国外化学名著系列

（影印版）3

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An Introduction for Scientists and Engineers

化学传感器

——科学家与工程师入门

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Preface

When this book appeared in German, its main task was to bridge the gap between the traditional ways of thinking of scientists and engineers. The differences in how scientists and engineers think stem from the fact that chemical sensors may be interpreted, on the one hand, as a kind of artificial sense organ developed by engineers to equip automatic machines. On the other hand, chemical sensors are not unlike the other myriad small analytical instruments common in analytical chemistry.

The book was written with the aim of providing students of technical disciplines with a basic understanding of certain aspects of chemical science as well as providing students of chemistry with a basic knowledge of electronics and other technical aspects of their discipline.

When the book first appeared, the author was unaware of a single publication that he could recommend to his students without reservations. It seems that this situation has not changed markedly in the time since then. Thus, the author feels encouraged in presenting this English version of his textbook, which is more or less a translation of the German edition.

November 2006 *Peter Gründler*

Contents

1 Introduction

1.1
Sensors and Sensor Science

Sensors belong to the modern world like the mobile phone, the compact disc or the personal computer. The term 'sensor' is easily understood. People may imagine a sensor similar to a sensing organ or a tentacle of an ant. *Chemical sensors*, as a special variety of sensors, can be found, for example, in a cold storage place in the form of a freshness sensor which detects spoiled food. A generation ago, the word sensor was not widely used. Today, however, sensors are becoming ubiquitous in our daily lives. Our world is changing rapidly, and sensors play an important role in this process.

Chemical sensors analyse our environment, i.e. they detect which substances are present and in what quantity. Generally, this is the task of analytical chemistry, which aims to solve such problems by means of precise instruments in well-equipped laboratories. For a long time there was a trend towards increased centralization of analytical laboratories, but in certain respects we now see a reversal of this tendency away from instrumental gigantism. Such a tendency to build smaller devices instead of ever bigger ones occurred many years ago when the personal computer appeared and started to replace the large, highly centralized data processing centres. A similar development brought about a rapid expansion in the use of chemical sensors.

1.1.1
Sensors – Eyes and Ears of Machines

The term 'sensor' started to gain currency during the 1970s. This development was caused by technological developments which are part of a technical revolution that continues to this day. Rapid advances in microelectronics made available technical intelligence. Machines became more 'intelligent' and more autonomous. There arose a demand for artificial sensing organs that would enable machines to orient themselves independently in the environment. Robots, it was believed, should not execute a program blindly. They should be able to detect barriers and adapt their actions to the existing environment. In this respect, sensors first represented *technical sensing organs*, i.e. eyes, ears and tentacles, of automatic machines. With our senses we can not only see, hear and feel, but also smell and taste. The latter sensations are the results of some kind of chemical analysis of our environment, either of the surrounding air or of liquids and solids in contact with us. Consequently, chemical sensors can be considered *artificial noses* or *artificial tongues*.

If we accept that sensors are technical sensing organs, then it might be useful to compare a living organism with a machine. When we do this, it is plausible that the term sensor came into use simultaneously with the advent of the microprocessor and the mobile personal computer. Figure 1.1 illustrates the similarities between biological and technical systems.

In a living organism, the *receptor* of the sensing organ is in direct contact with the environment. Environmental stimuli are transformed into electrical signals conducted by *nerve cells* (*neurons*) in the form of potential pulses. Strong stimuli generate a high pulse frequency, i.e. the process is basically some kind of frequency modulation. Conduction is not the only function of neurones. Additionally, signal amplification and signal conditioning, mainly in the form of signal reduction, take place. In the brain, information is evaluated and, finally, some action is evoked.

We see many similarities between living organisms and machines when we compare how modern sensors and living organisms acquire and process signals. As in a living organism, we find a *receptor* which is part of the technical sensor system. The receptor responds to environmental parameters by changing some of its inherent properties. In the adjacent *transducer*, primary information is transformed into electrical signals. Frequently, modern sensor

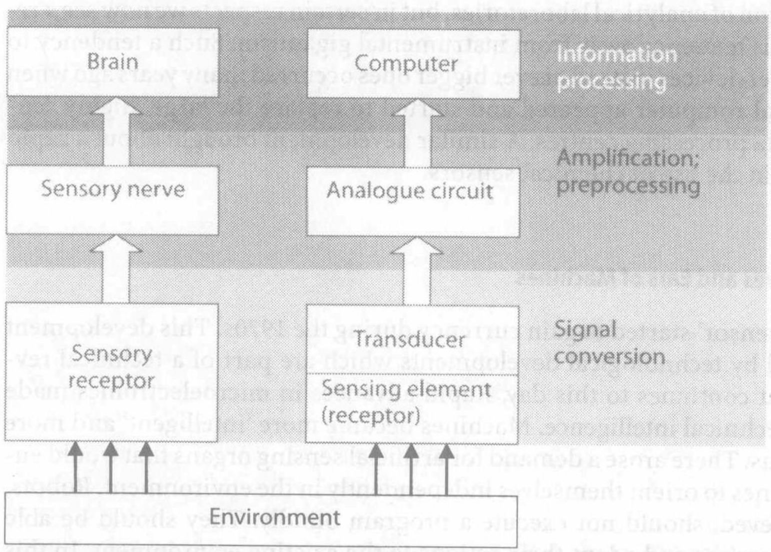

Figure 1.1. Signal processing in living organisms and in intelligent machines

systems contain additional parts for signal amplification or conditioning. At the end of the chain, we find a microcomputer working like the central nervous system in a living organism.

The above considerations, although simplified, demonstrate that signal processing by electronic amplifiers or by digital computers is indispensable for sensor function, like the indispensability of neurones and the brain for physiological processes in organisms. As a consequence, we should accept the fact that 'sensor' does not mean simply a new expression for well-known technical objects like the microphone or the ion selective electrode. Indeed, use of these objects takes on a new meaning in the emerging sensor era.

1.1.2
The Term 'Sensor'

It would not be sufficient to see sensors merely as some kind of technical sensing organs. They can be used in many other fields besides just intelligent machines. A modern definition should be comprehensive. Actually, there is still no generally accepted definition of the term. On the other hand, it seems to be rather clear what we mean when we talk about a sensor. We find, however, differences regarding whether the receptor alone is a sensor or whether the term encompasses the complete unit containing receptor plus transducer.

Regardless of such differences, there is broad agreement about attributes of sensors. Sensors should:

- Be in direct contact with the investigated subject,
- Transform non-electric information into electric signals,
- Respond quickly,
- Operate continuously or at least in repeated cycles,
- Be small,
- Be cheap.

It seems astonishing that sensors are expected to be cheap. Such an expectation can be understood as the expression of the self-evident requirement that sensors be available in large quantities, above all as a result of mass production.

1.2
Chemical Sensors

1.2.1
Characteristics of a Chemical Sensor

The term 'chemical sensor' stems not merely from the demand for artificial sensing organs. Indeed, chemical expertise was necessary to design chemical sensors. Such expertise is the subject of analytical chemistry in its modern, instrumental form. Initially, chemists hesitated to deal with sensors, but later their interest in them grew. The field of chemical sensors has been adapted and is now largely considered a significant subdiscipline of analytical chemistry. On the other hand, the field is given little space in analytical chemistry textbooks. This is true mainly in European textbooks. Sensors do not fit smoothly into traditional concepts and appear to belong to an unrelated field. Up to now, they have not been a typical constituent of analytical chemistry lectures in Europe. There is no doubt, however, that chemical sensors comprise a branch of analytical chemistry. The latter by definition aims to '... *obtain information about substantial matter, especially about the occurrence and amount of constituents including information about their spatial distribution and their temporal changes* ...' (Danzer et al. 1976).

There are two obvious sources for the formation of sensor science as an independent field. One of these sources is the above-mentioned development of microtechnologies, which stimulated a demand for sensing organs. The second source is a consequence of the evolution of analytical chemistry which brought about a growing need for mobile analyses and their instrumentation. Figure 1.2 attempts to outline the formation of sensor science as a bona fide branch of science.

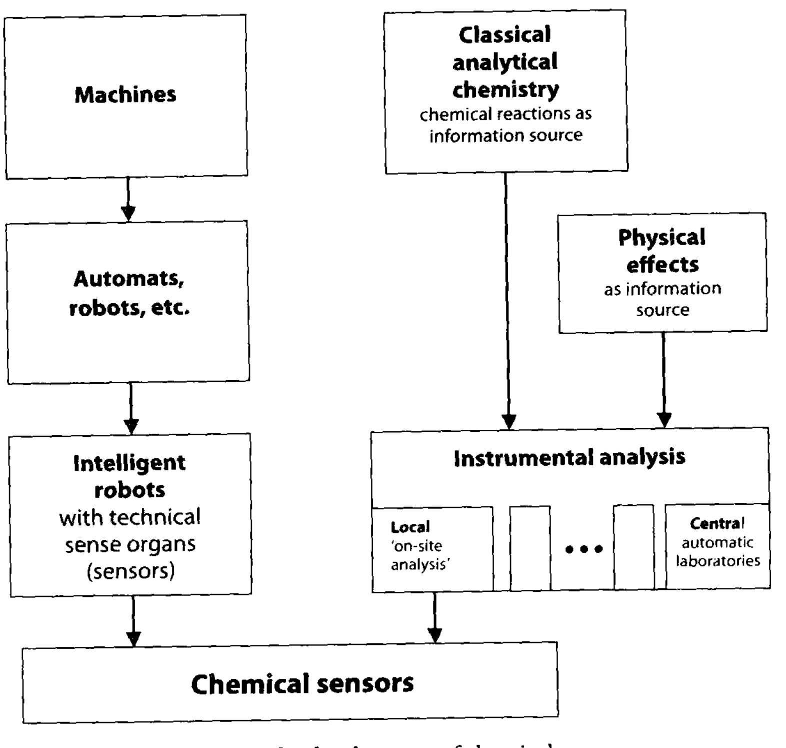

Figure 1.2. Two sources in the development of chemical sensors

As a science, chemistry from the very beginning required information about chemical composition. In other words, analytical chemistry comprises one of the earliest foundations of chemical science; it is as old as general chemistry. The high degree of importance of this field is a result of the natural interest of humans in the composition of our environment. The systematic development of analytical chemistry started with the work of Robert Boyle in the 17th century. Since that time, when we speak about 'analysing' mixtures, we do not mean simply decomposing them. In fact we often carry out a chemical reaction with the express purpose of obtaining knowledge about the composition of the chemicals or materials involved in the experiment. So, for example, since ancient times a well-known indication of the presence of the element chlorine has been the formation of a white precipitate with the addition of silver nitrate solution. Since that time, Boyle's 'wet analysis' has reached a high degree of perfection. Much later, in the middle of the 19th century, the arsenal of analytical chemistry was perfected by the addition of new tools, namely the evaluation of physical properties like light emission. Meanwhile, today instrumental techniques are a significant part of analytical chemistry. Spectroscopy and chromatography are examples of such techniques.

In the final decades of the last century, a strong tendency towards automation appeared in chemical analysis. Big central laboratory complexes were established. One reason for centralizing the resources is the high costs of modern instruments. However, at a certain point, it became obvious that not every problem could be solved smoothly in this way. In many cases, it was difficult or impossible to transport samples long distances without decomposition. This is a typical problem in environmental analysis, a branch of growing importance. Commonly, it proved to be much more simple to bring the instrument to the sample rather than the sample to the instrument. Mobile techniques of chemical analysis attracted increasing interest. Analysts started to look for small, transportable analytical probes which could be stuck smoothly into a sample. Probes of this kind are e.g. the well-known ion selective electrodes, among them the glass electrode for measuring pH. With the growing popularity of sensors in technical applications, it turned out that analytical chemistry already possessed some types of chemical sensors. Thus, during the 1970s, the term 'sensor' became increasingly popular for well-established devices as well.

Now, having discussed the problems associated with defining the sensor in general, we can seek a definition of the chemical sensor. Such a definition was given by IUPAC in 1991:

A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal.

This is rather general. Thus, many pragmatic descriptions exist in the literature. Consider the following definition by Wolfbeis (1990):

Chemical sensors are small-sized devices comprising a recognition element, a transduction element, and a signal processor capable of continuously and reversibly reporting a chemical concentration.

The attribute of *reversibility* is considered important by many authors. It means that sensor signals should not 'freeze' but respond dynamically to changes in sample concentration in the course of measurement. The following characteristics of chemical sensors are generally accepted. Chemical sensors should:

- Transform chemical quantities into electrical signals,
- Respond rapidly,
- Maintain their activity over a long time period,
- Be small,
- Be cheap,
- Be *specific*, i.e. they should respond exclusively to one analyte, or at least be *selective* to a group of analytes.

The above list could be extended with, e.g., the postulation of a *low detection limit*, or a *high sensitivity*. This means that low concentration values should be detected.

Classification of sensors is accomplished in different ways. Prevalent is a classification following the principles of *signal transduction* (IUPAC 1991). The following sensor groups result:

- Optical sensors, following absorbance, reflectance, luminescence, fluorescence, refractive index, optothermal effect and light scattering
- Electrochemical sensors, among them voltammetric and potentiometric devices, chemically sensitized field effect transistor (CHEMFET) and potentiometric solid electrolyte gas sensors
- Electrical sensors including those with metal oxide and organic semiconductors as well as electrolytic conductivity sensors
- Mass sensitive sensors, i.e. piezoelectric devices and those based on surface acoustic waves
- Magnetic sensors (mainly for oxygen) based on paramagnetic gas properties
- Thermometric sensors based on the measurement of the heat effect of a specific chemical reaction or adsorption which involves the analyte
- Other sensors, mainly based on emission or absorption of radiation

Alternative classification schemes do not follow the principles of transduction but prefer to follow the appropriate application fields or receptor principles. In this way is the large and important group of biosensors defined.

Biosensors are often considered to be an independent group in sensor science. In this book, however, we will regard them as a special type of chemical sensor. Consequently, they will be integrated into the appropriate chapters of the book. This concept corresponds to that of the responsible IUPAC commission which has expressed in an official document (IUPAC 1999): *Biosensors are chemical sensors in which the recognition system utilizes a biochemical mechanism.*

Since there cannot be found a perfect classification scheme for chemical sensors, in what follows an attempt will be made to find a compromise between the various concepts.

1.2.2
Elements of Chemical Sensors

Section 1.1.1 showed that the functions of a chemical sensor can be considered to be tasks of different units. This is expressed typically in statements like the following (IUPAC 1999): *Chemical sensors usually contain two basic compo-*

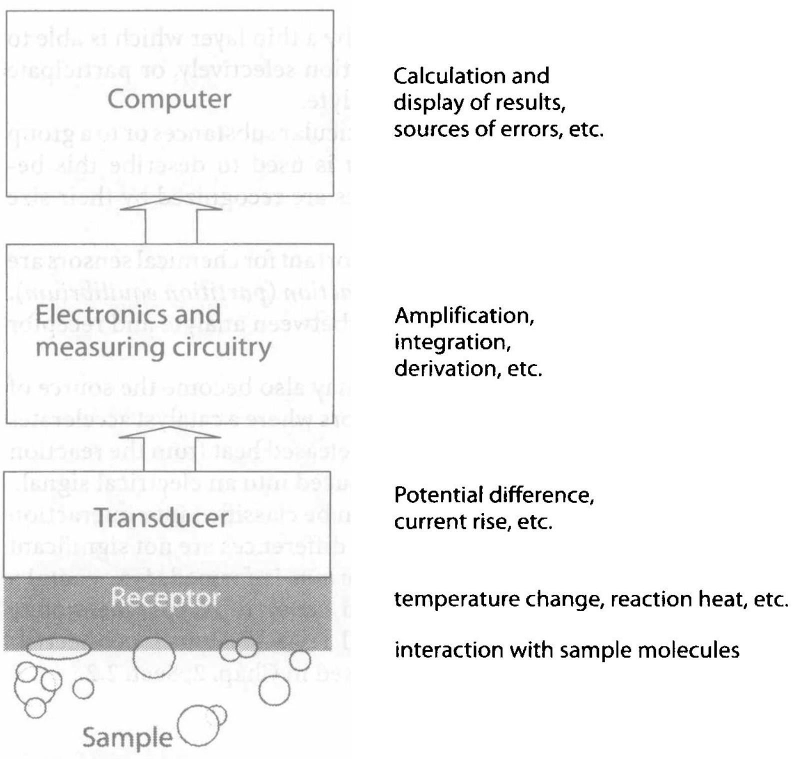

Figure 1.3. Scheme of a typical chemical sensor system

nents connected in series: a chemical (molecular) recognition system (receptor) and a physicochemical transducer. In other documents, additional elements are considered to be necessary, in particular units for signal amplification and for signal conditioning. A typical arrangement is outlined in Fig. 1.3.

In the majority of chemical sensors, the receptor interacts with analyte molecules. As a result, its physical properties are changed in such a way that the appending transducer can gain an electrical signal. In some cases, one and the same physical object acts as receptor and as transducer. This is the case e.g. in metallic oxide semiconductor gas sensors which change their electrical conductivity in contact with some gases (Chap. 5, Sect. 5.2). Conductivity change itself is a measurable electrical signal. In mass sensitive sensors, however, receptor and transducer are represented by different physical objects. A piezoelectric quartz crystal acts as transducer. The receptor is formed by a sensitive layer at the crystal surface. The latter is capable of absorbing gas molecules. The resulting mass change can be measured as a frequency change in an electrical oscillator circuit.

Receptor

The receptor function is fulfilled in many cases by a thin layer which is able to interact with analyte molecules, catalyse a reaction selectively, or participate in a chemical equilibrium together with the analyte.

Receptor layers can respond selectively to particular substances or to a group of substances. The term *molecular recognition* is used to describe this behaviour. Typical for biosensors is that molecules are recognized by their size or their dimension, i.e. by *steric recognition.*

Among the processes of interaction, most important for chemical sensors are adsorption, *ion exchange* and *liquid-liquid extraction* (*partition equilibrium*). Primarily these phenomena act at the interface between analyte and receptor surface, where both are in an equilibrium state.

Instead of equilibrium, a chemical reaction may also become the source of information. We find this, for example, in receptors where a catalyst accelerates the rate of an analyte reaction so much that the released heat from the reaction creates a temperature change that can be transduced into an electrical signal.

Processes at the receptor-analyte interface can be classified into interaction equilibria and chemical reaction equilibria. The differences are not significant for work with sensors. A true chemical equilibrium is formed, for example, in electrochemical sensors where receptor and analyte are partners of the same redox couple. The fundamental chemical relationships in connection with signal formation at the receptor are discussed in Chap. 2, Sect. 2.2.

Transducer

Today, signals are processed nearly exclusively by means of electrical instrumentation. Accordingly, every sensor should include a transducing function, i.e. the actual concentration value, a non-electric quantity, must be transformed into an electric quantity—voltage, current or resistance.

The pool of transducers can be classified in different ways. Following the quantity appearing at the transducer output, we encounter types like 'current transducer', 'voltage transducer' etc. In the international literature, there exists no systematic concept for classification. In what follows, an attempt is made to find a classification scheme which reflects the inner function of the transducers using only a few transducer principles. It is based on a scheme developed by electronics engineers but has not been applied to sensors till now (Malmstadt et al. 1981). Among the examples given are those that develop their sensor function only in combination with an additional receptor layer. In other types, receptor operation is an inherent function of the transducer.

Energy-Conversion Transducers The principle of energy conversion means that electrical energy is produced by the sensor. Many of these kinds of sensors are able to operate without external supply voltage. In Fig. 1.4, we see two examples together with their measuring circuitry.

The photovoltaic cell, taken as an example of an energy-conversion transducer, converts radiation energy into electrical energy. It is intended to mea-

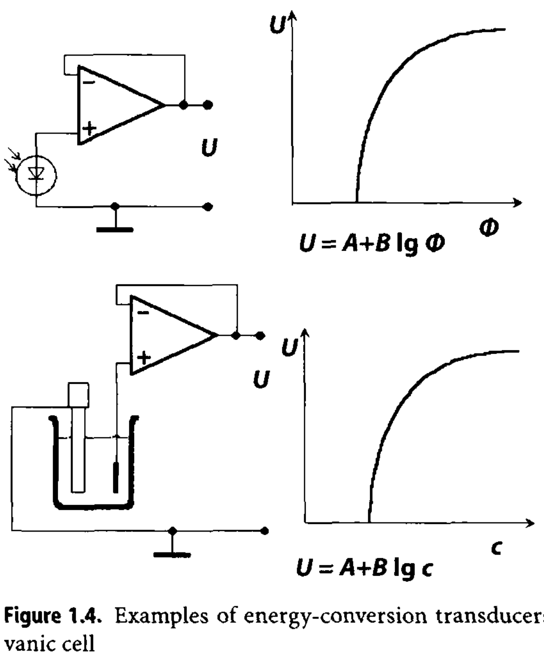

Figure 1.4. Examples of energy-conversion transducers. *Top*: Photo element, *bottom*: galvanic cell