

Automatic Neutralization and Determination of Acid Addition With Electrolytically Generated Base

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Introduction

The coulometric method of titration using electrolytically generated reagents has recently made a rapid progress, which is attributed to its advantages over conventional volumetric method. First the reagent for titration is produced, or the substance to be titrated is changed, by electrode reaction. In other words the titrant is the electricity itself instead of the standard solution in conventional titrations. If the current efficiency is maintained at 100% for the concerned reaction throughout the process, the required amount of electricity is calculated from Faraday's law. As this law holds accurately for all possible electrode reactions, the coulometric method furnishes a very accurate means of titration especially for microanalysis, provided a sensitive end-point detection is feasible. Second the titration cell can be tightly closed if necessary and the reaction solution is kept free from atmospheric influences, because no additional solution is needed. In case a labile reagent is employed as titrant and it is produced by an electrode reaction with an efficiency of 100%, the coulometric titration surpasses over the conventional method. Third the titration procedure can be easily automatized by suitable electrical control. Since it is recently a general tendency to automatize analytical procedures, several authors have already reported the automatization of coulometric titrations.¹⁾⁻⁸⁾

In the course of research the present writer demanded a means with which the acid solution intermittently added into an unbuffered neutral solution is immediately neutralized with any basic reagent to keep the latter solution almost neutral and that the amount of added acid is to be determined. For this purpose the coulometric titration technique will answer the requirement if it is automatically controlled. This paper describes the procedure to maintain the pH of an aqueous solution of sodium sulfate at about 7 even when aliquots of an aqueous hydrochloric acid solution are added drop by drop and to determine the total amount of added acid by that particular time.

A pH meter with a glass electrode was employed to indicate the pH of the solution. While the solution remains acid it was electrolysed to generate base or to annihilate the acid by the cathode reaction. At pH 7 (an arbitrary settled end-point) a trigger operates to open the gene-

rating circuit and the next increment of acid solution makes the circuit closed again repeating the process. By combining a timer to a constant current source the total amount of electricity was measured according to Faraday's law, which was equivalent to the total amount of acid neutralized.

Apparatus

Each component was constructed separately and operates as a single unit. These components are connected each other directly or through the controller. Fig. 1 gives the block diagram of the assembly.

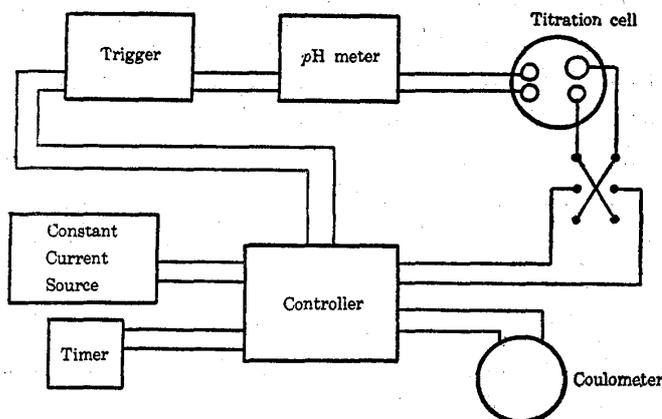


Fig. 1. Block diagram of the titration assembly

Constant current source The constant current source is nearly the same as Carson's.⁹⁾ This source is satisfactory for current up to 20 ma. The exact value of current was measured in an ordinary way from the iR drop through a

[standard resistor.

Timer When the electrolysis is performed with a constant current, use of timer is essential for measuring the total amount of electricity. The timer must cooperate with the make and break of the electrolysis current, but the usual electric timer is not available because of the unstability of AC line supply in our country. Instead a spring-driven precise stop-watch was reconstructed to start and stop with a lever operation managed by an electromagnet. The controller circuit connects this timer to the constant current source as to run while the electrolysis current flows and to stop when the current is cut off, thus the time of current flow is integrated. This timer is accurate enough for the present purpose the error being less than 0.1%.

Coulometer To check the total amount of electricity a coulometer was inserted in the electrolysis circuit. This is not always necessary if a constant current and the timer are used, but is indispensable when an instabilized current is employed or even in case of stabilized current it is so intermittent that the exact value is not to be measured. The coulometer is the so-called coulometric coulometer described by Ehlers and Sease¹⁰⁾ consisting of a platinum foil (6×8 mm) and copper wire electrode system. As the current flows copper in the electrolyte deposits on the platinum cathode. After the electrolysis the deposited

copper is stripped off by a constant current reversing the polarity. Time for complete strip is measured with the timer mentioned above until the potential difference between the two electrodes suddenly rises. In the latter case the electrodes of the coulometer are connected to the input of the trigger. The efficiency of this coulometer was $99.6 \pm 0.1\%$, nearly equal to $99.7 \pm 0.1\%$ as Ehlers and Sease say. In some experiments this coulometer was used, but the values of total amount of electricity calculated directly from the current and time was practically equal to those from the coulometer, so that the coulometer was often omitted.

Titration cell The titration cell is a weighing bottle of about 50 ml capacity. Electrodes are inserted through the rubber stopper fitted to the cell. One of the generator electrodes is a platinum foil (6×15 mm) electrode while another is an electrode isolated from the solution to be titrated by a fritted glass disk and agar, the latter being saturated with sodium sulfate. The two electrodes are arranged closely as indicated in Fig. 2 to minimize the influence to the indicator electrodes. The indicator electrodes are a glass electrode and a silver-silver chloride reference electrode, those attached to the pH meter. The platinum foil electrode is settled on a level with the working part of the glass electrode because the geometrical arrangement of electrodes is important. As electrolyte about one fourth formal solution of sodium sulfate was used and the solution was vigorously stirred with a magnetic stirrer.

pH meter A direct-indicating pH meter of vibrating capacitance type manufactured by Mitamura Co. was employed. The iR drop through a resistance in the output circuit is fed to the input of the trigger.

Trigger The essential part of this trigger circuit shown in Fig. 3 is generally identical to that of Takahashi and others.¹¹⁾ One half of the circuit serves as a valve voltmeter whereas the other half a DC amplifier. At moment the signal developed by the pH meter exceeds a settled value which corresponds to a certain pH, the galvanometer relay operates to set the magnetic relay of the controller in action, which causes to cut off the electrolysis current and at the same time to stop the timer. This response was enough sharp to repeat the action with the discrepancy of less than 0.1 in term of pH value.

Controller This controller was provided to combine the components of titrator as indicated in Fig. 1 and to set those in action at one

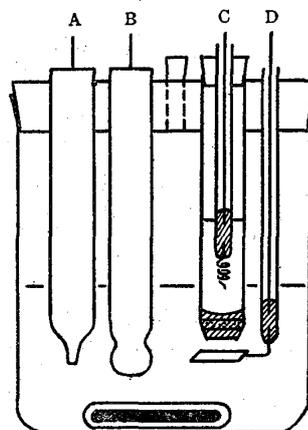


Fig. 2. Schematic diagram of titration cell

- A: Ag-AgCl reference electrode
- B: Glass electrode
- C: Isolated generator electrode
- D: Working generator electrode

stroke. The controller consists of a mutiple switch and a magnetic relay connected to the galvanometer relay in the trigger. The circuit

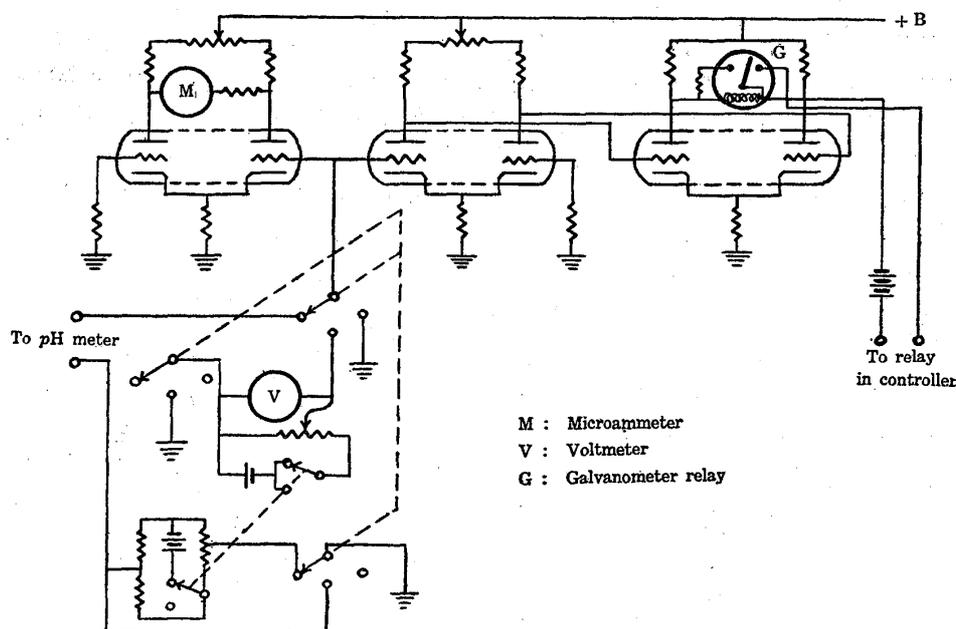


Fig. 3. Circuit diagram of trigger

is simple and may be designed in an arbitrary convenient way. The controller performs in the process as follows:

1. At the (a) position of the switch the circuit to the titration cell is open and the current flows only in a solid resistor instead of the cell. The timer remains stopped.

2. Let the switch at the (b) position, the current flows into the cell through the coulometer and the timer runs on. At the end-point of titration the galvanometer relay in the trigger works to operate the magnetic relay, as the result of which the electrolysis current is switched to flow through the solid resistor and at the same time the timer stops.

3. The (c) position of the switch is used to measure the total amount of electricity. In this case the electrolysis current flows only through the coulometer and in an opposite direction as in 2. The behavior of other parts is entirely the same as in 2.

Experimentals and discussions

Equivalency of generated acid and base When an aqueous sodium sulfate solution is electrolysed as working platinum electrode being anode, acid is generated as the electrode reaction product. Similarly base is generated if the polarity is reversed. To examine the equivalency of those generated acid and base for the equal amount of electricity, the following experiment was performed.

About 20 ml of one fourth formal solution of sodium sulfate was taken into the cell and the electrodes were inserted. After adjusting the trigger to stop the electrolysis at pH 7, acid was generated with about 10 or 20 ma for 100 to 200 sec. The exact value of current was measured from the iR drop through a standard resistor. The acid was then neutralized with the generated base to the automatically controlled end-point, that is to pH 7. If the electrodes are adequately arranged a false end-point appears a little before the true end-point, because the solution around the indicator electrode becomes partially less acid than the bulk of solution. But the electrolysis soon recontinues and the second false end-point will come, thus several small increments must be included before the true end-point is reached. The results are summarized in Table 1, the determination error being satisfactorily small for these microchemical scale.

Table 1. Equivalency of generated acid and base

Generation of acid			Generation of base			Error (%)
Current (ma)	Time (sec)	Amount of electricity (coulomb)	Current (ma)	Time (sec)	Amount of electricity (coulomb)	
20.106	200.0	4.021	20.108	199.3	4.008	-0.32
20.114	200.0	4.023	20.114	199.7	4.017	-0.15
20.114	200.0	4.023	20.114	200.4	4.031	0.20
20.114	100.0	2.011	20.114	100.1	2.013	0.10
20.118	150.1	3.020	10.036	300.8	3.019	-0.03
10.048	250.1	2.513	10.050	248.7	2.499	-0.56

Determination of standard hydrochloric acid solution Standard hydrochloric acid solution (0.0249N) was pipetted into the cell and determined with the electrolytically generated base. At first the trigger was adjusted to work at pH 7 with the blank solution of sodium sul-

Table 2. Determination of hydrochloric acid

Hydrochloric acid solution (0.0249N)		Generation of base			Error	
Taken (ml)	Equivalent amount of electricity (coulomb)	Current (ma)	Time (sec)	Amount of electricity (coulomb)	%	$\mu\text{g-HCl}$
1.010	2.427	9.74	251.7	2.452	1.03	9.4
2.020	4.854	19.50	249.0	4.856	0.04	0.8
"	"	19.49	250.0	4.873	0.39	7.2
"	"	19.55	246.9	4.827	-0.56	-10.2
"	"	19.52	250.0	4.880	0.54	9.8
"	"	9.70	500.7	4.857	0.06	1.1

fate, therefore the condition of the solution is almost the same as that at the end-point of titration. Then hydrochloric acid solution was pipetted into it and titrated with the generated base. Table 2 gives the results.

Neutralization and simultaneous determination of increasingly added acid To the cell adjusted beforehand to the same condition as at the end-point, the standard hydrochloric acid solution (0.0249N) was added drop by drop from a microburet in various speeds. When the first drop falls into the cell the electrolysis current begins to flow to neutralize the acid and maintain the neutrality of the solution.

The electrolysis current of 20 ma corresponds to the generation speed of 1.244×10^{-5} equiv./min. of base. Therefore the same addition speed of acid is critical to maintain the solution neutral, because the maximum current is limited by the capacity of the current source used. The experiments were performed within this limit. If the acid solution adds in small increments, the electrolysis follows them, hence the current is interrupted. These numbers of interruption are shown on the third column in Table 3. No definite correlation is found between these numbers and the determination error.

Table 3. Generation of base for neutralizing hydrochloric acid solution (0.0249N) droppingly added
Total added amount of acid: 2.020 ml
Corresponding amount of electricity: 4.854 coulombs

Current (ma)	Time (sec)	Number of interruption	Amount of electricity (coulomb)	Error	
				%	$\mu\text{g-HCl}$
19.00	254.0	21	4.826	-0.58	-10.6
19.10	253.3	14	4.838	-0.33	- 6.1
19.08	253.6	41	4.839	-0.31	- 5.7
19.08	253.0	98	4.812	-0.87	-15.9
19.07	353.2	3	4.829	-0.51	- 9.5

Except at the moment where drops of acid solution were added, the solution in the cell remained within the range of pH 7.0 to 7.5 in case of a 20 ma generation. A very slight overtitration was inevitable and this resulted in an increase of pH in such an unbuffered solution.

To maintain the neutrality of a solution against the addition of acid and to simultaneously determine it, the above procedure will be satisfactory. But the experiment was performed against the addition of such a strong acid as hydrochloric. If this technique is applied in case of any weak acid, for example in order to eliminate the influence of carbon dioxide in the atmosphere and determine it, the error of determination error will considerably extend, though an exact determination is possible in principle. For such cases substitution of any strong acid

for the weak one by some chemical means will solve the problem, which however remains in the future plans of the present writer.

Summary

The electrolytical generation of base in an aqueous sodium sulfate solution was applied to keep an unbuffered solution neutral, when a strongly acid substance was continuously or intermittently added. The total amount of added acid was also determined by the coulometric titration method. The process was automatized. With the generation speed of 20 ma, the pH of the solution could be maintained within the range of 7.0 to 7.5 in terms of pH. The errors of determination of total acid amounted to several tenths percent for milligram quantities.

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