

Linearity Range of Gran Plots for the End-point in Potentiometric Titrations

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Simple criteria and procedures to assess which part of a potentiometric titration curve can be used to obtain an appreciably linear Gran plot and an accurate extrapolation to the equivalence volume are discussed for one-step precipitation, complexometric, redox and acid - base titrations. Equations were derived for calculating the limiting values of the experimental parameters that prevent titration errors higher than an assigned value.

Keywords: Potentiometric titration; Gran plots

Gran's method for the determination of the equivalence point in potentiometric titrations¹ is becoming increasingly popular. It has been applied in a large number of analytical procedures, particularly with ion-selective electrodes,²⁻⁵ and microprocessor-controlled potentiometric titrators programmed to use it have been manufactured.⁶

Gran titrations are based on the linearisation of the potentiometric titration curve.^{1,7} For each experimental point, the value of an appropriate function of the measured variables (the "Gran function") is calculated. The form of the function depends on the nature of the titration reaction and on which part of the titration curve (*i.e.*, whether before or after the equivalence point) is linearised. The equivalence volume is found by linear extrapolation of this function to zero added titrant volume. In order to be exactly linear, any function should be chosen in such a way as to be equal, or proportional, to the amount (number of moles) of the stoichiometric excess of one of the reactants (either the analyte, before the equivalence point, or the titrant, after it).

The simple functions originally developed by Gran¹ are formulated as being equal, or proportional, to the amount of either reactant actually unreacted at equilibrium, on the assumption that the equilibrium constant of the titration reaction (as expressed by the titration equation) is very large (infinite), that is, that the titration reaction is "complete" or "quantitative." In a real titration, the equilibrium constant has a finite value and therefore the amount of unreacted reactant differs from the stoichiometric excess. As a consequence, the relevant Gran function¹ is not strictly linear, and the linearly extrapolated end-point volume is not, in principle, exactly coincident with the true equivalence-point volume. If approximations have been introduced in calculating the equilibrium amount of the reactant of interest, the linearity of the Gran plot can be further affected.²⁻⁵

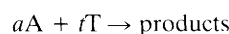
It is important to anticipate whether, and to what extent, such deviations from linearity affect the accuracy of a titration, and whether it is possible to improve the result by exploiting only a selected number of the experimental points. In fact, if the use of the Gran method had to be restricted to appreciably "quantitative" reactions, its main advantage over other end-point methods⁷ would be lost.

Merely indicative linearity conditions for Gran plots are frequently given. On the other hand, very rigorous methods and computer programs for the evaluation of linearity limits and of deviations from linearity have been developed.⁸⁻¹² In this paper, a method is described that is rapid and easy to apply and sufficiently correct for any practical purpose. Equations are derived by means of which the indications sought can be immediately obtained.

Causes of deviation from linearity different from those inherent in the titration equilibria (for instance, deviations of the electrode response from ideal behaviour) will not be considered.

The "Ideal" Case: Quantitative Reactions

As indicated above, the Gran functions are derived on the assumption that the analyte A and the titrant T react quantitatively in accordance with a specified reaction equation:



On this assumption, the equilibrium amount (in moles) of the analyte, n_A , before the equivalence point is exactly equal to the stoichiometric difference between the amount of analyte initially present, n^0 , and the amount of titrant added at any particular time, n' :

$$n_A = n^0 - (a/t)n'$$

Hence n_A decreases linearly with the progress of the titration, which is expressed by n' . After the equivalence point, $n_A = 0$ and the amount of free titrant increases linearly with the progress of the titration:

$$n_T = n' - (t/a)n^0$$

The Gran functions can be formulated to be equal to n_A before and to n_T after the equivalence point.¹ Using the value of n' to express the progress of the titration, an "ideal" Gran plot is composed of two straight lines with slopes of $-a/t$ (before the equivalence point) and $+1$ (after it), and crossing the abscissa and each other at $n' = (t/a)n^0$, *i.e.*, at the equivalence point.

In current practice, quantities simply proportional to n_A or n_T are used as the dependent variable, and the added titrant volume, V , which is proportional to n' , is used as the independent variable. For sake of generality, n_A , n_T and n' will be used in the following; in some instances we shall find it convenient to use the titration ratio, f :

$$f = (a/t)n'/n^0$$

in place of n' .

In any event, the equivalence point can be accurately located as the intercept with the abscissa of a straight line drawn through at least two points, arbitrarily chosen in either the first or second part of the titration. The problem of the propagation of random errors will not be examined here; however, it is clear that the effect of such errors can be reduced by using a larger number of points, and especially by taking points near to the equivalence point.

Real Cases: Incomplete Titration Reactions

Deviations from the linear ideal behaviour described above can be due to two reasons: the unreacted amount of the relevant reactant (n_A before and n_T after the equivalence point) is not equal to its own stoichiometric excess, because the reaction is incomplete; and the Gran function is not

proportional to the unreacted amount of the relevant reactant, because of some approximation (here including the hypothesis of a quantitative reaction) assumed in expressing the equilibrium amount of unreacted reactant as a function of the experimentally measured variable. As the second type of deviation depends on the nature of the titration reaction, and is absent in some instances, only the first one will be discussed here in a general form.

Deviations due uniquely to the incompleteness of the titration reaction can occur in principle in all kinds of titrations (acidimetric, complexometric, redox and precipitation titrations). Owing to the finite value of the equilibrium constant of the titration reaction, the equilibrium amount of the analyte before and of the titrant after the equivalence point is always larger than the respective stoichiometric excess of reagent:

$$\begin{aligned} n_A &> n^0 - (a/t)n' \\ n_T &> n' - (t/a)n^0 \end{aligned}$$

The Gran functions, still equal or proportional to n_A or n_T , are thus no longer linear functions of n' (or f or V), the deviation from linearity increasing on approaching the equivalence point from either side. In view of this, the use of points near to the equivalence point instead of being advantageous can introduce a systematic titration error. This error is, of course, significant only when it is comparable to, or higher than, the random titration error produced by random errors in the values of the Gran function. This point will not be discussed here, however, and we shall simply assume that the maximum allowable systematic contribution, δ , to the relative titration error is a conveniently small, but arbitrary, value [e.g., 0.01 (i.e., 1%) or possibly 0.001].

We need a convenient criterion for deciding which part of the titration curve can be exploited for the Gran extrapolation of the equivalence point. Let us discuss first the region before the equivalence point of an isovalent reaction ($a = t$). In this region any deviation from linearity due to an incomplete reaction can only cause a positive titration error. In Fig. 1, line A represents n_A (i.e., the Gran function) for an incomplete reaction, the straight line B represents the ideal plot for a complete reaction and the straight line C represents the "experimental" line which would give a determinate error exactly equal to δn^0 . The vertical distance between the actual Gran curve A and the ideal line B is $n_A - (n^0 - n')$. The vertical distance between C and B is $n'\delta/(1 + \delta) \approx \delta n'$ (the approximation $1 + \delta \approx 1$ holds for any reasonable value of δ). This distance increases from zero at the beginning of the titration to about δn^0 at the equivalence point.

Let us assume that only two points are employed for the extrapolation: the initial point, P_0 , and a point P at a generic

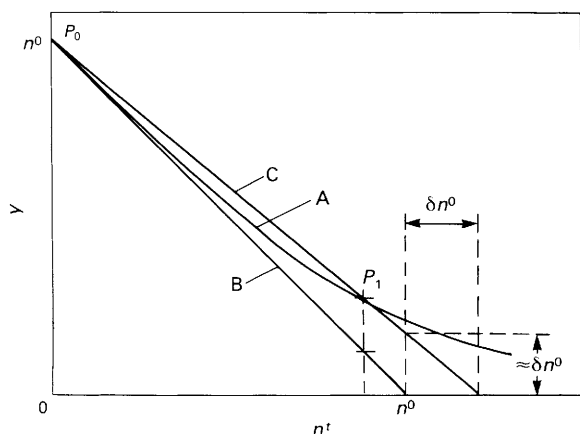


Fig. 1. Real, ideal and extrapolated Gran plots for a generic titration, before the equivalence point. A, $y = n_A$, the equilibrium amount of analyte; B, $y = n^0 - n'$, the stoichiometric excess of analyte; and C, linear extrapolation giving an absolute titration error δn^0 . For clarity, a very large value has been assumed for δ

value of n' . The maximum value of n' that we can use in order to have an extrapolation error not higher than δn^0 is that corresponding to point P_1 , where the actual Gran plot intersects the line C. At this point we have

$$n_A - (n^0 - n') = \delta n' \quad \dots \quad (1)$$

By solving the algebraic system formed by equation (1), the equations of the mass balances of the solutes and the expression of the conditional equilibrium constant of the titration reaction, the "critical value" of a relevant "experimental" variable (e.g., the equilibrium concentration of a reactant) which gives a relative titration error lower than δ can be calculated.

If, in addition to P_0 and to P_1 , also some intermediate points are employed for the extrapolation, they contribute to make the systematic error lower than δn^0 , because their deviation from linearity is less than $\delta n'$. Therefore, the use of points regularly distributed between P_0 and P_1 ensures a safety factor, which is the larger the more experimental points are used. If, as often applies, P_1 is not too far from the equivalence point, that is, the critical value of n' is not much smaller than n^0 , then equation (1) can be approximated to

$$n_A - (n^0 - n') = \delta n^0 \quad \dots \quad (2)$$

Equation (2) is suitable when equation (1) leads to cumbersome expressions. Although it must be applied cautiously, it is certainly reliable when the critical n' value is larger than 0.8 or 0.9 times n^0 (depending on the number of experimental points).

Sometimes the initial point and, in general, points near to the beginning of the titration cannot be used (e.g., when the electrode does not respond properly in the absence of the titrant or in the titration of a moderately weak acid; see below). If the first useful point is taken at $f = f_m$, equation (3) replaces equation (1) as the limiting condition:

$$n_A - (n^0 - n') = \frac{\delta(n' - f_m n^0)}{1 - f_m} \quad \dots \quad (3)$$

However, equation (1) [or (2)] can still be used, provided that at least half of the part of the titration preceding the equivalence point can be linearised and that the number of experimental points is large enough.

The treatment of the second part of the titration (after the equivalence point) is similar to the above, the only differences being that any deviation from linearity due to an incomplete reaction causes a negative titration error and that, whereas before the equivalence point the range of n' values is limited ($0 < n' < n^0$), after the equivalence point their range ($n' > n^0$) does not, in principle, have an upper limit. If we assume that the last experimental point is taken at $f_M = 2$, we have a plot symmetrical with that in Fig. 1, from which it is easily seen that in order to obtain a systematic error smaller (in absolute value) than δn^0 , it is sufficient to use only points at n' values larger than the critical value given by

$$n_T - (n' - n^0) = \delta(2n^0 - n') \quad \dots \quad (4)$$

The corresponding equation for a generic value of f_M is

$$n_T - (n' - n^0) = \delta(f_M n^0 - n')/(f_M - 1) \quad \dots \quad (5)$$

The simplified form of conditions (4) and (5) ($n' \approx n^0$ in the right-hand member)

$$n_T - (n' - n^0) = \delta n^0 \quad \dots \quad (6)$$

gives a linearity range that can be taken as safe provided that it begins not too far from the equivalence point and the value of f_M is 2 or larger.

For a heterovalent titration reaction ($a \neq t$), for which the equivalence condition is $tm^0 = an'$, the critical n' value before the equivalence point is given by

$$n_A - (n^0 - an'/t) = \delta an'/t \quad \dots \quad (7)$$

and, looking for a linearity range reaching a n' value not much lower than tn^0/a ,

$$n_A - (n^0 - an'/t) = \delta n^0 \quad \dots \quad (8)$$

After the equivalence point it must be

$$n_T - (n' - tn^0/a) = \delta[(t/a)f_M n^0 - n']/(f_M - 1) \dots \quad (9)$$

and, for a critical n' not much higher than tn^0/a , we have

$$n_T - (n' - tn^0/a) = \delta tn^0/a \quad \dots \quad (10)$$

Assessment of the Linear Range of Incomplete Reactions

In this section, equations (1)–(10) will be applied with the main objective of finding the range of the measured potential values in which useful experimental points can be collected. Therefore, we shall answer (or suggest the way to answer) the following questions:

(a) Given an estimate of the analytical concentration of A, C^0 , and the value of the conditional equilibrium constant of the titration reaction, K_T , state the critical value of the equilibrium amount, and therefore of the concentration, of the ion sensed by the electrode (e.g., [A] or [T]) which gives a relative titration error lower than δ . If the calibration parameters of the indicating electrode are known, the critical value of the measured potential can then be calculated.

(b) With the same information as above, state the critical value of n' or, more conveniently, of the titration ratio, f_c . It can be shown that the approximate expressions for f ,

$$f = 1 - n_A/n^0 \quad \dots \quad (11)$$

before the equivalence point,

$$f = 1 + n_T/n^0 \quad \dots \quad (12)$$

after the equivalence point of an isovalent titration reaction and

$$f = 1 + (a/t)n_T/n^0 \quad \dots \quad (13)$$

after the equivalence point of a heterovalent reaction, by which the values of f_c are calculated by substitution into equations (11)–(13) of the critical values of n_T or of n_A obtained as in point (a), are consistent with the approach described above.

(c) Given the value of K_T , state the minimum value of the initial analyte concentration, C^0 , for which the Gran function can be safely extrapolated from points lying in a given f range (for instance, between $f = 0$ and 0.9 or for $f > 1.05$) with a relative titration error lower than δ .

(d) Given the minimum value of C^0 that we want to determine with an assigned accuracy, state the K_T value to be sought (for instance, by choosing the titrant or the titration conditions such as temperature or the solvent) in order to obtain a linear Gran function in a sufficiently large f range.

The "exact" solution of the problem (a) is found by solving the algebraic system formed by one of the "exact" equations given above, the equations of the mass balances of the solutes and the expression of the conditional equilibrium constant of the titration reaction. When this approach would be impractical, it is possible to introduce reasonable simplifications. The validity of the latter increases with the number of the experimental points pertaining to the linear range. The procedure involving simplified expressions of the linearity criterion, such as equations (2), (6), (8) and (10), gives reliable results when the above criteria are met.

When a cause of deviation other than that considered in equations (1)–(10) is present, its effects will be discussed and compared.

Isovalent Precipitation Titrations

The application of the above criteria is straightforward for isovalent precipitation titrations. Taking as an example the argentimetric titration of chloride with a silver indicating electrode, it is easily seen that the Gran function used before

the equivalence point, $(V^0 + V)10^{-E/S}$, (where E is the electromotive force of the measuring cell, S is the experimental slope of the electrode response and V^0 is the initial volume of the analyte solution) is exactly proportional to the amount of unreacted chloride:

$$\begin{aligned} n(\text{Cl}) &= (V^0 + V)[\text{Cl}^-] = (V^0 + V)K_s/[\text{Ag}^+] \\ &= \text{constant} \times (V^0 + V)10^{-E/S} \end{aligned}$$

(remember that, from the Nernst equation, $[\text{Ag}^+] = 10^{-E^0/S} \times 10^{E/S}$). Here and in the following, $n(\text{X})$ represents the equilibrium amount, in moles, and $[\text{X}]$ the equilibrium concentration, in M, of the species X.

In order to find the useful linearity range of this function we combine equation (1) with the mass balances of the reactants:

$$\begin{aligned} n^0 &= n(\text{Cl}) + n(\text{AgCl}) \\ n' &= n(\text{Ag}) + n(\text{AgCl}) \end{aligned}$$

obtaining

$$(1 - \delta)n(\text{Ag}) = \delta[n^0 - n(\text{Cl})]$$

i.e.,

$$(1 - \delta)(V^0 + V)[\text{Ag}^+] = \delta\{V^0 C^0 - (V^0 + V)[\text{Cl}^-]\} \quad (14)$$

If the titrant is at least ten times more concentrated than the analyte, as usual, then V can be neglected with respect to V^0 (the "dilution effect" will always be neglected in the following). If δ is also neglected with respect to 1, equation (14) reduces to

$$[\text{Ag}^+] = \delta(C^0 - [\text{Cl}^-]) \quad \dots \quad (15)$$

We can calculate the critical value of $[\text{Ag}^+]$ by substituting $[\text{Cl}^-]$ into equation (15) by means of the expression for the solubility product constant, K_s , and solving the quadratic equation for $[\text{Ag}^+]$:

$$[\text{Ag}^+]_c = \frac{\delta C^0 + \sqrt{(\delta C^0)^2 - 4\delta K_s}}{2}$$

Likewise, the limiting value of the chloride concentration is

$$[\text{Cl}^-]_c = \frac{C^0 - \sqrt{(C^0)^2 - 4K_s/\delta}}{2} \quad (16)$$

Equation (2) gives, more simply

$$[\text{Ag}^+]_c = \delta C^0$$

and

$$[\text{Cl}^-]_c = K_s/\delta C^0 \quad \dots \quad (17)$$

The corresponding value of f_c is obtained by substitution of the expression for the critical value of analyte concentration into equation (11); for instance, equation (18) is obtained by using equation (17) and again neglecting dilution.

$$f_c = 1 - [\text{Cl}^-]_c/C^0 = 1 - K_s/\delta(C^0)^2 \quad \dots \quad (18)$$

As an example, both the exact and the approximate equations show that, taking $K_s = 10^{-9.5}$ (25 °C, ionic strength 0.1 M), at $C^0 = 10^{-3.0}$ M a systematic error lower than 1% is given by points up to $[\text{Ag}^+] = 10^{-5.0}$ M, $E = 0.30$ V vs. SCE, $f_c = 0.98$. Conversely, the minimum initial concentration of analyte, C^0 , for which a Gran plot using points up to a given titration ratio, say 0.90, gives a systematic error lower than say 1% is obtained by rearranging equation (18):

$$C^0 = [K_s/(1 - f_c)]^{1/2}$$

The result is 5×10^{-4} M, which is not appreciably different from the value obtained by the use of "exact" equations. In contrast, a systematic error lower than 0.1% can hardly be obtained; in fact, the exact equation (16) does not admit solution, as the argument of the square root term is negative, in substantial agreement with the result of the approximate equation (18), which gives $f_c \approx 0.7$, a value outside its range of validity. It is clear from above that the approximate equations

Table 1. Linearity critical conditions for different types of titrations

Types of reaction	Species sensed	Part* of titration	$[A_c]^\ddagger$	$[T_c]^\ddagger$	f_c or E_c
Isovalent precipitation§	A or T	B.E.P.	$\frac{C^0 - \sqrt{(C^0)^2 - 4K_s/\delta}}{2}$	$\frac{\delta C^0 + \sqrt{(\delta C^0)^2 - 4\delta K_s}}{2}$	$\frac{1 + \sqrt{1 - 4K_s/\delta(C^0)^2}}{2}$
		A.E.P.	$\frac{\delta C^0 + \sqrt{(\delta C^0)^2 - 4\delta K_s}}{2}$	$\frac{C^0 - \sqrt{(C^0)^2 - 4K_s/\delta}}{2}$	$\frac{3 - \sqrt{1 - 4K_s/\delta(C^0)^2}}{2}$
Heterovalent precipitation¶	A or T	B.E.P.	$K_s^{1/a}(a/t\delta C^0)^{1/a}$	$\delta(t/a)C^0$	$1 + K_s^{1/a}(a/t\delta)^{1/a}/(C^0)^{(a+t)/a}$
		A.E.P.	δC^0	$K_s^{1/t}/(\delta C^0)^{a/t}$	$1 + (a/t)K_s^{1/t}/\delta^{a/t}(C^0)^{(t+a)/t}$
Chelometric titrations (direct and reverse)§	M	B.E.P.	$1/\delta K_f$	$\delta C^0 - 1/K_f$	$1 - 1/\delta K_f C^0$
		A.E.P.	$\frac{\delta C^0 + \sqrt{(\delta C^0)^2 - 4\delta C^0/K_f}}{2}$	$\frac{C^0 - \sqrt{(C^0)^2 - 4C^0/\delta K_f}}{2}$	$\frac{3 - \sqrt{1 - 4/\delta K_f C^0}}{2}$
Oxidation titration:§					
$aA_{rd} + tT_{ox}$	$\frac{[A_{ox}]}{[A_{rd}]}$	B.E.P.	$[T_{ox}] = \delta[T_{rd}] = \delta t[A_{ox}]/a$		$E_c = E_A^0 + (0.06/z_A) \log \delta$
$aA_{ox} + tT_{rd}$	$\frac{[T_{ox}]}{[T_{rd}]}$	A.E.P.	$[A_{rd}] = \delta[A_{ox}] = \delta a[T_{rd}]/t$		$E_c = E_A^0 - (0.06/z_A) \log \delta$
Reduction titration:§					
$aA_{ox} + tT_{rd}$	$\frac{[A_{ox}]}{[A_{rd}]}$	B.E.P.	$[T_{rd}] = \delta[T_{ox}] = \delta t[A_{rd}]/a$		$E_c = E_A^0 - (0.06/z_A) \log \delta$
$aA_{rd} + tT_{ox}$	$\frac{[T_{ox}]}{[T_{rd}]}$	A.E.P.	$[A_{ox}] = [A_{rd}] = \delta a[T_{ox}]/t$		$E_c = E_A^0 + (0.06/z_A) \log \delta$

* B.E.P. = before the equivalence point; A.E.P. = after the equivalence point.
 \ddagger Critical value of the analyte equilibrium concentration.
 \ddagger Critical value of the titrant equilibrium concentration.
 \S Exact solution.
 $\|$ For $f_M = 2$.
 \P Approximate solution.

* B.E.P. = before the equivalence point; A.E.P. = after the equivalence point.

† Critical value of the analyte equilibrium concentration.

‡ Critical value of the titrant equilibrium concentration.

§ Exact solution.

|| For $f_M = 2$.

¶ Approximate solution.

give reliable results but in extreme, easily recognisable instances.

The deductions above are independent of whether the electrode responds to the analyte or to the titrant (although the respective Gran functions differ in the sign of the exponential term). The corresponding equations valid after the equivalence point can be easily obtained by following the same reasoning as above, and are reported in Table 1 (for $f_M = 2$). The simplified forms of the critical conditions [independent of f_M , see equation (6)] can be deduced from those for heterovalent titrations putting $a = t$.

Heterovalent Precipitation Titrations

Similar considerations also hold for heterovalent precipitation titrations. Combining the mass balances

$$\begin{aligned} n^0 &= n_A + an_p \\ n^t &= n_T + tn_p \end{aligned}$$

(p = precipitate) with equation (8), one obtains

$$n_T = \delta(t/a)n^0$$

as the approximate critical value of n_T and

$$[T]_c = \delta(t/a)C^0 \quad \dots \quad (19)$$

as the approximate critical value of $[T]$ before the equivalence point.

By using equation (19), the expression of the solubility product, $K_s = [A]^a[T]^t$, and equation (11) the expressions for the critical concentration of analyte and for f_c reported in Table 1 are obtained. Likewise, the approximate expressions to be employed in the second part of the titration are obtained from equation (9) or (10).

Titration of Strong Acids or Bases

The titration of a strong acid with a strong base, and the reverse titration, are formally identical with a precipitation titration with $K_s = K_w$. For instance, for the linearisation of the titration of a strong acid before the equivalence point, one obtains as the approximate limiting condition $pH = pK_w + \log \delta C^0$.

It is not surprising that this equation gives a pH value larger than 7, but for very small values of δ and/or C^0 . These pH values, although being after the equivalence point, have an intercept on the ordinate of zero on the Gran plot and on the abscissa of $f = 1$ both on the Gran plot and on the experimental titration curve, within the chosen value of δ . (The same consideration is valid for all kinds of titration, when the calculated limiting value of the equilibrium concentration of the primary ion for either part of the titration curve lies on the other side with respect to the equivalence point.)

Complexometric (Chelometric) Titrations of Metals

In the chelometric titration of a metal M with a chelating agent Y, monitored by an electrode sensing the analyte cation, the form of the Gran function generally employed $(V^0 + V)10^{E/S}$ is plotted before the equivalence point. This function is again exactly proportional to the unreacted amount of metal, $n(M)$:

$$n(M) = (V^0 + V)[M] = \text{constant} \times (V^0 + V)10^{E/S}$$

(conditional amounts and constants¹³ can be conveniently used if the necessary conditions are maintained throughout the titration). Therefore, condition (1) can be immediately applied. By substitution with the mass balances of the reactants:

$$n^0 = V^0 C^0 = n(M) + n(MY) = (V^0 + V)([M] + [MY]) \quad (20)$$

$$n' = VC = n(Y) + n(MY) = (V^0 + V)([Y] + [MY])$$

it becomes

$$(1 - \delta)n(Y) = \delta n(MY)$$

i.e.,

$$(1 - \delta)[Y] = \delta[MY]$$

from which, for negligible dilution, the critical concentrations

$$[M]_c = \frac{(1 - \delta)}{\delta K_f} \approx \frac{1}{\delta K_f}$$

and

$$[Y]_c = \frac{\delta C^0}{1 - \delta} - \frac{1}{K_f} \approx \delta C^0 - \frac{1}{K_f}$$

are obtained ($K_f = [MY]/[M][Y]$ is here the conditional stability constant of the chelate complex). The approximate equation (3) gives the limiting condition

$$[Y]_c = \delta C^0$$

After the equivalence point of the same titration, a second cause of deviation, not taken into consideration in the introductory discussion, affects the deviation of the Gran plot from the ideal behaviour. The form of the Gran function generally employed, which in this instance is $10^{-E/S}$, is not proportional to the amount of unreacted chelating agent:

$$\begin{aligned} n(Y) &= (V^0 + V)[Y] = \frac{(V^0 + V)[MY]}{K_f[M]} \\ &= \text{constant} \times (V^0 + V)[MY]10^{-E/S} \end{aligned}$$

unless the amount of complex formed, $(V^0 + V)[MY]$, can be considered to be constant, equal to the initial amount of analyte, $n^0 = C^0 V^0$. The difference between the approximate value $n'(Y)$ (proportional to the Gran function) and the true equilibrium amount is

$$n'(Y) - n(Y) = \frac{C^0 V^0 - (V^0 + V)[MY]}{K_f[M]}$$

and, with equation (20),

$$n'(Y) - n(Y) = \frac{(V^0 + V)}{K_f} \approx \frac{V^0}{K_f}$$

Although the linearity of the Gran plot is not affected by this deviation (itself a linear function of the added volume), the intercept on the V axis is; the extrapolation error (in moles of analyte) is approximately $V^0(C^0 + C)/K_f C$, where C is the concentration of the titrant solution. For negligible dilution, the deviation tends towards the constant value V^0/K_f . It becomes negligible when

$$V^0/K_f \leq \delta n^0, \quad \text{i.e.,} \quad C^0 \geq 1/\delta K_f \quad \dots (21)$$

However, errors from this source are generally smaller than those due to the first type of deviation. Therefore, the limiting condition for the linearity of the Gran plot after the equivalence point,

$$(1 - \delta)[M] = \delta(C^0 - [Y])$$

can be deduced from equation (4). From this (introducing some minor simplifications), the equations reported in Table 1 are obtained. In this part of the titration the approximate equation (6) gives the much simpler expressions

$$[M]_c = \delta C^0$$

and

$$f_c = 1/\delta C^0 K_f$$

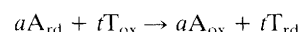
for the critical values of the variables.

As an example, calculations with the above equations show that when a chelating agent having $K_f = 10^{5.0}$ is employed, a 1.0×10^{-2} M solution of a metal ion can be titrated with a systematic error smaller than 1% by linearising the experimental points at $[M] > 10^{-3.0}$ M, $f < 0.9$, or at $[M] < 10^{-4.0}$ M, $f > 1.1$. If an accuracy of better than 0.1% is wanted, the analyte concentration must be higher than 0.09 M when points at $f < 0.9$ are intended to be used, and higher than 0.1 M for $f > 1.1$. These results are obtained both from the exact and the approximate equations. In every instance condition (21) is fulfilled.

Identical equations represent the critical analyte and titrant concentrations for the reverse titration of a chelating agent with a metal ion. In this instance, condition (21) must be fulfilled before the equivalence point.

Redox Titrations

Gran plots are seldom applied to redox titrations, because only a few redox titration couples give a Nernstian response at the indicator electrode. However, this type of titration deserves to be treated at least briefly, even though it is not possible to give a single treatment valid for the wide variety of titration systems. Let us take as an example the homogeneous oxidation titration



for which the equilibrium redox potential can be written as

$$\begin{aligned} E &= E_A + (0.06/z_A) \log[n(A_{ox})/n(A_{rd})] \\ &= E_T + (0.06/z_T) \log[n(T_{ox})/n(T_{rd})] \quad \dots (22) \end{aligned}$$

with $a = z_T$ and $t = z_A$.

Before the equivalence point, the correct equivalence volume is obtained if points are only extrapolated for which the Gran function $V \times 10^{-tE/0.06}$ is proportional to the truly linear amount $n^0 - (a/t)n'$. For our purpose, this amount can be identified with the amount of unreacted analyte, $n(A_{rd})$, down to the value expressed by equation (7), which, by substitution with the expressions of the mass balances of the reactants and of the electron balance

$$n(A_{ox}) = (a/t)n(T_{rd})$$

becomes

$$(1 - \delta)n(T_{ox}) = \delta n(T_{rd}) \quad \dots (23)$$

Using equation (22), we obtain

$$\begin{aligned} n^0 - (a/t)n' &= 10^{tE/0.06} n(A_{ox}) \times 10^{-tE/0.06} \\ &= 10^{tE/0.06} (a/t)n(T_{rd}) \times 10^{-tE/0.06} \\ &\approx \text{constant} \times V \times 10^{-tE/0.06} \end{aligned}$$

The approximation

$$n(T_{rd}) \approx n(T_{rd}) + n(T_{ox}) + n' = CV$$

which eventually makes the Gran function linear, is allowed when the neglected term is lower than the limiting value

$$n(T_{ox}) = \delta n(T_{rd})/(1 - \delta) \approx \delta n(T_{rd})$$

again corresponding to condition (23). Equation (23) can also be written as

$$[T_{ox}] = \delta [T_{rd}] = \delta (t/a) [A_{ox}]$$

The limiting value of the electrode potential is immediately obtained:

$$E_c = E_T + (0.06/z_T) \log \delta$$

The expressions for the part after the equivalence point and for the reverse titration (reduction of A_{ox}) can be obtained in a similar way and are reported in Table 1. These expressions are easily handled by means of logarithmic diagrams.¹⁴

Titration that do not obey the above reaction scheme need separate treatment.

Titration of a Weak Acid with a Strong Base

Gran plots of titrations of weak acids (here indicated as HB), in addition to positive deviations from linearity in the proximity of the equivalence point, can also show negative deviations from linearity (decreasing with the progress of the titration) in the initial part of the titration.^{9,11,12} Both types of deviation can be ascribed, although to different extents, to two facts. First, the excess amount of analyte is not identical with the equilibrium amount of undissociated acid, and second, this last amount is not exactly proportional to the Gran function, $V \times 10^{-\text{pH}}$.

Positive Deviations Before the Equivalence Point

Let us consider first the effect of the difference between $n(\text{HB})$ and $n^0 - n'$ in the proximity of the equivalence point. A low equilibrium constant of the titration reaction, $K_T = K_a/K_w$, gives, as usual, positive deviations. In most instances, as discussed above, equation (1) rather than equation (3) may be taken as the linearity criterion for $n(\text{HB})$ (which, however, is not exactly proportional to the plotted function, see below). Using the mass balances of the reactants

$$n^0 = n(\text{HB}) + n(\text{B}^-) \quad \dots \quad (24)$$

$$n' = n(\text{Na}^+) \quad \dots \quad (25)$$

and the charge balance

$$n(\text{Na}^+) + n(\text{H}^+) = n(\text{B}^-) + n(\text{OH}^-) \quad \dots \quad (26)$$

equation (1) becomes

$$(1 - \delta)[n(\text{OH}^-) - n(\text{H}^+)] = \delta n(\text{B}^-)$$

and, putting $1 - \delta \approx 1$,

$$[\text{OH}^-] - [\text{H}^+] = \delta[\text{B}^-] \quad \dots \quad (27)$$

while equation (2) gives

$$n(\text{OH}^-) - n(\text{H}^+) = \delta n^0$$

and, neglecting dilution,

$$[\text{OH}^-] - [\text{H}^+] = \delta C^0 \quad \dots \quad (28)$$

Equations (27) and (28) represent the critical condition only if the plotted Gran function, $V \times 10^{-\text{pH}}$, is proportional to the equilibrium amount of undissociated acid, $n(\text{HB})$:

$$n(\text{HB}) = n(\text{B}^-) \left(\frac{10^{-\text{pH}}}{K_a} \right)$$

that is, when this amount can be correctly calculated by means of the approximate equation

$$n'(\text{HB}) = n' \left(\frac{10^{-\text{pH}}}{K_a} \right) = \frac{CV10^{-\text{pH}}}{K_a}$$

For this purpose, the difference between the equilibrium amount of conjugated base (the reaction "product"), $n(\text{B}^-) = (V^0 + V)[\text{B}^-]$, and the amount of added titrant, $n' = CV$, must be negligible. When, as seen, on approaching the equivalence point n' becomes appreciably higher than $n(\text{B}^-)$, $n'(\text{HB})$ becomes larger than the real equilibrium value (represented by line A in Fig. 1). The deviation remains negligible down to the point where

$$n' - n(\text{B}^-) = \delta n(\text{B}^-)$$

i.e., again up to the conditions (27) and (28).

Negative Deviations in the Initial Part

An acid that is only moderately weak is partly dissociated from the very beginning of the titration, so that the equilibrium amount of undissociated acid is lower than its stoichiometric amount:

$$n(\text{HB}) < n^0 - n'$$

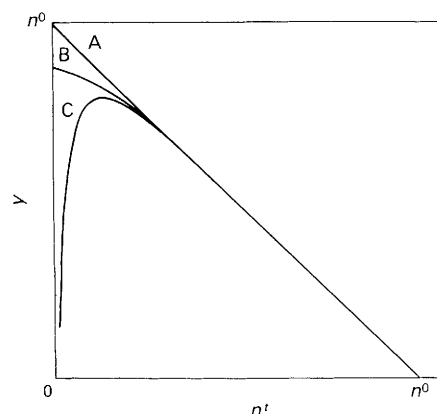


Fig. 2. Titration of a moderately weak acid ($\text{p}K_a = 4.75$, $C^0 = 10^{-3.00} \text{ M}$) before the equivalence point. A, Ideal Gran plot, $y = n^0 - n'$; B, $y = n(\text{HA})$, the equilibrium amount of undissociated acid; and C, the Gran function $CV \times 10^{-\text{pH}}/K_w$.

Therefore, the curve representing the real amount of undissociated acid (line B, Fig. 2) shows negative deviations from linearity, which decrease as n' increases. Negative deviations in the initial part of the titration give rise in turn to a positive extrapolation error. However, they have a small effect on the error if the upper limit of the linearity range is near enough to the equivalence point (as happens when the moderately weak acid is not extremely diluted). Therefore, we can consider for our purpose that the curve of $n(\text{HB})$ merges with the ideal straight line when

$$(n^0 - n') - n(\text{HB}) = \delta n^0$$

$$[\text{H}^+] - [\text{OH}^-] = \delta C^0 \quad \dots \quad (29)$$

However, when n' is appreciably lower than $n(\text{B}^-)$ (see above), $n'(\text{HB})$ (exactly proportional to the plotted function) is lower than the real equilibrium value (line C in Fig. 2). The difference becomes negligible starting from the point where

$$n(\text{B}^-) - n' = \delta n(\text{B}^-)$$

$$[\text{H}^+] - [\text{OH}^-] = \delta[\text{B}^-] \quad \dots \quad (30)$$

Condition (30) is much more demanding than condition (29), as $[\text{B}^-]$ in the initial part of the titration is generally much smaller than C^0 ; therefore, it represents the true critical conditions.

After the Equivalence Point

After the equivalence point, the Gran function $(V^0 + V)10^{\text{pH}}$ is actually proportional to the amount of free titrant (hydroxide ion), and therefore equations (4)–(6) do express the corresponding linearity limit. By using the mass and charge balances, equation (4) becomes

$$(1 - \delta)[n(\text{HB}) + n(\text{H}^+)] = \delta[n^0 - n(\text{OH}^-)]$$

$$[\text{HB}] + [\text{H}^+] = \delta(C^0 - [\text{OH}^-]) \quad \dots \quad (31)$$

The approximate condition obtained from equation (6) is

$$[\text{HB}] + [\text{H}^+] = \delta C^0 \quad \dots \quad (32)$$

Explicit Equations for Critical Conditions

For the present type of titrations, the equations for the critical values of $[\text{H}^+]$, f and C^0 are not as simple as in previous instances.

Regarding the initial part (negative deviations), by substitution with the expressions for K_w and K_a and the mass balance of analyte, a third-degree equation in $[\text{H}^+]$ is obtained from equation (30). However, the same equation requires a pH value not higher than 7, as both members must be positive; the

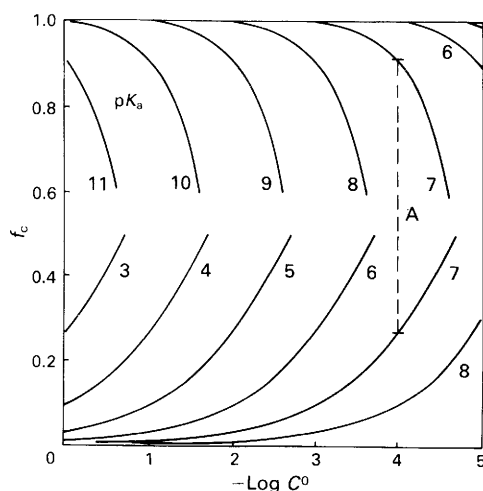
Table 2. Linearity critical conditions for the titration of a weak acid with a strong base

Part of titration	Critical condition	$[H^+]_c$	f_c	Observations*
B.E.P. (initial part)	$[H^+] - [OH^-] = \delta[A^-]$ $[H^+] = \delta[A^-]^{\ddagger}$	$\frac{\sqrt{K_a^2 + 4\delta C^0 K_a} - K_a}{2}$	$\frac{[H^+]_c}{\delta C^0}$	$pH_c < 6.5$
B.E.P. (final part)	$[OH^-] - [H^+] = \delta[A^-]$ $[OH^-] = \delta[A^-]^{\ddagger}$ $[OH^-] = \delta C^0$	$\frac{K_w K_a}{\delta C^0 K_a - K_w}$ $\frac{K_w}{\delta C^0}$	$\frac{K_a}{[H^+]_c + K_a}$ $\frac{\delta C^0 K_a}{K_w + \delta C^0 K_a}$	$pH_c > 7.5$ $f_c < 0.8$
A.E.P.	$[HA] + [H^+] = \delta(C^0 - [OH^-])$ $[HA] = \delta(C^0 - [OH^-])^{\ddagger}$ $[HA] = \delta C^0$	$\frac{\delta(C^0 K_a - K_w) + \sqrt{\delta^2(C^0 K_a - K_w)^2 - 4\delta C^0 K_a K_w}}{2C^0}$ δK_a	$1 + \frac{K_w}{[H^+]_c C^0}$ $1 + \frac{K_w}{\delta C^0 K_a}$	$f_M = 2$

* Conditions for the validity of approximate solutions.

† Approximate condition.

‡ Ultimate approximation.

**Fig. 3.** Critical values of the titration ratio, f_c , for the titration of weak acids of different strengths before the equivalence point, as a function of concentration. The allowed extrapolation error, δ , is 1%. The pK_a values are indicated on the lines. For $\delta = 0.1\%$, the pK_a values of the lower lines must be increased by 1 and those of the upper lines must be decreased by 1. Distance A: linearity range of the titration of a $10^{-4.00}$ M acid, $pK_a = 7.00$

term $[OH^-]$ can be reasonably neglected in most instances. A second-degree equation and, from it, the simplified equations in Table 2 are obtained, which are valid as long as a critical pH value lower than 6.5 is calculated.

In the proximity of the equivalence point (positive deviations), the third-degree equation in $[H^+]$ corresponding to equation (27) can be reduced to the first degree by neglecting $[H^+]$ with respect to $[OH^-]$ [note that equation (27) requires basic pH values], the validity of the approximation being confirmed by a resulting pH value larger than 7.5. Equation (28), which is quadratic in $[H^+]$, with the same consideration as above reduces to

$$[H^+]_c = K_w / \delta C^0$$

By combination with equation (11) and with the expressions of the equilibrium constants, the other equations in Table 2 are obtained.

In Fig. 3, the values of f_c for titrations of weak acids or bases, obtained through the above equations for various K_a values, are plotted against C^0 . The useful ranges for the linearisation of titrations can be directly obtained from this diagram.

The expression for the critical value of $[H^+]$ after the equivalence point in Table 2 is deduced from equation (31) for an acid sufficiently weak and concentrated to make $[H^+]$ negligible with respect to $[HB]$. From equation (32) the approximate value

$$[H^+]_c = \delta K_a$$

is obtained.

As examples of application of the above deductions, we shall consider the titrations of 1.2×10^{-3} M pyridinium chloride ($pK_a = 5.24$ at 25°C) and of 1.0×10^{-2} M ammonium chloride ($pK_a = 9.30$). In the first instance, the linear range for $\delta = 0.01$ starts at $pH = 5.23$, $f = 0.49$, while the condition $\delta = 0.001$ is fulfilled from $pH = 5.99$, $f = 0.85$ up to the equivalence point. It follows that only the part of the titration following the equivalence point can in principle give accurate results. For the weaker acid, only points in the immediate vicinity of $f = 0$ show an appreciable negative deviation. However, the condition for $\delta = 0.01$ ceases to be fulfilled at $pH = 9.90$, $f = 0.80$, and begins to be valid again at $pH = 11.43$, $f = 1.27$. The above values can be compared with $pH = 10.0$, $f = 0.83$ and $pH = 11.3$, $f = 1.20$, respectively, resulting from approximate equations. It can be shown that, after the equivalence point, the exact critical values approach nearer to the approximate values (independent of f_M) the higher is f_M .

In practice, it must be remembered that small amounts of acidic or basic impurities in the reactants can introduce appreciable differences with respect to theoretical expectations (the effect of carbon dioxide contaminating strong bases is well known¹⁵).

The critical conditions for the titration of a weak base can be deduced in exactly the same way and are reported in Table 3.

Conclusions

In developing the present approach to assessing the linearity of Gran plots, we have tried to make it simple enough to be useful to non-expert "consumers" of potentiometric titrations, and to make clear the chemical meaning of the Gran plots and of their deviations from linearity. The present approach has been tested by comparison with other formally different approaches and with "exact" Gran plots obtained from synthetic titration curves. Details have been omitted for brevity. For the same reason, only a few numerical examples have been discussed, and the experimental confirmations we have obtained have not been reported.

The deviations from linearity inherent in the original Gran functions can be avoided by the use of functions that correctly express the stoichiometric excess amount of either reactant

Table 3. Linearity critical conditions for the titration of a weak base (*e.g.*, NaA)

Part of titration	Critical conditions	$[H^+]_c$	f_c	Observations*
B.E.P. (initial part)	$[OH^-] - [H^+] = \delta[HA]$			
	$[OH^-] = \delta[HA]^\dagger$	$\frac{K_w + \sqrt{K_w^2 + 4\delta C^0 K_a K_w}}{2\delta C^0}$	$\frac{[H^+]_c}{[H^+]_c + K_a}$	$pH_c > 7.5$
B.E.P. (final part)	$[H^+] - [OH^-] = \delta[HA]$			
	$[H^+] = \delta[HA]^\dagger$	$\delta C^0 - K_a$	$1 - \frac{K_a}{\delta C^0}$	$pH_c < 6.5$
	$[H^+] = \delta C^0^\ddagger$	δC^0	$\frac{\delta C}{\delta C^0 + K_a}$	$f_c > 0.8$
A.E.P.	$[A^-] + [OH^-] = \delta(C^0 - [H^+])$			
	$[A^-] = \delta(C^0 - [H^+])^\dagger$	$\frac{C^0 - K_a - \sqrt{(C^0 - K_a)^2 - 4C^0 K_a / \delta}}{2}$	$1 + \frac{[H^+]_c}{C^0}$	$f_M = 2$
	$[A^-] = \delta C^0^\ddagger$	$\frac{K_a}{\delta}$	$1 + \frac{K_a}{\delta C^0}$	

* Conditions for the validity of approximate solutions.

† Approximate condition.

‡ Ultimate approximation.

as a function of the titration parameters and of the experimentally measured variables.^{16–20} However, neither these procedures, nor the previous methods for the evaluation of linearity of original Gran plots,^{8–12,21} have until now received the attention they deserve among the users of Gran plots and of potentiometric methods. It is hoped that the present approach will persuade a larger number of analysts to expand the use of the Gran method beyond the more obvious applications, and on the other hand to avoid its improper application.

The approach illustrated here could be adapted to other types of segmented titrations, such as photometric titrations. In this paper this approach has been illustrated with reference to one-step titration reactions, but it can be fruitfully extended to more complicated situations (*e.g.*, titrations of polyfunctional analytes and of mixtures; back-titrations). In this connection, the use of logarithmic diagrams of equilibrium concentrations of the titrated systems¹⁶ is particularly convenient and will be discussed in a future paper.

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