An optical Chemical Sensor Based on polymer Swelling for pH and Metal Ions Determination

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1.1 Chemical sensors

Chemical sensors constitute new analytical devices that provide experimental response related to the quantity of a chemical species. These devices are designed to operate in a continuous and reversible fashion in real time. The sensor may be constructed to monitor a specific analyte present in a variety of sample matrices, including liquids, and gases[1,2].

Chemical sensors consist of chemical recognition phases coupled to transduction elements[1]. The chemical recognition phase interacts with the analyte of interests and is detected by the transduction element. Typically, it converts current, potential, or light intensity into an electrical signal. The electrical signal is proportional to the concentration of the analyte in the sample being measured. A general construction principle of a chemical sensor is illustrated in figure 1.

To achieve good chemical sensors, they should have a variety of aspects such as high selectivity only to analyte in question, high sensitivity, long lifetime, short response time, ruggedness, stability, reliability, inexpensive,

small, simple to operate, reversible, easily calibrated, and can analyze nondestructively, rendering accurate information in a short time[3]. They are electrically passive, and can safely be used in vivo[10]. The signal is not subject to electrical interference. Light can be transmitted through fibers over long distances, the fibers are mechanically flexible[11].

1.1.1 Selectivity

Selectivity can be simply defined as the sensors ability to respond to one particular analyte of interest in the presence of other analytes. The sensing elements are constructed to provide selective measurement of analyte based upon its chemical reactivity, electrical, mass, or optical properties. The use of chemometric and pattern recognition techniques in combination with arrays of sensors is a strategy has been used successfully to overcome the lack of selectivity of individual sensors [3].

The selectivity is the most important parameter associated with a chemical sensor because it largely determines the accuracy of the analytical method. Since selectivity is always limited, all chemical sensors are prone to report higher concentration than a sample actually contains[4]. In the environmental field, this positive error can be considered as a safety margin

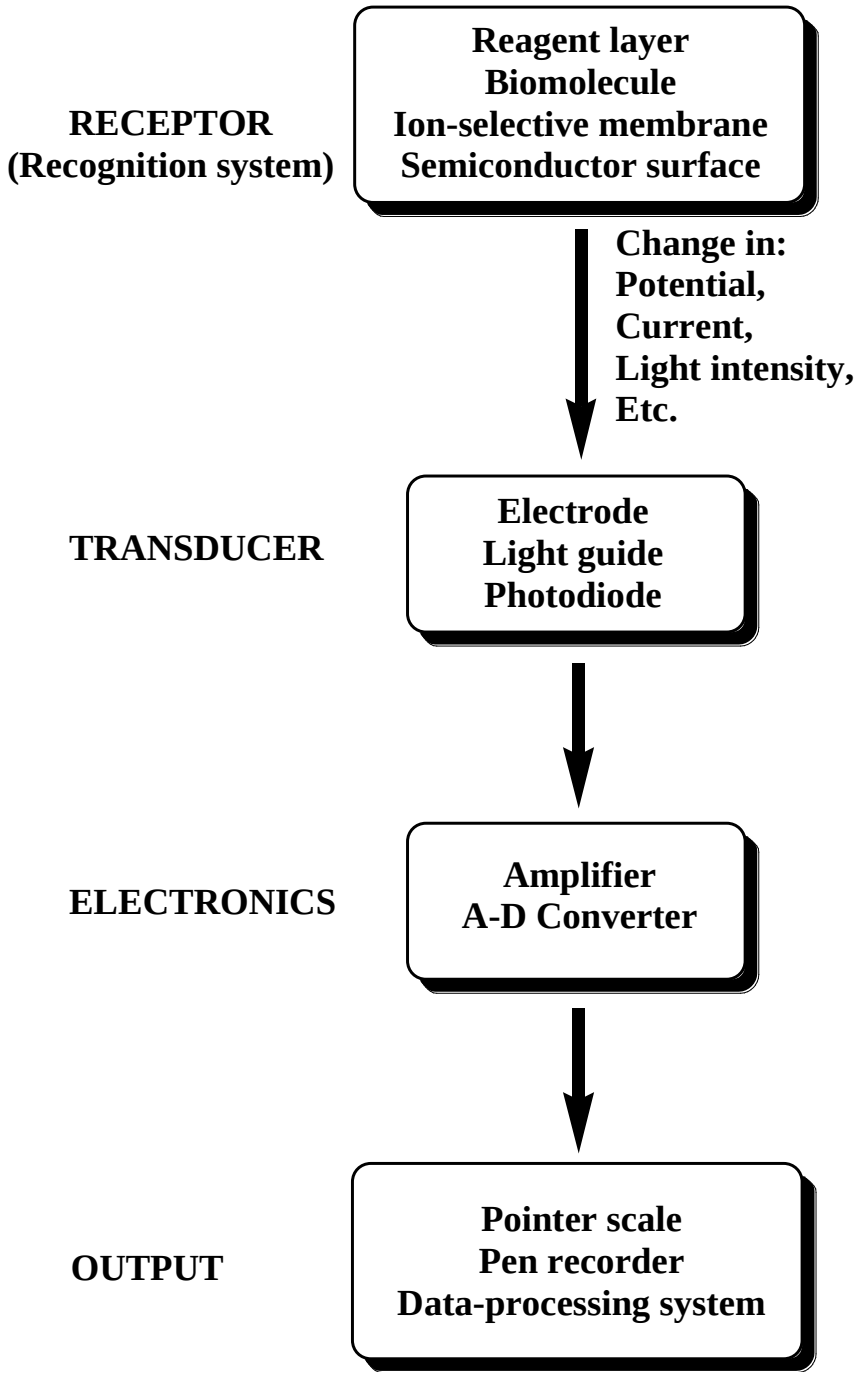

Figure 1.1: Generalized scheme of the main elements of a sensor.

if relevant interferents are also present[4]. Over the past decade; the possibility of selectivity and quickly sensing of a specific analyte with optical fibers has been the center of much research[3].

1.1.2 Sensitivity

The sensitivity of a sensor is defined by the signal it generates, expressed in the concentration units of the substance measured[4]. With some sensors the sensitivity rises to a maximum during the device's lifetime. Sensitivity depends on some parameters such as sample matrix, temperature, pressure, and humidity. All these parameters must remain constant during calibration and in the analysis of real samples. Our chemical sensor with the dicarboxylate group has a good sensitivity with different concentrations of samples used.

1.1.3 Lifetime

Many factors affect the lifetime of a sensor. For optical sensors based on membrane-bound recognition, molecules lose their ability to function by leaching-out effects. Photodegradation may occur if the readout device

requires absorption of light such as most types of optically sensitive materials. Photodegradation of chromophores can occur when absorption is used for sensing. This will limit the lifetime of the sensor. Also the photo bleaching effect on optical sensors may reduce the lifetime to less than a year[4].

1.1.4. Response Time

Some manufacturers define it as the time required for a signal to reach about 90% of its final value. While others sometimes prefer the 95% or even 99% level[4]. The response time should be ranged from several seconds to a few minutes, depending on the thickness of the sensing element, and the extent to which the analyte has to be interacted with the sensing element. Response times for chemical sensors are in the range of seconds, but some biosensors require several minutes to reach a final reading, sometimes in environmental control, the time is reasonable; it is in minutes.

The response time for a sensor is generally greater for low analyte concentration than for higher concentration, this is related to the diffusion factor. There are some factors that affect the response time such as the surface roughness of the sensor and the dead volume of the measuring cell.

In the presence of strongly interfering substances, the response time for a chemical sensor might increase as a result of an increase in the time required to reach final equilibrium[4].

1.1.5. Stability

The stability of a chemical sensor is usually subject to a significant aging process. In this process, most sensors lose some of their selectivity, sensitivity, and stability. Some sensors can be rejuvenated, such as the glass pH electrode[4]. Some sensors based on polymer swelling lose their stability due to mechanical stresses associated with swelling and shrinking, and cracking or other forms of mechanical deterioration. The forces that cause the polymer to swell create internal stresses that often cause the polymer to crack. If the polymer is immobilized in a solid substrate, then it is constrained so that it can only swell in the direction perpendicular to the surface. This leads to shear forces at the polymer/substrate interface that can cause delamination[5]. These factors are in minimum if the microspheres polymer dimensions are in the order of few micrometers. By suspending the microspheres in a hydrogel membrane allows them to swell freely in all directions, increasing the volume change due to swelling and circumventing the problem of delamination.

1.1.6. Limit of Detection

The limit of detection (LOD) is defined as three times the standard deviation of the blank value (the lowest measurable level), expressed in concentration units. The definition used when traces of the analyte would be present or might easily be carried out into the calibration process by solvents or reagents. This case is found in extremely sensitive sensors[4].

1.1.7. Reliability

It is defined as the extent to which an experiment, or measuring procedure yields the same results on repeated trials. Analytical results are incomplete without an estimate of their reliability.

1.1.8 low cost

Both the preparation and instrumentation of a sensor should have low cost.
For example, some optical sensors, such as optical sensors based on polymer swelling use low cost LEDs as light source and photodiode as detectors. While conventional methods require sampling as well as sample preparation, and expensive instrument.

1.2 Classifications of chemical sensors

There are four major subclasses of chemical sensors: thermal, mass, electrochemical, and optical; they are based upon the measurement of heat, mass, electronic, and optical quantities, respectively.

1.2.1 Thermal Sensors

These chemical sensors use the heat generated by a specific reaction as the source of analytical information. These sensors represent a form of in situ microcalorimetry, which could be performed in a batch mode. The general strategy is to place the chemically selective layer on top of a thermal probe and measure the heat evolved in the specific chemical reaction taking place in that layer, as the change in temperature of the sensing element. Thermal sensors constitute the smallest class of sensors. Thermistors and pyroelectric devices are two thermal probes used for monitoring thermal processes[1].

1.2.2 Mass Sensors

Microbalances and microgravimetry can be regarded as mass sensors. Piezoelectric crystals have been used as microbalances due to their small size, high sensitivity, and stability. They are relatively inexpensive, and readily available. α-Quartz is the material selected for the most piezoelectric sensor applications, because it is inexpensive and has a relatively high piezoelectric coefficient. The sensor operates by applying a voltage -created by an applied pressure- to the crystal, which causes it to propagate a wave across the crystal at a certain frequency. Since the chemical sensing layer which interacts with the analyte of interest is applied to the top of the crystal. The interaction between the sensing layer and the chemical causes an increase in the mass crystal. The addition of mass to the crystal changes the frequency of the propagating wave, which can be easily measured[1].

The major advantages of mass sensors are their simplicity of construction and operation, their light weight, and the low power required. They also have high sensitivity and can be used for a very broad range of compounds[1].

1.2.3 Electrochemical Sensors

Electrochemical sensors are the largest and oldest group of chemical sensors. They are divided by their mode of measurement into potentiometric, amperometric, and conductimetric sensors. There are some common rules, which apply to all electrochemical sensors, the cardinal one being the requirement of a closed electrical circuit that is at least two electrodes constitute an electrochemical cell. From an electrical point of view, the two electrodes can be a sensor electrode and a signal return[1].

Electrochemical sensors have certain advantages. Measurements can be made on exceedingly small volumes of sample with miniaturized electrodes. Also the signal from electrochemical cell is electrical. So, no conversion to an electrical signal for the measurement process is required. Electrochemical cells exhibit certain disadvantages, which have restricted their implementation as sensors. The main one is their inherent lack of selectivity in comparison with electrical techniques. A second disadvantage is the necessity of the references electrode in order to maintain constant half cell potential[2].

1.2.4 Optical Chemical Sensors

Fiber optic chemical sensors (FOCS) are based upon the interaction of electromagnetic radiation passed through fiber with matter presented at one end of the fiber optic chemical sensor. Optical fibers and waveguides can transmit light over large distances and with minimal loss of intensity. This makes optical sensors particularly attractive for remote sensing and for applications where the use of electricity may be hazardous[1]. FOCS has essentially three major components: light source, optical fiber, and a photodetector[6-8]. The advent of optical fibers has initiated a revolution in telecommunications technology and is producing a subsequent and possibly equal impact on chemical sensor technology[2].

Since optical fibers can be many meters in length, are flexible, and have diameters typically 125-1000μm, it is feasible to perform continuous spectroscopy in inaccessible or remote sites. Sensors based on fiber optic technology provide some interesting advantages over other sensors. Their sturdy and simple construction permits placement in harsh environments[2]. They are immune to electromagnetic interference, and require no reference electrode, and no electrical shocks happen[2,9]. Also their low cost permits the sensors to be useful for many applications[2]. There is a great degree of selectivity inherent in the transduction part of optical sensors given by the choice of wavelengths, polarization, etc[1].

Fiber optic sensors are classified as intrinsic or extrinsic sensors[2]. With an intrinsic sensor the optical fiber itself acts as an optical component and is modulated directly by the change in a physical parameter, thus altering the transmitted light. Intrinsic sensors exist for the measurement of temperature, magnetic field, acoustics, strain and electrical current as well as other physical parameters. These sensors use the fiber as the chemically sensitive component. They use developed fibers in which, the core, cladding or jacket materials are used as the transduction element. Essentially, a physical property of the analyte can be measured directly through the fiber with or without a specific chemical sensing element. An example of this type of sensor is the evanescent wave sensor. Extrinsic sensor is used for specific chemical detection and requires the association of an optical transducer with the fiber. The transducer must induce an optical signal change in response to the selective detection of an analyte in a complex mixture. The transduction of chemical information usually takes place outside of the fiber. A chemical recognition element is attached to the tip of the fiber, and fluorescence or absorbance measurement is monitored.

FOCS have a variety of applications in different areas, such as water analysis, biological and medical research, industrial bio processes corrosion

and combustion. Several papers on gas, vapor, and humidity sensors have been produced[12]. Gas sensors such as hydrogen[13], methane and related hydrocarbons[14], oxygen[15], NO gas[16], and CO_2 gas sensor[17,18]. Humidity sensors have been described that are based on highly different schemes[19]. Numerous fiber ion sensors for all kinds of inorganic ion including the proton (pH), and salinity have been reported. Also sensors for organic compounds such as pollutants, agrochemicals, explosives, drugs and pharmaceuticals have been developed. In biosensors, a biological component is used in the recognition process[12]. Typical components include enzymes[20], antibodies, oligonucleotides, and whole cells[21].

1.3 Types of Optical Sensors

1.3.1 Optical Sensors Based on Indicator

There has been an interest in chemical sensors consisting of immobilized indicators coupled to a spectrometer through fiber optics. It is necessary to add reagents that interact with the analyte to form a product, which is optically detectable. There should be a convenient method for formulating the polymeric indicator substrate and coupling into fiber optics. Different methods for immobilizing indicators and coupling them to optical fibers

have been employed. Although these methods offer advantages and disadvantages, none of them combines convenience with the ability to reproducibly control both the amount of indicator and the amount of immobilization substrate. A method for immobilizing indicator for fiber optic sensing has been reported[22]. Cyanuric chloride is used to couple indicator to poly (vinyl alcohol) (PVA), which, is then cross-linked with glutaraldehyde in the presence of acid, which acts as a catalyst. Further work describes the response characteristics of sensors for pH and Mg^{2+} prepared using PVA as the indicator substrates[2]. This kind of sensor has some limitations, such as indicator instability, because of leaching and photodegradation.

1.3.2 Optical Sensors based on polymer swelling

Sensors based on polymer swelling include chemical functional group as the chemically selective, and sensitive layer. This type of chemical sensor has been investigated several years ago. In 1990, the first fiber optic chemical sensor based on polymer swelling was developed using ion exchange materials of sulfonated polystyrene and sulfonated dextran to detect changes in the ionic strength of aqueous solution. Interaction between the analyte and the functionalized polymer caused the bead to shrink[23]. This polymer bead