_2 concentration in the external solution and the hydrogen ion activity in the internal solution. The conventional glass electrode is used as hydrogen ion-selective electrode and calibration is based on the Nernst equation. It is also possible to use pH measurements to determine other gases, such as SO_2 or NO_2 . The pertinent chemical reactions are given in Table 7.7-3.

For membrane electrodes interference is restricted to gases that react with the internal solution in a way similar to the analyte gases. This is observed, e.g., when determining NO_2 in the presence of CO_2 or SO_2 . In such cases, the pH glass electrode is replaced by an ion-selective electrode. For the determination of NO_2 ,

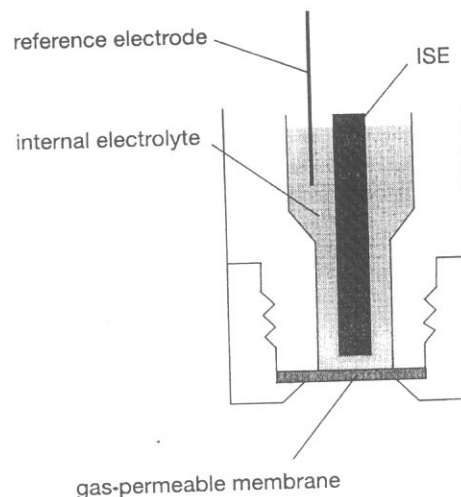


Fig. 7.7-1. Scheme of a gas-sensitive probe based on potentiometric measurements

Table 7.7-3. Types of commercial potentiometric gas sensors

Analyte	Reaction in the internal solution	Sensitive electrode
CO_2	$CO_2 + 2 H_2O \rightleftharpoons HCO_3^- + H_3O^+$	pH glass
NO_2	$2 NO_2 + 3 H_2O \rightleftharpoons NO_2^- + NO_3^- + 2 H_3O^+$	pH glass or NO_3^- ISE
SO_2	$SO_2 + 2 H_2O \rightleftharpoons HSO_3^- + H_3O^+$	pH glass
NH_3	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	pH glass
H_2S	$H_2S + 2 H_2O \rightleftharpoons S^{2-} + 2 H_3O^+$	Ag_2S ISE
HCN	$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$	Ag_2S ISE
HF	$HF + H_2O \rightleftharpoons F^- + H_3O^+$	LaF_3 ISE

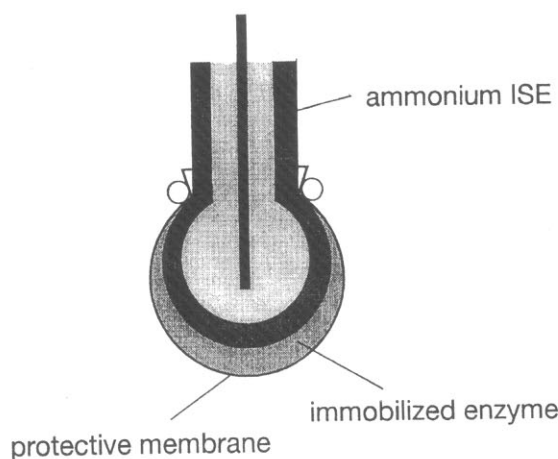


Fig. 7.7-2. A biocatalytic membrane sensor based on an ISE for ammonium ions and the enzyme urease

a nitrate ISE can be used, as can be understood from the reaction equation in Table 7.7-3. This Table gives some additional examples for using ISEs as sensitive electrode. The slow response times and low sensitivities of this kind of gas sensor are disadvantageous.

Biocatalytic membrane sensors

ISEs may be covered with an enzyme that catalyzes a biochemical reaction. For example, the enzyme urease catalyzes the hydrolysis of urea to give ammonia and carbon dioxide. The reaction products can be monitored by means of the above gas-sensitive ISEs. The combination of appropriate enzymes with electrodes allows, numerous organic species to be detected. These represent one possibility for the construction of *biosensors* (cf. Sec. 7.8). The application of enzymes as biocatalysts leads to reactions that occur under mild conditions of pH and temperature, that are selective, and consume minimal amounts of substrate.

In order to minimize the consumption of the relatively expensive enzymes, devices are preferred where the enzyme can be immobilized. Immobilization is performed either directly on the surface of the electrode, or the enzyme is immobilized in a solid state reactor and the sample is passed through the reactor and the products are detected at its end.

An example of a substrate-specific membrane electrode is the determination of urea by means of an ammonium-sensitive glass electrode as the ISE. The enzymatic reaction is based on the hydrolysis of urea in the presence of the enzyme urease:



Urease is immobilized in a polyacrylamide layer mounted on the surface of the NH_4^+ glass electrode as the ISE. Figure 7.7-2 shows a schematic arrangement of this biosensor. Problems with this device may arise from the limited selectivity of this type of ammonium ISE. In most biological matrices, interferences occur with respect to sodium and potassium ions. As an alternative the detection may be replaced by a gas-sensitive ammonia electrode (Table 7.7-3). In this case, however, the sensitivity is restricted because the pH value necessary for the detection and the enzymatic reaction are different. Maximum sensitivity for the gas-sensitive ammonia sensor is obtained at pH between 8 and 9, where most of the NH_4^+ is converted to ammonia. The enzyme reaction, however, is optimal at about pH 7.

Commercial systems for routine analysis of urea work on the basis of a bead reactor with the immobilized enzyme. The sample solution passes through the reactor. After alkalization of the solution, the ammonia is detected by a gas-sensitive ammonia ISE.

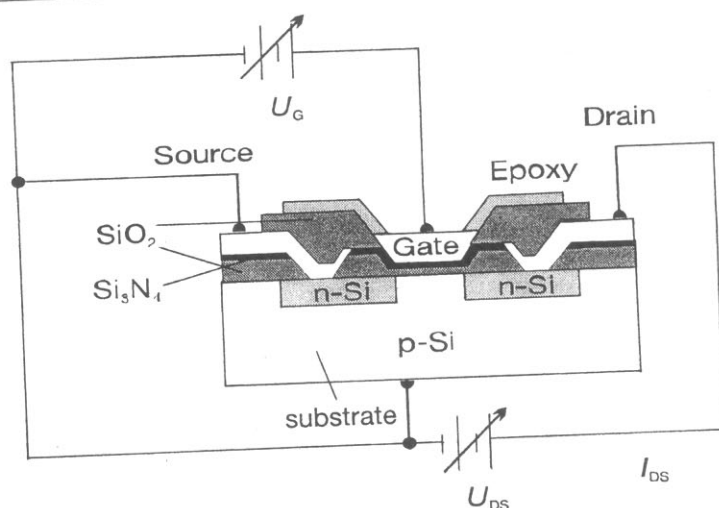


Fig. 7.7-3. Schematic of a metal oxide field-effect transistor (MOSFET)

Field-effect transistors

The potentiometric sensors considered up to now consist in general of a sensitive membrane connected to the measuring instrument by a solid contact or an ion-conducting salt bridge. Electrical amplification and digitization occur separately in the voltage recording device.

Microelectronic integration of the sensor and signal processing is possible, if the potentiometric sensor is based on a *field-effect transistor*. This chip may be chemically sensitive (CHEMFET) or specifically ion selective (ISFET). Bergveld developed FET sensors on the basis of metal oxide silicon field effect transistors (MOSFET).

The structure of such a transistor is shown in Fig. 7.7-3. The transistor consists of a substrate of p-type Si, with two n-type Si-enriched regions formed on its surface. The n-type Si region electrodes, source and drain, are connected to the surroundings via metal contacts such as vapor-deposited aluminum electrodes. By means of an insulator, SiO_2 , the Si regions are almost completely covered so that connection feasible only through the drain and source electrodes. The silicon nitride layer, Si_3N_4 , can be recognized as an additional passivation layer (Fig. 7.7-3).

If a voltage U_{DS} is applied between the source and drain, no current flows along the connection channel since the pn-diode channel is shut, either between the source electrode and the substrate or between the drain electrode and the substrate. In the chip, however, there is a further contact, consisting of a metal oxide layer (the "gate"). This layer is electrically separated from the substrate by the SiO_2 insulator.

If an additional voltage U_G is applied between gate and substrate an electric field is produced in the n-channel between the n-Si regions, so that a current I_{DS} flows between drain and source. The size of the current is determined by the voltage. Of course, a minimum voltage is necessary to produce a current. Because of the high resistance between gate and substrate, the input current becomes negligible. The high resistances of field-effect transistors make them very suitable as inputs for pH or ion meters and for signal amplification in conventional voltmeters. The influence of the drain source voltage is due to changes in the electrical characteristic of the transistor (Fig. 7.7-5).

For construction of an ion-selective FET, the original gate has to be removed or replaced by another material. If removed, the lower Si_3N_4 -layer acts as conductive layer. If replaced by a new ion-selective layer, e.g., a membrane of a suitable ionophore (Fig. 7.7-4) it acts as an ISE. Electrical contact is obtained by a reference electrode, as commonly used for potentiometric measurements. The potentials resulting from the applied gate voltage U_G and from the ion-selective layer, add together, and the measured current I_{DS} depends on the activity of the potential-forming ions. As a result, the electrical characteristic of the FET changes. In the optimum case, the change of the characteristic is 59 mV for a one-electron step for concentration changes of one order of magnitude (Fig. 7.7-5).

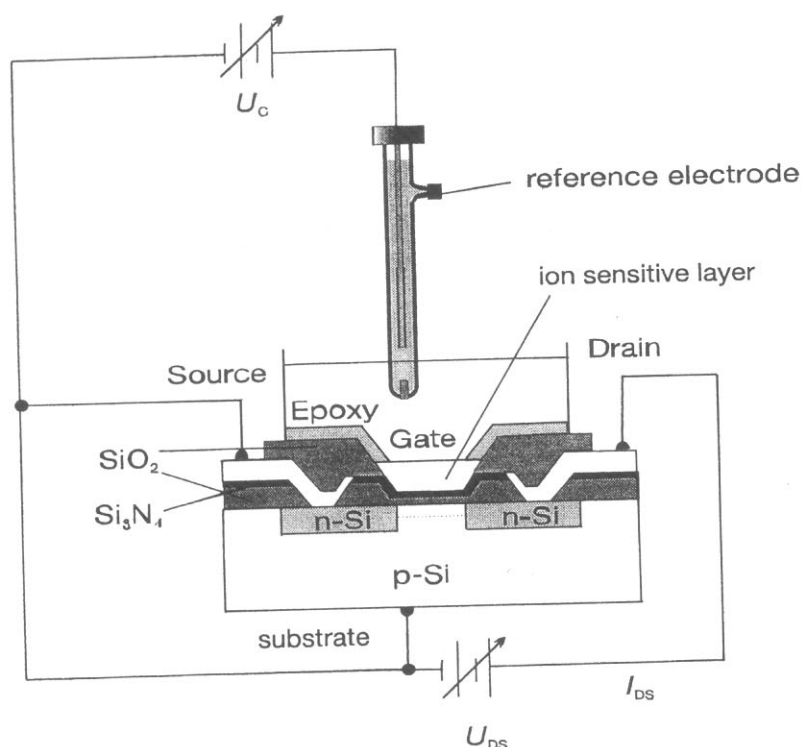


Fig. 7.7-4. Sensor based on an ion selective field-effect transistor (ISFET)

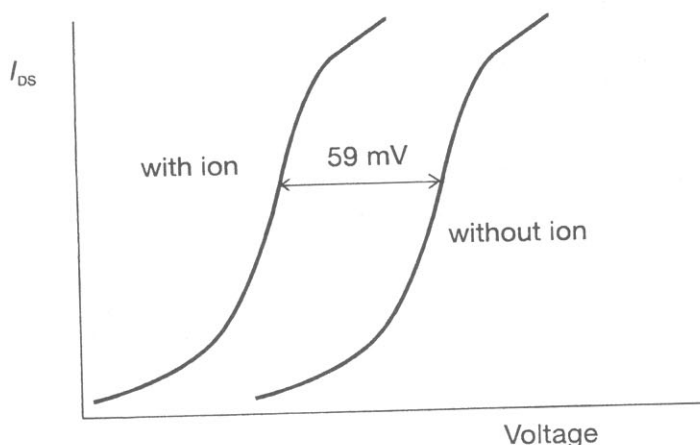


Fig. 7.7-5. Electrical characteristics of an ISFET: the drain current I_{DS} depends on the sum of the applied gate voltage U_G and the potential of the ion-sensitive layer

For practical measurements with an ISFET, the drain source current is kept at a constant working level. The change of the gate voltage with ion concentrations is compensated by an additional control voltage. This feedback voltage is proportional to the activity of dissolved ions as for the case of conventional measurements according to the Nernst equation. The first application of an ISFET was for pH measurement, and the best Nernstian response is obtained if the gate is made of Ta_2O_5 .

Further applications of FETs for the determination of other ions, but also of gases, enzymes, and antibodies, are given in Table 7.7-4. In principle, all layers applied to ISEs can also be transferred to microelectronic sensor devices.

The performance of an enzyme-coated macrosensor is discussed in detail in Section 7.8.3. Immunosensors, in turn rely on the basic principles of radioimmunoassay (Sec. 7.8.3).

The many methodological variations for developing sensors based on micro-lithographics are hindered by severe problems. In microelectronic circuits, the sites used for chemical sensing are usually hermetically sealed in metal cans or encapsulated in plastic or ceramic blocks. This is because of the high sensitivity of these devices to changes in the ambient environment, such as alterations in humidity, irradiation, or temperature. These interactions are based on forces that can usually be neglected in the macro range, e.g., surface tension, diffusion effects, van der

Table 7.7-4. Chemically selective field-effect transistors

Type	Gate	Analyte
Gas-sensitive FET (GASFET)	Pd	H ₂ , NH ₃ , CO
Ion-sensitive FET (ISFET)	Ion-selective layers: Ta ₂ O ₅ , Al ₂ O ₃ , BN Gas-permeable membrane + Al ₂ O ₃ Valinomycin	H ⁺ NH ₃ , CO ₂ K ⁺
Enzyme-coated FET (ENFET)	Gel- or polymer layer with immobilized enzyme	Urea, glucose, penicillin, H ₂ , acetylcholine
Immuno FET (IMFET)	Antigen or antibody	Albumin

Table 7.7-5. Examples of amperometric gas sensors

Analyte	Reaction	Working electrode
CO	$\text{CO} + 3 \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2 \text{H}_3\text{O}^+ + 2\text{e}^-$	Pt
NO ₂	$\text{NO}_2 + 3 \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + 2 \text{H}_3\text{O}^+ + \text{e}^-$	Au
SO ₂	$\text{SO}_2 + 6 \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 4 \text{H}_3\text{O}^+ + 2\text{e}^-$	Au
Cl ₂	$\text{Cl} + 2\text{e}^- \rightleftharpoons 2 \text{Cl}^-$	Pt
H ₂ S	$\text{H}_2\text{S} + 2 \text{Ag} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Ag}_2\text{S} + 2 \text{H}_3\text{O}^+ + 2\text{e}^-$	Ag
HCN	$\text{Ag} + \text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{AgCN} + \text{H}_3\text{O}^+ + \text{e}^-$	Ag

Waals forces, or quantum tunneling effects. In the field of microelectronic chemical sensors, these interactions become very important.

Amperometric sensors

The use of voltammetric measurements as a sensor principle is well known for the amperometric Clark sensor for oxygen measurements (Sec. 7.3). The working electrode of the Clark sensor is a platinum electrode linked to a silver anode. The sensor can be modified to circumvent the need for regeneration of the silver electrode. For example, silver can be used in the working electrode and lead in the auxiliary electrode. Potassium hydroxide serves as the electrolyte. In contrast to the reduction of oxygen at the silver working electrode, oxidation of lead represents the electron-generating anodic reaction:



Since lead hydroxide is soluble, there is no increase in the resistance which is in contrast to the Clark electrode, where silver hydroxide precipitates at the silver anode.

Amperometric sensors for other gases are also known (Table 7.7-5). Sensors without a membrane are used for monitoring chloride in drinking water. Sensors for carbon monoxide are common in the coal mining industry. This kind of semi-quantitative sensor responds rapidly in emergencies, but cannot compare – in terms of resolution of the signal – to membrane sensors, such as the Clark electrode.

A combination of the Clark sensor with an enzyme layer is discussed in Section 7.8.3 for the determination of glucose by glucose oxidase. This scheme can be transferred to other oxidative enzymatic reactions, e.g., for the determination of galactose based on galactose oxidase, or of uric acid by means of uricase.

Conductivity sensors

Electrical conductivity is another principle that can be used for gas sensing purposes. The respective sensors consist of metal oxides, such as SnO₂, ZnO, TiO₂ or Fe₂O₃ with *n*-type conductivity. The scheme of a SnO₂ thin-layer sensor is shown

Combination of semiconducting sensors in an array is sometimes called an *electronic nose*. Based on pattern recognition methods, the responses can be used to analyze an unknown gas, both qualitatively and quantitatively.

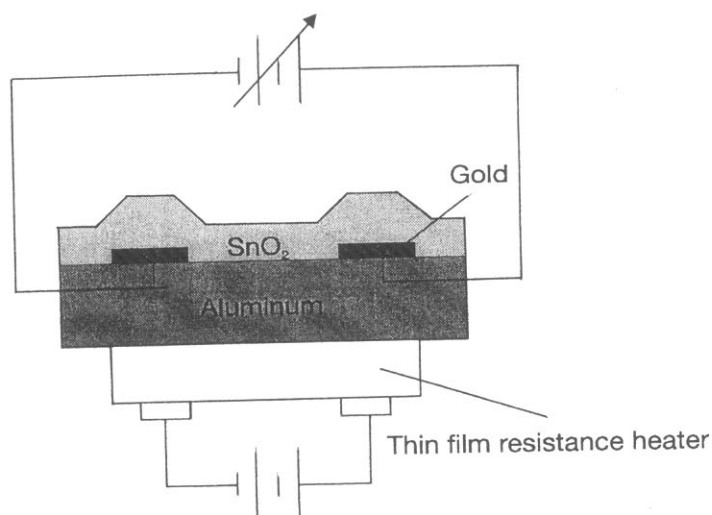
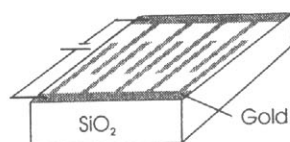
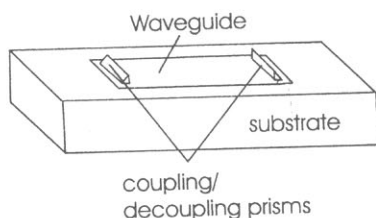


Fig. 7.7-6. Gas sensor based on an aluminum substrate covered with a semiconductor



Interdigitized electrodes



Planar waveguide

in Fig. 7.7-6. Oxygen is adsorbed at the heated surface of this sensor and reacts with reducing gases as the analytes. As a result, the conduction characteristics of the device are changed and can be measured as a nonspecific signal.

The simple structure of conductivity sensors has led to a broad range of industrial and domestic applications for detection of H_2 , PH_3 , NH_3 , SO_2 , CO , CH_4 , O_2 , and other gases.

Conductivity is also exploited in so-called *chemiresistors*. This kind of sensor is constructed from a thin film of an organic semiconductor laid down over interdigitized electrodes. Typical film materials are phthalocyanines, which have a chemical structure similar to hemin and chlorophyll. Depending on the central atom of the complexing agent, sensors for CO (Zn-phthalocyanine) or NO_2 (Pb-phthalocyanine) can be prepared.

7.7.4 Optical sensors

The development of optical sensors became feasible with the availability of optical fibers in the visible range. Recent developments are concerned with the extension of the visible spectral range to include fiber-optic sensors in the UV, near- and mid-IR range. Apart from fiber-optical sensors, there is also an interest in sensors based on planar optics.

In general, fiber optical sensors generate an optical signal in proportion to the analyte concentration.

Measuring inherent optical properties

The simplest type of optical fiber sensor involves coupling an optical fiber to a spectrophotometer. With this device, the color or fluorescence of solutions or of biological matter can be measured. In order to illustrate the applicability of fiber-optical sensors some fundamentals of *waveguides* are considered.

Fiber cables consist of a core (the waveguide) and a cladding both made from glass, quartz, or plastic. The cable diameters range from $0.05\ \mu m$ to $0.6\ cm$. The light propagates down a single fiber or a fiber bundle. The bundles can be arranged randomly or in a fixed position at the input and output of the fiber. In the latter case, a whole picture can be transmitted by the fiber cable. These fibers are important in medical diagnosis (endoscopy) for inspecting organs, such as the stomach.

Guiding light through an optical fiber is demonstrated in Fig. 7.7-7. When light reaches the waveguide, part of it is transmitted and part is totally reflected. For the total reflection of light to occur, a critical angle θ is necessary, and the refractive index of the core n_1 has to be higher than the refractive index of the cladding

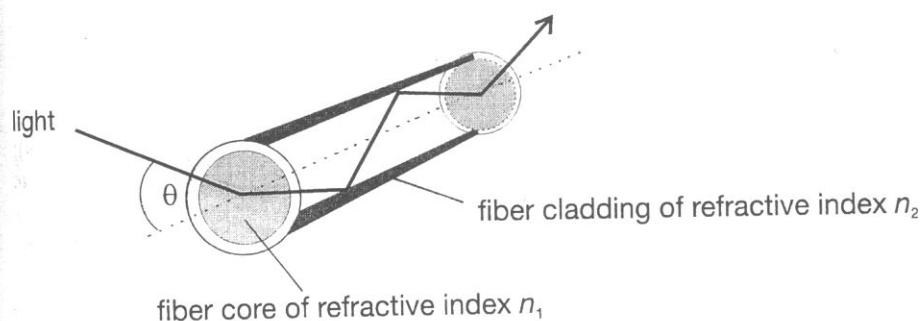


Fig. 7.7-7. Reflection of light in an optical fiber

n_2 . The refractive index of a glass core is ~ 1.6 and that of glass cladding ~ 1.5 . For measurements in the mid-IR range other materials are necessary, such as chalcogenide glasses (AsSeTe) or polycrystalline silver halide fibers, that are transparent between 2 and 20 μm . The refractive index of a silver halide fiber consisting of 75% AgBr and 25% AgCl is 2.21. This core material is cladded by a plastic cover of refractive index 1.5.

The critical angle θ is determined by the *numerical aperture (NA)* of the waveguide. NA depends on the refractive index of the core n_1 and of the cladding n_2 :

$$NA = \sin \theta = \sqrt{n_1^2 - n_2^2} \quad (7.7-6)$$

The larger the numerical aperture, the more light the waveguide can capture and transmit.

Commonly, *multimode waveguides* are used. In these fibers the light propagates in many modes down the waveguide. Attenuation of light does not occur in the same proportion for the different modes. The refractive index is uniform and changes abruptly at the cladding interface. *Monomode waveguides* possess a very small core diameter, typically 2–10 μm , so that the light propagates almost linearly down the fiber. The thickness of the optical cladding should be at least ten times that of the core. The coupling of light into a monomode fiber is difficult, since a narrow angle of incidence has to be achieved. Therefore, highly focused light sources, such as lasers or laser diodes are needed.

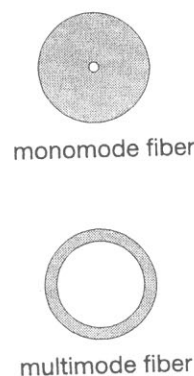
Waveguides are coupled to a spectrophotometer as bifurcated fibers (*Y-cables*). Figure 7.7-8 shows a typical arrangement of a plain fiber “sensor” for measuring the absorption in liquid samples. Light propagates down the fiber into the sample solution and is redirected at a reflector into a second fiber to the spectrophotometer. The path-length of the light is twice the distance between the end of the fiber and the reflector.

The waveguide merely serves to transfer the radiation. Instead of a photometer the fibers may be linked by means of an *optoelectronic circuit*; in this case, the light source is a light emitting diode (LED) and the detector a photodiode.

Applications of plain optic fiber sensors are given in Table 7.7-6. Whereas a photometric titration based on an optoelectronic sensor is easily achieved, monitoring of chemical processes or ground-water is much more complicated. For example, the direct detection of *organic compounds* in ground-water is feasible by fluorescence measurements. Although individual chemicals cannot be determined, the quality of water can be monitored by a combination of fiber optics, laser enhancement, and quantitative Raman spectroscopy. With such a system, contaminants in the ppb-range can be monitored at distances up to 1000 m, assuming that at least some of the contaminants are fluorescent.

Table 7.7-6. Applications of plain fiber optic sensors

Analyte	Measured optical property	Application range
Copper ions	Absorption at 930 nm	Copper electroplating
Organic compounds	Fluorescence	Ground-water monitoring
Hemoglobin	Diffuse reflectance at 600–750 nm	Blood oximetry
Halothane	Absorption in the NIR	Anesthetics



multimode fiber

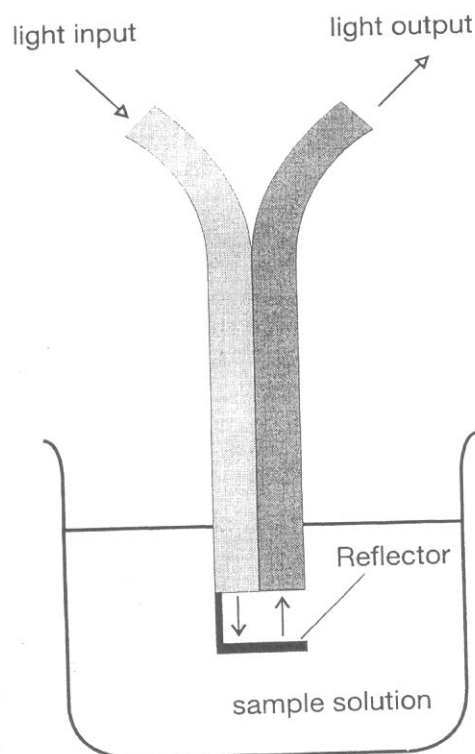


Fig. 7.7-8. Fiber optic sensor for measuring light absorption in a sample solution. The fiber cables consist either of single fibers or of fiber bundles

Immobilization can be mechanical, electrostatic, or covalent.

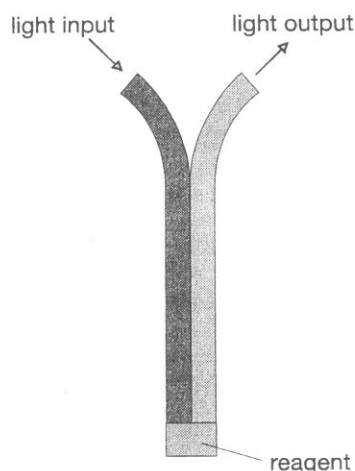


Fig. 7.7-9. Optical sensor using an immobilized reagent

Sensors with recognition systems

Measuring analyte concentrations in samples for which no inherent optical properties can be used requires a recognition system with a measurable color change. For this purpose, an indicator is frequently bound directly to the fiber (Fig. 7.7-9); common immobilization techniques are based on adsorption on (ion) exchange resins, inclusion into polymers, or by covalent immobilization.

Such sensors, also called *optrodes* or *optodes*, have been developed for measuring pH, oxygen, CO₂, NH₃, heavy metal ions, and several other species. The respective indicator is immobilized at the fiber tip and its color change is measured.

In order to obtain a reversible sensor, the chemical equilibria between the immobilized reagent and the analyte in solution (or in the gas phase) have to be taken into account. Consider the simplest case of a reaction of analyte A with the immobilized reagent \bar{R} :



(To distinguish species in solution, such as A, from those at the resin the bar is used for characterizing immobilized species.)

For equilibrium formation between the complex at the fiber, \bar{AR} , and the immobilized reagent \bar{R} it is valid:

$$K = \frac{[\bar{AR}]}{[A][\bar{R}]} \quad (7.7-8)$$

In the case of measurement of the optical properties of \bar{AR} we obtain for the signal to concentration relationship:

$$[\bar{AR}] = K[A][\bar{R}] \quad (7.7-9)$$

Under the assumption that the equilibrium concentration of A is almost identical to the total concentration of the analyte in solution, $[A] = c_A$ and that the concentration of the immobilized reagent equals the difference between the total reagent concentration c_R and the product concentration, i.e., $\bar{R} = c_R - \bar{AR}$, Eq. (7.7-9) can be rewritten in terms of the constant quantities K and c_R as follows:

$$[\bar{AR}] = \frac{Kc_Ac_R}{1 + Kc_A} \quad (7.7-10)$$

Figure 7.7-10 shows a typical dependence of complex concentration in the immobilized layer on analyte concentration.

The calibration curves are linear only at low analyte concentrations, i.e., for $Kc_A \ll 1$ or $c_A \ll 1/K$. At high analyte concentrations, the curve approaches a limiting value because of saturation of the reagent by the analyte.

The nonlinearity of the calibration curves is not a significant problem if a microprocessor is used for data evaluation. The decrease in sensitivity with increasing concentration remains a disadvantage. Often, however, the sensors are needed only for narrow concentration ranges where linearity can be achieved.

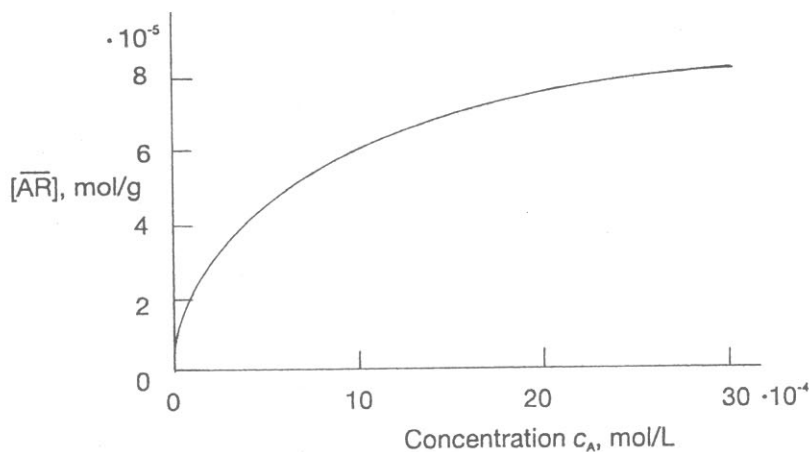


Fig. 7.7-10. Relationship between concentration of complexed reagent $[\bar{AR}]$ and analyte concentration c_A . The optical signal is usually directly related to $[\bar{AR}]$. Equilibrium constant $K = 1660 \text{ L/mol}$, $\bar{R} = 10^{-4} \text{ mol/g}$

Table 7.7-7. Chemical immobilization techniques for optical sensors and methods for surface modification

Polymer	Reactive group	Modified by reaction with	Partner
Cellulose	Aminoethyl Carboxyethyl	Bromocyan, ethylenediamine Chloroacetic acid	Carboxylate, sulfonic acids Amines
Glass, silica gel	Aminopropyl Vinyl	γ -aminopropyl-triethoxysilane Triacetoxysilane	Carboxylic acids, aldehyde Nucleophiles
Polyacrylamide	Carboxyethyl	Strong alkalis and acids	Amines, proteins

Table 7.7-8. Fiber optic sensors with immobilized reagents (optodes)

Analyte	Reagent/immobilization	Measuring principle
pH (2–5)	Congo red/cellulose acetate	Reflectance
pH (4–7)	Fluoresceinamine/glass	Fluorescence
Al ³⁺	Morin/cellulose	Fluorescence
K ⁺	Valinomycin + MEDPIN/PVC	Reflectance
Cl [−]	Fluorescein/silver colloid	Fluorescence
Humidity	CoCl ₂ /Co(H ₂ O) _n Cl ₂ /gelatine	Reflectance
O ₂	Ru-trisbipyridyl/silicone	Phosphorescence
NH ₃	Bromothymol blue (silicone)	Evanescent waves
Albumin	Bromocresol green/cellophane	Reflectance

Selection of the indicator reagent must take into consideration that reagents are to be applied which form less stable complexes. This guarantees that the reagent concentration can be adjusted to the range of analytical interest. This is in contrast to classical analytical applications of equilibrium reactions, where high equilibrium constants and reagent excess are the rule.

Chemical immobilization is based on covalent binding of the indicator to the fiber matrix. This kind of immobilization provides a rather strong coupling of the indicator and minimizes *leaching*. A prerequisite for chemical immobilization is the availability of reactive groups at the indicator or the support matrix. As a rule, these groups are generated by preliminary activation steps at the matrix. The most frequently used support materials are cellulose, dextrane, or agarose. In addition, artificial polymers are used, e.g., polyacrylamide. Examples of chemical immobilization techniques are given in Table 7.7-7. The techniques can be taken over from the research experience in polymer and surface chemistry as well as from modification of stationary phases in chromatography.

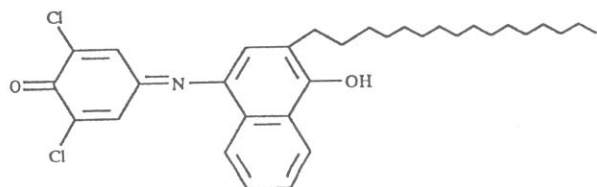
Fiber-optic sensors are not restricted to the determination of pH. Optodes have been developed for cations, anions, gases, organic compounds, and for measuring ionic strength (Table 7.7-8). Absorption and reflectance based sensors are less common than fluorescence sensors because of the higher sensitivity of the latter.

Transfer of the ion-selective electrode principle to optical sensors has led to the development of *ion-selective optodes*. One possibility consists in the application of ion exchange equilibria between the solution and the PVC membrane of the optode. Determination of potassium ions is feasible on the basis of the equilibrium:



where \overline{HC}^+ , \bar{C} are the protonated and deprotonated form, respectively, of the chromophore immobilized in PVC, and \bar{I} and \overline{KI}^+ , respectively, are the ionophore and its complex with potassium ions in PVC. The equilibrium is driven by the electroneutrality condition.

A versatile ionophore is valinomycin, familiar from ion-selective electrode applications. The chromophore is a hydrophobic compound, e.g., MEDPIN (Miles (Bayer)):



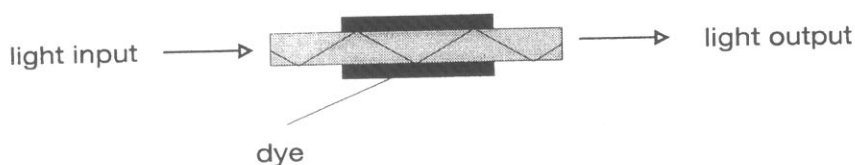


Fig. 7.7-11. Optical sensor for measurement of evanescent waves

The advantage of ion-selective optodes is their large working range, similar to that of ISEs. In addition, the many ionophores developed for ISEs can also be used in optodes.

Optodes based on evanescent waves

The measurement of *evanescent waves* is feasible if the indicator is immobilized on the core of a waveguide (Fig. 7.7-8). For determination of ammonia, a solution of bromothymol blue in silicone is deposited on the waveguide (Fig. 7.7-11). At each internal reflection in the waveguide, a fraction of the beam extends into the coating and interacts with the indicator. The same phenomenon is known in IR spectroscopy as the ATR technique (Sec. 9.2).

In the determination of ammonia the evanescent wave is affected by the actual color of the dye in proportion to the ammonia concentration. The differences can be quantified, e.g., by measuring absorbance.

Table 7.7-8 gives some further examples for developing fiber-optical sensors.

Advantages of optical sensors over electrochemical sensors are the following:

- All the spectroscopic information is available. If necessary, this information can be monitored at several measuring sites (multiplex advantage).
- There is no electrical interference, so that measurements are possible in high electric fields, e.g., during electrolysis or in transformers.
- No reference electrode is necessary.
- The reagent phase can be made low-cost, so that one-way sensors can be designed.

Disadvantages of optical sensors are:

- Ambient light influences the measurements. This interference has to be reduced, e.g., by pulsing the light source.
- The reversibility of optodes in liquid samples is often poor and repeated regeneration of the sensor becomes obligatory.
- The long-term stability is frequently limited, owing to leaching of the indicator.
- The establishment of an equilibrium between the analyte in solution and the immobilized reagent (Eq. 7.7-10) results in relatively narrow working ranges, apart from ion-selective optodes with a logarithmic signal-concentration relationship.

7.7.5 Thermal sensors

The measurement of reaction enthalpy is utilized in gas sensors based on a catalytic reaction (*pellistors*). Such catalytic sensors consist of a heating wire embedded in a sinter pearl and a catalytically active layer doped with Pt or Pd metal (Fig. 7.7-12). The wire coil is heated to about 550 °C. Reducing gases, such as CO or CH₄, are oxidized by adsorbed oxygen, and the heat of reaction can be measured by the increasing resistance of the coil. The oxidation rate at the surface of the sensor is proportional to the concentration of the analyte gas. The precision of this unspecific resistance measurement can be enhanced by reference measurements with respect to an inactive sinter pearl.

Calorimetric sensors are based on miniaturized calorimeters and are applied to solutions (cf. Sec. 7.5). In the simplest case the sample passes through a reactor at

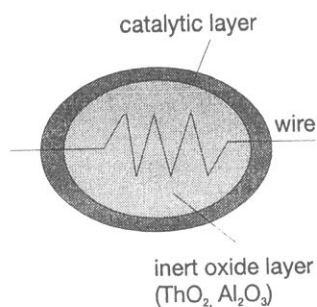


Fig. 7.7-12. Pellistor consisting of a catalytically active Pt or Pd layer and an inactive sinter pearl made of an oxide

the end of which the heat of reaction is measured by a thermistor. For determination of substrates (cf. Sec. 7.8) an enzyme is immobilized in the reactor. Such devices are not sensors in the strict sense of our definition since monitoring is discontinuous. Conventionally they are termed sensors. The detection of reaction heat becomes practicable by utilizing a particular enzyme reaction. Determination of urea, penicillin, glucose, sucrose, cholesterol, or lactate is feasible.

7.7.6 Mass-sensitive sensors

The change of mass and the subsequent change in resonance frequency in the presence of an analyte gas is used in mechano-acoustic sensors. The most important are the piezoelectric quartz crystal resonator and surface acoustic wave (SAW) sensors.

The principle of a quartz crystal resonator is explained in Fig. 7.7-13. A quartz crystal resonator that has been freed from its encapsulation is covered by an organic, gas-absorbing layer. The quartz is arranged as a frequency-determining element in an oscillator circuit. By deposition of gas onto the planar crystal surface the mass is changed. As a result the resonant frequency changes as well. Operation is performed in the thickness shear mode. In this mode the surfaces of the crystal are moved against each other. The following relationship holds between mass change Δm and the change in frequency Δf :

$$\Delta f = -2.3 \times 10^6 f_0^2 \left(\frac{\Delta m}{A} \right) \quad (7.7-12)$$

where A is the quartz surface area, and f_0 is the resonant frequency of the uncovered quartz.

Frequencies of 10–15 MHz can be resolved with resolution of up to 0.01 Hz. Thus masses as low as 10 pg can be determined. Different coatings are used as absorbing layers. For example, organophosphorous compounds can be determined by means of a copper diamine substrate linked to a polymer resin. With this material, a reversible sensor is formed that responds to diisopropyl methylphosphonate at 20 ppb concentrations. Mass-sensitive sensors are also used for monitoring gas pollution or for determination of dust in air.

More sensitive devices can be obtained by surface acoustic wave (SAW) sensors. This is because of the higher frequencies involved. According to Eq. 7.7-12, resonant frequencies f_0 up to 1 GHz are common, yielding detectable masses down to the femtogram level. The operation of an SAW sensor is explained in Fig. 7.7-14.

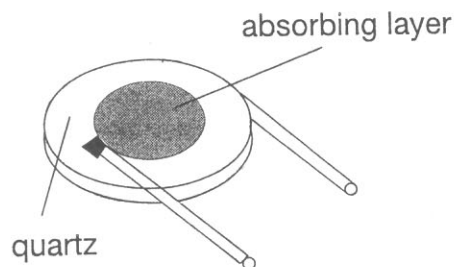
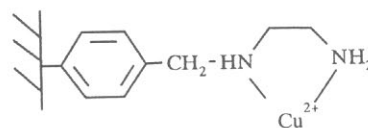


Fig. 7.7-13. Piezoelectric crystal resonator sensor

The piezoelectric quartz crystal resonator is also termed a *quartz microbalance*.



thickness shear mode



The piezoelectric quartz crystal resonator generates *bulk acoustic waves* in contrast to *surface acoustic waves* observed with an SAW device.

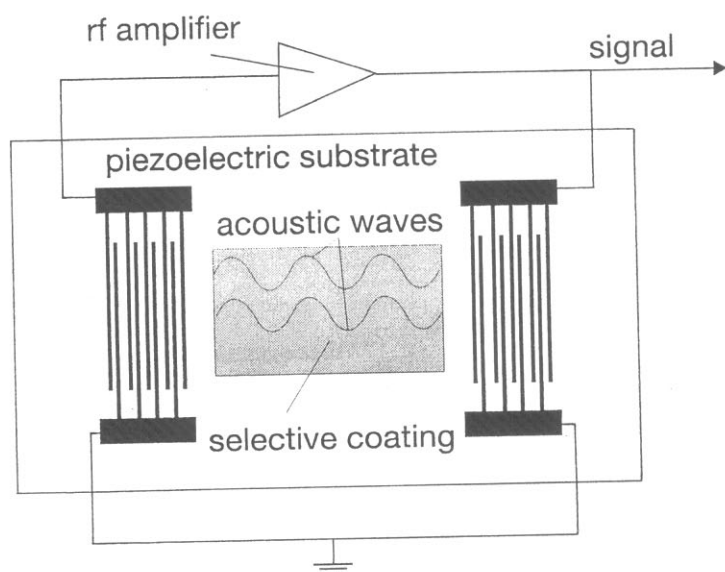


Fig. 7.7-14. Surface acoustic wave (SAW) gas sensor, e.g., for determination of styrene vapor at 5 ppm with $\text{PtCl}_2(\text{ethylene})(\text{pyridine})$ as the selective coating

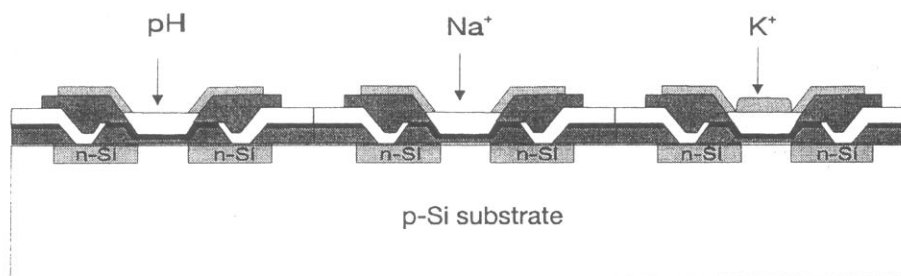
On the surface of a piezoelectric substrate a set of interdigitized electrodes is laid down by integrated circuit technology. After applying an rf signal to this transmitter a seismic Rayleigh wave passes along the surface. If the substrate is covered with a gas-sensitive coating, changes in the ambient gas can be detected by frequency measurements. The selectivity of the device is determined by the chemically sensitive coating.

7.7.7 Sensor arrays

Most sensors are not specific, but respond simultaneously to several species. In order to compensate for the lack of selectivity, measurements over several sensor channels are necessary, i.e., at several wavelengths, potentials, currents, or resonant frequencies.

Multiple channel sensors or sensor arrays can be formed by aggregation of several single sensors. For example, piezoelectric quartz crystals may be coupled in an array to form a novel device and operated simultaneously. Sensor arrays based on field-effect transistors consist of a single circuit, where individual sensors are formed of different coatings (Fig. 7.7-15). Optical sensors can also be run in the multiple channel mode, if a spectral range is evaluated, rather than a single

Fig. 7.7-15. Array of ISFETs for analysis of blood electrolytes. The pH-sensitive layer is based on a Si_3N_4 gate. For measurement of sodium, the $\text{Si}_3\text{N}_4/\text{SiO}_2$ insulator is doped with Al and Na; potassium is measured via a sensitive layer containing valinomycin



wavelength, e.g., by means of a diode array spectrophotometer. The channel is then the recorded wavelength.

Data evaluation for multiple channel sensors is carried out by the principles of simultaneous multicomponent analysis, as explained in Sec. 12.5.4.

Up to now sensor development has been concentrated on the construction of sensors for the analysis of individual chemical species. Thus, the general approach adopted in off-line analysis has merely been transferred to the development of sensors. For example, assessment of wine quality is performed by determination of individual components, followed by data evaluation on the basis of some trace components or by means of chemometric methods of pattern recognition. A much more natural approach would be to employ a taste sensor, that could be used to judge the quality of wine in the same way that humans do.

The development of sensors for solving this kind of problem is still in its infancy. The routine use of such sensors will also depend on their acceptance by official organizations.

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- [7.8-2] Wolfbeis O.S. (Ed.), *Fiber Optical Chemical Sensors and Biosensors*, CRC Press, Boca Raton, Florida, 1991, Vols. I and II.
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Questions and problems

1. Electrochemical measurements of ions in solutions are strongly influenced by the ionic strength. What effect of ionic strength is to be expected if optodes are used?
2. Voltammetric sensors are usually based on amperometry. Does a polarographic sensor make sense?
3. Optodes exploit the color change of the immobilized indicator. What does the shape of the calibration curve look like?
4. How can one correct for a lack of specificity and/or selectivity of a sensor?
5. What are the differences and what are the similarities between diode arrays and sensor arrays?

