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Optical chemical sensors and biosensors for food safety and security applications

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ABSTRACT Over the past two decades or so, the incorporation of optical techniques in the development of chemical sensors and biosensors have been investigated resulting in novel and very interesting devices with great promise for many areas of applications. These are truly integrated and interdisciplinary systems that invoke expertise from the fields of chemistry, biochemistry, physics and electronics. Optical chemical sensors and biosensors utilise immobilised reagents and novel materials that can result in a variety of optode designs that are suitable for a variety of measurements in environmental, biomedical, industrial and process control areas.
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KEY WORDS

biosensor
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Chemical sensors and biosensors are really sensing devices that utilise the principles of optical molecular spectroscopy in conjunction with chemical systems for use in a variety of applications. The term '**optode**' is sometimes used, as in this paper, which represents the combination of **opt**ical measurements with configurations and performance that are similar to electr**ode**. Optodes represent a group of integrated analytical systems, where chemical and biochemical measurements are performed based on the interaction of light with the chemical/biochemical media followed by conversion of optical signals into readable electrical signals. In this group of devices, optical fibres are often employed as the medium that conveys optical signal to the measurement system and to the detection system. Chemical and biochemical media contain immobilised reagents that are capable of interaction with the measurand of interest, and thus provide the molecular recognition element generating optical signals. Thus the optical signal returned from the recognition element will be encoded with chemical/bio-chemical information conveyed by optical fibres to suitable detectors.

The incorporation of optical fibres in optodes imparts a number of advantages in measurements such as miniature device application, geometrical flexibility and ruggedness, small sample volumes, remote signal detection, multisensing capabilities and low cost. In addition, the use of immobilised reagents enables the development of specific and sensitive optodes in several fields of applications. A few disadvantages such as ambient light interference, limited dynamic range, long response times and reagent stability, may exist with optodes. These can be overcome by proper sample preparation and engineering appropriate instrumentation. Optodes have been developed and employed for chemical and biochemical analytes in environmental monitoring, chemical industrial process control, biotechnology (e.g. food science) and biomedicine, and many more are possible. The development of new materials and optode designs is continuously being pursued broadening the scope of applications of optodes.

This paper presents a brief review of the state-of-the-art of this optode technology, and covers briefly the principles and applications of these devices in a number of areas including food safety and security, with an insight to its future trends.

Principles of transduction

The basic concept of a chemical and bio optode is simple and can be represented as in Figure 1. The molecular/ionic recognition is carried out by the transducer containing immobilised reagents and the measurement involves optical signals that are conveyed by optical fibres. In fact light is launched into the optical fibre from a suitable light source and directed to the measurand region and the returned light is collected by the same or another optical fibre to be measured by the detector. This optical signal may be absorption, emission, transmission, reflection or scattering of light by the transducer in the optode. Various model equations that relate the signal measured to concentration of optical species by the above mentioned techniques of interaction of light have been used (Narayanaswamy and Sevilla 1988). In addition, evanescent waves have been used in optodes, which refers to the light that penetrates into the surrounding medium from optical fibres; have been employed in optode development (Harmer and Narayanaswamy1988, Narayanaswamy 1993a). Such phenomenon is extensively utilised in sensors based on Surface Plasmon Resonance (SPR) of analyte specific coatings

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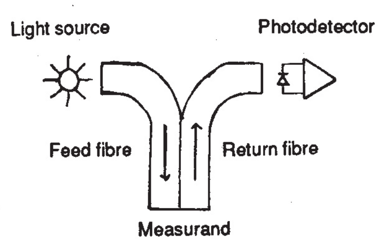

Figure 1. Schematic of an optode (from Narayanaswamy and Sevilla 1988).

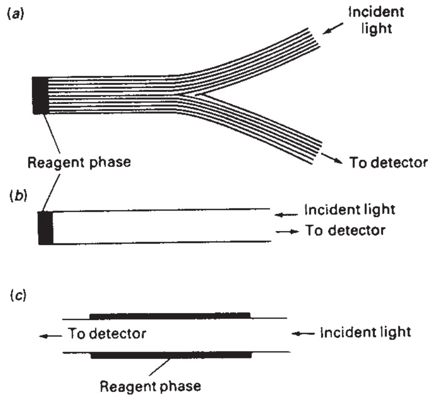

Figure 2. Common optode designs (from Narayanaswamy 1993a).

on waveguides (Harmer and Narayanaswamy 1988).

A variety of sensing mechanisms have been adapted in optodes. These include reversible binding of analyte to a reagent/sensor surface, irreversible chemical interactions between analyte and reagent, specific binding of analytes (e.g. biomolecules) and direct spectroscopic examination of analyte. The sensor chemistry may utilise a single or a mixture of such different mechanisms to produce an overall optical response that can be measured and correlated to analyte concentrations.

Immobilisation of reagents

Immobilisation of reagents for optodes is a key operation that determines a number of their characteristics such as response times, lifetimes and also robustness. They are commonly used in solid state to provide ease of interfacing to optical fibres and this allows simple measurements to be carried out with facilitates the reuse of reagents, if needed.

Physical and chemical methods have been used for the immobilisation of reagents in optodes. Physical immobilisation is achieved through adsorption, entrapment, encapsulation or electrostatic attraction between the reagent(s) and polymeric solid supports(s). In adsorption, the reagent molecules are held on the surface of the support by physical forces such as hydrogen bonding or hydrophobic interactions. In entrapment/encapsulation, the reagents molecules are confined in the lattice structure of the support, while electrostatic attraction involves interactions between ionic groups present in the reagents and in the support material. Some recent work incorporate reagents imprinted on specially designed polymers and this field is of growing interest (Al-Kindy et al. 2000). These physical immobilisation procedures are simple and involve mild reaction conditions. As a result, the binding strength of the reagent molecules on the support will be weak and result in problems of reagent being leached from the support surface. Chemical methods involve the formation of covalent bonds between the reagent and the polymeric support via reactive functional groups such as $-NH_2$, $-OH$, $-CHO$, $-SO_3H$, $-Cl$, $-COCl$, etc. Reactive polymeric supports that have been used in optodes range from inorganic materials (e.g. glass, sol gel, etc.) to organic polymers (e.g. XAD polymers, nylon, cellulose, silicone, etc.). Chemical immobilisation provides stable reagent matrices for optodes. In addition, polymeric membranes may constitute part of the optode design which can provide analyte selectivity to be achieved and thus, improve the optode performance characteristics.

The reagent immobilised materials can then be fabricated into several configurations such as thin films, solids in columns, gels, etc., to be interfaced with optical fibres.

Optode designs

The integral part of many optode designs incorporates optical fibres, which are either optical fibre bundles or single optical fibres (Figure 2). Fibre bundles are bifurcated so that separate fibres can transmit incident and detected radiation (Fig. 2a), while with single fibres, the transducing element can be interfaced at the end of the fibre (Fig. 2b) or applied as a coating on the fibre surface as a cladding material (Fig. 2c). The reagent cladding-based optode design utilises the evanescent waves of optical radiation passing through the optical fibre. Many other designs have been studied for optodes depending on the nature of their application (Wolfbeis 1991).

Instrumentation

The instrumentation associated with optodes is similar to those of common spectrophotometers, and include components such as a light source, a wavelength selector, a photo detector and a display of output (Narayanaswamy and Sevilla 1988, Narayanaswamy 1993a). In addition, optical components such a lens, optical couplers and connectors are used for coupling of light into optical fibres. Commercial portable instrument systems have been developed incorporation solid-state opto-electronic components (Ocean Optics Inc). A review has been published in the literature that deals specifically with instrumentation for use with optodes (Taib and Narayanaswamy 1995). As far as optical fibres are concerned, depending on the fibre material, different range of wavelengths of light can be transmitted through the fibre medium. For example, while glass and plastic optical fibres are useful in the visible and near infra-red region of the electromagnetic spectrum, quartz optical fibres can be used to transmit ultraviolet, visible and near infrared wavelengths of light.

Applications

A number of optodes have been developed for monitoring dissolved and gaseous chemical and biochemical analytes in a variety of fields of applications. For example, pH optodes have been fabricated with different transduction systems and optical principles, and all of these involve the use of pH indicators (acid-base type) that have been immobilised using physical and chemical procedures (Swindlehurst and Narayanaswamy 2004). Sensors for CO_2 are based on changes in pH of the environment of the sensing reagent. This has been the basis of development of a CO_2 sensor employing dual luminophore referencing for application in food technology, by measurements of the analyte in Modified Atmosphere Packaging applications (von Bültzingslöwen et al. 2002), which has major advantage in food safety.

Oxygen optodes for biomedical and process control applications have been developed based on the quenching of fluorescence of an immobilised luminescent indicator, yielding good precision. The signals measured are correlated to O_2 concentrations using the Stern-Volmer equation. Measurement of luminescence lifetimes has been the basis of measurements in an oxygen sensor that has been used in biotechnology and food industries (Köneke et al. 1999).

Covalently immobilised enzymes have been used in the development of bio-optodes for glucose, urea, etc. The use of competitive binding reactions of glucose and of fluorescein-labelled dextran with Concanavalin A (antigen) has resulted in a reversible optode system for detection of low levels of glucose. A recent review paper has been dedicated to the use of immobilised enzymes in the development of bio-optodes (Kuswandi et al. 2001).

Heavy metal ions (Al^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, etc.) in the environment and food have been determined using optodes that utilise immobilised chelating ligands that nearly specifically interact with metal ions. These optodes require fairly rigorous control of pH of the medium and can result in devices with very low detection limits. Several optodes have been developed for the monitoring of gaseous and vapour chemical species and these systems could be adapted for detection of the analytes in dissolved state (Narayanaswamy 1993b). Here gases include NH_3, CO_2, Cl_2, NO_2, SO_2, H_2, etc., and vapours such as water, volatile organics. The use of novel electrochromic polymers in the development of gas optodes have been investigated with very reasonable detection levels (Kondratowicz et al. 2001). Humidity sensors, that can be used in the manufacture and storage of food products, has been the subject of a recent review (Moreno-Bondi et al. 2004), and many types of optical humidity sensors have been investigated by many researchers.

Recently, research has been concentrated for developing optode systems that are capable of multi-analysis. In these, novel signal processing techniques have been employed to analyse the differences in absorption/reflectance wavelengths and reaction kinetics. For example, humidity and NH_3 have been simultaneously determined with a single optode based on Nafion® immobilised crystal violet reagent (Raimundo Jr and Narayanaswamy 2001). Simultaneous determination of Zn(II), Cd(II) and Hg(II) in water has been studied utilising a single reagent adsorbed on a polymeric material (Raimundo Jr and Narayanaswamy 2003). The use of integrated technology in a multifunctional biochip has been described recently that utilises two different bioreceptors on a single platform for application in medical diagnostics and quantitative detection of pathogen (Vo-Dinh et al. 2003). Toxins in food have been detected using an optical fluoro-immunosensor in an array biosensor configuration that is capable of detecting multiple targets (mycotoxin, bacterial toxins, etc.) have been investigated (Ligler et al. 2003). An extended study involving the use of SPR biosensors for detection of food safety-related analytes including chemical contaminants, foodborne pathogens and toxins, has been recently reviewed (Homola 2004).

Though publications concerning applications of optical chemical sensors and biosensors for food safety and security have been dearth in the literature, several workers have attempted to use the novel sensor technique as described below. An optical sensor to detect diacetyl vapours that is evolved at the onset of spoilage of meats has been investigated (Shiers and Honeybourne 1993). The detection of bacterial contamination and food processing with optical sensors has been described in a short review presented in a conference (Wolfbeis 1995). Likewise, robust and inexpensive integrated optical sensors based on the use of Mach-Zehnder interferometers have been studied for beverage analysis (Luff et al. 1998). A patent describes the detection of bacterial volatiles in food analysis by using gas sensors and spectral footprints with advantages of identification of particular microorganisms (Alocilja et al. 2002). Based on the analysis of vapours emanating from food, several researchers are currently studying the development of optical sensors, and the results of such work would cause a mini explosion of publications in the near future.

Summary

Chemical and bio optodes that have been developed over the past two decades have shown considerable promise and many more are being researched. The optode devices need to be combined with advanced signal processing techniques (pattern recognition, artificial neural network, principle component analysis, etc.) in order to improve their characteristics and capabilities. Many new materials such as electrochromic compounds and molecularly imprinted polymers can be exploited in the molecular recognition element of the optode. New sensing schemes and the use of integrated technologies are being investigated that can result is novel and very useful devices for food safety and food security applications.

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