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**AN ELECTROCHEMICAL DEVICE FOR
MEASURING OXYGEN**

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**SCHOOL OF AEROSPACE MEDICINE
USAF AEROSPACE MEDICAL CENTER (ATC)
BROOKS AIR FORCE BASE, TEXAS**

AN ELECTROCHEMICAL DEVICE FOR MEASURING OXYGEN

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61-79

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INTRODUCTION

In recent years many practical applications have been made of the ability to detect and measure oxygen by electrochemical means. Basically, the bulk of this effort has been adapted from the technic of polarography as introduced by Heyrovsky (1) in 1922. The unique advantages of this technic for chemical analysis have been widely recognized, and these advantages are especially striking in the case of oxygen, as shown by several early investigations (2, 3) utilizing the dropping mercury electrode.

In attempting to apply the polarographic method to a broader range of problems in which the measurement of oxygen was of interest, the dropping mercury electrode proved in many cases to be somewhat cumbersome if not completely impractical. Thus Blinks and Skow (4) in 1938 utilized a solid platinum electrode in place of the dropping mercury electrode to measure the time course of oxygen tension changes during photosynthesis. They were able, by this means, to chart the rather rapid changes in oxygen concentration which occur on illumination of chlorophyll-containing green plants. A number of investigators have improvised on this particular technic (5, 6). Whereas the solid electrode permitted procedures impossible with the dropping mercury electrode, it was not so stable nor were the results as reproducible as with the latter. This was due primarily to the obvious inability to continuously renew the electrode surface, as with the dropping mercury electrode, and due also to the less well-defined diffusion barrier produced around the solid electrode.

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A number of technics have been utilized to circumvent the disadvantages of solid electrodes. Laitinen and Kolthoff (7) studied diffusion at electrodes of various shapes and explained the diffusion processes and the geometric considerations involved. The same investigators (8) showed the advantage of a rotated electrode over a stationary one. Davies and Brink (9) experimented with the recessed electrode. They also first reported on the promising method of covering the electrode with a semipermeable membrane. Olson et al. (10) applied alternating potentials to the electrode and reported that this was of advantage in measuring oxygen. In 1954 Stow and Randall (11) reported on an electrochemical cell for measuring carbon dioxide in which both the measuring and the reference electrodes were completely separated from the composition being measured. Later, this design was applied to the measurement of oxygen in blood by Clark (12). An encapsulated pressure-insensitive unit for measuring oxygen has been described by Neville (13). More recently, Kreuzer (14) has described a fast-responding, catheter-type electrode system for oxygen which can be inserted into the pulmonary passages.

The present paper describes an electrochemical device for measuring oxygen which is basically a simple polarographic unit, but has, at the same time, certain details and characteristics which it may be worthwhile to report at this time. The device was designed primarily to measure oxygen in gases rather than in liquids, and this design has allowed applications under many adverse field conditions over relatively long periods of time. Essentially, the design involves the use of

suitable electrodes placed in an insulated electrode housing. An electrolyte is added and a gas-permeable membrane applied in such a manner as to encapsulate the electrodes and fluid after suitable degassing procedures have been carried out. An additional feature is a protective cover which holds the membrane in place and prevents its displacement or rupture through rough handling.

PHYSICAL DESCRIPTION OF THE CELL

Electrodes

The indicator or polarizable electrode of solid metal polarographic assemblies has generally been constructed of platinum; however, Kolthoff and Jordan (15), in a report on the use of both platinum and gold for the measurement of oxygen, state that gold is generally superior for this purpose. Initial experiments with both platinum and gold indicated that for long-term use in a device of the kind envisioned, gold is definitely more stable and gives more reproducible results than platinum. It gives a wide, flat plateau on running the current-voltage curve or polarogram of oxygen, indicating as Jordan and Kolthoff had found, a relatively large hydrogen overvoltage.

Silver-silver chloride, mercury, and calomel are the most commonly used reference electrodes in polarographic work, and for many purposes they are excellently suited. Other possibilities present themselves, however, and one of these is described here. The electrode which was finally chosen for a reference—cadmium—made possible the elimination of the polarizing voltage in the determination of oxygen. In other words, such a reference electrode made possible the spontaneous electrochemical reduction of oxygen on the gold electrode when the external circuit was closed.

Normally, one applies approximately -0.5 volt vs. the SCE (saturated calomel electrode) in order to maintain solid inert indicator electrodes within the diffusion-controlled region of the polarogram of oxygen. If a suitable reference electrode could be chosen which was already approximately -0.5 volt vs. the SCE,

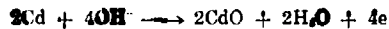
then the need for a polarizing voltage would be circumvented, at least in a device intended only to measure oxygen. The reference electrode for the device described here must, of course, be a solid at ordinary temperatures, and its anode film products should have both a low solubility and a low resistivity; it should preferably form the oxide of the metal rather than the salt of the anion in the electrolyte; it should, furthermore, produce a relatively stable potential for long periods of time. Finally, the material used should not be plated out at the cathode under the conditions required for reduction of oxygen.

Of the metals that were considered, three appeared most promising because of the position which they occupied in the electromotive series and the fact that they could be easily procured and worked with. These were iron, zinc, and cadmium. Iron, possibly because of autoxidation processes and the nature of the oxide films that are formed, was not stable enough for reference purposes. Zinc proved too reactive, actively "gassing" in the electrolyte solution and thus making it unsuitable for the sealed or encapsulated type of device that was required. Cadmium, on the other hand, proved very suitable for the purpose at hand. Not only did cadmium provide the proper voltage, making the reduction of oxygen proceed spontaneously when the external circuit of the cadmium-gold cell was closed, but it also maintained a voltage over a long period of time which was quite suitable for the present purpose. Furthermore, the predominant feature of the anode process appeared to be an oxide or hydroxide formation.

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



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



Therefore, the overall cell reaction can be depicted simply as:



Consequently, the electrolyte solution is not depleted and does not limit the useful life of the cell. The lifetime of the cell will be discussed later.

Figures 1 and 2 show cells of the type described. The cadmium ring electrode is visible in those which are dismantled. The gold electrode can also be seen in the center of the

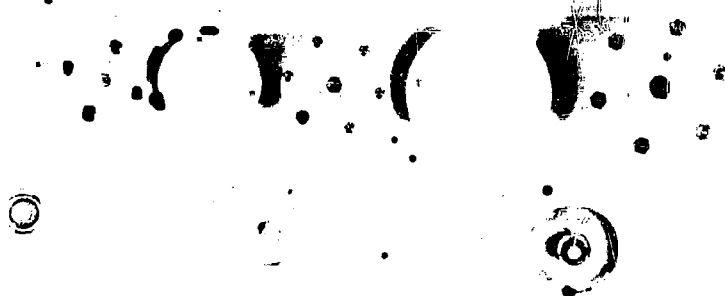


FIGURE 1
Unassembled cells.



FIGURE 2
Loaded cells (see text for size of largest unit).

electrode housing unit. The latter electrode is so fashioned as to be flush with the upper surface of the electrode housing. The gold will thus be directly beneath the membrane when the latter is applied, making a minimum diffusion pathway between the gas phase and the surface of the gold electrode.

Size

The physical dimensions of the cell can be varied within comparatively wide limits. Generally speaking, the smaller the unit, the more difficult it will be to construct, load, and make appropriate electrical connections. Also, the current obtained from a cell under a given set of circumstances will be directly proportional to the area of the gold electrode.

The area of the reference cadmium electrode should be larger than that for the gold electrode, and we have normally used an area ratio of at least 40 to 1 in order to insure a non-polarizing reference even with high oxygen partial pressures. A critical evaluation of this ratio in the present case has not been made; however, evidence of reference electrode polarization was obtained with an area ratio of about 5 to 1. A number of factors, such as total current and the geometry of the cell, would be expected to influence such polarization, but they have not been evaluated in relation to the present device. Practically, however, the 40 to 1 ratio appears to be satisfactory for most cases.

As shown in figures 1 and 2, most of the cells we have constructed were cylindrical, about $3\frac{1}{2}$ cm. in diameter and $2\frac{1}{2}$ cm. long. The weight of the usual unit, when fully loaded, was about 40 gm. Smaller units, weighing as little as 10 gm. have been used.

It has been mentioned that the unit requires no polarizing voltage, the reduction of oxygen proceeding spontaneously on closing the external circuit between the electrodes. This is, of course, convenient for general usage; it can also be an important feature for certain

¹Refers to the process of adding electrolyte fluid, degassing, sealing with a membrane, and applying the protective cover.

applications in the field, where weight, space, and power are at a premium, as in the instrumentation of space capsules. The fact that only a small amount of electrolyte is required also enhances the capabilities for miniaturization and long-term use of the device.

Insulating material

As an insulating material for housing the electrodes, a variety of materials can be used. Nylon has been found suitable for the purpose because it machines and molds well and presents no special aging problems as do some plastics. Nylon also is highly resistant to cracking or shattering on impact. When constant handling of the unit is required, such resistance is important since even slight cracks or leaks, especially around the electrodes, can be very detrimental to the function of the device. Nylon has the disadvantage, as do many plastics, of adsorbing water, swelling, and losing its original dimensions. The dimensions of the center gold electrode area are especially critical to the function of the cell, and proper treatment of the nylon as well as careful sealing of the gold electrode is extremely important. A leakproof, completely encapsulated cell is essential for successful long-term operation of the unit. This is especially true where operation at varying total pressures is required.

Membrane

The membrane used to encapsulate the device has two functions. It must prevent the evaporation of water (while allowing free diffusion of oxygen), and also it must form and retain a very thin layer of electrolyte solution above the gold electrode. Although a number of plastic membranes are suitable for this purpose, superior performance has always been obtained with polyethylene films of about 1 mil thickness or less. The membranes are stretched rather tightly over the top of the electrode housing and excess fluid is pressed away with the fingers in the loading process. This leaves a drum-tight membrane which forms an excellent barrier to the escape of water and also retains its shape for long periods of time, thus preventing changes in the dimensions of the

diffusion barrier between the gold electrode and the ambient gas. The permeability of polyethylene to oxygen is comparatively high and, when protected by the retaining cover as described above, the membrane will remain intact for long periods under fairly extreme working conditions.

Electrolyte

The electrolyte used has normally been potassium chloride, although sodium chloride works as well. The electrolyte concentration is not especially critical, but we are currently studying various additives in an attempt to extend the low temperature range of the unit. More will be said on temperature effects in the following section.

FUNCTIONAL CHARACTERISTICS

Some of the more usual functional characteristics which may be of interest here are discussed under the various headings below.

Response time

The response time will be influenced by the diffusion coefficient of oxygen through the media and by the thickness of the diffusion path between the gas phase and the gold electrode. These factors can be varied within certain limits, but it should be pointed out that the very fastest response times will not always be compatible with certain other desired characteristics, such as shock and vibration resistance, general ruggedness, and so on. Normally, units which have been made for field applications have a response time of 10 to 15 seconds for essentially complete equilibration. The use of very thin membranes (0.2 mil), together with elevated temperatures (40° C.), causes the cell to respond to a change in oxygen partial pressure in approximately 1 second. It will be noticed in figure 3, which shows typical response curves, that a large part of the change which occurs is concluded within a fraction of the above-cited response times.

Range

The usual range in which the unit functions with linear output is between zero and about

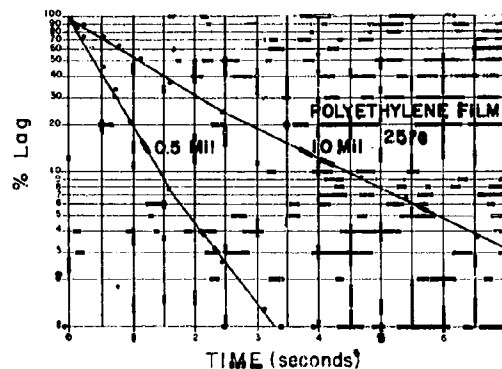


FIGURE 3

Response time of oxygen cell.

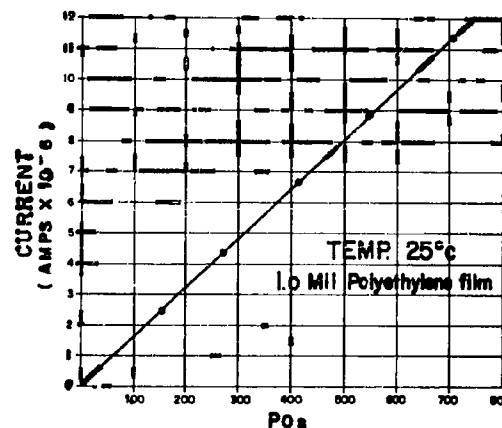


FIGURE 4

Range and output of oxygen cell.

1 atmosphere oxygen. Since the signal-to-noise ratio can be made comparatively large, rather narrow ranges can also be monitored under suitable conditions. Figure 4 shows a typical graph relating current to oxygen partial pressure between zero and about 745 mm. Hg.

Sensitivity

The output of the cell, other things being equal, will depend on the area of the gold electrode exposed to the electrochemical action of oxygen. The units we have used normally

produce about 2.5×10^{-8} amperes per mm. Hg oxygen. When a temperature-compensating thermistor of about 10,000 ohms is used at 25°C ., the output will be about 40 mv. on air at sea level. The uncompensated unit is rather sensitive to temperature, but appropriate thermistors give reasonably good compensation between 5° and 45°C . These limits can be exceeded, but such temperature ranges have not been thoroughly explored. Uncompensated, the cell output changes about 4 or 5 percent for each degree centigrade. This can be decreased tenfold or more with appropriate thermistors.

Accuracy

Although the device potentially has a comparatively high signal-to-noise ratio, expressions of accuracy will depend on a number of factors extrinsic to the function of the transducer itself; consequently, isolated figures intended to portray this characteristic often will not be too meaningful. It is fair to say, however, that readings obtained during unattended and long-term monitoring procedures can be accurate to within ± 5 percent, and short-term frequently calibrated runs can approach accuracies of ± 1 percent.

Calibration

Calibration of the device is simplified by the fact that the zero oxygen current is quite small, amounting usually to the equivalent of about 2 mm. Hg oxygen pressure or less, and also by the fact that the response is linear. Therefore, for many purposes, a single check of the output on air, or other known gas, is all that is required for calibration. Where more care is required, of course, calibration with several known gases in the range of interest is preferred.

Specificity

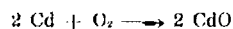
Of gases encountered in normal breathing mixtures, including carbon dioxide, the device is highly specific to oxygen. Water vapor does not affect the readings except so far as such

vapor pressure would normally be expected to influence the gas pressures.

When properly loaded, the device does not respond to changes in ambient pressure except as such pressure change will affect the oxygen pressure. In addition, artifacts due to shock, vibration, or gravity-loading are usually minor or transitory.

Operating time

Since the device is electrochemical in nature and since such devices characteristically have finite operating times, discussion of this factor is appropriate. As mentioned earlier the overall reaction of the cell may be represented as:



This indicates that the materials consumed in the process of utilizing the device are the cadmium anode and oxygen from the gas being sampled. 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 (0.34 cc., STPD). The mass of the anode will normally be several grams and consequently will obviously not be a limiting factor in regard to operating time. It is equally apparent that the small amount of oxygen that is consumed by the cell also will be of no consequence. It can be calculated that the device should have a theoretic chemical lifetime in excess of 1,000,000 hours. Unfortunately, it is found in practice that the cells will normally require servicing sooner than this. This requirement is related to the physical rather than chemical changes which occur in the cell. Experience with the device has indicated that the most critical factor affecting the lifetime of the unit 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 will most favorably

influence the service-free lifetime of the oxygen sensor described here. Some variability is found in the units we have built and tested, as might be expected, but three to six months, depending on the kind of treatment afforded the unit, now seems to be a reasonable expectation for the lifetime before servicing is required. When evidence of deterioration occurs, either from decreased output or slowed response time, the difficulty, without exception in my experience, is remedied by attention to the seal and the position of the gold electrode.

APPLICATIONS

In discussing applications of the device, I wish primarily to elaborate in some detail on the basic functional characteristics that have already been discussed. Most of the applications will be rather obvious, but the discussion

will possibly serve to emphasize those characteristics of the unit which may be used to advantage when oxygen analysis is indicated. It should be recalled that the device described here was designed primarily for use in the gas phase; consequently, the examples given below are all related to this particular problem.

Very convenient and time-saving application can be made of the device for simple routine oxygen analysis. A sample of only 1 or 2 cc. is required in washing out the sensory area, or the unit can be placed directly in a gas line or other system containing the gas to be analyzed.

The unit has been used to monitor cabin or capsule oxygen pressure in a number of Air Force projects in which the School of Aerospace Medicine has participated. Figure 5 shows a

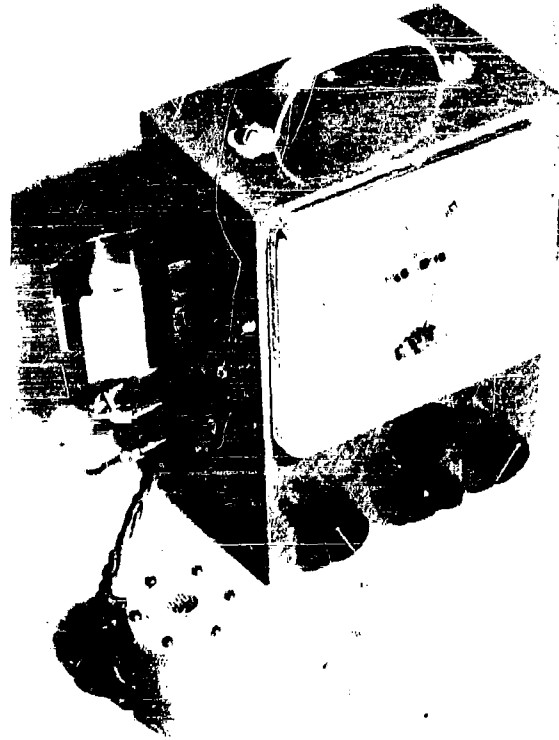


FIGURE 5

Portable unit for monitoring oxygen pressure.

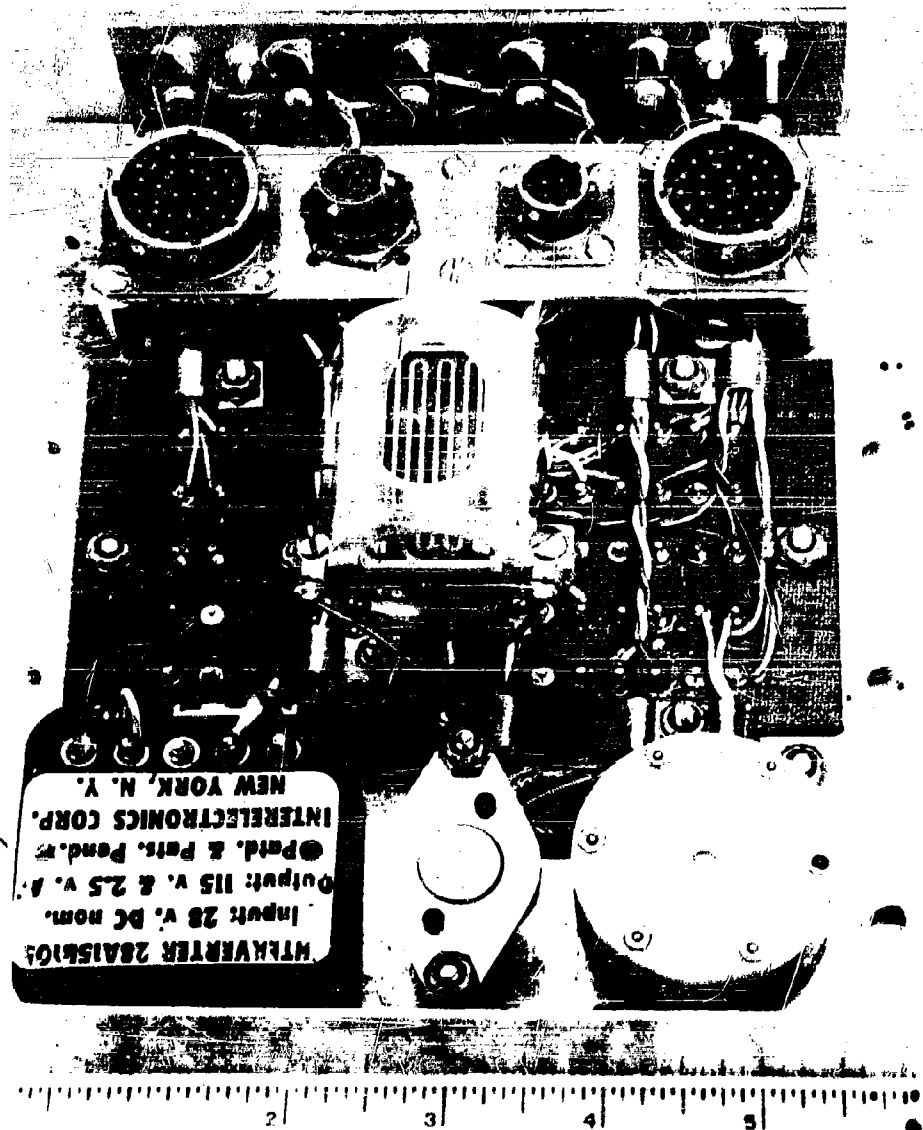


FIGURE 6

Environmental sensors used in the "Little Joe" biopack.

small portable unit which was used in the Man High balloon program. The amplifier in this case is completely transistorized and a direct meter readout is provided. Figure 6

shows the so-called "sensor deck," a compact grouping of environmental sensors used to monitor the capsule environment of what has been called the "Little Joe" biopack. The



FIGURE 7
Aircrew hypoxia warning device.

signal from the oxygen sensor was recorded on board. In later biopack experiments, the information from the sensors was telemetered. The Mercury capsule is scheduled to use a device similar to the one described here. In addition to a direct readout and telemetering of the signal, a provision will also be included to give a visual warning should the oxygen partial pressure drop below a predetermined value.

Figure 7 shows a unit designed at the School of Aerospace Medicine expressly for use as an aircrew hypoxia warning device. The unit can be installed in aircraft with a minimum of modification since it needs merely to be connected to a 400-cycle electrical system. It is completely safe in operation, presents no interfering electrical signals and has proved reliable in airborne tests with the F-100.

As indicated earlier, it is possible to obtain relatively fast response times by using thin

membranes and elevated temperatures. This presents the possibility of breath-by-breath recording of oxygen in respired gas. Figure 8 shows the typical breathing pattern given by

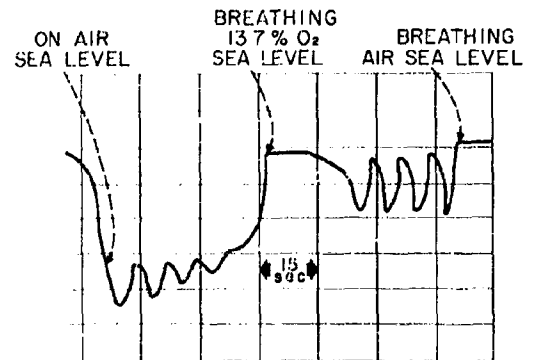


FIGURE 8

Breath-by-breath response recorded with cell in oxygen mask.

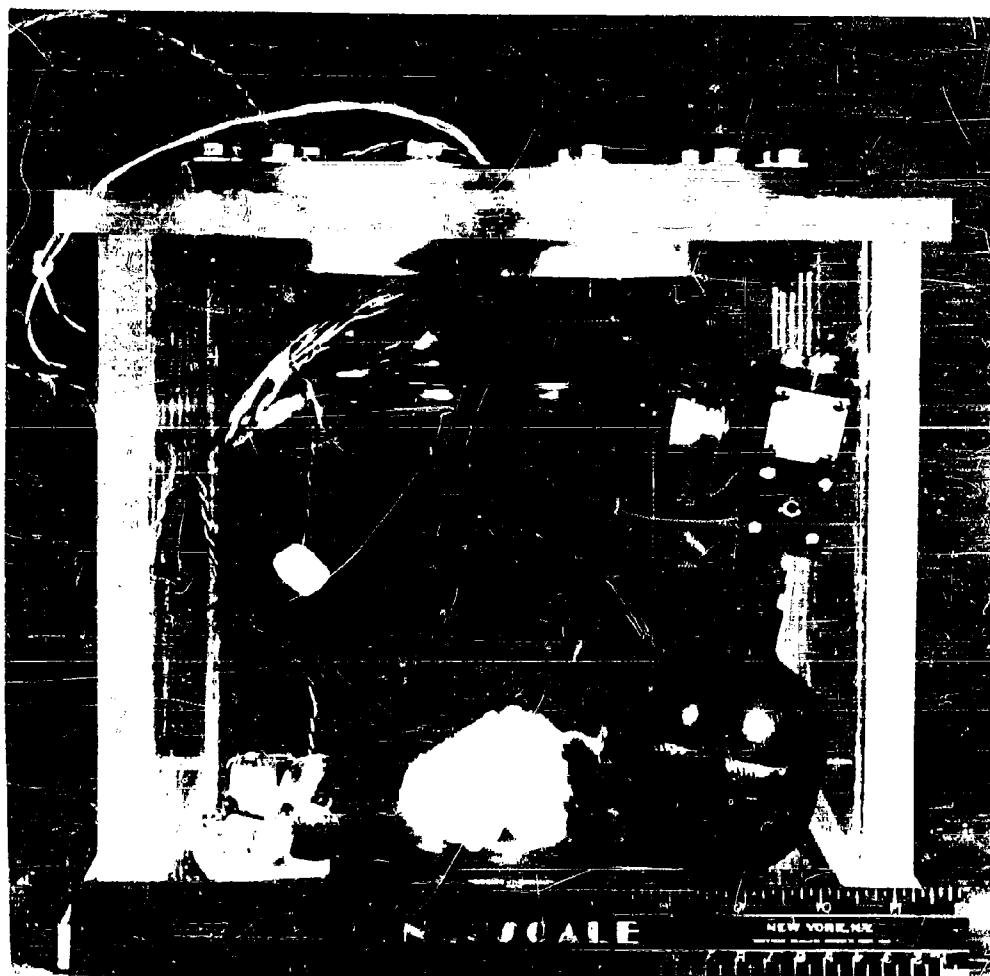


FIGURE 9

Use of the device in metabolic studies.

the cell when mounted in an oxygen mask. Although the unit displays some lag in response, it is faithful enough in this respect to suggest a number of possibilities with regard to the evaluation of pulmonary function.

Figure 9 demonstrates a type of application possible in the study of metabolism and oxygen consumption. More recently a unit was installed in a sealed tissue-culture flask and changes in oxygen tension were followed during

the growth of the culture. The possibilities of such "electrical Warburg" techniques are receiving attention in the author's laboratory at this time.

SUMMARY

An electrochemical device has been described which utilizes a gold indicator electrode and a cadmium reference. This cell, when

filled with electrolyte and encapsulated with a thin polyethylene membrane, gives a current proportional to the oxygen partial pressure in the ambient gas. Protected with a special plastic cover, the unit is relatively rugged,

specific, and fast response. It is suitable for power or potentiometric use. It has been attended for relatively long periods in the Laboratory, clinical, and field use. It has been illustrated and discussed in the literature.

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