A New Titration Method Based on Concentration-Variable Patterns. Principles and Applications to Acid–Base and Redox Titrations

Chong-Liang Zhang and Yoshio Narusawa*

Department of Chemistry, College of Science, Rikkyo (St. Paul's) University, 3-34-1, Nishi-Ikebukuro, Toshima-ku, Tokyo 171

(Received August 27, 1996)

A new titration method based on concentration-variable patterns is presented. Since this titration method is characterized by a non-dilution and a non-gradient operation, no volume correction is necessary, and the influence of the matrix is indifferent. The proposed method is applied to acid–base and redox titrations. In addition, a new approach for equivalence-point detection is established, where the equivalence point can be mathematically determined by solving simultaneous linear equations before and after the equivalence point. Indicators or first-derivative and second-derivative treatments are no longer necessary, and the accuracy and precision in the equivalence point have been improved, compared with the traditional titration method. The titration error has been decreased to such levels as 0.1 pH for acid–base titrations, and of 0.01 V unit for redox titrations.

Titrimetry is one of the oldest analytical methods, and is still developing; it plays an important role in various analytical fields as well as routine studies.[1] The aim in titrimetric analysis is to observe the exact point at which a reaction has completed. Traditionally, most titration methods, for example, acid–base, redox, complexometric and potentiometric methods, were based on volume-variable patterns due to the use of a burette, except for some methods with special techniques, such as a test-paper titration method.[2] The titration error depends mainly on two parameters: The first is the one-drop volume of the solution from the titrant, no matter how the addition of the solution is carried out, in a batch or an automatic manner; the second is the sensitivity and location of indicators, which take place along with some changes in the color. Generally, a sudden change in pH through the equivalence point caused by the last one drop of the titrant would cause an uncertainty of the end-point pH; the change becomes at least two units of pH in an acid–base titration. Since the addition of an indicator would distort the original chemical equilibrium, the system to be titrated would no longer be true. In two cases, a positive error is always given. Moreover, if titration is carried out in a rather dilute solution, it may have no appropriate indicator, single or mixed, with a sufficiently sharp change which would allow the location of the equivalence point to have good precision, especially in redox titration.

In traditional titrations, since the volume of the solution increases as the titration proceeds, a correction is necessary for the volume effect, in spite of whether the equivalence point is obtained from the titration curve directly or from the derivative curve in automatic titration or not. The Gran method is excellent as an analytical method for the titration curve, because data points are analyzed as a linear regression with a least-squares method of the data between the titration volume and the hydrogen-ion concentration. Unfortunately, the analytical curve deviates almost in front of the equivalence point.

On the whole, all of the conventional titration methods based on volume-variable patterns are influenced by the dilution effects. Although the dilution effects in those titrations with indicators are always ignored, they should be strictly corrected.

There have been many investigations reported on Gran methods.[3—21] Freiser[22] presented a monograph on pH titration in analytical chemistry, and pointed out that the Gran method is effective for evaluating the equivalence point of the titration method.

Although the new titration method based on concentration-variable patterns proposed in this paper is totally different from the traditional titrations, it is one of the true titrations according to IUPAC's definition.[23] Both the titrant and titrand are taken in a given volume of solution, respectively, at every measurement, so that the total volume of the mixed solution is kept constant throughout the titration processes. Therefore, the obtained signals can be treated as a function of the titrant concentration instead of its volume. Since the concentrations of all but one are known, the unknown can be simply calculated and referred to the concentration of the original sample.

The objectives of this paper are as follows: The first is to discuss the applicability of two-thirds section method as an end-point detection method in various non-linear titration systems; the second is to discuss the titration error and the applicability of the ionic-strength correction. This optimization procedure was carried out in our own computer program software written in BASIC language. The present authors call the new titration approach the concentration-variable titration method (CVTM) due to its characteristics.

In addition, a new titration error is defined in the method, and the influence of the ionic strength is also discussed compared with a "classical" method without an activity concept. The proposed method is applied to acid-base and redox titrations.

Principle

A "classical" approach, involving the molar concentration instead of the activity, is used in the following discussion. Of course, the influence of the ionic strength on the detection error is also discussed in some cases.

Linear Photometric Titration. As a matter of convenience, a self-indicating reaction is considered,

$$A + B = P. \tag{1}$$

Assume a titrand (A) to react with a titrant (B) to form a product (P), and that P is the only absorbing species at the wavelength used, and obeys Beer's law. Let the volumes of the titrand and titrant (V_A and V_B) be kept constant, so that the total volume of the reaction solution (V) or the ratio of the volume (V_A/V_B) is maintained constant during the titration. It is necessary to mention here that the partial molar volumes of the titrand and the titrant are assumed to have no significant difference from their molar volumes, which should be reasonable for these solutions used in general titrations. For a "complete" reaction, a titrant solution at different concentrations of B ($C_{B,0}$) in a given volume of V_B is added to a titrand with a volume of V_A and an initial concentration ($C_{A,0}$), respectively. According to the stoichiometric relationship of the titration reaction above, the concentration of P ($C_{P,eq}$) can be written as a function of the concentration of B ($C_{B,0}$),

$$C_{P,eq} = f(C_{B,0}). \tag{2}$$

Before the equivalence point (B.E.P.), the equilibrium concentrations of A, B, and P are

$$C_{A,eq} = (C_{A,0}V_A - C_{B,0}V_B)/V,$$
$$C_{B,eq} = 0,$$
$$C_{P,eq} = C_{B,0}V_B/V,$$

respectively. Hence, the absorbance of the solution at B.E.P. (Abs_b) holds, as follows:

$$Abs_b = kC_{P,eq} = kC_{B,0}V_B/V = k_1C_{B,0}, \tag{3}$$

where k and k_1 are constants and $k_1 = kV_B/V$.

After the equivalence point (A.E.P.), $C_{A,eq}=0$; $C_{B,eq} = C_{B,0}V_B/V$; $C_{P,eq}=C_{A,0}V_A/V$. Hence, the absorbance of the solution at A.E.P. (Abs_a) is given as

$$Abs_a = kC_{P,eq} = k_2 = \text{constant}. \tag{4}$$

The relationship between Eqs. 3 and 4 is shown in Fig. 1a. At the equivalence point, since Abs_b is equal to Abs_a, the equilibrium concentrations of A, B, and P are $C_{A,(EP)}=0$, $C_{B,(EP)}=0$, $C_{P,(EP)}=C_{A,0}V_A/V$. Therefore, the equivalence-point concentration of the titrant ($C_{B,0(EP)}$) can be established by two different methods: the first is to plot the absorbances vs. $C_{B,0}$; the second is to solve the simultaneous Eqs. 3 and 4 mathematically. From the latter, we can obtain

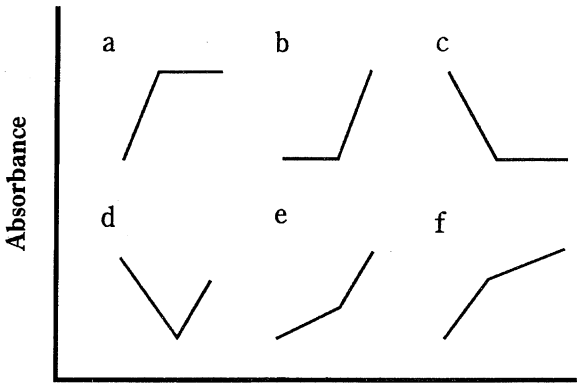

Fig. 1. Typical curves of photometric titration with concentration-variable patterns. a: $\varepsilon_P > \varepsilon_A$, $\varepsilon_B = 0$; b: $\varepsilon_B > \varepsilon_A$, $\varepsilon_P = 0$; c: $\varepsilon_A > \varepsilon_P$, $\varepsilon_B = 0$; d: $\varepsilon_A > \varepsilon_P$, $\varepsilon_B > 0$; e: $\varepsilon_P > \varepsilon_A$, $\varepsilon_B > \varepsilon_P$; f: $\varepsilon_P > \varepsilon_A$, $\varepsilon_B < \varepsilon_P$. Where, the ε_A, ε_B, and ε_P are the molar absorptitivities of the titrand, titrant, and product, respectively.

$$C_{B,0(EP)} = k_2/k_1. \tag{5}$$

Thus, the concentration of A can be determined stoichiometrically,

$$C_{A,0} = C_{B,0(EP)}V_B/V_A. \tag{6}$$

Figure 1 (b—f) illustrates some other typical types of photometric titration curves.

Acid–Base Titrations. Tanaka and Nakagawa[24] precisely discussed the acid–base titrations about thirty years ago. Other types of titration methods with a concentration-variable titration method will be introduced in this section, the methods of which are in line with the recent recommendation of IUPAC.[23]

Two kinds of acid–base titrations are discussed here; the others should be obtained in the same way.

Strong Acid and Strong Base. For a reaction of a strong acid (A) with $C_{A,0}$ mol dm^{-3} (M) and a volume of V_A and a strong base (B) with $C_{B,0}$ M and V_B, the base is assumed to be titrant, and the same titration procedure mentioned in the previous section (cf. **Linear Photometric Titration**) is used.

Before the equivalence point, according to the proton condition and the ion product of water, the equilibrium concentration of the hydrogen ion can be represented as

$$[H^+] = K_w/[H^+] + C_A - C_B \tag{7}$$

in the acidic side, because $[H^+] \gg K_w/[H^+]$; hence,

$$[H^+] = C_A - C_B = C_{A,0}V_A/V - C_{B,0}V_B/V$$
$$= k_0 - m_1C_{B,0}, \tag{8}$$

where V is the total volume of the mixed solution, and $k_0 = C_{A,0}V_A/V$, $m_1 = V_B/V$.

After the equivalence point, similarly, the following relationship is obtained:

$$[OH^-] = K_w/[OH^-] + C_B - C_A, \tag{9}$$

since $[OH^-] \gg K_w/[OH^-]$; thus,

$$[OH^-] = -C_{A,0}V_A/V + C_{B,0}V_B/V = -k_0 + m_1 C_{B,0}. \quad (10)$$

The equivalence concentration ($C_{B,0(EP)}$) can be obtained by two methods: Solving the simultaneous Eqs. 8 and 10; plotting $[H^+]$ as well as $[OH^-]$ vs. $C_{B,0}$. In the latter, the left and the right vertical axes are graduated by $[H^+]$ and $[OH^-]$, respectively; then, $C_{B,0(EP)}$ can be determined by the intersection point of two straight lines. From Eqs. 8 and 10, it can be seen that the sensitivity of this method depends on the ratio of the titrant volume to the total volume. The detection of the equivalence point is shown in Fig. 2.

Besides, another solution technique is presented as follows. The simultaneous Eqs. 8 and 10 can be rewritten as

$$pH = -\log\{(C_{A,0}V_A - C_{B,0}V_B)/V\}, \quad (11)$$

$$pH = pK_w + \log\{(C_{B,0}V_B - C_{A,0}V_A)/V\}. \quad (12)$$

In view of the traditional method, it seems impossible to solve Eqs. 11 and 12, because they contain an unknown factor, $C_{A,0}$. Therefore, a new optimum approach has been proposed to solve this problem. The details are discussed in a later section (cf. **Determination of the Equivalence Point**).

Weak Acid and Strong Base. If a weak acid (HA) with $C_{A,0}$ M and V_A and a strong base (B) with $C_{B,0}$ M and V_B are mixed, the reaction can be written as

$$\begin{array}{lccccc} & HA & + & OH^- & = A^- + H_2O & (13) \\ \text{at equilibrium} & C_A - C_X & & C_B - C_X & C_X, & \end{array}$$

where C_X is the concentration of the product (A^-). According to the law of mass action, one can express these equilibrium concentrations as follows:

$$\frac{C_X}{(C_A - C_X)[OH^-]} = K = K_a/K_w. \quad (14)$$

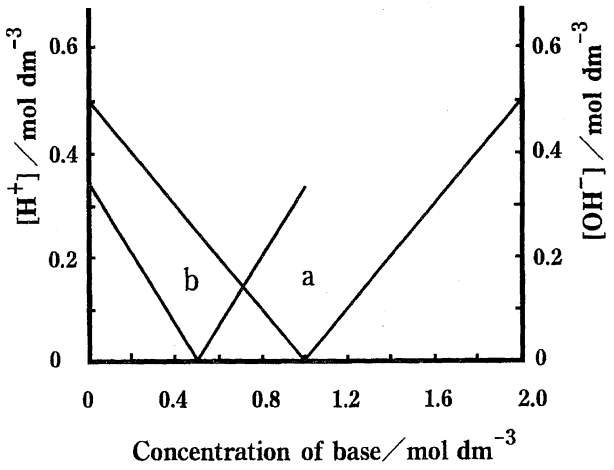

Fig. 2. Titration of strong base with strong acid based on concentration-variable pattern. Detection of the equivalence point of 1 M strong acid with a strong base using direct concentration statement: (a) $V_B = V_A$; (b) $V_B = 2V_A$.

For a reaction with an equilibrium constant of K more than 10^8, some satisfactory approximations are given: before the equivalence point, $C_X = C_B$; after the equivalence point, $C_X = C_A$. Therefore, Eq. 14 can be written as

$$\text{B.E.P.} \qquad [H^+] = K_a(C_A - C_B)/C_B \quad (15)$$

or

$$pH = pK_a - \log\{(C_{A,0}V_A - C_{B,0}V_B)/C_{B,0}V_B\}. \quad (16)$$

Of course, the relationship of $[OH^-] = C_B - C_X$ is also valid throughout titration. Hence,

$$\text{A.E.P.} \qquad [H^+] = K_w/(C_B - C_A) \quad (17)$$

or

$$pH = pK_w + \log\{(C_{B,0}V_B - C_{A,0}V_A)/V\}. \quad (18)$$

Similarly, the equivalence point pH_{EP}, $C_{B,0(EP)}$, and $C_{A,0}$ can be obtained by solving the simultaneous Eqs. 16 and 18.

The titration of a weak base with a strong acid can be carried out in the same way and, obviously, the same approach should be applicable to those cases of polyprotic acids or bases. Some typical acid–base titration curves are shown in Fig. 3; their detections of the equivalence points are shown in Fig. 4.

Redox Titration. A simple redox reaction of a titrand (Red_1) with $C_{A,0}$ M and a volume of V_A and a titrant (Ox_2) with $C_{B,0}$ M and V_B, is considered as

$$\begin{array}{lccccc} & Red_1 & + & Ox_2 & = Ox_1 + Red_2 & (19) \\ \text{at equilibrium} & C_A - C_X & & C_B - C_X & C_X \quad C_X. & \end{array}$$

Assume that the reaction is "complete", meaning that it has a very large equilibrium constant, the following approximations are reasonable: before the equivalence point, $C_X = C_B$; after the equivalence point, $C_X = C_A$. By the Nernst equation,

$$E_1 = E_1^0 + (RT/nF)\ln([Ox_1]/[Red_1]), \quad (20)$$

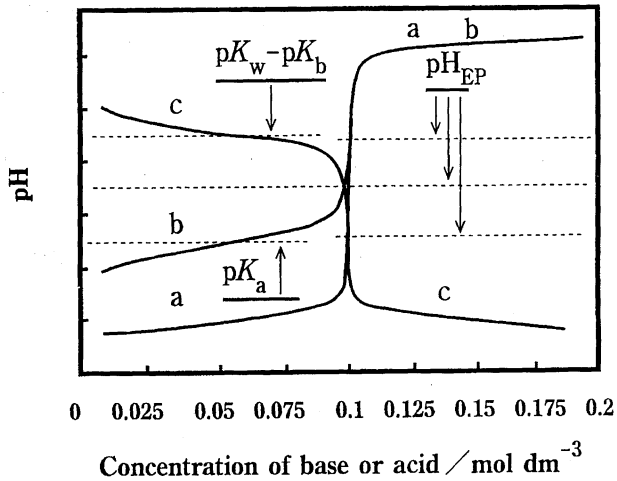

Fig. 3. Theoretical titration curves of acid-base titrations using concentration-variable patterns. $V_B = V_A$, $C_{A,0} = 0.1$ mol dm^{-3}: (a) strong acid with strong base; (b) weak acid ($K_a = 1.0 \times 10^{-5}$) with strong base; (c) weak base ($K_b = 1.0 \times 10^{-5}$) with strong acid.

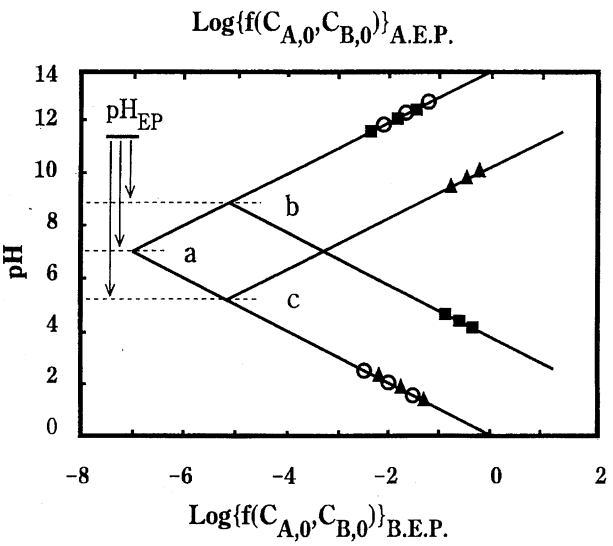

Fig. 4. Detection of the equivalence point for the Fig. 3 (a), (b), and (c).

$$E_2 = E_2^0 + (RT/nF)\ln([Ox_2]/[Red_2]), \quad (21)$$

where E is the measured potential, E^0 is the standard electrode potential of the redox ion pair to be determined, T is the absolute temperature, n is the number of electrons involved in the half-cell concerned, R is the gas constant and F is the Faraday constant. Since the potential of the reaction system can be expressed by either the potential of the half cells (1 or 2), and $V_A=V_B$ is assumed, the relationships between the potential and the concentrations of the titrand and titrant, before and after the equivalence point, are given by the following equations:

$$\text{B.E.P.} \quad E_1 = E_1^0 + (RT/nF)\ln\{C_{B,0}/(C_{B,0} - C_{A,0})\}, \quad (22)$$

$$\text{A.E.P.} \quad E_2 = E_2^0 + (RT/nF)\ln\{(C_{B,0} - C_{A,0})/C_{A,0}\}. \quad (23)$$

Assume that the number of electrons in the half-cell reaction is 1, the equivalence-point potential can be given by

$$E_{EP} = (E_1^0 + E_2^0)/2. \quad (24)$$

Of course, the equivalence concentration ($C_{B,0(EP)}$) and the unknown ($C_{A,0}$) can be obtained by solving the simultaneous Eqs. 22 and 23. Figure 5 shows a typical redox titrimetric curve, and Fig. 6 shows the relationship between the potential and the logarithmic variable in Eqs. 22 and 23.

Determination of the Equivalence Point. In order to solve those simultaneous equations mentioned above, how to calculate the unknown factor ($C_{A,0}$) must be overcome. The redox titration is one example to be explained.

Since a linear relationship between the potential and the logarithmic variable exists in both Eqs. 22 and 23, a least-squares method (LSM) should be appropriate for treating Eqs. 22 and 23. Since the biggest first-derivative value of $dE/dC_{B,0}$ should be obtained when the equivalence point is reached, the end-point concentration of the titrand and/or titrant should be located within the range between the two

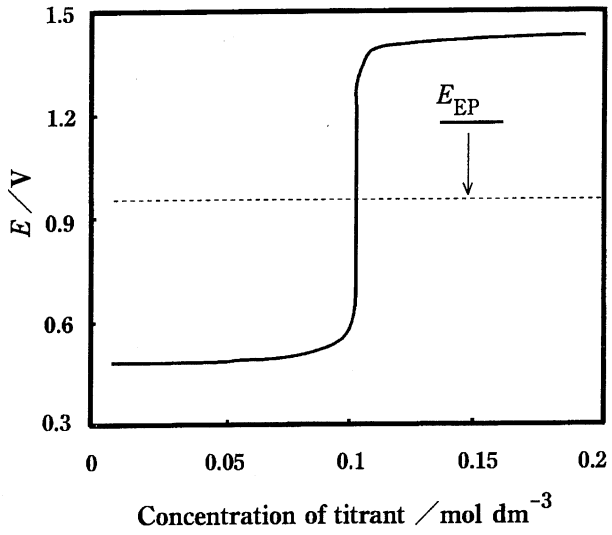

Fig. 5. Theoretical titration curve of redox titration $Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$ using concentration-variable pattern. $C_{Fe^{2+}}=0.1$ mol dm^{-3} and $V_{Fe^{2+}} : V_{Ce^{4+}}=1:1$.

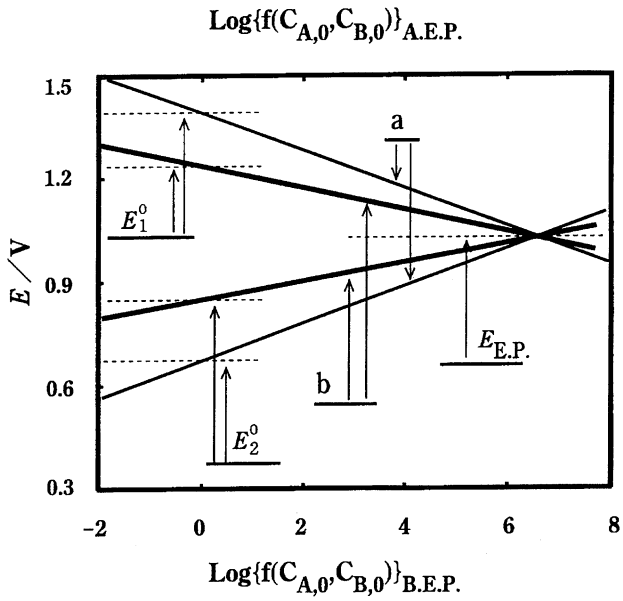

Fig. 6. Detection of the equivalence point with two-thirds section method, the number of electron in the half-reaction: (a) n=1; (b) n=2.

points nearest to the equivalence point, which gives the biggest first-derivative value.

A function defined as

$$f = \sum(E_{calc} - E_{exp})^2 \quad (25)$$

was proposed to estimate the correlativity of the calculated values and the experimental values. Here, E_{calc} is the calculated value, which can be obtained by using LSM. A "true" value of the unknown concentration ($C_{A,0}$) should make the function f minimum. However, a "bad" $C_{A,0}$ value would distort the linearity of Eq. 22 or Eq. 23, and lead to a larger value of f. Therefore, an objective function,

$$F = f_b + f_a, \quad (26)$$

has been proposed for searching for the $C_{A,0}$ value, where f_b and f_a have the same definition as f, but correspond to those data before and after the equivalence point, respectively. The smaller is the function, the better is the $C_{A,0}$ value. When a minimum or a required value of the function is reached, the "true" $C_{A,0}$ value can be considered to have been obtained. The objective function is continuous and monotonous, which suggests that an optimization approach would be valid.

The first approximation value of $C_{A,0}$ was selected from the range which is regarded to be the maximum value of $\Delta E/\Delta C_{B,0}$. According to the calculated result, the range to be researched is contracted, from which the next approximation value is taken. In a preliminary study, some optimum methods, such as the golden-section and half-section methods, were tried; unfortunately, those methods failed because the best point was always missing. in order to keep the best point from leakage, a new optimum approach was designed. The present authors propose this approach as the two-thirds section method. In this method, the optimized range was equally divided into three parts by four points in every computation. Since the worst part was disposed after each optimization had been completed, the best range containing the "true" $C_{A,0}$ value was absolutely retained. The convergence of the range can be carried out at a speed of the (n_C)th power of two-thirds, where n_C is the number of computations. This means that a precision of less than 4×10^{-5} of the initial range can be reached within twenty-five repetitive computations. Therefore, it was programed that the repetitive computation did not stop until the objective function decreased to a required value of 1×10^{-20} or twenty-five repetitive computations had been completed.

Titration Error. The error incurred in titration with the concentration-variable patterns is defined as

$$\text{error} = \frac{\Delta C_{\text{titrant}}}{\text{equivalence point concentration of titrant}}, \quad (27)$$

where $\Delta C_{\text{titrant}}$ equals the difference between the equivalence-point concentration and the end-point concentration of the titrant. The percentage error is obtained by multiplying this value by 100.

As an example concerning the titration of a strong acid with a strong base, the equivalence point would be located at a pH or pOH of 7; hence, Eq. 27 can be expressed as

$$\text{error} = \frac{C_{B,0(EP)} - C_{B,0(ep)}}{C_{B,0(EP)}}. \quad (28)$$

If $pH_{(eq)} < 7$,

$$\text{error} = \frac{10^{-7} - 10^{-pH(ep)}}{C_{B,0(ep)} + 10^{-7} - 10^{-pH(ep)}}.$$

If $pH_{(ep)} > 7$,

$$\text{error} = \frac{10^{-7} - 10^{-pOH(ep)}}{C_{B,0(ep)} + 10^{-7} - 10^{-pOH(ep)}}.$$

We now consider the influence of the titrant volume on the measured values in a simple acid-base titration. By differentiating Eq. 11, we obtain

$$\frac{dpH}{dV_B} = \left(\frac{C_{B,0}}{C_{A,0}V_A - C_{B,0}V_B} + \frac{1}{V}\right) / \ln 10. \quad (29)$$

If $C_{B,0}=C_{A,0}/2$ and $V_A=V_B$ are assumed, the first-derivative value of dpH/dV_B, at the point at which the titrand is neutralized to half, is given by $3/(2V_B\times\ln 10)$. Therefore, the volume error of a titrant of 1.5% is allowable when a precision of 0.01 pH is required under the condition that $V_B=0.005$ dm^3, which can be easily achieved in conventional batch operation.

Experimental

Reagents and Apparatus. All of the chemicals were of analytical reagent grade unless otherwise noted. Ultra-pure water was used to prepare the solutions throughout. The standard solutions of sodium hydroxide (0.1 M (M=mol dm^{-3}), factor=1.000 at 20 °C) and hydrochloric acid (0.1 M, factor=1.000 at 20 °C) (Yoneyama) and potassium permanganate (0.02 M, factor=1.003) (Wako) were used. Cerium(IV) sulfate, iron(II) sulfate and sulfuric acid (Wako) were used. Aqueous solutions of the following acid–base indicators were also used: phenolphthalein (50 mg dm^{-3}) in 2.5% ethanol, methyl orange (50 mg dm^{-3}) in 2.5% ethanol. The sodium hydroxide solution was used without further standardization. The iron(II) sulfate solution was standardized proir to titration.

Some laboratory glasswares were used. A pH meter (HM-20S, TOA) equipped with a glass electrode (GST-5211C) and a complex electrode (PTS-5011C) was used.

Computer Analysis. NEC PC-98 series computers (9801RA, 9801FA, 9801BX3, 9801NS/A (Note-type), 9821Ap2, 9821V10, and 9821Xa16) were used. Several versions of MS-DOS (Ver. 3.3B, 5.00, 5.0A, 5.0A-H, and 6.20) were used for evaluating the equivalence-point information. MS-DOS in Windows 95 was also used for comparisons. Machines without a math-coprocessor did not work well in regarding both speed and precision. All of the data computed by twenty-five repetitive computations with the PC-9801FA (with the math-coprocessor) and PC-9801RA (without the math-coprocessor) were checked by twenty-five and thirty-five repetitive calculations with the UBASIC program.[25]

Results and Discussion

In a linear spectrophotometric titration, in order to correct any dilution-induced curvature, all appreciable absorbance values should be multiplied by a volume-correction factor, $(V+v)/V$, where V is the initial volume of the titrand and v is the added volume of the titrant. Therefore, although a relatively concentrated titrant is commonly added from a small burette care must be taken so that S_X, the standard deviation of the titrant volume, does not contribute very markedly to S_A, the standard deviation of the absorbance. It should, however, be emphasized that the accuracy still depends upon the dilution effect as well as the chemical balance, glassware calibration, temperature effects from stirring, etc.

The equivalence point, or "equivalence concentration", can be related to the analyte concentration by two different procedures. First, the determined values against the concentration of the titrant can be used for plotting. However, it is limited to an instance which does not contain the unknown concentration of the sample in the linearization relationships.

Second, the detection method of the equivalence point proposed in the present paper can be applied. Of course, it suits all types of titrations.

Acid–Base Titration. Different types of acids were titrated. A NaOH solution was used as the titrant. Then, 0.1 M HCl solutions with 0.00500 dm^3 were titrated with NaOH solutions at different concentrations (from 0.00 to 0.10 M) with 0.010 dm^3. The results obtained from the simultaneous Eqs. 8 and 10 were as follows:

$$\text{B.E.P.} \quad [H^+] = 0.03189 - 0.6345C_{B,0} \qquad (r = 0.9997)$$
$$\text{A.E.P.} \quad [OH^-] = -0.02449 + 0.4925C_{B,0} \qquad (r = 0.9997)$$

From $C_{B,0(EP)}$=0.05002 M, the concentration of the titrand solution was obtained to be 0.10004 M. The accuracy, shown as the relative deviation for the certified value was 0.04%. The reproducibility, expressed as the relative standard deviation (R.S.D.) was 0.3%. The two coefficients of the correlation mentioned above showed very good linear relationships between the hydrogen-ion concentration and the concentration of the titrant before the equivalence point, and between the hydroxide-ion concentration and the concentration of the titrant after the equivalence point.

The two-thirds section method was also applied to the strong acid–base titration mentioned above. The obtained results are listed in Table 1. The pH at the end point and the original concentration of acid ($C_{A,0}$) were found to be 6.946 and 0.100006 M, respectively. The equations between the pH and the concentration of the titrant before and after the end point showed the following very good linear relationship:

$$\text{B.E.P.} \quad \text{pH} = 0.0087 - 1.005 \log\{(C_{A,0} - 2C_{B,0})/3\}, \qquad (r=0.9998)$$
$$\text{A.E.P.} \quad \text{pH} = 13.88 + 1.005 \log\{(2C_{B,0} - C_{A,0})/3\}. \qquad (r=0.9998)$$

The detailed optimum results are listed in Table 2. From

Table 1. Determination of the Titrand Concentration by the Two-Thirds Section Method

$C_{B,0}$ / M	pH detn.	pH calcd	Relative error of pH/%
0.00	1.50	1.4934	−0.44
0.01	1.59	1.5908	0.05
0.02	1.71	1.7164	0.37
0.03	1.89	1.8934	0.18
0.04	2.20	2.1959	−0.19
	$\text{pH}=0.0087-1.005\log\{(C_{A,0}-2C_{B,0})/3\}$		
0.06	11.69	11.694	0.03
0.07	12.00	11.997	−0.03
0.08	12.18	12.174	−0.05
0.09	12.30	12.299	−0.01
0.10	12.39	12.397	0.05
	$\text{pH}=13.88+1.005\log\{(2C_{B,0}-C_{A,0})/3\}$		

$pH_{(ep)}$=6.946, $C_{A,0}$/M=0.100006. HCl solutions with 0.00500 dm^3 were titrated with NaOH solutions at different concentrations from 0.00 to 0.10 M with 0.010 dm^3. Computer used was PC-9801FA with the math-coprocessor.

Table 2. Optimization of the End Point Concentration of Titrand by the Two-Thirds Section Method

No.	Points remained[a)]	$pH_{(ep)}$	Objective function/10^{-4}	Concentration of titrand/M
1	1,2,3	6.013	10.1	0.09335
2	2,3,4	6.638	3.04	0.09778
3	2,3,4	7,047	2.34	0.10074
4	1,2,3	6.775	2.50	0.09877
5	2,3,4	6.956	2.26	0.10008
6	1,2,3	6.835	2.36	0.09921
7	2,3,4	6.916	2.26	0.09979
8	2,3,4	6.970	2.26	0.10018
9	1,2,3	6.934	2.26	0.09992
10	2,3,4	6.958	2.26	0.10009
11	1,2,3	6.942	2.26	0.09998
12	2,3,4	6.953	2.26	0.10005
13	1,2,3	6.946	2.26	0.10000
14	1,2,3	6.941	2.26	0.09997
15	2,3,4	6.944	2.26	0.09999
16	2,3,4	6.946	2.26	0.10001
17	2,3,4	6.947	2.26	0.10002
18	1,2,3	6.947	2.26	0.10001
19	1,2,3	6.947	2.26	0.100006
20	1,2,3	6.946	2.26	0.100003
21	2,3,4	6.946	2.26	0.100005
22	2,3,4	6.946	2.26	0.100006
23	1,2,3	6.946	2.26	0.100005
24	2,3,4	6.946	2.26	0.100006
25	1,2,3	6.946	2.26	0.100006

a) The starting points ($C_{A,0}$) were: 0.08004, 0.0933467, 0.106653, 0.11996 M. Titration and computer used were the same as described in Table 1, note.

Table 2, it can be seen that the $C_{A,0}$ value became better with an increase of the optimum computation. The first approximate value of $C_{A,0}$ gave a bad detection curve, and had an end point pH of 6.03; the concentration of the titrand was 0.09335 M. After twenty-five calculations, a $C_{A,0}$ value was obtained at a precision of 0.05%. The detection curves drawn at the first and the twenty-five optimizations by computations with the two-thirds section method are shown in Fig. 7. From these results, it can be seen that the agreement between the calculated and theoretical equivalence point pH was sufficiently good, and that the titration error was 0.06 pH unit, less than that of any cases with pH indicators. By a simple calculation, it was found that a titration error of 0.06 pH unit between pH 7.0 and 6.946 corresponds to a volume error of 5×10^{-7} dm^3 in a 0.05 M NaOH solution, which means that the titration precision increased up to a level of 1×10^{-4} drop.

A ca. 0.05 M acetic acid solution was titrated with NaOH solutions at a volume ratio of 1. The computed data were as follows:

$$\text{B.E.P.} \quad \text{pH} = 4.691 - 0.9613 \log\{(C_{A,0} - C_{B,0})/C_{B,0}\}, \qquad (r=1.000)$$
$$\text{A.E.P.} \quad \text{pH} = 14.14 + 1.182 \log\{(C_{B,0} - C_{A,0})/2\}. \qquad (r=0.9994)$$

The pH at the end point was 8.93, which agreed very closely

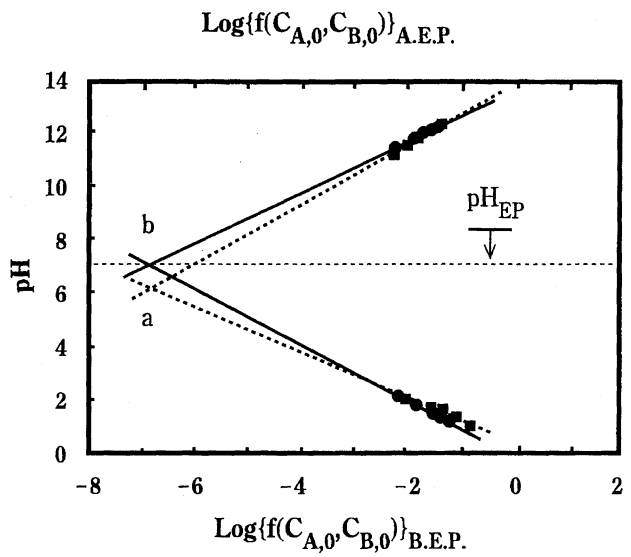

Fig. 7. Optimization of the original concentration of titrand in acid–base titration using the two-thirds section method. Graphical curves in the optimization process of the end point, where titrand is 0.1 M HCl with 0.005 dm^3 and titrant is 0.01—0.1 M NaOH with 0.01 dm^3: (a) the first computation; (b) the twentieth computation (cf. Table 2).

with the theoretical value of 8.6. If pH 8.6 is taken as the true value, the titration error of 0.33 pH means a 1/123 drop in the titration error, and that a sample concentration error of 1×10^{-5} M was obtained. The concentration of the titrand solution was found to be 0.04771 M. The same acetic acid solution was titrated with 0.05 M NaOH using phenolphthalein as an indicator. Its concentration, obtained as an average value for three determinations, was 0.04802 M.

A Na_2CO_3 solution was titrated with HCl solutions. Since the titration system contained two analytes, they were treated with the optimum approach independently. For the first equivalence point,

$$\text{B.E.P.pH} = 10.04 - 0.8963 \log\{C_{B,0}V_B/(C_{A,0}V_A - C_{B,0}V_B)\} \quad (r = 0.9998),$$

$$\text{A.E.P.pH} = 6.32 - 1.216 \log\{(C_{B,0}V_B - C_{A,0}V_A)/(2C_{A,0}V_A - C_{B,0}V_B)\} \quad (r = 0.9996).$$

For the second equivalence point,

$$\text{B.E.P.pH} = 6.26 + 1.225 \log\{(C'_{A,0}V_A - C_{B,0}V_B)/(C_{B,0}V_B - C'_{A,0}V_A/2)\} \quad (r = 0.9997),$$

$$\text{A.E.P.pH} = 0.7104 - 0.6852 \log\{(C_{B,0}V_B - C'_{A,0}V_A)/V\} \quad (r = 0.9999),$$

where $C'_{A,0}$ is the apparent concentration of HCO_3^-. In fact, it should be twice the concentration of CO_3^{2-}. The pH values at the first and second end points were 8.42 and 3.5, which agree very closely with the theoretical values of 8.3 and 3.8, respectively. From the calculated results, we obtained $C_{A,0}$ and $C'_{A,0}$ concentrations of 0.04765 and 0.09682 M, respectively. Therefore, the concentration of CO_3^{2-} was found to be 0.04765 from $C_{A,0}$, or 0.04841 from $C'_{A,0}$. There is a 1.6% relative error between these two values. A conventional batch operation using the mixed indicators of phenolphthalein and methyl orange gave values of 0.04950 and 0.04870 M, respectively.

After the second end point, the solution's pH depended only on the hydrogen-ion concentration, no matter whether the carbonic acid escaped out from the system or not. Therefore, the CVTM method presents an effective approach to avoid any influence from CO_2 gas if the solution is sufficiently dilute.

Redox Titration. A cerium(IV) sulfate solution of ca. 0.025 M was titrated with iron(II) sulfate solutions in a medium of 0.5 M H_2SO_4 solution using the proposed methodology. The obtained results were as follows:

$$\text{B.E.P.} \quad E = 1.438 + 0.06621 \log\{(C_{A,0}V_A - C_{B,0}V_B)/C_{B,0}V_B\} \quad (r = 1.000),$$

$$\text{A.E.P.} \quad E = 0.6871 + 0.05114 \log\{C_{A,0}V_A/(C_{B,0}V_B - C_{A,0}V_A)\} \quad (r = 0.9999).$$

The potential at the end point was 1.02 V, which gave a markedly concordant answer for a theoretical value of 1.06 V. The concentration of cerium(IV) sulfate was found to be 0.02604 M. The same solution was titrated by a conventional batch method, and was found to be 0.02611 M, which also agreed very well with the obtained result. Also, much information can be simultaneously obtained using the proposed method. The formal electrode potentials of the iron(III)–(II) and cerium(IV)–(III) half cells in 0.5 M H_2SO_4 were obtained from the intercepts of the equations; they agreed very well with the literature values of 0.68 and 1.44 V.

Correction for Ionic Strength. All of the discussions presented above are not associated with the ionic strength. In solutions with concentrations higher than about 10^{-3} M, the activity coefficients must be taken into account, and the relationship between the activity and the concentration of an ion is $a_i = C_i f_i$.

For the titration of a weak acid with a strong base, Eqs. 16 and 18 can be rewritten as

$$\text{B.E.P.} \quad \text{pH}_b = \text{p}K_a - \log(f_{HA}/f_{A^-}) - \log\{(C_{A,0}V_A - C_{B,0}V_B)/C_{B,0}V_B\}, \quad (30)$$

$$\text{A.E.P.} \quad \text{pH}_a = \text{p}K_w + \log f_{OH^-} + \log\{(C_{B,0}V_B - C_{A,0}V_A)/V\}. \quad (31)$$

Because the activity coefficient of a single ion cannot be measured, the mean activity coefficient was used. According to the Debye–Hückel limiting law and $f_{HA} = 1$, the following equations were obtained:

$$\text{B.E.P.} \quad \text{pH} = \text{p}K_a - 0.5(C_{B,0}V_B/V)^{1/2} - \log\{(C_{A,0}V_A - C_{B,0}V_B)/C_{B,0}V_B\}, \quad (32)$$

$$\text{A.E.P.}\quad \mathrm{pH} = \mathrm{p}K_w - 0.5(C_{B,0}V_B/V)^{1/2} + \log\{(C_{B,0}V_B - C_{A,0}V_A)/V\}. \quad (33)$$

Equations 32 and 33 were used to solve the titration data of the acetic acid mentioned above, and the following results were obtained:

$$\text{B.E.P.}\quad \mathrm{pH} = 4.747 - 0.9933 \log\{(C_{A,0} - C_{B,0})/C_{B,0}f_{A^-}\},$$
$$\text{A.E.P.}\quad \mathrm{pH} = 14.45 + 1.256 \log\{(C_{B,0} - C_{A,0})f_{OH^-}/2\}.$$

The pH at the end point and the concentration of the acetic acid solution were found to be 9.03 and 0.04785 M, respectively. The equivalence-point pH was calculated to be 8.6 using the equation $(\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}C_{A^-})/2$. It was found that the titration error decreased to 0.43 pH, due to a correction of the ionic strength. From the results it can be seen that the ionization constant of the acetic acid was effectively corrected on the acidic side, and that the ion product of water was bigger than the theoretical value. The reason may be attributed to the base-error in measurements with a glass electrode on the strong base side. In a range of over 0.05 M in concentration of the titrant, Davies's equation is rather appropriate. By making a correction with this equation, the following results were obtained:

$$\text{B.E.P.}\quad \mathrm{pH} = 4.746 - 0.9926 \log\{(C_{A,0} - C_{B,0})/C_{B,0}f_{A^-}\},$$
$$\text{A.E.P.}\quad \mathrm{pH} = 14.26 + 1.196 \log\{(C_{B,0} - C_{A,0})f_{OH^-}/2\},$$

where the pH and $C_{A,0}$ were 9.06 and 0.04792, respectively. It is obvious that the Davies correction is effective.

It is very interesting that some useful information, such as $\mathrm{p}K_a$ and $\mathrm{p}K_w$, can be obtained directly from the solved results. However, there was no significant difference between the acetic acid concentration and the obtained result without correction of the ionic strength; the ionization constant of the acetic acid was in accord with its reference value of 4.74, less than a relative deviation of 0.2%.

Conclusions

The concentration-variable titration method has been demonstrated to be useful in acid–base and redox titrations. This method can surely be applied to other titrations, such as spectrophotometric, complexometric, amperometric, conductometric, and nonaqueous titrations. The following advantages of the method have been shown: The measured signals are independent of the volume of the titrant solution and indicators are unnecessary; a dilution correction is no longer necessary and the titration precision and accuracy are greatly improved. Certainly, it should be especially valuable for those titration reactions without proper indicators. Since this method can work at a classical chemical-equilibria and steady-state operation,[26,27] it is expected to be applied to continuous-flow analyses as well as automatic titration.

The authors thank Nomura Micro-Science Co. for providing ultra-pure water.

References

1) E. Bishop, in C. L. Wilson, "Theory and Principles," Wilson and Wilson's "Comprehensive Analytical Chemistry," Elsevier, Amsterdam (1960), Vol. IB, Chap. VII, pp. 5—117.
2) I. M. Korenman, "Novel Titration Methods," Himiya, Moscow (1983), Translated in Japanese by S. Aoyama, Japan–Russia Information Service (1985).
3) S. Ebel, *Chem. Ing. Tech.*, **46**, 811 (1974).
4) J. Zsako and F. Makkay, *Zh. Anal. Khim.*, **29**, 1894 (1974).
5) B. M. Mar'yanov, *Zh. Anal. Khim.*, **30**, 1892 (1975).
6) P. Chakurova, P. Zikolov, G. Velinov, and O. Budevski, *Farmatsiya (Sofia)*, **26**, 8 (1976).
7) G. G. Clemena, J. W. Reynolds, and R. McCormick, *Transp. Res. Rec.*, **651**, 1 (1977).
8) J. Zsako and F. Makkay, *Chem. Anal. (Warsaw)*, **25**, 95 (1980).
9) H. Marquardt, *Z. Chem.*, **20**, 264 (1980).
10) J. F. Magallanes and A. F. Caridi, *Anal. Chim. Acta*, **133**, 203 (1981).
11) R. Pardo, J. L. Bernal, and E. Barrado, *Anal. Chim. Acta*, **142**, 285 (1982).
12) L. Anderson and M. Wedborg, *Oceanol. Acta*, **6**, 357 (1983).
13) J. Hazi, L. Daruhazi, O. Pinter, and Z. Szakaly, *Mikrochim. Acta*, **2**, 379 (1986).
14) J. Hazi, Z. Szakaly, and L. Fonyo, *Magy. Kem. Foly.*, **96**, 241 (1990).
15) M. Paul, *Rocz. Glebozn.*, **38**, 31 (1987).
16) L. G. Anderson, C. Haraldsson, and R. Lindegren, *Mar. Chem.*, **37**, 179 (1992).
17) Y. I. Tur'yan, G. V. Ivanova, and V. F. Pokhodzei, *Zh. Anal. Khim.*, **47**, 715 (1992).
18) B. Wang, W. Wu, and X. Fan, *Fenxi Huaxue*, **10**, 618 (1982).
19) V. Pavlova and M. Wedborg, *Water Res.*, **22**, 497 (1988).
20) A. Vesala, *J. Chem. Educ.*, **69**, 577 (1992).
21) S. B. Mokrov and N. N. Markuzina, *Vestn. S.-Peterb. Univ., Ser. 4: Fiz. Khim.*, (**3**), 55 (1994).
22) H. Freiser, "Concepts and Calculations in Analytical Chemistry," CRC Press Inc., Boca Raton, Florida (1992). Translated in Japanese by O. Tochiyama, "Analytical Chemistry — Theory and Calculations —," Tokyo Kagaku Doujin, Tokyo (1994).
23) H. Freiser and G. H. Nancollas, "IUPAC Compendium of Analytical Nomenclature," 2nd ed, Blackwell, Oxford (1987).
24) M. Tanaka and G. Nakagawa, "Jikken-Kagaku-Kouza (Zoku), Vol. 7, Reactions and New Technologies in Analytical Chemistry," Maruzen, Tokyo (1966), pp. 54.
25) Y. Narusawa and Y. Miyamae, *J. Chem. Software*, **1**, 99 (1993). cf. Homepage of Chemical Software Society of Japan (CSSJ): URL is "http://cssjweb.chem.eng.himeji-tech.ac.jp".
26) C. -L. Zhang, Y. Narusawa, and S. Kitahama, *Chem. Lett.*, **1993**, 877.
27) C. -L. Zhang and Y. Narusawa, *Bull. Chem. Soc. Jpn.*, **67**, 2994 (1994).