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A Coulometric-Titration Coulometer

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A highly precise coulometer is described which permits time integration of currents totaling 100 coulombs or more with a precision of about 1 part in 100,000. The current to be integrated oxidizes hydroquinone in an electrolysis cell, producing quinone and acid. The quinone is then reduced by constant-current coulometric titration, the end point being indicated by hydrogen-ion concentration measurements.

1. Introduction

The increased interest in coulometric methods of chemical analysis has created a need for a current integrator of higher precision than the mechanical, electrical, or electrochemical devices now available. Such an integrator should be simple to operate and give precise results for small quantities of electricity.

Overall considerations indicated that it should be possible to integrate a total charge of 100 coulombs, corresponding to 1 milliequivalent of chemical reaction, with a precision of about 1 part in 100,000, using an electrochemical coulometer. The purpose of this investigation was to develop such a device.

The simplest arrangement which might be expected to fulfill the requirements is an acidimetric type of electrochemical cell in which the current to be integrated generates strong acid in a neutral electrolyte. The amount of acid so generated is then determined precisely by constant-current coulometric titration.[2] A titration coulometer of the acidimetric type has been reported in the literature,[3] but preliminary investigations showed that the electrode reactions involved were not efficient to the degree required for this application.

As a result of the experiments which showed the defects in this method, it was decided to use an oxidation-reduction type of reaction. Upon investigation of several possibilities, the hydroquinone coulometer was selected as best fitting the requirements placed on the method. The reaction involves the oxidation of hydroquinone to quinone by the current to be determined, and the subsequent reduction back to hydroquinone by constant-current coulometry. The reactions may be represented as follows:

$$\text{Hydroquinone} + \text{integrated current} \rightarrow \text{quinone} + H^+ \quad (1)$$

$$H^+ + \text{quinone} + \text{constant current} \rightarrow \text{hydroquinone} \quad (2)$$

Reaction (2) is the reverse of (1), so that the quantity of electricity required to return the cell to the starting point, reaction (2), is equivalent to that responsible for reaction (1).

Since hydrogen ions are involved in the reaction, it is possible to use a hydrogen-ion concentration (pH) measurement as the means for detection of the end point, that is, when the reverse reaction is complete. This has the distinct advantage over other possible systems in that an indicating electrode system and related measuring equipment are readily available which are very stable and of a high degree of refinement, making additional investigation in this area unnecessary.

2. Reagents and Apparatus

The supporting electrolyte is made up from reagent-grade sodium chloride, precipitated from the saturated solution by hydrogen chloride gas, and recrystallized from water.

The hydroquinone is recrystallized once from air-free water and dried under reduced pressure. The product of the recrystallization consists of white needles appearing slightly violet in large quantities.

The electrical system used is shown in figure 1. The voltage is supplied by a 48-v lead storage battery isolated from ground. Variable resistor R_1, a voltage dropping resistor, supplies several ranges of current. Switch S_2 is a double-pole, double-throw knife switch of the Leeds and Northrup potentiometer type. When in position (1), the current is passed through a dummy resistor R_2 which is ad-

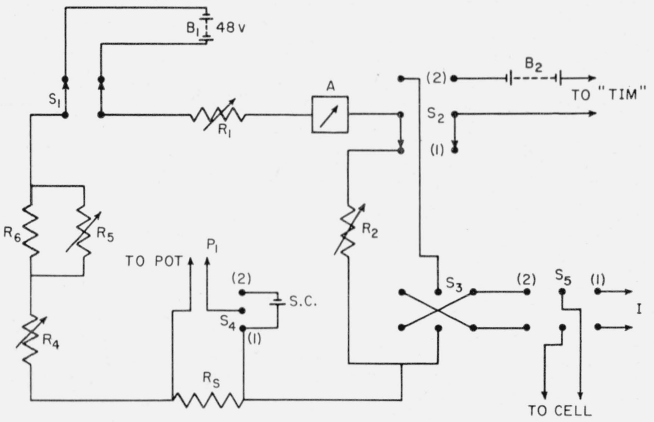

FIGURE 1. *Schematic diagram of electrical circuit.*

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justed to have the same resistance as the cell. When switch S_2 is thrown in position (2), the current flows through the cell and simultaneously the quartz crystal controlled time-interval meter, TIM, Berkeley Model 7250 CD, is triggered by the pulse from battery B_2.

Switch S_3 is a reversing switch, allowing the current to flow through the cell in either direction. When switch S_4 is in position (1), the voltage drop across standard resistor R_3 is measured by the precision potentiometer P_1. When switch S_4 is in position (2), the voltage across R_3 opposes the standard cell, *S.C.*, and the difference is measured by P_1. The resistor network R_4, R_5, and R_6 is for adjustment of the current. The coarse adjustment, R_4, is composed of resistance decade boxes. Fine regulation is obtained by means of a fixed resistor and a carbon compression resistor, R_5. The resistance range of the network, R_5–R_6, is approximately 18 ohms, and the range of R_4 is 2,000 ohms in 0.1 ohm steps. The resistance is adjusted during a determination to maintain a null deflection of the galvanometer of potentiometer P_1.

Switch S_5, when in position (1), connects the cell to the source of current to be integrated according to reaction (1). Position (2) is used for the coulometric titration according to reaction (2).

The end point is determined by a commercial *p*H meter equipped with standard glass and reference electrodes. In addition, a precision potentiometer is connected across the recorder terminals of the *p*H meter, allowing a precision of 0.002 *p*H units in determining the end point.[2]

The stability of the *p*H meter is of prime importance, since the reproducibility of the end point is directly related to this factor. A commercial meter providing automatic zero standardization is very satisfactory in this respect.

The cell and associated equipment are shown in figure 2. Water-pumped nitrogen is passed successively over copper at 500° C to remove oxygen, through ascarite to remove carbon dioxide, through a 1-*N* sulfuric acid wash-solution to entrap any dust from the ascarite, and finally through two wash-solutions of distilled water to remove traces of acid and saturate the gas with water vapor. The function of the stopcock arrangement will be explained under experimental procedure.

The cell consists of two electrode compartments, 4.5 by 10 cm, connected by a bridge containing 3 sintered glass disks, of which (1) and (2) are of medium porosity and (3) is of fine porosity. An agar plug at the entrance port of compartment *C* effectively prevents transfer of solution to or from this compartment. The bridge is provided with tubes for blowing the solution from its compartments by means of nitrogen pressure.

The stopper assembly which closes working compartment *A* is filled with three glass tubes: one for bubbling nitrogen through the solution for the purpose of removing carbon dioxide and oxygen; one for flowing nitrogen over the solution during the determination; and one for exit of the nitrogen from

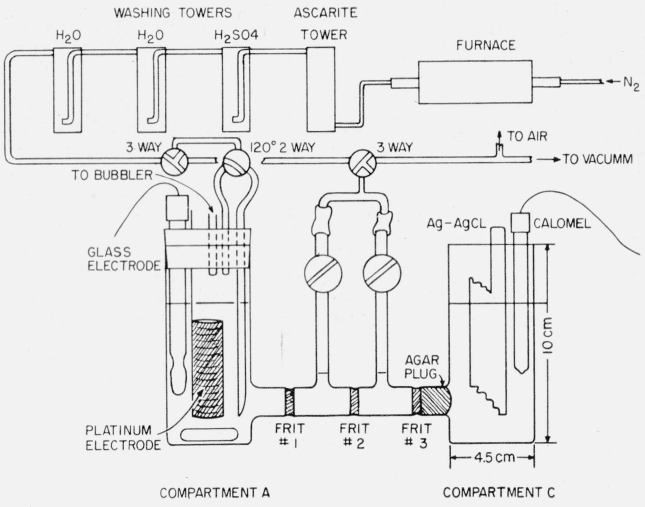

FIGURE 2. *Coulometric cell and associated apparatus.*

the cell through a water trap. A hole is provided for the introduction of the glass electrode. A cylindrical platinum gauze electrode, 5 by 1.5 cm in diam, completes the assembly.

Compartment *C* is separated from the rest of the cell by a 5-percent agar plug as described above. It contains the silver–silver chloride working electrode, constructed from a piece of fine silver 5 by 10 cm, and the calomel reference electrode.

To hasten the rate of attainment of equilibrium at the end point, it is desirable to immerse the cell in a water bath maintained at 45° C. A satisfactory arrangement is to place the cell in an aluminum pan sitting on a combination hotplate-magnetic stirrer to provide both stirring and temperature control.

3. Experimental Procedure

Before assembly, the cell is cleaned in hot sulfuric acid-chromic acid solution and rinsed by drawing large quantities of hot distilled water through the sintered glass disks to ensure removal of all traces of the cleaning solution.

The agar plug is formed in the side arm of the clean cell as follows. An agar solution, made by dissolving 5 g of agar-agar in 100 ml of a 2-*M* sodium chloride solution and heating to near boiling, is poured into the side arm. The gel sets on cooling and will not soften unless the temperature is raised above 60° C.

The supporting electrolyte is prepared by adding 10 g of sodium chloride to each compartment, plus sufficient distilled water (approximately 85 ml) to cover the platinum electrode when the bridge is filled. After the stirring bar is added, the stopper assembly is fitted to the cell and it is placed in position in the water bath. The nitrogen manifold connections are then made as shown in figure 2.

After the *p*H electrodes have been standardized in a buffer solution at the operating temperature,

45° C, the glass electrode is inserted in the stopper assembly. The reference electrode is placed in the isolated compartment with the silver–silver chloride electrode. Nitrogen is then bubbled through the cell and the bath temperature is raised to 45° C. After purging for 20 to 30 min, the stopcock is turned to allow the gas to flow over the surface of the solution. The bridge is then filled by applying suction to the center compartments.

The current is adjusted to 10 ma and passed through the cell until the *p*H reaches 7. At this point, the solution in both central compartments is pushed into compartment *A* by nitrogen pressure. After mixing, it is drawn back into the bridge. The *p*H is again brought to 7 by electrolysis and the process is repeated until there is no change in *p*H.

Hydroquinone (0.50 g) is now added to compartment *A* and allowed to dissolve. The equilibrium *p*H (approximately 5.6) is recorded and used as the end point.

For accurate results, the cell is preconditioned in the following manner. With the platinum electrode as anode, the current is adjusted to 100 ma and acid is generated for approximately 1,200 sec. The polarity is then reversed and base is generated for about 1,150 sec. The current is then changed to 10 ma and the generation of base is continued to the end point. The bridge is emptied, then refilled, and the solution is brought to the end point again. This rinsing process is continued until no change occurs. The cell is now ready to be used as a coulometer.

Performance testing is carried out in the following manner. The current is adjusted through the dummy resistor to 100 ma. With the platinum electrode as anode, acid is generated for about 1,000 sec, while the current is monitored continuously to maintain a constant and known value.

The acid so produced is then titrated by reversing the polarity, and passing a constant and accurately measured current of about 100 ma until approximately 95 percent of the acid is neutralized. The current is then reduced to 10 ma and the end point (original equilibrium *p*H) is reached by the same process as described for conditioning the cell.

The procedure is the same for integrating an unknown current. However, if the total quantity of charge is not known approximately, the *p*H must be observed occasionally to avoid generating past the end point. When the solution is back to the end point, the cell is ready for another determination.

4. Results

When following the procedure described in section 3, a precision of approximately 1 part in 100,000 may be obtained. The results of a number of determinations made over a period of 10 months are given in table 1. These data were all obtained with approximately 100 coulombs input and are given as percent recovery; namely, (coulombs, oxidation/coulombs, reduction)$\times$100.

TABLE 1. *Performance data*

1958	Recovery	1958	Recovery
	%		%
Jan. 14	100.000	Jan. 30	100.001
Jan. 15	100.001	Feb. 27	99.999
Jan. 16	100.002	Oct. 13	99.999
Jan. 16	99.999	Oct. 14	100.002
Jan. 29	100.000	Oct. 14	100.001

5. Discussion

The method does not involve any precision chemical operations which would require the services of a highly skilled chemist.

The precision and accuracy of this method depend on the control maintained over a number of factors, including: Accidental loss of electrolyte, diffusion and migration of ions, efficiency of electrode reactions, slope of the *p*H-time curve, stability and calibration of the circuitry, and freedom from ground loops.

Accidental loss of electrolyte could occur through the gas exit tube, around the stopper assembly, or through the bridge into the isolated compartment. If the nitrogen is flowed over the solution during the entire run and the stopper assembly is carefully made and fitted, there is no appreciable loss from this source. The possibility of loss through the bridge is negligible if the agar plug is firm and does not soften at the temperature of operation. It has been demonstrated experimentally that only a minute amount of acid reaches the second bridge compartment, mainly by convection through the frits (1 and 2). None is transferred through an agar plug in good condition.

The use of a rather concentrated salt solution to carry the current effectively minimizes electromigration of hydrogen ions across the bridge during reaction (1).

The reactions at the platinum electrode are 100 percent efficient as long as the silver–silver chloride electrode is maintained in a separate compartment. In experiments where this electrode was installed in the same compartment with the generating electrode, the efficiency of the reduction reaction (2) was found to be less than 100 percent due to the finite solubility of silver chloride in the electrolyte and the subsequent reduction (plating out) of silver on the cathode.

It is necessary, of course, to exclude all traces of foreign acid or alkali from the cell. For example, the leaching of 10^{-4} ml of cleaning solution from the walls of the cell would result in an error of about 3 parts in 10,000.

The precision of the detection of the end point depends on the reproducibility of the *p*H-meter readings and on the slope of the *p*H-time curve. Experience has shown that the experimental arrangement is of sufficient stability and sensitivity to make the *p*H measurements reliable to about ± 0.002 unit.

The slope depends on the concentration and volume of the electrolyte in the cell. Hydroquinone is a very weak acid, $K_1 = 1.1 \times 10^{-10}$, and exhibits slight

buffering action at the end point. Since the slope increases as the solution is diluted, it is desirable to use the most dilute solution practicable. At the same time, the volume of the working compartment of the cell must be kept small to insure significant changes in the *p*H for small amounts of reduction near the end point.

Theoretically, 55 mg of hydroquinone is oxidized by 100 coulombs of electricity. To minimize concentration-polarization effects, a larger amount must be used. For example, poor results were obtained with a two-fold excess of hydroquinone present, but a six-fold excess was found to be adequate for efficient operation of the cell. As a conservative measure, a nine-fold excess of hydroquinone was adopted, corresponding to 500 mg or to a concentration of 6 g/liter in the 85-ml cell.

The variation of the *p*H of the electrolyte with concentration of hydroquinone is shown in figure 3. The theoretical curve is shown for comparison. The *p*H value indicated at the operating concentration of 6 g/liter is 5.63 (average deviation $= \pm 0.10$) and is the average of the end-point values for 20 integrations.

Figure 4 shows the variation of the *p*H of the cell as the end point of reaction (2) is reached, for two different concentrations of hydroquinone. For the cell containing 50 mg of hydroquinone, approximately the theoretical amount for 100 coulombs, 0.0004 coulomb produces a change in *p*H of 0.002 unit. For the cell containing 500 mg of hydroquinone, the same change in *p*H requires 0.001 coulomb.

With reference to the data of table 1, the reproducibility found is what would be expected from the uncertainty of the end point.

If the components of the electrical circuitry are properly calibrated, any errors from this source will be at least an order of magnitude below the other errors in the method. However, it is necessary to control the temperature of the standard resistor and the standard cell for high accuracy. Also care must be exercised to prevent the formation of accidental ground loops (high resistance pathways to ground) in the system, particularly through the reference electrode of the *p*H meter, since the system as described is grounded only at this point. Errors from this source could be as much as several parts in one thousand.

The performance of the coulometer was studied extensively at the 100-coulomb level because this amount of charge corresponds to 1 milliequivalent, a convenient amount of chemical reaction. For small amounts of electricity, a somewhat lower precision of integration would be expected. Larger amounts of current should be integrable with precision comparable to that found here, provided appropriate modifications of the technique, including concentration of electrolyte and electrode dimensions, were made.

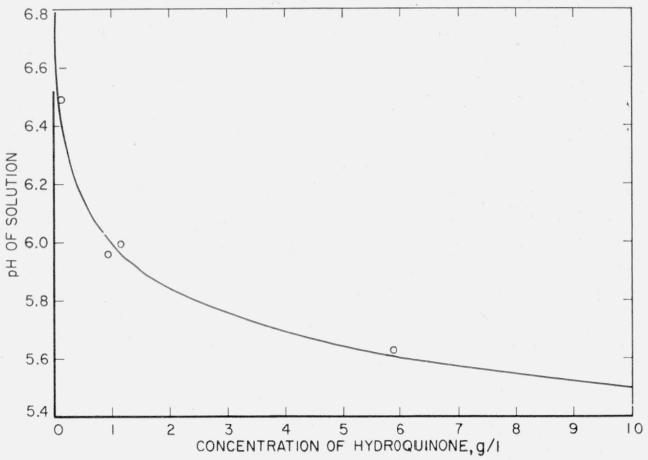

FIGURE 3. *The dependence of the pH value of the cell-electrolyte on the concentration of hydroquinone.*

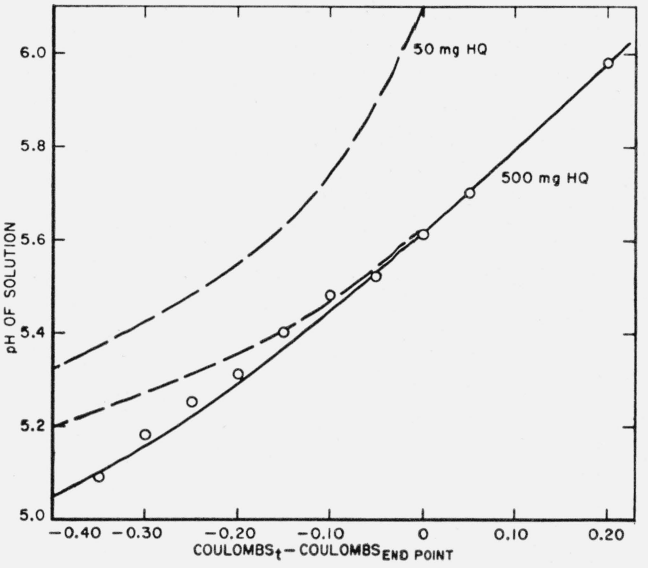

FIGURE 4. *Titration curves at the end point of reaction (2).*

Calculated and experimental values are represented by the broken curves and the solid curve, respectively. The current is 10 ma, corresponding to 0.05 coulomb for each 5-sec titration interval.

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