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The Precise Coulometric Titration of the Acidic Primary Standard using Amperometric End-point Detection

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The sensitive amperometric end-point procedure (*Anal. Chem.*, **23**, 1662 (1951)) with an antimony electrode is used in the titrations of acids. The cyclic voltammetric curves of the electrode indicate the possibility of the use of the above method for the titration of acids. The purities of potassium biphthalates (primary standard substances) are determined directly by precise coulometric titration with this end-point location. The standard deviations of the results (99.999%) are 0.007 or 0.008%. The purity of the benzoic acid prepared as the standard material for the calorimeter is also determined by this method. The standard deviation of these results (99.993%) is 0.009%.

Many investigations have indicated that coulometric titration is the most precise and accurate method in analytical chemistry. The purities of several primary standard substances have been directly determined by this method.[1-5]

Although the relative standard deviation by this method has been 0.003% in the most accurate studies, there are several problems in obtaining this value in ordinary laboratories without atmospheric control. Among these problems, the location of the end-point of the titration is the most important, especially in the titration of an acid or a base.[6] A pH meter with a glass electrode has been preferably used in locating the end-point of the titration. This potentiometric method has, however, several disadvantages because of the very high impedance of the electrode.

In the direct determination of the bulk material in a sample, a large amount of the sample should be taken in order to decrease the error in weighing. This causes the need to use a correspondingly large electrolytic current; otherwise, the electrolysis cannot be finished within a reasonable time interval. The electric field in the titrating cell caused by such a large electrolytic current then interferes with the high impedance circuit, that is say, the indication of the pH meter for end-point detection. After the current is cut off, it is necessary to wait several minutes in order to measure the pH value of the titrating solution. Furthermore, it is also necessary to measure many pH values in order to draw the titration curve clearly.

On the other hand, the circuit for the amperometric end-point location has a low impedance. Therefore, the disturbance caused by the electrolytic current disappears; also, only a few measurements are enough to locate the end-point. Chris-

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[1] J. K. Taylor and S. W. Smith, *J. Res. Nat. Bur. Stand.*, *A*, **63**, 153 (1959).

[2] G. Marinenko and J. K. Taylor, *ibid.*, *A*, **67**, 31; 453 (1963).

[3] E. L. Eckfeldt and E. W. Shaffer, Jr., *Anal. Chem.*, **37**, 1534 (1965).

[4] G. Marinenko and J. K. Taylor, *ibid.*, **39**, 1568 (1967).

[5] J. Knoeck and H. Diehl, *Talanta*, **16**, 181 (1969).

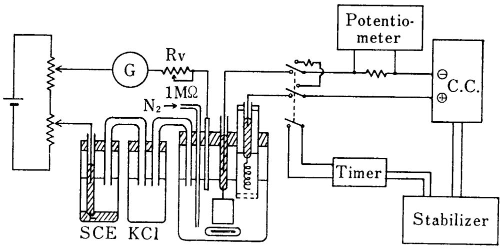
[6] T. Yoshimori and I. Hikawa, *Bunseki Kagaku*, **16**, 927 (1967).

tian[7] has already recommended the use of the amperometric method in locating the end-point of a coulometric titration, and the present authors have had the same experience. However, only a few amperometric methods have yet been used in the case of the titration of an acid or a base.

The present authors have now tried to use an antimony electrode with the aid of a sensitive amperometric end-point procedure,[8] they have obtained fairly satisfactory results.

Experimental

Apparatus and Reagents. The apparatus used for the amperometric titration with an antimony electrode and that used for the coulometric generation of hydroxyl ions are shown in Fig. 1. The generating current was measured with a standard resistor and a potentiometer. The error in the measurement of the current had a standard deviation of less than 0.005%. As the Faraday constant, 96487.2 coulomb was used. The generating current was kept constant by the following method; the fine adjuster of the constant-current source was regulated so as to keep as small as possible the deflection of the galvanometer (Sens. 10^{-6} V) connected to the potentiometer in the electrolytic circuit.



G: Galvanometer (2×10^{-9} A) C.C.: Constant current source

Fig. 1. Apparatus.

The 50-Hz oscillator of a quartz crystal and a cycle counter were used to measure the time interval of the electrolysis.[9]

The potential between the antimony electrode and a saturated calomel electrode was 0.50 volt for the titration of potassium biphthalate and 0.58 volt for benzoic acid. According to the character of the electrode, and also according to the pH value at the end-point, this potential should be chosen from the titration curve obtained by a preliminary potentiometric titration of the sample.

All the weights were corrected to standard weights. A weighing bottle of nearly the same weight as that containing the sample was used as a counterpoise. A lipless beaker made from polystyrene (about 200 m*l*) was used as the cell. An auxiliary electrode compartment, made from a polyethylene tube with an agar-agar diaphragm,[6] was installed through a silicone rubber stopper. About a 100-mg portion of barium carbonate was added into the compartment in order to neutralize the acid produced by the anodic reaction.

All the reagents were of an analytical grade, and all were used without further purification. For the purity determination of potassium biphthalate, a 0.5 M potassium chloride solution was used as the electrolyte, while for benzoic acid a 30% v/v ethanolic solution of 0.7 M potassium chloride was used.

Procedure. *Drying of the Sample.* Potassium biphthalate was heated at 120°C for 4 hr and then cooled in a desiccator containing concentrated sulfuric acid for 1.5 hr.

Benzoic acid was dried by the following two methods. First, the acid was dried in the desiccator containing concentrated sulfuric acid for 72 hr. Secondly, it was melted in a platinum crucible at 135°C,[10] cooled under the same conditions as above for 1.5 hr, and then weighed and introduced into the cell.

Coulometric titration. Place an electrolytic cell containing 100 m*l* of a potassium chloride solution (0.5 M) in a thermostat. Introduce nitrogen (free from carbon dioxide) for more than 40 min; then neutralize the solution with electrolytically-generated hydroxyl ions until the galvanometer in the indicator circuit shows zero. At this point, the potential of the antimony electrode (*vs.* SCE) coincides with the voltage of the potentiometer in the indicator circuit.

A weighed sample is introduced into the solution, and nitrogen is allowed to flow through for about 10 min. The solution is then electrolyzed with a constant current until it is neutralized to the previous pH value. The end-point of the electrolysis can be located by the point at which the galvanometer in the indicator circuit reaches zero. During the electrolysis, nitrogen must be allowed to flow over the electrolyte (not through the solution). Early in the titration, the indicator current through the galvanometer must be regulated with a variable resistor (1 MΩ).

Results and Discussion

Before the practical use of the antimony electrode, the cyclic voltammetric curves of the electrode were recorded with the instrument named Electroscan 30 (Beckman Instrument Co.). Typical cyclic voltammetric curves thus obtained at pH 4.0, 7.0, and 9.0 are shown in Fig. 2 (a).

Figure 2 (b) is an example of the curve obtained at pH 4.0. Identical curves were obtained at pH 7.0 and 9.0. This figure shows that the potentials of the zero-current point in cathodic curves (from the positive to the negative direction) coincide with one another. Since the pH of the electrolyte changes from acidic to basic near the end of the titration, the good reproducibility of the zero-current potential of the electrode from the positive to the negative direction demonstrates

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[7] G. D. Christian, *J. Electroanal. Chem.*, **11**, 94 (1966).

[8] W. D. Cooke, C. N. Reilley and N. H. Furman, *Anal. Chem.*, **23**, 1662 (1951).

[9] T. Miwa, T. Yoshimori and T. Takeuchi, *Kogyo Kagaku Zasshi*, **67**, 2045 (1964).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd. Ed., MacMillan Co., New York (1952), p. 529.

that the electrolyte has the same pH value when the indicator current becomes zero (galvanometer zero). Thus, the titration of acid with electrolytically-generated hydroxyl ions will be possible with the antimony electrode and a sensitive amperometric end-point procedure.

Determination of the Purities of Potassium Biphthalates. The results obtained for the analyses of potassium biphthalates are shown in Table 1. In this case, the samples were weighed with a semimicrobalance; the error in the measurement of the electricity was less than 0.01% as a standard deviation. These accuracies are the same as those of the potentiometric method reported previously.[6]

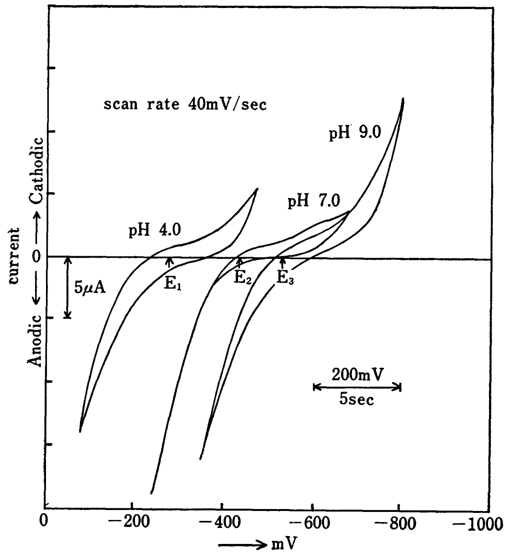

Fig. 2(a). Current-voltage curves of antimony electrode

$E_1 \sim E_3$: equilibrium potentials of the electrode measured by the very high impedance circuit.

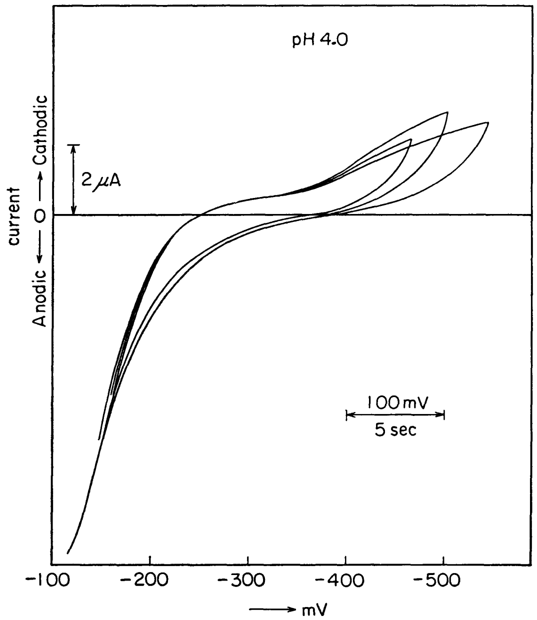

Fig. 2(b). Cyclic voltammetric curves of antimony electrode.

When the relative standard deviation in Table 1 is compared to that of the previous potentiometric method,[6] it is seen to be considerably decreased (nearly one-half). In this case, the time necessary for a single determination does not exceed

TABLE 1. PURITY TEST OF POTASSIUM BIPHTHALATE

(Current = about 210 mA)

Sample	Sample taken (mg)	Current of electrolysis (mg)	$KHC_8H_4O_4$ found (mg)	Purity (%)	Deviation from mean (%)
NBS standard sample	481.38	210	481.28	99.97_9	-0.01_2
	425.95		425.92	99.99_3	$+0.00_2$
	499.37		499.32	99.99_0	-0.00_1
	522.88		522.99	100.02_1	$+0.03_0$
	465.62		465.49	99.97_2	-0.01_9
			Mean	99.991%	R = 0.049%
					$\hat{\sigma}$ = 0.021%
Standard sample 100.00%*	545.94	200	545.77	99.96_9	-0.02_1
	518.89		518.74	99.97_1	-0.01_9
	388.83		388.91	100.02_1	$+0.03_1$
	411.76		411.85	100.02_2	$+0.03_2$
	382.21		382.08	99.96	-0.02_4
			Mean	99.990%	R = 0.056%
					$\hat{\sigma}$ = 0.024%

* Certificated value by Industrial Inspection Institute (Japan).

1 hr. By the potentiometric method, more than 3 hr are needed.

Next, the error due to the measurements of the electricity decreased to about 0.005% as the standard deviation, and the samples were weighed with a microbalance. In order to verify the error in the weighing of the sample, the following experiment was carried out. The potassium biphthalate in a weighing bottle (0.5 g) was dried at 110°C for 4 hr, cooled in the desiccator for 1.5 hr, and then weighed with the microbalance. This procedure was repeated 6 times.

TABLE 2. ERROR OF WEIGHING

Weight of sample (mg)
433.429
433.429
433.412
433.414
433.416
433.406
Mean 433.418
$\hat{\sigma}=9.12\,\mu g$

TABLE 3. PURITY TEST OF POTASSIUM BIPHTHALATE
(Current: about 160 mA)

Sample	Sample taken (mg)	$KHC_8H_4O_4$ found (mg)	Purity (%)	Deviation from mean (%)
NBS Standard sample	279.323	279.317	99.998	−0.001
	421.849	421.860	100.003	+0.004
	402.995	403.025	100.007	+0.008
	353.535	353.545	100.003	+0.004
	393.055	393.009	99.988	−0.011
	407.154	407.167	100.003	+0.004
	403.716	403.672	99.989	−0.010
			Mean 99.999%	$\hat{\sigma}=0.007\%$
Standard sample 100.00%*	494.551	494.555	100.001	+0.002
	491.758	491.738	99.996	−0.003
	505.377	505.435	100.011	+0.012
	457.803	457.766	99.992	−0.007
	506.761	506.724	99.993	−0.006
			Mean 99.999%	$\hat{\sigma}=0.008\%$

* Certificated value by Industrial Inspection Institute (Japan).

TABLE 4. PURITY TEST OF BENZOIC ACID
(Calorimetric standard sample)

Sample	Sample taken (mg)	C_6H_5COOH found (mg)	Purity (%)	Deviation from mean (%)
Stored in the desiccator containing conc. H_2SO_4 for 72 hr	265.140	265.119	99.992	+0.001
	218.390	218.367	99.989	−0.002
	236.576	236.579	100.001	+0.010
	262.040	262.032	99.997	+0.006
	265.032	264.974	99.978	−0.013
			Mean 99.991%	$R=0.023\%$ $\hat{\sigma}=0.010\%$
Melted at 135°C	256.173	256.129	99.983	−0.010
	323.689	323.695	100.002	+0.009
	234.715	234.697	99.992	−0.001
	245.042	245.054	100.005	+0.012
	287.920	287.875	99.984	−0.009
			Mean 99.993%	$R=0.022\%$ $\hat{\sigma}=0.009\%$

The results thus obtained are shown in Table 2; there may be some problems in the above method for drying, because it seems that the weight of the sample decreased gradually. The decrease is, however, very small, and may be considered at a later time. When the overall difference is regarded as the error of drying and weighing of the sample, the standard deviation of the error does not exceed 0.003%.

The results obtained by the procedure described previously are shown in Table 3. The standard deviation of these results was 0.007%, somewhat larger than the value to be expected from the errors in samplings and in coulometric titration. The difference may be based on the errors connected with the location of the end point. Material transference through the diaphragm used should also be considered. Taylor's method[1] is very time-consuming, and the diaphragm proposed by Eckfeldt and Shaffer[3] is not suitable either because the condition of the electrolyte at the end-point does not coincide with that at the beginning of the electrolysis. Although the diaphragm used here does not have as many advantages as the above two types, it is simple and useful when the electrolysis is finished within one hour.

Determination of the Purity of Benzoic Acid. The purity of the benzoic acid was determined by the proposed method. The acid was prepared as a standard material for a calorimeter and could be obtained from the Resources Research Institute (Japan). Two drying methods shown previously were used here.

The results obtained are shown in Table 4. These results indicate that there are not much difference between the above methods for drying; the purity of the acid was somewhat lower than 100% when the acid was evaluated as the "acidic" standard.