H. PORTABLE ELECTROCHEMICAL SENSOR METHODS
by W. J. Woodfin, NIOSH/DPSE

Contents: Page

1. INTRODUCTION

Portable electrochemical sensor methods include instruments employing this technology in the determination of oxygen and several toxic gases in the field, using battery-supplied power. They range in size from those small enough to fit into a shirt pocket and weighing less than one pound (0.45 kg) to larger units that weigh as much as six pounds (2.7 kg).

2. PRINCIPLES OF OPERATION

The basis for all electrochemical sensors is the use of a porous membrane (normally PTFE) or capillary system which allows the gas to diffuse into the cell containing the liquid or gel electrolyte and the electrodes (Figure 1). The exact configuration will vary with manufacturers and between different toxic gases. When the gas comes into contact with the electrolyte, a change in electrochemical potential between the electrodes is produced. Associated electronic circuitry then will measure, amplify, and control this electronic signal. Because the reaction is proportional to the concentration (partial pressure) of gas present, the signal is easily translated into parts per million, percent, or ppm-hrs, and read on the readout meter or stored in microprocessor circuits for later readout.

3. SAMPLING CONSIDERATIONS

a. Safety

Some portable electrochemical monitors have been designed for intrinsic safety, i.e., for use in potentially explosive atmospheres. Check with the manufacturer to ensure that a specific instrument meets the appropriate intrinsic safety requirements (e.g., Underwriter's Laboratory or Mine Safety and Health Administration).

b. Applications

Electrochemical sensors are available for, e.g., SO_2, H_2S, NO_2, $COCl_2$, CO and O_2 [1,2,3]. Except for O_2, the widest application for electrochemical sensors has been as alarm/dosimeter systems rather than as continuous monitors. Because of the low power requirements and small size, the electrochemical sensor is ideally suited for use in combination monitors, that is, those that are able to monitor two or more substances at once. Many combination monitors are available, including in one package the sensors for oxygen deficiency, combustible gas, and toxic gas. The oxygen and toxic gas sensors are usually electrochemical. Electrochemical sensors may be located several meters away from the electronics/readout unit in order to facilitate remote or pre-entry monitoring.

Because of the low power requirements of these devices, it is possible for them to be used in lightweight, personal monitor/alarm devices. Electrochemical sensors for oxygen deficiency, H_2S, HCN, and others have been designed into monitor/dosimeter/alarm packages that are small enough to fit into a shirt pocket, that weigh less than one pound (0.45 kg) and that operate continuously for as long as four months without changing the replaceable battery. Also, because of the low power required, it is relatively easy to design them to be intrinsically safe.

c. Environmental Conditions

The environmental conditions (temperature, relative humidity, barometric pressure) of the monitor at the time of calibration should be as near as possible to those that will be encountered during use. Of these three, temperature is most important because changes in temperature are most often encountered in the field and can cause bias in the readings obtained. Even with the temperature compensating circuitry employed in most sensors, some time is required for equilibrium to be reached. If it is not possible to calibrate at the working temperature, the user must allow sufficient time for field equilibration of temperature. Changes in barometric pressure are usually less significant than temperature changes and so are of less concern to the user. Oxygen monitors with pressure compensating circuitry should be employed whenever pressures differing by 5 kPa (0.05 atmosphere) or more from the calibration pressure [1,4] are encountered.

4. DATA ACQUISITION AND TREATMENT

a. Calibration

The most simple example of field calibration of an electrochemical sensor is the oxygen monitor which may be calibrated by placing it in fresh (outdoor) air and adjusting the calibration potentiometer to make the readout meter read 20.9% O_2. To determine if it responds to oxygen deficiency, hold the breath for a few seconds, then slowly exhale, directing the exhaled breath to the sensor. If it is functioning properly, the meter will deflect downscale and the alarm circuit will be activated.

For electrochemical sensors used to monitor other chemicals (e.g. H_2S, CO, NO_2, SO_2), stable cylinders of calibration gases in the concentration range of interest as well as other, less convenient chemical generation systems (e.g., permeation tubes) may be used for calibration. These sensors may also be zeroed in fresh air or zero air from a compressed gas cylinder or clean air prepared by filtration. The frequency of calibration cannot be prescribed exactly, but a good rule is to calibrate at least once a day at the start of a shift. Manufacturers instructions or user experience may dictate more frequent calibration.

Always carry out the calibration procedure for toxic gases in a well-ventilated area, preferably in a fume hood if one is available. Make sure that the calibration procedure itself does not pressurize the sensing cell. This is especially important to observe when pressurized cylinders of standard gases are used for calibration. Overpressurization of the sensor can be avoided by using a pressure regulator on the calibration gas cylinder or by installing a "tee" fitting in the line to reduce the stream to atmospheric pressure. Another method is to fill a bag with gas from the cylinder so that it can be presented to the sensor at atmospheric pressure from the bag. Sensors should be replaced when they can no longer be calibrated or zeroed easily during the routine calibration procedure.

b. <u>Sampling and Measurement Procedure</u>

(1) Toxic Gases

Electrochemical sensors used for toxic gases are normally used as dosimeter/alarms, which means that the electronic circuitry provides a time weighted average (TWA) but not necessarily a continuous readout of the concentration. The alarm circuit is designed to activate whenever the preselected value is reached or exceeded for a predetermined time (or number of counts). On some systems, the TWA value may be obtained from the systems' microprocessor at the end of the shift by attaching it to an accessory printer or plotter designed to display this information. Some units provide a display of the current TWA which can be updated periodically or at the user's command.

(2) Oxygen

Oxygen electrochemical sensors provide either a continuous or on demand display of the present percent oxygen in the atmosphere, and the alarm circuitry is designed to activate at the moment the concentration drops to 19.5% O_2. Some models, designed to be used in hospitals or as area monitors, have both upper and lower alarm levels so that oxygen-enriched atmospheres may also be monitored. Many of these models have output suitable for a strip chart recorder so that a permanent record of the oxygen in the atmosphere may be maintained. The output of these devices is in % O_2. Method 6601 gives a recommended procedure for the use of oxygen monitors.

c. Limits of Performance

(1) Temperature Limits

Most manufacturers of electrochemical sensors specify the lower temperature limits, usually 32 to 50 F (0 to 10 C), and upper limits, typically 120 to 140 F (50 to 60 C). These do not present a problem for most applications, but the user should be aware that lower temperatures tend to result in longer response times. When used outdoors in cold climates, ambient temperatures should be monitored to assure that the lower limits are not exceeded.

Since many electrochemical sensors are battery-operated, it should be noted that temperature extremes can adversely affect the performance or life of the batteries used in these devices [5,6].

(2) Interferences

Electrochemical sensors designed to measure toxic gases may be non-specific (i.e., cross-sensitive to other compounds). Response specificity is determined by the semi-permeable membrane selected, the electrode material, and the retarding potential (the potential used to retard the reaction of species other than the analyte). Filtering or pre-scrubbing of the sampled atmosphere is also an effective method that has been employed by some manufacturers for some applications. However, not all interferences have been eliminated.

5. MANUFACTURERS

Manufacturers of electrochemical sensors are too numerous to list. For example, there are at least 16 companies that manufacture oxygen monitors with electrochemical sensors. Consult current publications in the field of industrial hygiene and safety for manufacturers of specific sensors [7,8].

6. REFERENCES

[1] Woodfin, W. J. and M. L. Woebkenberg. An Evaluation Of Portable Direct-Reading Oxygen Deficiency Monitors, (NIOSH, unpublished, 1984).
[2] Air Sampling Instruments, 7th ed., Ch. V, ACGIH, Cincinnati, OH (1989).
[3] Methods of Air Sampling and Analysis, 2nd ed., Morris Katz, Ph.D., Editor, Library of Congress No. 77-6826, American Public Health Association (1977).
[4] NIOSH Criteria for a Recommended Standard...Working in Confined Spaces, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 80-106 (1979).
[5] Parker, C. D., et al. An Evaluation of Personal Sampling Pumps in Sub-Zero Temperatures, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-117 (1978).
[6] Evaluation of Rechargeable Batteries Used in Industrial Hygiene Equipment, Final NIOSH Contract Report No. 210-78-0090 (1980).
[7] American Laboratory 1993 Buyers Guide, Am. Lab., 25(5) (February 28, 1993).
[8] Pollution Equipment News 1993 Catalog and Buyers Guide, Rimbach Publishing, Inc., 25(6) (November, 1992).

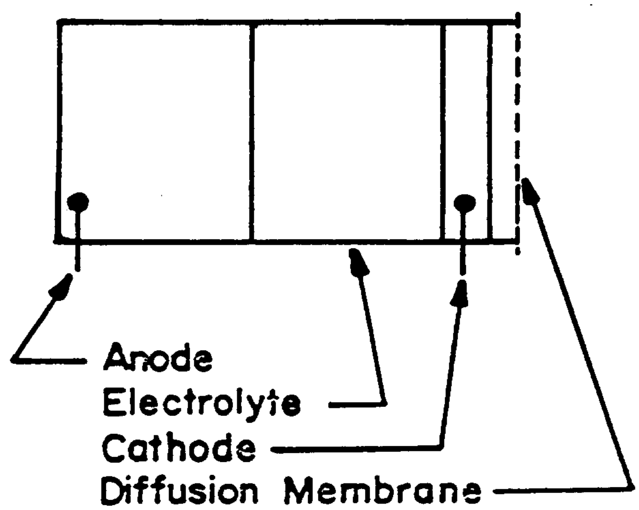

Figure 1. Electrochemical cell schematic.