Optical fibre chemical sensors

John F. Alder
DIAS, UMIST, P.O. Box 88, Manchester M60 1QD, UK

Faseroptische chemische Sensoren

Zusammenfassung. Faseroptische chemische Sensoren erlauben die Bestimmung einer großen Zahl von Anionen, Kationen, Gasen und organischen Verbindungen in Lösung oder Gasphasen. Für den direkten Einsatz in Komplexen oder aggressiven Mischungen stellen die Ansprüche hinsichtlich Selektivität, Empfindlichkeit, Langlebigkeit und Reproduzierbarkeit hohe Anforderungen an die Sensorreagentien und das schützende Membransystem. Diese Anforderungen werden dadurch gemildert, daß Probenvorbereitung und Trennverfahren vorausgeschickt werden, was die beste Ausnutzung der Sensoreigenschaften ermöglicht. Für einfachere Matrices oder solche, die im wesentlichen unveränderlich bleiben, stellen maßgeschneiderte Sensoren ein nützliches Mittel für die spezifische Bestimmung dar.

Die Notwendigkeit liegt auf der Hand, daß die Reagentien über einen möglichst großen Bereich von Einsatzbedingungen hohe Empfindlichkeit und hohe Selektivität aufweisen — eine wichtige Anforderung.

Summary. Optical fibre chemical sensors permit the determination of a wide range of anions, cations, gases and organic compounds in solution or gas phases. For in-line operation in complex or aggressive mixtures the requirements of selectivity, sensitivity, longevity and reproducible response impose great demands on the sensor reagents and protective membrane system. These demands will be alleviated by preceding the sensors with sample pretreatment and separation procedures and permit the best exploitation of their characteristics. For simpler analytical matrices, or those which are largely unchanging, tailored sensors provide a very useful means of specific determination. There is a clear need for high sensitivity and high selectivity of the reagent over as wide a range of conditions as possible — a demanding requirement.

Introduction

There has been considerable interest shown over recent years in the development of chemical sensors. As with many developments in science and society this has been brought about by economic pressure, stimulated by academic and entrepreneurial interest and made possible by contemporary technological developments.

The economic pressure to develop sensors has arisen largely from the need to rapidly acquire data on chemical compositions of manufacturing plant process streams; in vivo body fluids; gaseous atmospheres, for personal protection; the atmosphere, ground and river waters, for pollution monitoring etc. The desire to make chemical manufacturing process more efficient by closer and more informed control of the chemistry, is certainly one of the primary economic pressures and has extended into the domain of combustion control and monitoring for engine performance optimisation and fuel conservation from ships to space vehicles.

These pressures have demanded that the analytical scientist take his chemical analysis out of the laboratory environment and into the place where the monitoring needs to be done. Consequently, a quite different approach to chemical analysis has had to be taken compared with the normal process of sampling, transport to the laboratory, sample preparation, analysis, data reduction and reporting to the customer who makes decisions based on this analysis.

Now, there is a desire to carry out all of these steps on-site, clearly a very demanding operation in all but the simplest of cases.

Of equal severity is a firm desire by the customer that all this analysis be carried out automatically with little operator skill or interpretation, minimum maintenance, low installation cost and a long, 99%-plus reliable lifetime.

Only in recent years has the pressure to carry out these analyses become so great, due possibly to the economic recession of the last decade and the significant rise in fuel costs after 1974, demanding greater efficiency all round.

There is little doubt that the most important technological development which has permitted this move towards sensor-based chemical analysis is the development of microelectronics; not only the digital microcomputation ability but also the enormous developments in semiconductor technology, surface science and the availability of cheap, high quality components for the analytical chemist to build upon. Associated with the microelectronics and computer technology advances came a requirement for very wide bandwidth communication links for data video and voice channels; this led in turn to a rapid and capital intensive development of microwave and optical communication technology, from which low cost, high quality optical fibre has become available.

It is natural that the increased chemical analysis requirements should be contemporary with the developments in the enabling technology, they both being associated with increased automation and instrumentation of our technology based society. The analytical scientists have naturally taken example and material from these new technologies and are rapidly responding to the challenge set before them.

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in the field of chemical analysis. Semiconductor sensors and surface acoustic wave devices [1], piezoelectric crystal mass sensors [2], microwave technology and [3] optical waveguide technology is an incomplete list of the spin-off developments in chemical analysis which have arisen from the mainstream technology explosion that has occurred over the last quarter century.

The marriage of the technological developments to the analytical requirements is now moving apace and it is appropriate at this stage to consider the merits of certain approaches to the problems. In this paper specific reference will be made to optical waveguide chemical sensors, which are currently generating considerable interest in the analytical community.

**Optical fibre chemical sensors**

The most commonly met optical waveguide is the fibre-optic which has the property of being able to transmit light over considerable distances. More important to the chemist is the way the light is transmitted through the fibre rather than the distance. The light propagates by total internal reflection from the waveguide/air or waveguide/cladding interface, with a small fraction of the light, the evanescent wave, penetrating a small distance (typically of the order of the wavelength) into the adjacent medium [4].

On reaching the end of the fibre the wave is launched into the adjacent medium; if the ray is scattered or reflected it can be gathered within the optical aperture of the waveguide and propagate back down the fibre. As with microwave guides, one can employ optical couplers to separate the forward and reflected wave thus permitting reflection measurements, or by placing a detector at the exit of the guide, forward intensity attenuation can be measured.

Many optical fibre chemical sensors use the waveguide only to transmit and receive the light to and from a reagent phase. The chemically selective spectrophotometric reagent being held at the end of the fibre. This technique has been exploited for a variety of applications and the subject has been extensively reviewed in recent years [5—8]. Methods have been developed for the determination of pH, pO2, pCO2, glucose [5], Cl2, I2, Fe(III), UO2(II), Pu, HCHO, NH3 [6], Al and Be [8] amongst others.

**The problems with spectrophotometric analysis**

In most of these methods a specific chemical reagent is employed to give a colour or intensity change on reaction with the analyte species. As would be expected, none of these reagents is totally specific for a single analyte and the question of interferences and how they can be overcome, arises. With most spectrophotometric reagents, colour complexes can be formed with a variety of species. The interference to the desired determination has to be overcome by a gamut of separation, masking and buffering techniques of greater or less complexity depending upon the reagent system and the analytical matrix. The translation of these reagents from the "analytical laboratory" to the end of an optical fibre has not relieved any of these problems and one is faced with a dilemma of how to make the fibre-optic sensor suitable for its application.

**Overcoming the problems**

The way the problem of specificity is overcome using pre-made chemical sensors is to define quite closely the analytical matrix composition. For some applications this is quite straightforward. For example, human body fluids, even though complex are quite constant in gross terms from day to day or between individuals. One can therefore tailor the probe to that situation. This is normally achieved from three directions: first, a reagent with a high specificity is found for the analyte of interest and immobilised within the fibre-optic optical aperture. Second, it is maintained in a suitable environment, that is to say it is buffered at the correct pH and ionic strength. Third, it is protected from gross interference from the matrix by a protective, species selective membrane (Fig. 1). In this way, the reagent is kept in a condition which is optimum for its performance and the probe is able to give a reproducible response to the analyte under those conditions.

Clearly, many different approaches to these three steps can be taken and much depends on the reagent, analyte and matrix. For some circumstances, a reagent in a liquid film protected by an analyte permeable shear with a configuration identical to Fig. 1 can be used. In other cases, it is necessary to have the reagent bound to the matrix either by electrostatic binding or occlusion, as one would achieve by dispersing the reagent in a resin or cellulose for example. The working conditions are then defined by impregnating the matrix with a solution of the buffers.

In other probe examples it is necessary to chemically bind the molecule to the matrix. Here, it is important that the covalent binding does not drastically alter the reagent properties or chromophore characteristics and it is usually necessary to distance the reagent from the matrix using spacer molecules. Using this method, it may be possible to do away with the buffering medium and protective sheath, depending upon the robustness of the reagent. If this is done, however, the reagent molecule is wide open to attack by the analyte matrix, changes due to differing matrix pH, ionic strength, fouling etc. as is commonly found in electrochemical sensors.

The optical fibre chemical sensor is therefore usually specifically designed for a given set of conditions and for a known analyte. Its application will be necessarily user-oriented as indeed are other simple chemical sensors.

This is, indeed like conventional chemical analysis where different analytes and different matrices require modified analytical methods. The difference between the two approaches is quite clear however, whereas with a common set of instruments and reagents the chemist can carry out virtually any analysis in the laboratory, for the specific chemical sensor the conditions must always be worked out prior to the application which means that the application must always be known in detail. In commercial terms that means that the optical fibre chemical sensors offered for sale must be either for a specific task or be configured to be as widely applicable as possible, that is, to be highly specific and tolerant of a wide range of conditions.