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Review

# Amperometric sensing in the gas-phase

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## Abstract

The design of amperometric sensors for gaseous species presents a challenge as the gas phase has to be brought into contact with a solid electrode as well as an electrolyte phase which usually is liquid. However, many species of analytical interest are electroactive, such as $SO_2$, $NO_x$, $O_3$, CO, formaldehyde or ethanol, and electrochemical means are always attractive in designing sensors because the electronic signal is obtained directly. Therefore, different approaches have been implemented and some types of such sensors have been available commercially for quite some time. Nevertheless, many new developments with regard to an improvement of sensitivity, selectivity and in the construction of these devices have been reported over the last few years, as well as approaches to miniaturization. In this review it is attempted to give an overview of the state of the art of this field, highlighting recent developments.

*Keywords:* Sensor; Amperometric; Gas; Gas-diffusion electrode; Solid polymer electrolyte

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## 1. Introduction

The monitoring of gaseous species, such as $H_2$, $SO_2$, $NO_x$, CO, $H_2S$, $Cl_2$, $NH_3$, ozone, propane or ethylene oxide is of wide interest for industrial safety and hygiene applications, as well as in environmental monitoring. Chemical sensors, rather then conventional analytical instrumentation, are the preferred solution to this demand. Electrochemical transduction principles provide the most direct path to the electrical signals required by the data processing circuitry and for this reason most chemical sensors in use are based on either a change in resistance, the development of a potential or the measurement of a redox current. A range of electrochemical sensors has therefore also been designed for gas phase applications.

Most widely used are semiconductor sensors relying on the change in conductivity of a heated substrate of tin oxide or similar material when exposed to reducing or oxidizing gases. These types of gas sensors are readily available commercially even from catalogue distributors of electronic components. They are employed, for example, for the detec-

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tion of flammable gases (such as propane in fuel applications) or of carbon monoxide in enclosed environments. These sensors have the advantage that they are completely solid state and therefore have long shelf lives and show little deterioration in use. However, they have limited selectivity and sensitivity and a relatively high electrical power consumption as they must be resistively heated. Modern automobiles contain a different solid state sensor, the lambda probe which is a potentiometric sensor for oxygen. This sensor is very widely used, but the principle cannot be extended readily to other applications.

The amperometric gas sensors, which are the subject of this review, are the second most important group of electrochemical gas sensors. These usually contain a liquid electrolyte solution and are therefore not as robust, but generally have higher selectivity and sensitivity as the resistive semiconductor sensors. Amperometric gas sensors have been designed in different forms and are significant also in commercial terms.

In this review an introduction to amperometric sensors for gaseous samples is given and recent trends are discussed. Due to the multitude of publications in this area only a broad overview can be given and it is not possible to give a comprehensive listing of all relevant publications. Naturally such a survey has to be somewhat subjective. Please note that amperometric sensors for dissolved gases are not generally covered. Previous reviews are also available and general overviews on amperometric gas sensors have been presented by Stetter and coworkers [1,2] while Bontempelli et al. [3], Alber et al. [4] and Opekar and Štulík [5,6] have focussed on solid state devices.

## 2. Sensor configurations

Amperometric sensors are based on electrochemical cells consisting of a working electrode and counter and reference electrodes which are in connection through an electrolyte phase. This electrolyte phase has to carry the cell current by enabling the transport of charge carriers in form of ions and often has to provide co-reactants (usually water, protons or hydroxide ions) to the electrode as well as to allow the removal of ionic products from the reaction site. Note, that counter and reference electrodes may be combined into a single electrode for non-critical applications. For gas sensors the main challenge lies in the creation of a working electrode which is accessible for the sample gas, while still being in contact with the usually liquid internal electrolyte solution. Either, the gas must become dissolved in the electrolyte solution before coming in contact with the electrode, or so-called triple points are required where the gas, liquid and the solid electrode phases meet.

The development of amperometric gas sensors can be traced back to the introduction of the Clark-electrode in the mid-1950s [7], which is well known for the determination of dissolved oxygen. As shown in Fig. 1, it consists of a compartment filled with electrolyte solution incorporating a working electrode and a second electrode serving as counter and reference. The electrochemical cell is separated from the sample by a gas-permeable membrane which is pressed against a flat electrode leaving only a thin layer of electrolyte solution between electrode and membrane. The membrane has the important role of eliminating the interference of redox-active substances other than oxygen which might be present in the sample and the prevention of fouling of the working electrode. Prior to the introduction of this arrangement dissolved oxygen was measured with electrodes immersed directly in the sample solution (this can also be done with a dropping mercury electrode as used in polarography). These days bare electrodes are only rarely used, an exception is the determination of oxygen in sewage with electrodes which are regularly abraded mechanically for cleaning. Membranes are not suitable for this matrix. The membrane also allows the internal use of a high concentration of an electrolyte in the electrochemical cell without having to modify the sample itself, thus eliminating errors due to the i·R-drop which would otherwise be present. Chloride ions in the electrolyte solution are involved in the counter electrode mechanism and also establish a constant reference potential. The analyte has to diffuse through the membrane, in order to become dissolved in the internal electrolyte solution, and then to the working electrode. Modern Clark electrodes are fitted with a porous poly(tetrafluoroethylene) (PTFE)-membrane. Due to the hydrophobicity of the material the pores (typical diameter 10 μm) are not wetted but allow the transport of dissolved gases. As the mass-transfer rate of the analyte is slow, the Faradaic current is controlled by diffusion rather than the kinetics of the electrode reaction and this assures a linear dependence of the current on concentration of the dissolved oxygen. The layer of electrolyte solution between membrane and electrode is kept thin in order not to compromise sensitivity and response time.

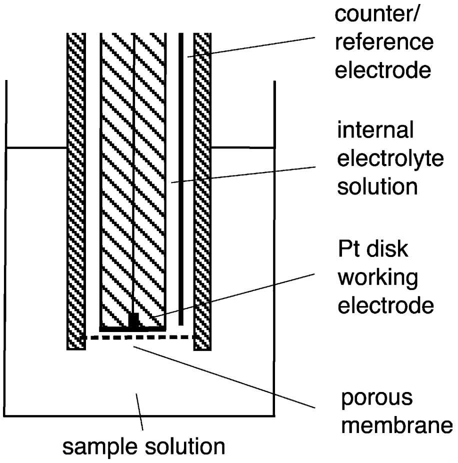

Fig. 1. Schematic drawing for a Clark-type sensor for the determination of dissolved gaseous species.

The arrangement is also used for the measurement of other dissolved electroactive gases, most notably for the determi-