A Simple Apparatus for Controlled-Potential Electrolysis

C. H. HOLTEN*

Kryolitselskabet Øresund A/S, Copenhagen Ø,
Denmark

Electrolysis at controlled potential has proved to be a valuable tool in polarographic work. Sand¹ introduced the method in electrogravimetric work, and Lingane² showed its utility for separations prior to polarography. In Lingane's first apparatus the control of the cathode potential was performed manually, and to eliminate this tedious work several varieties of automatic apparatus have been constructed³⁻⁹.

The purpose of this paper is to show the construction of an easily built apparatus for the performance of controlled-potential electrolysis. The reference voltage supply and zero-galvanometer relay in the potentiostats constructed by Lingane^{4,6} are replaced by a line-operated pH-meter, working as a voltmeter. This pH-meter is provided with a recorder connection which can be used to operate the control circuit.

Apparatus. The construction of the apparatus is shown in Fig. 1. Direct current is supplied from a voltage divider, connected to 110 V, d.c., or from any other convenient d.c. supply.

* Present address: Department of Chemistry, Danmarks Ingeniørakademi, Copenhagen K.

Fig. 1. Electrical circuit for electrolysis at controlled potential. A: Anode. C: Cathode. S.C.E.: Saturated calomel reference electrode. R: Contact meter with double electronic relay. M: Reversible condenser motor. G: Triple worm gear. P: Potentiometer (electrolysis current supply).

Fig. 2. Contact meter with double electronic relay. C: Contact meter (10 mA, 500 Ω). P₁, P₂: pH-meter recorder connection. S₁, S₂: Adjustable contacts, closed by the pointer, S₃. T: Transformer, 220 V/180 + 6.3 V. r₁, r₂, r₃, r₄: 100 000 Ω . c₁, c₂: 50 μ F. R₁, R₂: Magnetic relay, 4700 Ω . M_C, M₁, M₂: Motor connection, M_C: common lead. Valves EF 80.

This voltage which can be coarsely adjusted between 0 and 15 V is connected to a potentiometer, P (35 Ω , 100 W), used as a voltage divider. The electrolysis current is then conducted from the sliding contact and from one end of P to the working electrodes. Suitable meters are connected to this circuit to follow the progress of the electrolysis.

The electrolysis cell recommended by Lingane² has been used. The potential of the mercury cathode with respect to a saturated calomel electrode is measured with a pH-meter, type PHM 22 (Radiometer, Copenhagen), working as a voltmeter (range 0–2.2 V). The recorder connection of this pH-meter supplies through a resistance of 500 Ω a current proportional to the pointer deflection. This current amounts to 10 mA for full deflection. The recorder current is led to a 500 Ω ammeter, constructed to give the same pointer deflections as the pH-meter. This dependent instrument is provided with two adjustable limiting contacts, closing when the pointer passes above, respectively below the adjusted limits. The limiting contacts control a double electronic relay which in turn activates a reversible motor to revolve in one direction or the other, depending on which one of the limiting contacts has been closed. The contact instrument and the joined double relay (Fig. 2) has been constructed by Mr. Tynell, Jensen Electric

I/S, Copenhagen. The reversible motor (condenser motor, type 15GK, from Hans Heidolph, Ohg., Schwabach by Nürnberg) is connected to the shaft of the potentiometer, P, by means of a triple worm gear (from Hans Heidolph). The worm gear is constructed to move the potentiometer contact from one end to the other within one minute.

When the cathode potential differs from the desired value, adjusted at the limiting contacts, the electronic relay and the motor are activated to alter the electrolysis voltage from P in the appropriate direction, until the desired potential is reached.

The apparatus may be used to perform automatic potentiometric titrations when the relay is used to operate a magnetic valve for the standard solution. The magnetic valve must be connected at M_c and M_1 or M_2 (Fig. 2).

Experimental. To show the effectiveness of the apparatus the following experiment was performed: Copper sulfate (0.05 M) and lead nitrate (10^{-4} M) were dissolved in an ammonium acetate-acetic acid supporting electrolyte containing hydroxylamine as depolarisator (2 M $\text{CH}_3\text{COONH}_4$, 2 M CH_3COOH , 0.5 M $(\text{HO})\text{NH}_2\text{Cl}$). The hydroxylamine is necessary to avoid loss of lead deposited as PbO_2 on the anode. This solution was electrolysed using the apparatus. The cathode was a mercury pool kept in rapid motion by a glass propellor at the surface, and the anode was a platinum wire wrapped as a helix on the stirrer shaft. The cathode potential was controlled at -0.3 V vs. a saturated calomel electrode (Radiometer, type K4311). In the course of about 90 min the electrolysis current decreased from the initial 255 mA to less than 1 mA while the voltage between the anode and the cathode during the first 25 min decreased from 3.0 V to about 1.6 V and was then almost constant or slightly increasing. The effect of the electrolysis is shown in Fig. 3. Polarogram A is obtained from the electrolysed solution; a copper wave at -0.22 V and a lead wave at -0.50 V are observed. Polarogram B is obtained from a solution containing 10^{-4} Pb ion in the same electrolyte. It is obvious that the two lead waves are of the same magnitude, which indicates that no loss of lead ion has occurred. At the same time the copper ion concentration has decreased to the same order of magnitude as the lead ion concentration or to about 1/500 of its original concentration.

In the original solution the copper ion concentration was too large (0.05 M) to admit the recording of a polarogram. After 100-fold dilution with the electrolyte a polarogram showed a clean copper wave, but the lead

Fig. 3. Effect of electrolysis: Original solution contained 0.05 M Cu^{++} and 10^{-4} Pb^{++} (electrolyte: 2M $\text{CH}_3\text{COONH}_4$, 2 M CH_3COOH , 0.5 M $(\text{HO})\text{NH}_2\text{Cl}$). Polarogram A (abscissa at the top) obtained after electrolysis at cathode potential -0.3 V vs. S.C.E. Polarogram B (abscissa at the bottom) obtained from a solution containing 10^{-4} M Pb^{++} (no Cu^{++} added).

wave was hardly visible, even when the diffusion current compensation technique was used.

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