



POTENTIOMETRIC CHARACTERIZATION OF WEAK ACIDS BY MULTIPLE SAMPLE ADDITION—I. LINEAR EQUATIONS AND INTRINSIC PERFORMANCE OF THE METHOD

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Summary—The suitability of linearized multiple sample-addition for the potentiometric characterization of monoprotic weak acids is examined. Linear equations for the separate or simultaneous determination of the acidity constant and of the sample concentration by treatment of experimental data are introduced. The intrinsic performance of the method and the application range of the different equations are discussed with reference to the theoretical effect of measurement errors on the values of the quantities to be determined.

Titration with a standard solution of strong base is the method of choice for the characterization of a weak acid. Monitoring the titration progress by means of potentiometric measurements with a pH glass electrode allows the accomplishment of tasks of various complexity, from the simple quantitation of a single solute to the determination of the composition of multi-component mixtures together with the acidity constants of polyfunctional acids. Computer programs¹⁻³ at various levels of sophistication have been proposed, and are being continuously developed, in order to allow systems of increasing complexity to be dealt with in agreement with the principles of statistical analysis of data.

However, an examination of the literature reveals that, most commonly, experimental data are currently treated with simpler procedures. Very convenient computational and graphical procedures for processing titration data are based on various forms of linear equations, obtained by rearranging the rigorous equation of the titration curve (representing the theoretical dependence of measured pH on the added titrant volume) or an approximate form of it and employing auxiliary variables.⁴ The Gran function and the Gran plot are widely used,

mainly in their original approximate form,⁵ to locate the equivalence point; the rigorously linear Gran-type function⁶ requires the knowledge of the acidity constant (the dissociation constant K_a). Other linear equations⁴ can be employed when both the acidity constant and the concentration are unknown (this approach is frequent for the characterization of polyfunctional acids with several equivalent acidic functional groups).⁷

Most of these methods, because of the nature of the relevant equations,⁴ do not fulfill one or more of the prerequisites (for instance, normal error distribution, uncorrelated variables) to be treated with ordinary linear least squares methods. However, they can still be useful for preliminary screening of data and also yield reliable results, if appropriately used. Understanding the underlying principles and knowledge of their optimal application range, of their performance in the presence of interferences, and of other limitations are necessary for this purpose. Linearization methods of potentiometric titrations for the quantitation of monoprotic weak acids have been recently reviewed,⁴ with the purpose of giving some general hints about their correct application.

Potentiometric methods not requiring titration with a base, like sample addition or sample dilution, are seldom used. For instance, pH measurements of sample solutions at a

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single known concentration of weak acid are sometimes employed to calculate K_a for classification of the acid strength of series of similar substances.

In a previous paper,⁸ it has been shown that multiple addition of a standard solution of a weak acid to an unknown solution of the same acid, alone or in mixture with the conjugate base, can serve for the same purposes as the titration with a strong base. Linear equations for computational or graphical treatment of experimental data have been introduced and discussed. However, the need of a standard solution of the determinand sets some limit to the practical convenience of the method.

In this paper we will discuss a much more convenient application of the same principle, *i.e.* multiple addition of unknown sample, which can be described as a 'titration without titrant'. Measured volumes of the sample solution, containing a single weak acid at concentration C , are added stepwise to a known volume V^0 of water (the constancy of ionic strength being an important prerequisite for obtaining easily manageable data, an aqueous solution of inert electrolyte is preferable). In order to obtain either the concentration C or the acidity constant of the sample acid, K_a , or both, the experimental variables V (the total volume of sample added in correspondence of each step) and $[H^+]$ (the corresponding hydronium ion concentration measured by a calibrated glass electrode) can be processed by computational methods according to the basic equation describing the theoretical relation between these quantities.

Alternatively, by using expressly defined auxiliary variables, the basic equation can be rearranged to give linear equations which can be conveniently used to obtain, either by calculation or graphically, the quantities sought for. Equations for linearization of multiple addition of a single monoprotic weak acid are introduced and discussed in this paper. The intrinsic performance of the method and the application range of the different linear equations in dependence on the strength and on the concentration of the sample acid are evaluated, by calculating the theoretical effect of measurement errors on the results of simulated experiments.

The effect of interfering contaminants and the practical performance of the method will be investigated in a future paper.

THEORY

It is mainly matter of preference whether linear equations are obtained indirectly, by rearranging the basic equation relating the experimental variables V and $[H^+]$ with the physicochemical parameters of the system investigated, or by directly combining the equations of the mass balances of solutes and of the electroneutrality of the solution with the expressions of the equilibrium constants involved. The Gran-type equation is particularly suitable as the starting point for the following treatment, both because of its concrete meaning, which supports its derivation and interpretation,⁴ and because a general form for weak acid additions has been previously introduced.⁸

The rigorous Gran-type equation for multiple weak acid sample-addition

When an increasing volume V of a solution containing the weak acid HA at concentration C is added stepwise to a volume V^0 of solution containing the same acid at concentration $C^0 \geq 0$, the amount (moles) of weak acid in the solution, $C^0V^0 + CV$, increases proportionally to the added volume V (note that the same is not true for the concentration, unless $V \ll V^0$). By expressing this amount in terms of its functional relationship to the experimental variables, V and $[H^+]$, equation (1) is obtained⁸

$$F = (V^0 + V)([H^+] - K_w/[H^+])(1 + [H^+]/K_a) \\ = C^0V^0 + CV. \quad (1)$$

This equation defines an auxiliary variable F which is necessarily a linear function of V , in analogy with the 'rigorous Gran function' for weak acid titration.⁴ Application of equation (1) to the determination of the unknown concentration C^0 of a weak acid solution by multiple addition of a standard solution of the same acid at concentration C has been discussed.⁸

Equation (1) is, as stated above, only a particular form of the basic equation $f(V, [H^+], V^0, C^0, C, K_a, K_w) = 0$ relating the experimental variables V (the controlled variable) and $[H^+]$ (the measured variable) to the parameters V^0 , C^0 , C , K_a and K_w . By using other auxiliary variables, other linear equations have been introduced, by which one or two of the above parameters can be calculated from the experimental data. A more general equation has been also obtained that allows for the presence of the conjugate weak base at concentration C_b .

Table 1. Linear equations for the simultaneous determination of the acidity constant K_a and of the sample concentration C of a weak monoprotic acid by multiple sample addition [H , equation (4)]

Named after	X	Y	C	K_a	equation $Y = a + bX$	Nr.
Hofstee ¹¹	$H/[H^+]/V$	H/V	a	$-1/b$	$H/V = C - H/[H^+]/K_a V$	(8)
Scatchard ¹²	H/V	$H/[H^+]/V$	$-a/b$	$-b$	$H/[H^+]/V = K_a C - K_a H/V$	(9)
Lineweaver and Burk ¹³	$[H^+]$	V/H	$1/a$	a/b	$V/H = 1/C + [H^+]/K_a C$	(10)
n.n. ⁴	V/H	$[H^+]$	$-b/a$	$-a$	$[H^+] = -K_a + K_a CV/H$	(11)
Scott ¹⁴	$1/[H^+]$	$V/H/[H^+]$	$1/b$	b/a	$V/H/[H^+] = 1/K_a C + 1/C/[H^+]$	(12)
Briggs and Stuehr ¹⁵	$V/H/[H^+]$	$1/[H^+]$	b	$-1/a$	$1/[H^+] = -1/K_a + CV/H/[H^+]$	(13)

together with the weak acid at C° , in the measured solution.⁸

The case presently of interest, not previously considered, is multiple addition of a sample containing the weak acid at concentration C to a known volume of water or of an aqueous solution of an inert electrolyte. By putting the initial concentration of weak acid in the measured solution, C° , equal to 0, equation (1) reduces to equation (2):

$$F = (V^\circ + V)([H^+] - K_w/[H^+])(1 + [H^+]/K_a) = CV \quad (2)$$

or,

$$F = H(1 + [H^+]/K_a) = CV, \quad (3)$$

where

$$H = (V^\circ + V)([H^+] - K_w/[H^+]). \quad (4)$$

With moderately weak acids at moderate dilution ($\text{pH} < 5.5$), $K_w/[H^+]$ ($=[\text{OH}^-]$) is negligible with respect to $[H^+]$; therefore, equation (2) can, in most instances, be reduced to the approximate form

$$F = (V^\circ + V)[H^+](1 + [H^+]/K_a) = CV. \quad (5)$$

Equations (2)–(5) can be used, in principle, for the determination of the sample concentration C . In order to calculate the value of F for each sample addition, *i.e.* for every pair of experimental values of V and $[H^+]$, V° must be measured and K_a must be known. Moreover, the glass electrode must be calibrated to measure the hydronium ion concentration $[H^+]$ instead of pH .^{2,8,9} It is seen that F is proportional to V with C as the coefficient. Therefore, the unknown concentration of the added sample, C , is obtained either graphically from the slope of the plot of $F = Y$ against $V = X$, or by least-squares adjustment of the coefficient of the equation $Y = CX$.

Other linear equations

Equations (2)–(5) can be used as such for calculating the sample concentration only when the value of K_a is known. However, they can be

rearranged to give equations having a different scope or a wider one. For instance, to calculate K_a when C is known equation (3) can be written as

$$H/[H^+] = K_a(CV - H), \quad (6)$$

or, by defining the auxiliary variables $X = CV - H$ and $Y = H/[H^+]$, $Y = K_a X$. Therefore, equation (6) yields the acidity constant as the graphical or least-squares slope of the transformed experimental data.

It can be observed that an equation equivalent to equation (6), for instance equation (7),

$$K_a = \frac{[H^+]^2}{\frac{CV}{(V^\circ + V)} - [H^+]} \quad (7)$$

(valid at $\text{pH} < 5.5$) is used when K_a is calculated (in substance, as the ratio $K_a = Y/X$) from a single measurement of pH .

When both C and K_a are unknown, equation (2) can be employed to obtain these parameters with the usual computational methods.^{2,10} Alternatively, by defining other suitable auxiliary variables X and Y that can be calculated for each pair of experimental data V and $[H^+]$, it is possible to rearrange equation (2) to obtain six different linear equations of the form $Y = a + bX$. For each type of equation, the auxiliary variables X and Y have different definitions, and the linear parameters a and b are different combinations of C and K_a . Therefore, C and K_a can be obtained by numerical or graphical linear fit of the values of X and Y calculated from experimental data. These equations are collected in Table 1. Each equation is here named after the author of a linear equation formerly introduced for different purposes (for instance, for complexometric⁷ or acid–base⁸ titrations) that shows the same relationships between the linear parameters a and b and the sought after quantities C and K_a (4th and 5th columns of Table 1).^{11–15} It should be noted that equations (9), (11), (13) are the same as equations (8), (10), (12) respectively,

with interchanged coordinates. The variables X and Y of all the equations above are inter-related, because their expressions contain the same experimental variables V and $[H^+]$. Therefore, simple least-squares linearization is unsuitable in principle; however, it is commonly used to work out titration data with analogous linear functions, and is claimed to give reliable values of the unknown titration parameters when the precision of experimental data is good.¹⁶

DISCUSSION

The linear equation for the determination of acidity constant with known sample concentration

A simple evaluation of the suitability of the different linear equations for the determination of the acidity constant, either alone [equations (6) and (7)] or together with the sample concentration [equations (8)–(13)], has been made by investigating the effect of measurement errors on the relevant plots and on the resulting values of the parameter(s) sought. Errors of the measured variable, the hydronium ion concentration $[H^+]$, and of the controlled variable, the added volume V , have been considered separately.

Exact values of hydronium ion concentration, $[H^+]$, have been calculated¹⁷ theoretically for several simulated experiments, each one consisting of a series of equal additions of weak acid with given acidity constant K_a and concentration C (typically, 10 additions of 1 ml of sample to 100 ml of supporting electrolyte). Calculations were made for different values of K_a and for different ranges of values of the ratio C_{HA}/K_a , where $C_{HA} = CV/(V^0 + V)$ is the total concentration of weak acid in the measured solution after each addition.

For the evaluation of the separate determination of the acidity constant with equation (6), the deviation from the ideal behavior caused by error in $[H^+]$ has been investigated by calculating the auxiliary variables $X = CV - H$ and $Y = H[H^+]$ both for the exact values of $[H^+]$ and for pairs of corresponding values $(1 \pm \delta)[H^+]$, that is, for hydronium ion concentration affected by systematic relative error $\pm \delta$ (typically $\pm 4\%$, as due to a systematic absolute error of ± 1 mV in the measured e.m.f.).

Representative results are shown in Fig. 1, where the plot of equation (6) with exact data is compared with plots of corresponding points affected by systematic errors in $[H^+]$. For better comparison, reduced coordinates have been

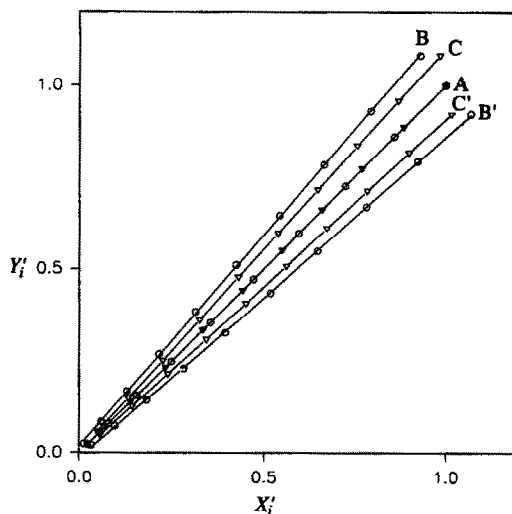


Fig. 1. Plot of equation (6) with synthetic data $X = CV - H$, $Y = H[H^+]$ [H , see equation (4)] calculated for 10 additions of weak acid sample, $pK_a = 4$; $V^0 = 100$ ml, $V_i = i$ ml, $i = 1 \div 10$. \circ , $C = 0.001M$ ($C_{HA}/K_a \approx 0.1 \div 1$); ∇ , $C = 0.01M$ ($C_{HA}/K_a \approx 1 \div 10$). Points on line A, calculated from theoretical values of $[H^+]$; upper points, calculated with 4% error in $[H^+]$; lower points, with -4% error in $[H^+]$. Reduced auxiliary variables are $X'_i = X_i/X_{10}$ and $Y'_i = Y_i/Y_{10}$, where X_{10} and Y_{10} are the exact values for the last point of the same simulated experiment. Lines B, B', C, C' are least-squares straight lines.

used; for any i -th point, $X'_i = X_i/X_{10}$ has been plotted as the abscissa and $Y'_i = Y_i/Y_{10}$ as the ordinate, where X_{10} and Y_{10} are the exact values at the maximum added volume of each experiment. Consequently, the straight line representing equation (6) for the exact values of $[H^+]$, line A, is the same for all the simulated experiments, with only a different distribution of all points but the last one. Synthetic data for $C_{HA}/K_a \approx 0.1 \div 1$ (circles and interpolated straight lines B, B') and for $C_{HA}/K_a \approx 1 \div 10$ (triangles and lines C, C') are represented. Plots affected by error for $C_{HA}/K_a \approx 10 \div 100$ or larger are very near to lines C and C'.

It is seen that a systematic error in $[H^+]$ can have an appreciable effect on the slope of the plot. The slope decreases with increasing concentration, becoming practically constant at higher concentrations. With $pK_a = 4$, for systematic +4% and -4% errors in $[H^+]$ the deviation of the linearized plot and, therefore, of the calculated value of K_a was respectively 14.7 and -12.9% in the range $C_{HA}/K_a \approx 0.1 \div 1$ (lines B and B', with correlation coefficient 0.9996), 9.5 and -9.0% at $C_{HA}/K_a \approx 1 \div 10$ (lines C and C', apparently through the origin, with correlation coefficient 1.0000), 8.5 and -8.2% at $C_{HA}/K_a \approx 10 \div 100$; with $pK_a = 7$, the

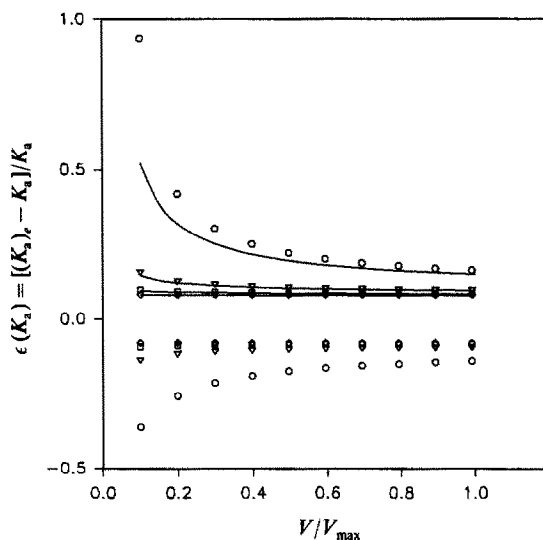


Fig. 2. Relative error of K_a calculated from theoretical values of $[H^+]$ with 4% (upper points) and -4% (lower points) systematic error by using equation (7). $V^0 = 100$ ml, $V_i = i$ ml, $i = 1 \div 10$; \circ , $C = 0.001M$, $pK_a = 4$ ($C_{HA}/K_a \approx 0.1 \div 1$); ∇ , $C = 0.01M$, $pK_a = 4$ ($C_{HA}/K_a \approx 1 \div 10$); \square , $C = 0.1M$, $pK_a = 4$ ($C_{HA}/K_a \approx 10 \div 10^2$); \diamond , $C = 0.1M$, $pK_a = 7$ ($C_{HA}/K_a \approx 10^4 \div 10^5$). Solid lines: relative standard deviation of K_a for 4% relative standard deviation of $[H^+]$ in the same C_{HA}/K_a ranges as the nearest series of points.

deviation was 8.2 and -7.8% at $C_{HA}/K_a \approx 10^4 \div 10^5$. Changing the values of C and K_a does not significantly alter the deviation of plots affected by error in given C_{HA}/K_a ranges. It is concluded that the effect of systematic errors on the determination of K_a is appreciably decreased by increasing the ratio C_{HA}/K_a over 1:1, while a scarcely significant improvement is obtained by further increasing this ratio over 10:1.

The investigation of the effect of random errors would require a separate treatment. For simplicity, the pairs of plots corresponding to opposite systematic errors can be taken as fairly indicative of the effect of a constant uncertainty of the measured variable on the auxiliary variables of the plot, and used for a qualitative comparison of the precision of the determination of slope, *i.e.* of the acidity constant, in the different experimental ranges. By comparing these pairs of plots for different simulated experiments it is concluded that, in order to obtain optimal accuracy and precision in the determination of acidity constant by multiple addition of sample at known concentration, it is sufficient to operate at $C_{HA} \geq K_a$.

Similar conclusions are reached by consideration of equation (7). Each series of points in Fig. 2 corresponds to multiple addition in

a different range of values of the ratio C_{HA}/K_a . Abscissa is the ratio V/V_{max} between the added volume at each point and the total volume added at the end of each series of additions. Ordinate is the relative error $\epsilon(K_a) = [(K_a)_e - K_a]/K_a$ of the determination of K_a , where $(K_a)_e$ is the value of acidity constant calculated point by point with equation (7) for $[H^+]$ values affected by $\pm 4\%$ error. Solid lines represent, for the same ranges of values of C_{HA}/K_a , the relative standard deviation $\sigma(K_a)$ of the calculated value of the acidity constant, for a standard deviation of 4% of measured $[H^+]$. It is seen that the theoretical lower limit of the relative systematic error and of the uncertainty of K_a (two times the systematic error and the uncertainty of $[H^+]$, respectively) is rapidly approached at $C_{HA}/K_a > 1$.

The effect of error in the controlled experimental variable, the added sample volume, has been also investigated. For each simulated experiment, the hydronium ion concentration, $[H^+]$, has been calculated for volumes affected by given errors. Either constant relative error or constant absolute error in V (total volume added after each addition step) have been assumed. The auxiliary variables $X = CV - H$ and $Y = H[H^+]$ of equation (6) have been calculated for these values of $[H^+]$ by using the nominal values of V .

Constant relative error in volume is brought about, for instance, by a calibration error of the volumetric apparatus by which sample additions are made. A +1% or -1% error (a very large value for this kind of error) has been seen to cause an error of K_a of opposite sign and having approximately the same magnitude, but in the lower range of the ratio C_{HA}/K_a (*i.e.* $0.1 \div 1$) where it is appreciably larger. Deviation from linearity is so small as to be inappreciable in practice; the interpolated straight line apparently goes through the origin as required by equation (6).

Constant absolute error in volume can be relatively more important, particularly when small volumes are measured for addition. Negative error of this kind can be caused, for instance, by the presence of an air bubble in the capillary tip of the delivery tubing of the dispensing microburette. However, it has been seen that errors of this kind do not affect the determination of acidity constant with equation (6). In our simulated experiments, a volume error of -10% in the first of 10 identical sample aliquots produced a very small variation of the

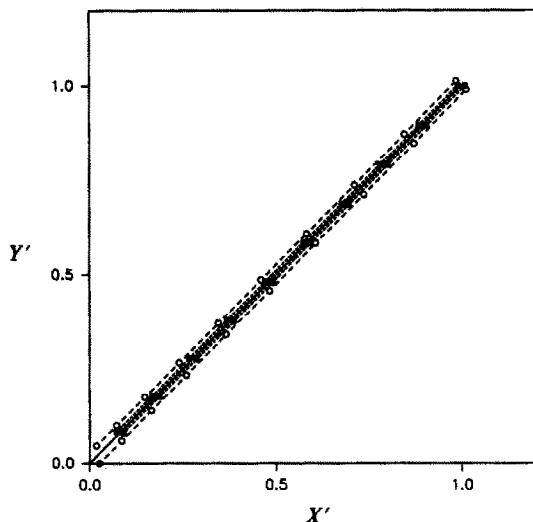


Fig. 3. Normalized plot of equation (6) with constant absolute error in volume. \circ , $pK_a = 4$, $C = 0.001M$ ($C_{HA}/K_a \approx 0.1 \div 1$); \square , $C = 0.1M$ ($C_{HA}/K_a \approx 10 \div 10^2$); other data and normalization as Fig. 1. Solid line, correct function without volume error; upper lines, values of $[H^+]$ calculated for $V = V_i + 0.1V_i$; lower lines, values of $[H^+]$ calculated for $V = V_i - 0.1V_i$.

slope of equation (6), while significantly displacing the intercept $Y(X=0)$ towards negative values. Although deviation increases with decreasing the C_{HA}/K_a ratio (Fig. 3), the error in K_a is only -0.2% in the range $C_{HA}/K_a = 0.1 \div 1$. Also in this instance, the pairs of plots in Fig. 3 corresponding to opposite systematic errors can be taken as indicative of the effect of the absolute precision of the controlled variable on the precision of K_a . It is concluded that the determination of K_a is not seriously affected by systematic or random volume errors.

Finally, the effect of the use of a wrong concentration value in calculations has been considered. The synthetic data $[H^+]$ against V for series of equal additions of weak acid have been used to calculate the auxiliary variable $X = CV - H$ of equation (6) after affecting C with a given relative error. The effect of error in C is found to be much more dependent on the ratio C_{HA}/K_a than on the single values of these two quantities. Even with large error in C , for instance $\pm 10\%$, apparently linear plots are obtained. However, the slope is not really independent of the C_{HA}/K_a ratio; indeed, deviations are larger at larger relative dilution. For instance, for a $\pm 1\%$ error in C , the relative error in K_a is practically identical with it at $C_{HA}/K_a > 100$, but is $\pm 1.3\%$ in the range $C_{HA}/K_a \approx 1 \div 10$ and increases to $\pm 2.5\%$ in the range $C_{HA}/K_a \approx 0.1 \div 1$.

The linear equations for simultaneous determination of acidity constant and sample concentration

The synthetic data $[H^+]$ and $(1 + \delta)[H^+]$ against V for series of equal additions of weak acid with given acidity constant K_a and concentration C have also been used to calculate the auxiliary variables X and Y of equations (8)–(13). Representative results are plotted in Figs 4–7.

Equation (8), normalized to the form $Y' = 1 + X'$ by putting $X'_i = X_i/CK_a$ and $Y'_i = Y_i/C$, is plotted in Fig. 4 for four series of synthetic data corresponding to $C_{HA}/K_a \approx 0.1 \div 1$, $1 \div 10$, $10 \div 10^2$, and $10^4 \div 10^5$, respectively. Data for $(1 + \delta)[H^+]$, with $\delta = 0.04$, are also plotted; for simplicity, only the two extreme points of each simulated experiment are shown, because a systematic error displaces the plot without affecting linearity. Indeed, the effect of systematic error $\pm \delta[H^+]$ on the slope (which yields K_a , see Table 1) and on the intercepts with abscissa, $X(Y=0) = CK_a$, and with ordinate, $Y(X=0) = C$, is constant, independently of the concentration range. Both the values of K_a and of C obtained by linear extrapolation of points with error are affected by a relative error equal to the error δ of the 'measured' variable ($+4$ and -4% for the upper and the lower plots of Fig. 4, respectively). However, the points of experiments at C_{HA}/K_a ratio higher than 10 are

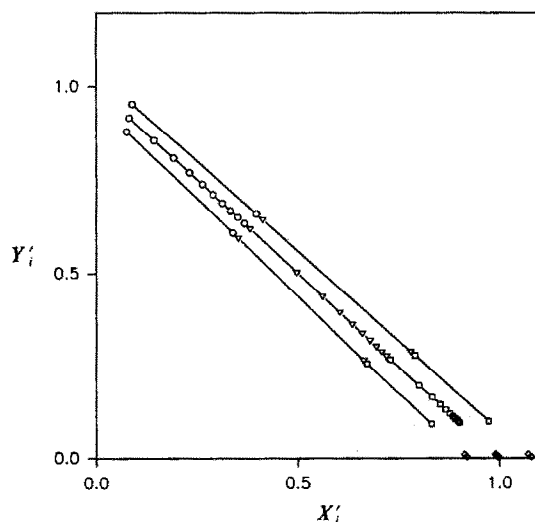


Fig. 4. Normalized plots of the Hofstee-type function, equation (8). Normalized auxiliary variables $X'_i = X_i/C$ and $Y'_i = Y_i/CK_a$ were calculated from synthetic values of $(1 + \delta)[H^+]$ with $\delta = 0.04$ (upper lines), 0, and -0.04 (lower lines). Symbols as Fig. 2. As X' increases, Y' decreases with actual weak acid concentration C_{HA} .

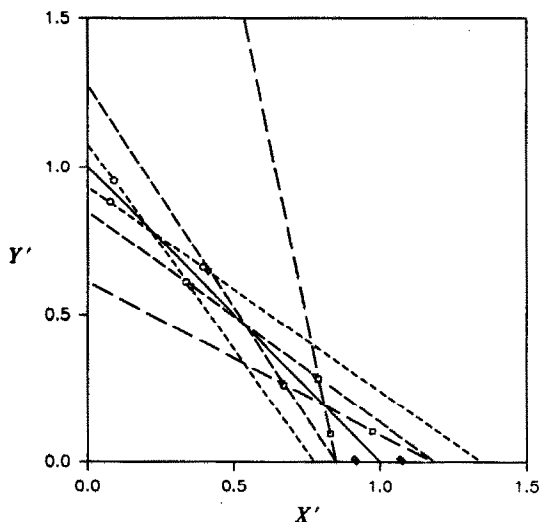


Fig. 5. Precision of the parameters of equation (8) in different C_{HA}/K_a ranges compared by extrapolating straight (dashed) lines through each pair of extreme points affected by opposite error of each series of synthetic data of Fig. 4. The solid line is the exact Hofstee-type equation.

more and more compressed towards $X' = 1$, $Y' = 0$ (while points of experiments at ratio smaller than 0.1, not shown, are compressed towards $X' = 0$, $Y' = 1$); therefore, the effect of random errors on the uncertainty of the experimental linear parameters and of the quantities drawn from them must be expected to depend heavily on the ratio C_{HA}/K_a .

A rather naïve approach to the evaluation of this effect, valid for mere comparison but effective and having a great visual impact, is introduced in Fig. 5. A straight line is interpolated through two points, calculated for opposite (positive and negative, respectively) values of error, at the beginning and at the end, respectively, of a simulated experiment. A second straight line is interpolated through the corresponding points calculated with inverted (negative and positive, respectively) values of error. Allowance made for the dramatic exaggeration, the span of the parameters of each pair of straight lines is sufficiently indicative for a comparison of the precision attainable in different C_{HA}/K_a ranges.

It is seen that the smallest span of slope (and, therefore, the smallest relative uncertainty of the calculated value of K_a) occurs at $C_{HA}/K_a \approx 0.1 \div 1$ and $1 \div 10$, it being approximately the same in both ranges; the uncertainty increases more and more both with increasing and (not shown) with decreasing this ratio. It is concluded that measurements restricted to C_{HA}/K_a ratios much larger than 10 or smaller

than 0.1 make the determination of the acidity constant by linearized multiple sample addition of sample at unknown concentration (*i.e.* the simultaneous determination of acidity constant and concentration) very uncertain and eventually unsuitable.

In contrast, the span of intercept with ordinate (and, therefore, of calculated value of C) decreases by decreasing the C_{HA}/K_a ratio. This finding is in agreement with the trivial consideration that at increasing dilution all acids behave as strong or nearly so; by consequence, the concentration of hydronium ion, losing its dependence on acidity constant, approaches the concentration of solute. The precision of the sample concentration improves to the detriment of the precision of the acidity constant.

The span of values of $X (Y = 0) = C_{HA}/K_a$ is indicative of the uncertainty of the determination of the product of the two unknown quantities; in Fig. 5, it is almost constant for $C_{HA}/K_a > 1$, but increases at lower values of the ratio. This finding is in agreement with the considerations above and also with the discussion of equation (6); indeed, if concentration is known, the whole uncertainty applies to the other quantity of the ratio.

Similar conclusion are drawn for the other linear functions, like Lineweaver–Burk-type (equation 10) and Scott-type (equation 12) functions plotted in Figs 6 and 7, respectively. It is also interesting to observe that with equation (12) (see Fig. 7) Y is more inclined to be affected by measurement errors than X ; with equation (10) (Fig. 6), both variables are about equally affected; with equation (8) (Fig. 4), at lower concentration (smaller X) Y is much more affected than X , while the opposite applies at higher concentration.

The auxiliary variables X and Y of equations (8)–(13) have been also calculated for simulated experiments with V affected by systematic error. The effect of a reasonably large constant relative error is moderate. For instance, with equation (8) (the Hofstee-type function) a -1% systematic error in the added volume yields errors in K_a and C that increase regularly from -0.3% and $+1\%$, respectively, in the range $C_{HA}/K_a \approx 0.1 \div 1$ to -1.3% and $+2.2\%$ in the range $C_{HA}/K_a \approx 10^2 \div 10^3$; deviations from linearity are inappreciable. Therefore, a moderately small error of this kind does not impair the determination of K_a with samples of unknown C .

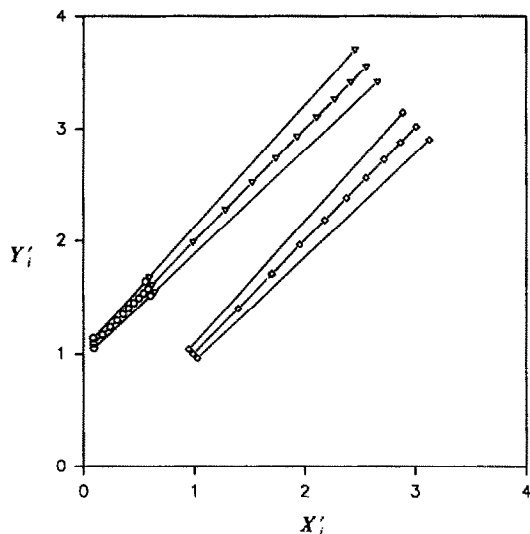


Fig. 6. Normalized plots of the Lineweaver and Burk-type function, equation (10). Normalized auxiliary variables $X'_i = X_i/K_a$ and $Y'_i = Y_i C$ were calculated from synthetic values of $(1 + \delta)[H^+]$ with $\delta = 0.04$ (upper lines), 0, and -0.04 (lower lines). Symbols as Fig. 2. \diamond , Scale reduced 100 times. Both X' and Y' increase with actual weak acid concentration.

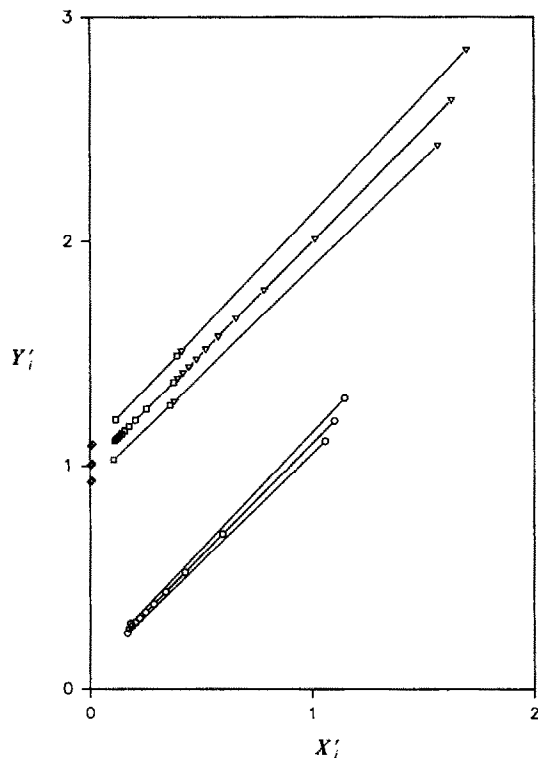


Fig. 7. Normalized plots of the Scott-type function, equation (12). Normalized auxiliary variables $X'_i = X_i/K_a$ and $Y'_i = Y_i C K_a$ were calculated from synthetic values of $(1 + \delta)[H^+]$ with $\delta = 0.04$ (upper lines), 0, and -0.04 (lower lines). Symbols as Fig. 2. \circ , Scale reduced 10 times. Both X' and Y' decrease with actual weak acid concentration.

The effect of a systematic absolute error in volume is more serious (Figs 8 and 9). The deviation of equations (8)–(13) from the linear behavior becomes appreciable, and the error in the parameters can grow unacceptably large even for small volume error. With equation (8), an error in the first sample aliquot added corresponding to -1% of its volume (which at the end of the series of 10 additions reduces to a 0.1% error of total volume added, the controlled variable) brings about errors in K_a and C that are, respectively, 2.7 and -1.0% in the range $C_{HA}/K_a \approx 0.1 \div 1$, 2.5 and -1.8% in the range $C_{HA}/K_a \approx 1 \div 10$, 5.1 and -4.4% in the range $C_{HA}/K_a \approx 10 \div 10^2$, 14 and -12% in the range $C_{HA}/K_a \approx 10^2 \div 10^3$. Dramatically large deviations are shown in Figs 8 and 9.

The linear rigorous Gran-type equation for determination of sample concentration

The previous discussion is focused on the use of multiple sample addition for the determination of the acidity constant. The equation from which all the other equations have been drawn, equation (2), is discussed last, because the determination of the sample concentration is possibly the less appealing application of the multiple sample-addition method. The Gran-type function for multiple sample-addition, equation (2) (or equation 5), always requires

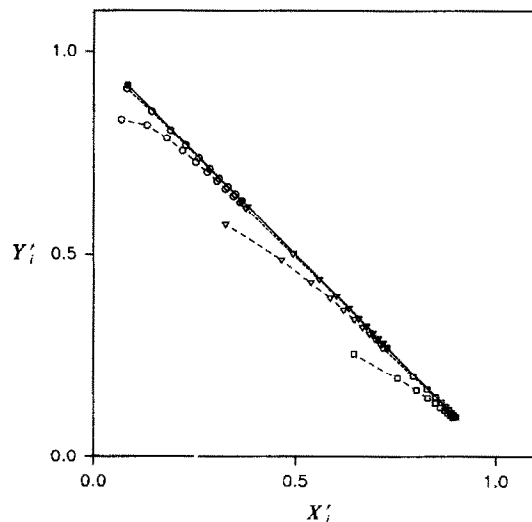


Fig. 8. Normalized plots of the Hofstee-type function, equation (8), with constant absolute error in volume. Symbols, data and normalization as Fig. 4. Solid line, correct function without volume error; dotted lines, values of $[H^+]$ calculated for $V = V_i - 0.01V_1$; dashed lines, $[H^+]$ calculated for $V = V_i - 0.1V_1$.

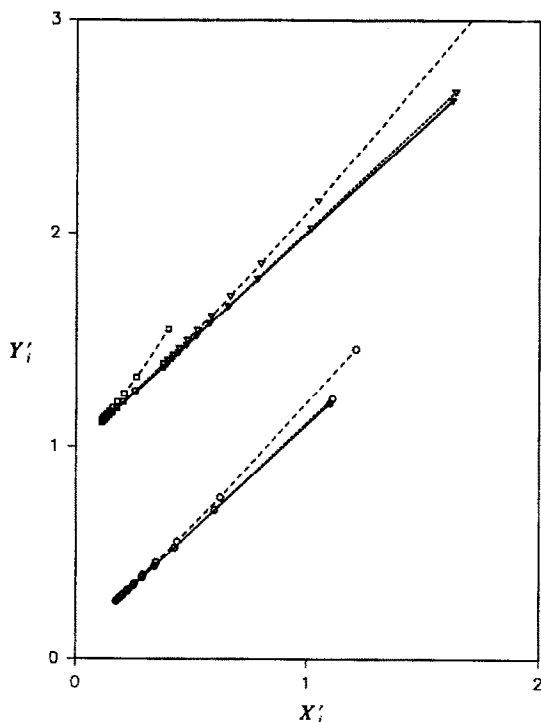


Fig. 9. Normalized plots of the Scott-type function, equation (8), with constant absolute error in volume. Symbols, data and normalization as Fig. 4. Solid line, correct function without volume error; dotted lines, values of $[H^+]$ calculated for $V = V_i - 0.01V_i$; dashed lines, $[H^+]$ calculated for $V = V_i - 0.1V_i$. \circ , Scale reduced 10 times.

careful electrode calibration and knowledge of the acidity constant. In contrast, the Gran function for titration of weak acid with strong base can be used, in most instances, in the approximate form (the original one),⁵ which simply requires the value of the slope factor of the electrode; only for titration of moderately strong acids is it necessary to resort to the rigorous equation which requires both calibration and K_a .¹⁸ Even in this instance, it is much less prone to errors due to inaccurate values of K_a than equation (2). Indeed, the Gran function for titration yields the sample concentration from the equivalence volume extrapolated as the intercept ($Y = 0$); in contrast, equation (2) yields the sample concentration from the slope, which is much more affected by errors in K_a than the intercept.

The synthetic data $[H^+]$ against V for series of equal additions of weak acid with given acidity constant K_a and concentration C have been used to calculate the auxiliary variable F of equation (2) with K_a values affected by error $\pm \Delta K_a$. Also the effect of the error in K_a is found to be much more dependent on the ratio C_{HA}/K_a than on the single values of these two quantities.

If the error in K_a is moderate, for instance $\pm 10\%$ (corresponding approximately to $pK_a \pm 0.05$), the variation of slope is barely appreciable within the range C_{HA}/K_a of a single simulated experiment, and an apparently linear plot is obtained. However, the slope is not really constant. Consequently, the deviation of the mean slope of error plots and, therefore, the error in C , depends on the C_{HA}/K_a range, it being smaller at smaller C_{HA}/K_a values. For instance, the relative error in C is $\Delta C/C \approx 0.4 \Delta K_a/K_a$ in the range $C_{HA}/K_a \approx 0.1 \div 1$, $\Delta C/C \approx 0.8 \Delta K_a/K_a$ in the range $C_{HA}/K_a \approx 1 \div 10$, and approaches $\Delta C/C = \Delta K_a/K_a$ at higher C_{HA}/K_a ratios.

It can be concluded that the accuracy with which the values of acidity constants in the experimental conditions are usually known is scarcely sufficient for satisfactory determination of concentration. A separate accurate determination of K_a can be worthwhile only with repetitive samples.

CONCLUSIONS

The above discussion suggests that 'titration-without-titrant' by multiple sample addition can compete with titration with strong base, or supplement it, for the characterization of weak acid samples. The intrinsic performance of this procedure and the optimal conditions for its application depend on the values of the analytical parameters of the sample, acidity constant and concentration of the acid, and on which of these must be determined.

The variety of samples and of conditions where the method is applicable is larger when only the acidity constant is wanted, the sample concentration being known. For optimal results, the relevant linear equation (6) requires in principle only that the stoichiometric concentration of acid in the solution where the hydronium ion concentration is measured is larger than the acidity constant. This prerequisite excludes only relatively strong acids. A sufficiently high concentration of the sample used for the additions is generally advantageous.

When both the sample concentration and the acidity constant are unknown, the range of conditions allowing optimal results with equations (8)–(13) is different, it also being narrower; indeed, the ratio between the total acid concentration in the measured solution and the acidity constant must preferably be higher than 0.1 and lower than 10. In this range, the

adverse effect of errors in either experimental variable are expected to be smaller. In principle, moderately weak acids are favored.

Finally, multiple sample addition cannot be safely recommended as a general method for the separate determination of the sample concentration using equation (2) by relying on literature values of the acidity constants. It is expected that acidic or basic interfering substances, inevitably present in real experiments, alter more or less the intrinsic performance of the method and set some other limits to its application. The performance of the method in the presence of possible interferences and its experimental validation are the subject of a further paper.

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