CXLII. A SIMPLE GLASS ELECTRODE OF SMALL CAPACITY

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Numerous glass electrodes in which the electrode is a relatively long thin-walled tube have been described in the literature [McInnes & Belcher, 1933; Michaelis, 1936; Pickford, 1937; Dill *et al.* 1937], but all demand for their manufacture considerable skill in glass-blowing. The following is a description of one which has a capacity of 0.2 ml. or less, which requires no special skill in manufacture, and which can be used for measurements at temperatures higher than room temperature. In conjunction with a McFarlane-Pye valve potentiometer, it has been found to give excellent results on a variety of biological fluids, including blood.

The membrane itself consists of a capillary of Corning No. 015 glass about 6–9 in. long and bent to the shape shown in Fig. 1. After bending, the electrode is mounted in a split rubber cork of suitable dimensions to fit the mouth of a cylindrical histological staining tube. This is best done by cutting two small grooves in one or both halves of the cork to allow the capillary to be held without distorting the shape of the cork. A suitably sized hole should be bored in each half of the cork, one to admit the tip of a calomel half-cell and the other to carry a small thermometer. When the capillary is placed in position between the two halves of the cork a wire band around the cork will hold it securely and facilitate subsequent handling.

After mounting in its cork, the capillary is filled with some conducting solution, e.g. a buffer, and the whole assembly inserted into a staining tube previously waxed on its internal surface and filled with hydrofluoric acid. A fine platinum wire is inserted into the interior of the straight limb of the electrode and a second platinum wire dips into the surrounding acid. These wires are connected through a galvanometer and 10 megohm grid leak resistance to a 60 V. battery (Fig. 1). The grid leak acts as a protection to the galvanometer in case of a sudden puncture of the electrode.

On first setting up, the galvanometer reading indicates a resistance across the glass membrane of some 300 megohms, but as etching proceeds the galvanometer reading rises as the resistance falls and gives an excellent indication of how the etching is progressing. It has been found advisable to remove the electrode every minute or so and wash under a gentle stream of water. This renders the etching more uniform, presumably by removing adherent particles of fluorides. With care an electrode may be brought to as low a resistance as 10–20 megohms without puncturing, but, while it is desirable to get the resistance as low as possible, satisfactory results have been obtained with electrodes of resistances up to 50 megohms.

After etching, the electrode is removed from the hydrofluoric acid and immersed for at least 24 hr. in distilled water. The water may then be replaced by a solution of $N/10$ KCl in a phosphate buffer of pH 6.8.¹ This fluid is identical

¹ 0.47 g. Na_2HPO_4 + 0.45 g. KH_2PO_4 to 100 ml. $N/10$ KCl.

with that used in one of the half-cells; consequently when the electrode system is fitted up, as in Fig. 2A, there is no contact potential between this half-cell and

Fig. 1. Etching apparatus.

Fig. 2A. Side-view of electrode system with heated water-jacket.

Fig. 2B. End-view of electrode system with heated water-jacket (half-cells omitted).

the fluid on the outer side of the glass membrane. A thermometer is inserted in one of the holes in the rubber cork and the electrode is ready for use.

In use, the capillary is filled simply by dipping the bent end into the fluid whose *pH* is to be determined, when the fluid will run in by capillary attraction.

The electrode assembly is connected to the half-cells as shown in Fig. 2 A. As previously stated, the tip of one of these half-cells dips into the fluid surrounding the capillary. The other half-cell, which contains 3.5 *N* KCl, ends in a U-shaped tube of narrow bore whose open end widens into a cup. The bent end of the capillary is slightly immersed below the surface of the KCl in this cup and the only liquid junction is at this point. In spite of its apparently crude nature, potentials stable over 2–3 hr. to within 0.2 mV. are obtainable in determinations on buffer solutions.

When measurements at body temperature are desired, the electrode is supported by a rubber ring in a rectangular specimen jar of suitable size filled with water. A glass tube passes down each end of this jar and along its bottom. The external ends of this tube are connected by rubber tubing to a copper spiral immersed in a heated water bath situated well below the electrode table. Convection maintains a circulation of hot water and, by manual adjustment of the flame below the water bath, it is possible to maintain the temperature around the electrode with sufficient accuracy for most purposes. A thermo-regulating system can be fitted if desired. Electrical heating of the water around the electrode was tried but had to be abandoned owing to interference with the potentiometer.

Used in conjunction with a McFarlane-Pye potentiometer, the following results were obtained on a series of twelve buffer solutions, ranging with varying intervals between pH 3.88 (No. 1) and pH 9.19 (No. 12). The potential differences between each pair of adjacent buffers was measured once by hydrogen electrode, and once by each of three glass electrodes of the above pattern. All measurements were made at, or corrected to, 20.5°.

Buffer no.	ΔE by hydrogen electrode mV.	ΔE by glass electrode I mV.	ΔE by glass electrode II mV.	ΔE by glass electrode III mV.	Diff. ΔE hydrogen and mean ΔE all glass electrodes mV.	Diff. hydrogen and glass electrodes pH
1	96.5	95.9	96.1	96.3	-0.4	-0.007
2	18.1	18.0	18.1	18.3	0	0
3	18.2	18.5	18.3	18.0	+0.1	+0.002
4	15.0	15.0	15.0	15.1	0	0
5	12.1	12.2	12.3	12.1	+0.1	+0.002
6	13.0	13.0	12.7	13.1	-0.1	-0.002
7	17.0	17.4	17.5	17.5	+0.5	+0.009
8	26.8	27.2	27.3	27.2	+0.4	+0.007
9	32.6	32.6	32.5	32.7	0	0
10	36.5	37.3	37.0	36.9	+0.6	+0.010
11	19.0	18.5	17.8	17.7	-1.0	-0.017
12						

SUMMARY

A capillary glass electrode of extremely simple construction is described.

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