A GLASS ELECTRODE WITH A COPPER AUXILIARY ELECTRODE

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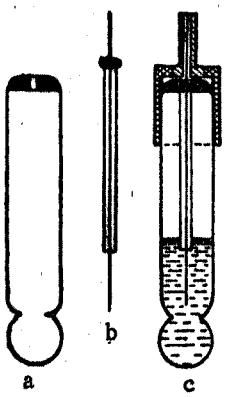
Silver and platinum are ordinarily used for the preparation of inner auxiliary electrodes.

We explored the possibility of using copper for inner electrodes.

The basic requirement for inner electrodes is that the potential jump at the electrode – solution interface remain constant, which is possible if the metal either does not dissolve or dissolves very slowly, i.e., when the concentration of the potential-determining ions remains practically constant. At the same time, another requirement is thereby satisfied, namely, the constancy of the solution acidity inside the electrode, and consequently, the constancy of the potential jump at the inner glass – solution interface. Since, in measuring the pH of solutions, both potential jumps are components of the emf, the degree of their constancy in time can be evaluated with respect to the change in the "zero point" of the glass electrode, i.e., with respect to the change in the pH of the solution in which the circuit emf is equal to zero.

In order to secure the constancy of potential jumps, the electrodes were filled with a 0.5 N copper sulfate solution acidified with sulfuric acid to a 0.2 N concentration. It is known that copper dissolves very slowly in sulfuric acid if acidifiers are not present. In preparing the electrodes, we were careful to remove oxygen from the electrodes and to secure a good airtightness in order to prevent the access of air.



Glass electrode with a copper auxiliary electrode.

The copper electrodes were made of standard 0.5 mm enameled copper wire of the type used in the radio industry for transformer windings. The wire was heated until it became red hot, after which it was sanded with fine emery paper and then dipped for a few seconds in a hot solution of nitric acid (1 : 2) and afterwards carefully rinsed in running water in order to remove the remnants of acid.

The figure shows the stages in preparing glass electrodes with copper auxiliary electrodes. The open end of a lithium-glass tube (a) which was provided with a bulb, was heated in flame until the thickness of the tube end part was 1-2 mm, and the opening diameter was 2.5-3.0 mm. The copper wire, which has been treated in the manner indicated above, was placed in a capillary (b) with an internal diameter of ~1 mm and an outside diameter of 2.5-3.0 mm. The capillary end was heated and shaped into a small bulb with a diameter somewhat larger than that of the tube opening. By means of the capillary, the electrode was approximately 1/3 filled with a solution of the indicated composition; the solution in the electrode was blown through with technical nitrogen in order to remove oxygen, after which an insert was provided and the electrode was sealed in it. The upper portion (4-5 cm) of tube a) was heated in burner flame almost to the softening point, after which the tube with the insert was intensively heated to the melting point. By this method of sealing, a slight rarefaction was secured inside the electrode, which prevented the bulging of tube walls usually observed in the sealing of closed volumes. An ebonite fitting with a pressed-in brass peg 3 mm in diameter and a channel for the copper wire was fixed on the electrode by means of the BF-2 paste.

The electrode characteristics of nine electrodes in this manner were plotted immediately after they were prepared and also after they have been stored in a 0.1 N solution of hydrochloric acid over periods of one and ten months. After their characteristics were plotted, electrodes 6-9 (see table) were kept in boiling distilled water over a period of 19 working days in order to accelerate the dissolution of the inner copper auxiliary electrode and, consequently, to secure the greatest change in the electrode "zero point". The electrode characteristics were plotted for 15-16° by means of an LP-5 potentiometer. A saturated calomel electrode was used as the comparison electrode.

As can be seen from the table, the difference in zero-point values for seven of the electrodes does not exceed ± 0.05 pH, which apparently can be explained by the difference in asymmetry potential values of these

Zero-Point Values and Electrode Sensitivity

Electrode No.	$pH_{E=0}$	ph after 1 month	$\Delta pH_{E=0}$	pH after 10 months	$\Delta pH_{E=0}$	$\Delta E/\Delta pH$	$\Delta E/\Delta$ pH after 10 months	Δ
1	1.60	1.65	+0.05	1.70	+0.10	56.5	55.8	—0.7
2	1.65	1.75	+0.10	1.75	+0.10	57.0	56.0	—1.0
3	1.65	1.70	+0.05	1.70	+0.05	56.0	55.8	—0.2
4	1.55	1.70	+0.15	1.75	+0.20	57.0	56.5	—0.5
5	1.65	1.65	0.00	1.67	+0.03	56.5	56.0	—0.5
6	1.85	1.80	—0.05	1.80	—0.05	56.5	55.8	—0.7
7	1.70	1.80	+0.10	1.90	+0.20	56.5	56.3	—0.2
8	1.65	1.60	—0.05	1.85	+0.20	56.5	55.6	—0.9
9	1.65	1.60	—0.05	1.80	+0.15	56.5	56.5	0.0

electrodes. Measurements performed one month after the electrodes were made showed that, for electrodes which were not heated, the zero point values were shifted, on the average, by 0.1 toward larger values. However, the zero-point values remained constant over a period of nine months of storage in a 0.1 N HCl solution, which indicated the constancy of potential jumps at the copper solution and glass solution (inside the electrode) interfaces. For electrodes which were heated, the zero-point values were shifted by approximately 0.05 pH (toward smaller values), however, during the subsequent storage over a period of nine months at room temperature, the zero-point values changed by approximately 0.2 pH. The decrease in the electrode sensitivity during this storage period was on the average equal to ~0.5 mv per unit of pH, as can be seen on the right-hand-side of the table; these changes characterize the electrode properties of lithium glass.

At higher temperatures, the "zero points" of electrodes are shifted toward larger pH values by an amount equal to 0.012 pH unit/°C; if the electrodes are filled with a saturated solution of cuprous chloride in water, the "zero points" are shifted by 0.003 pH unit/°C.

The satisfactory constancy of zero-point values of electrodes in storage over long periods of time indicates the possibility of using copper electrodes as auxiliary electrodes in an acidified solution of copper sulfate. Small variations of electrode zero-point values can be always corrected by changing the emf in standard buffer solutions.

A LABORATORY CELL WITH A GLASS ELECTRODE FOR MEASURING THE pH OF SOLUTION

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The LP-5 laboratory pH-meter, which is produced by the domestic industry, is provided with thin-walled glass electrodes enclosed in a protective tube with openings. In this design, the electrode must be repeatedly wetted with the solution to be analyzed, so that the solution is used up at a considerable rate.

The figure shows a laboratory vessel with a glass electrode, by means of which the pH determination of solution samples in amounts equal to 0.05-0.10 ml can be performed. The glass electrode, which has a diameter of 9-10 mm, is made of lithium glass.* The salt correction for a 3 N concentration of sodium ions does not exceed 0.1-0.2 pH for the interval of pH values from 12.5 to 13.0 at room temperature.

* N. A. Fedotov, Zavodskaya Lab. 24, 4, 498 (1958); G. Perley, Anal. Chem. 21, 394 (1949).