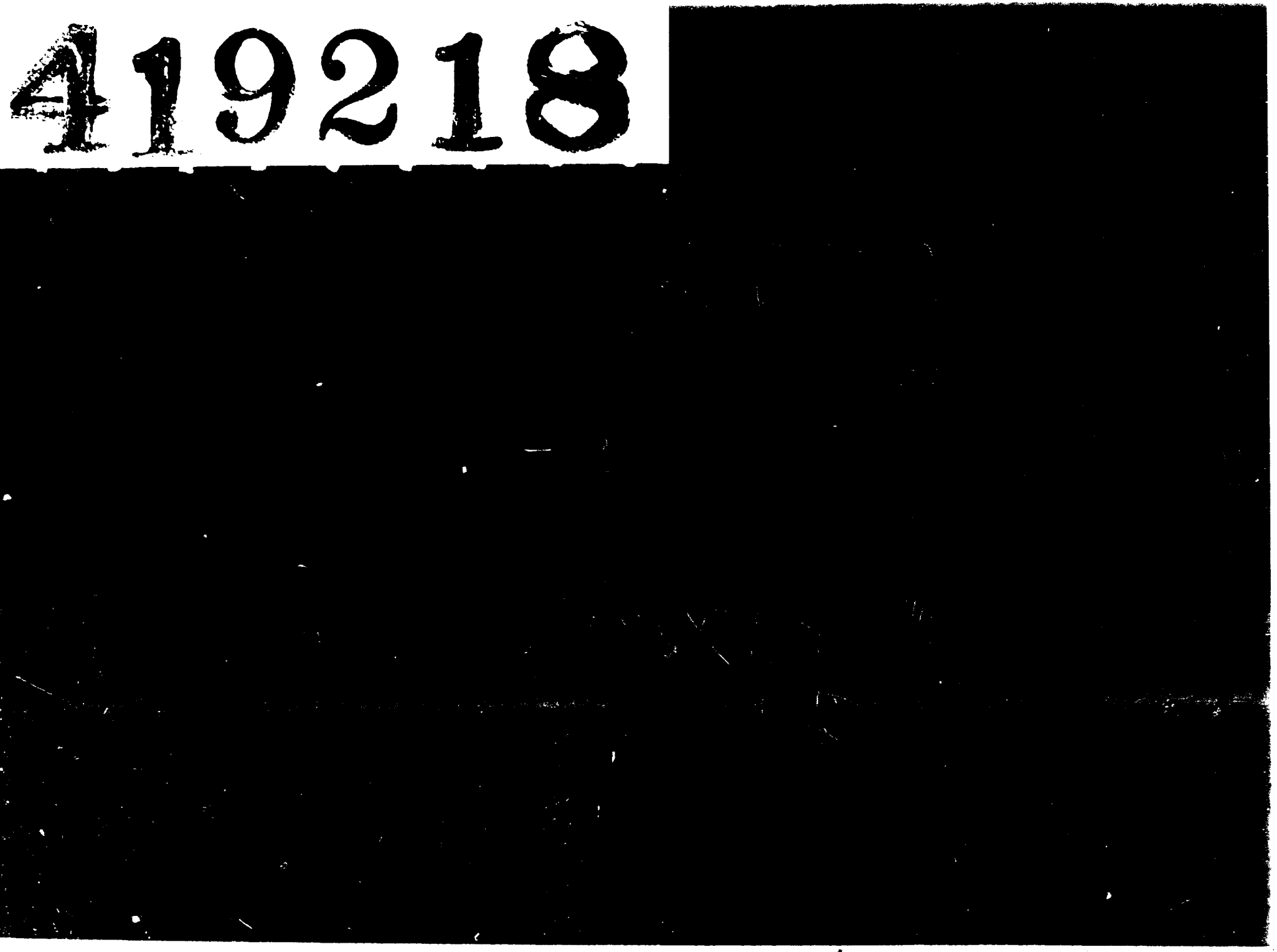

PHYSICAL TRANSDUCERS FOR SENSING OXYGEN

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INTRODUCTION

Among the continuing needs that man has for food, water, and oxygen, his need for oxygen is the most critical. He can go without food for many days and without water for several days, but without oxygen for only a few minutes he suffers irreversible damage or death. Man has no large internal stores of oxygen. If he is deprived of a source of oxygen, the oxygen in his tissues, his blood, and his lungs will be used up within eight minutes at rest and in a lesser time if he is active.

Not only is oxygen lack, or hypoxia, dangerous to man; hyperoxia, or excess oxygen, is also a dangerous condition that can lead to oxygen poisoning and to death.

Man must then live in an atmosphere where neither too little nor too much oxygen is provided. Figure 1 shows the range of oxygen pressure favorable to his subsistence.

Since an adequate amount of oxygen is usually obtained from the air which he breathes, man is not consciously aware of his need. There are special situations, however, where conditions require the control of respired gases to give the proper range of oxygen tension.

High-altitude aviation and operations in mines, submarines, and aerospace sealed cabins are examples of these special situations. In high-altitude operations, where the ambient air does not have sufficient oxygen pressure to support man, the interior of the

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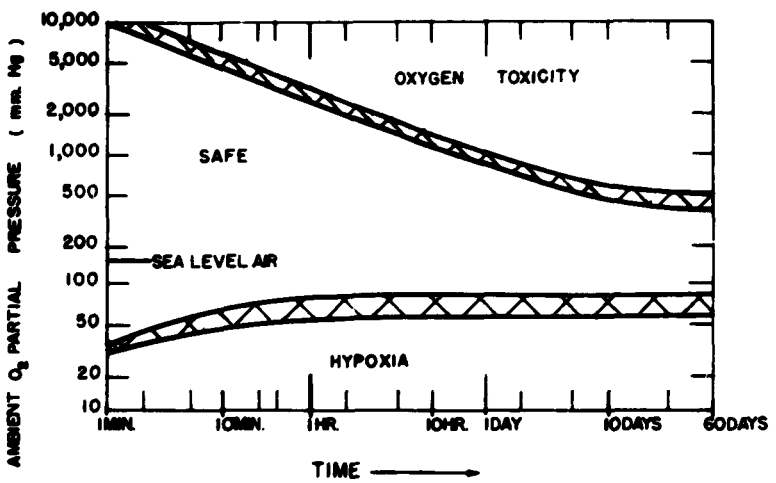

FIGURE 1

Human tolerance to oxygen.

aircraft may be pressurized to supply him with a sufficient pressure of oxygen; or each occupant of the aircraft may be equipped with a respiratory device through which he receives adequate oxygen. In mining operations, the oxygen pressure is usually adequate; however, pockets of gas may develop which are deficient in oxygen, and the miners must then be supplied fresh air by mask in order to live. In the sealed-cabin operations of submarines and aerospace vehicles, an atmosphere with adequate oxygen must be continuously provided from controlled sources.

Ideally, men who venture into these special situations should be provided with sensors to make certain that the gaseous environment is adequate. Especially for oxygen is it imperative to have a transducer to continuously perform this monitoring task.

A transducer usually converts some physiologic data to an electrical signal which can then be passed on to an amplifier and a recorder. As for other physical transducers, a transducer for sensing oxygen should be specific and accurate, have a rapid response time, a wide range of detection, and a long operating life, and be reliable. Since the situations where the oxygen transducer may be most needed are frequently hazardous and often confined spatially, the oxygen transducer should be continuous, automatic, small, light in weight, and easy to calibrate and operate for long periods of time.

METHODS FOR DETECTING OXYGEN

Let us consider some methods for detecting oxygen and see if these can reasonably be expected to meet the requirements of an oxygen transducer. For accuracy, the classical methods of Haldane (1) and Van Slyke and Neill (2) are extremely good. However, these methods require bulky equipment and skilled technical personnel to perform the determinations and are, hence, not suitable for continuous oxygen monitoring. The micromethod of Scholander (3), which can use a minute sample for analysis, also requires trained personnel for oxygen determinations and is not generally adaptable for use as a transducer.

The requirements for small size and continuous operation can be met in the oximeter (4), but it measures oxygen by an indirect method—namely, by the indirect measurement of the oxygen saturation of hemoglobin. It is difficult to calibrate and, during use, it must be attached to living tissue.

Other technics which might be considered for oxygen analysis are the paramagnetic oxygen analyzer (5), the mass spectrometer (6), the gas chromatograph (7), and the oxygen electrode (8).

These analyzers, with proper calibration and in good hands, are very satisfactory for most laboratory applications. The paramagnetic oxygen analyzer is too large for use as a transducer in cramped quarters. There is work in progress to reduce the size of the mass spectrometer and the gas chromatograph (9) for use as continuous gas monitors, but these efforts have not yet produced devices suitable for oxygen sensing in the special environmental situations mentioned above.

A continuous oxygen analyzer based on polarography or electrochemical principles was developed at the USAF School of Aerospace Medicine (10, 11). Because it shows great promise of fulfilling the requirements of a continuous oxygen transducer, it will be described in detail.

THE USAF SAM ELECTROCHEMICAL DEVICE FOR MEASURING OXYGEN

The device is basically a simple polarographic unit that requires no applied polarizing voltage, and its operation is feasible throughout wide ranges in environmental conditions because the electrolyte is completely encapsulated along with the electrodes. Its design involves the use of suitable electrodes placed in an insulated electrode housing. An electrolyte is added and a gas-permeable membrane applied so as to encapsulate the electrodes and fluid after degassing procedures have been carried out. A protective cover holds the membrane in place and prevents its displacement or rupture by rough handling. The device can be used in safety equipment and warning devices such as those required in aerospace operations, submarine operations, and mining, as well as for breath-by-breath monitoring in anesthesiology and tests of pulmonary function.

PHYSICAL DESCRIPTION OF THE DEVICE

Electrodes

Gold is used as the indicator or polarizable electrode. Gold gives a wide, flat plateau on the current-voltage curve or polarogram of oxygen.

The reference electrode is made of cadmium. The use of cadmium makes possible the elimination of the polarizing voltage in the determination of oxygen. With the use of cadmium, there is spontaneous electrochemical reduction of oxygen on the gold electrode when the external circuit is closed. The reference voltage given by cadmium is maintained reasonably constant for long periods. Slight changes in the reference voltage cause no adverse effects on the operation of the cell.

At the gold indicator electrode, the following reaction takes place:

$$O_2 + 4e + 2H_2O \rightarrow 4OH^-$$

At the reference cadmium anode, the following reaction probably takes place:

$$2Cd + 4OH^- \rightarrow 2CdO + 2H_2O + 4e$$

The overall cell reaction can be written as:

$$2Cd + O_2 \rightarrow 2CdO.$$

Consequently, the electrolyte solution is not depleted and does not limit the useful life of the device.

Materials

Nylon has been used to construct the electrode housing as well as other parts of the device. Nylon machines and molds well; it is highly resistant to cracking or shattering on impact and is resistant to chemical attack.

Polyethylene film of about 1 mil (0.001 inch) thickness has been used as a membrane to encapsulate the device. It prevents any detectable evaporation of water over long periods of time while permitting rapid diffusion of oxygen to the gold electrode. The technician applies the membrane by stretching it fairly tightly over the top of the electrode housing and pressing away excess fluid with the fingers. This leaves a tight membrane which retains its shape for long periods, thus preventing changes in the diffusion layer between gold electrode and ambient gas.

The electrolyte most often used is potassium chloride; sodium chloride works just as well. The electrolyte concentration is not a critical factor in most applications.

Size and configuration

The device most commonly used is a cylinder about 3½ cm. in diameter and 2½ cm. deep. Its weight is about 40 grams. Figure 2 shows three assembled cells. The gold electrode is flush with the upper surface of the electrode housing and directly beneath the polyethylene membrane, allowing a minimum diffusion pathway between the gas phase and the surface of the gold electrode.

The dimensions of the device can be varied within comparatively wide limits, but as a rule smaller units are more difficult to construct and assemble.

FIGURE 2

Oxygen sensors. The one on the left shows the circular gold electrode in its housing.

The current that one obtains from a given oxygen pressure is directly proportional to the active area of the gold electrode. This relation may have an upward limit, but it holds well below 0.05 square inch, the largest gold electrode that has been tried. The reference electrode requires a larger active area than the indicator electrode to insure that the former does not polarize. A ratio of the area of the cadmium to the gold electrode of 40 to 1 will give consistently reliable results.

FUNCTIONAL CHARACTERISTICS

Sensitivity

The electrical output of the device depends on the area of the gold electrode exposed to the electrochemical action of oxygen. The normally used units produce about 2.5×10^{-8} amperes per 1 mm. Hg of oxygen. When a temperature-compensating thermistor of about 10,000 ohms is used at 25° C., the output will be about 40 mv. for air at sea level. The uncompensated unit is sensitive to temperature changes, having a coefficient of about 4 or 5% for each degree centigrade. This change can be effectively compensated with appropriate thermistors.

Specificity

Of the gases encountered in normal breathing mixtures, the device is highly specific for oxygen. Artifacts due to shock, vibration, or gravity are usually minor or transitory.

Accuracy

As the device must be calibrated; the accuracy obtained is related to the stability achieved during a given time interval. Any factor which changes the diffusion coefficient, diffusion path, or the voltage of the electrodes can influence the stability. A low, constant zero-oxygen current, good linearity, and a relatively fast response time all favorably influence the ease with which calibrations can be performed and, hence, the ability with which a given

level of accuracy can be achieved. Readings obtained during unattended long-term monitoring procedures can be accurate to within ± 5 %, and short-term, frequently calibrated runs can approach accuracies of ± 1 %.

Calibration

The device has extremely good linearity within oxygen pressures under 1 atmosphere. The zero-oxygen current is quite small and usually does not exceed 1 mm. Hg of oxygen. Therefore, in many cases, a single check of the output on air, or other known gas, is all that is required for calibration.

Range

The usual range in which the device functions with linear output is between 0 mm. Hg of oxygen and 1 atmosphere of oxygen.

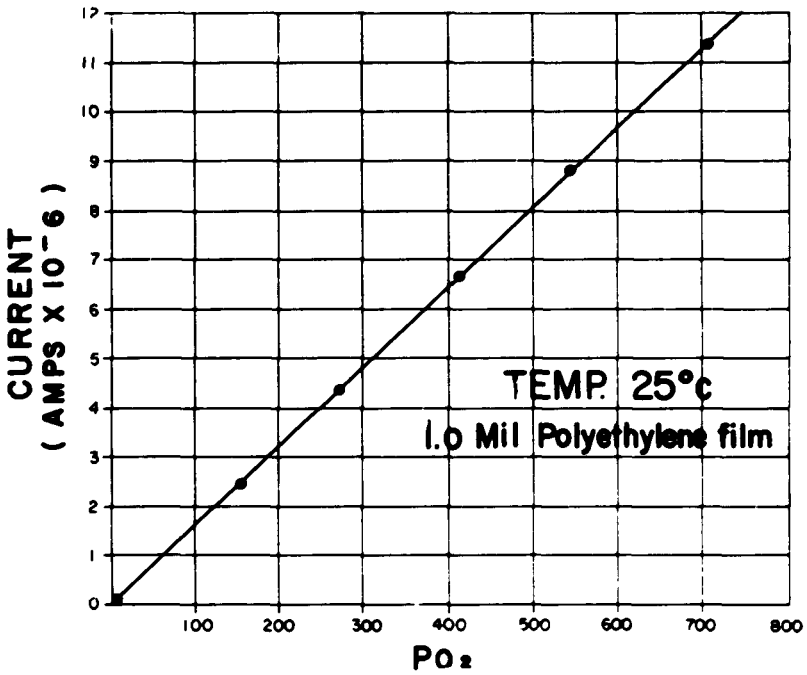

FIGURE 3

Electrical output of device with different oxygen pressures.

Since the signal-to-noise ratio can be made relatively large, rather narrow ranges can also be monitored under suitable conditions. Figure 3 shows a typical graph relating current to oxygen partial pressure between 0 and 750 mm. Hg oxygen tension.

Response time

The response time is influenced by the diffusion path between the gas phase and the gold electrode. These factors can be varied within certain limits. The fastest response times are not always compatible with certain other desirable characteristics such as shock and vibration resistance and general ruggedness. The time for 99% equilibrium varies between approximately 2 and 15 seconds, depending on membrane thickness and temperature. Figure 4 shows typical plots of the equilibration pattern.

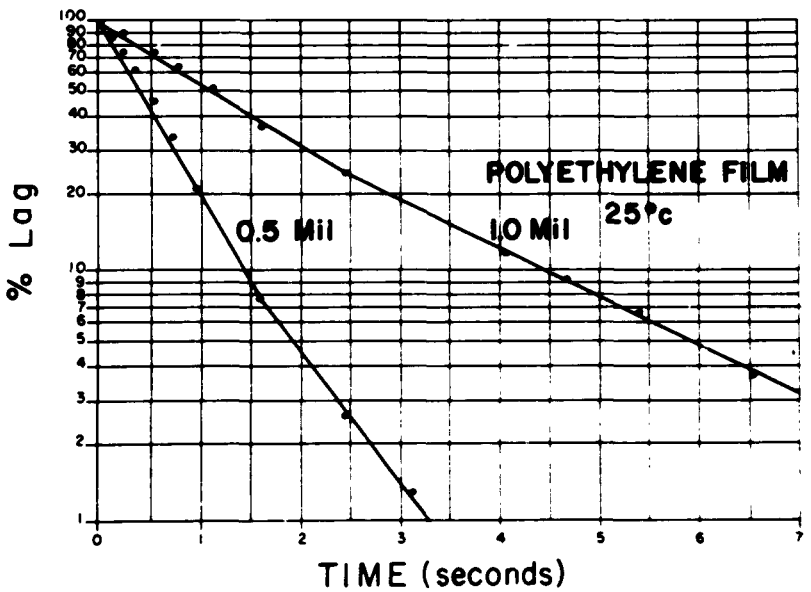

FIGURE 4

Response time of oxygen sensor.

Operating time

The operation of the cell involves only the chemical change of the cadmium electrode to cadmium oxide and the disappearance of an extremely small amount of oxygen from the sample being measured.

If the current given by 150 mm. Hg oxygen partial pressure is taken as being average, then 14.4 coulombs of electricity will flow for each 1,000 hours of use. This is equivalent to the conversion of approximately 8.4 mg. of cadmium and 1.2 mg. of oxygen (0.84 cc., STPD). The mass of the anode will normally be several grams and will not be a limiting factor in regard to operating time. The small amount of oxygen used will also be of no consequence. Theoretically then, the device should have a chemical lifetime in excess of 1,000,000 hours. However, changes in the physical characteristics of the cell require that servicing be performed sooner than this. The most critical factor affecting the lifetime of the device is the gold electrode, both its seal to the surrounding insulating material and its dimensional relation to the membrane. A lasting seal and dimensional stability of the insulating materials so as to keep intact the close spatial relationships between the surface of the electrode and the membrane most favorably influence the service-free lifetime of the device. In numerous tests of practicability, three to six months appears to be a reasonable expectation for the lifetime of the device before servicing is required. When evidence of deterioration occurs, either from decreased output or slowed response time, the difficulty is usually always remedied by repositioning the gold electrode or replacing the membrane.

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