

Overview on the Gran and other linearisation methods applied in titrimetric analyses

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Abstract

The paper provides some linearisation methods presented in modified (Gran I method), extended (pH-static titration) and generalised (Ni method) or corrected versions. Particularly, the modified Gran I method, based on the approximation $\ln(1+x) \cong x/(1+x/2)$, enables (a) significant error inherent in the original Gran I method of equivalence volume V_{eq} evaluation to be avoided, (b) greater portions of titrant to be added and (c) the points more approached to V_{eq} to be involved in calculation of V_{eq} , according to the linear model applied. Moreover, prior determination of the real slope of the (pX, E) characteristics for X-selective indicator electrode (inherent in Gran II method) is thus avoided. The modified Gran I method is particularly useful in potentiometric titrations where electromotive force (E) is measured. The pH-static titration has been extended on some complexometric and precipitation titrations. Among others, two new methods of cyanide determination and a three-component precipitation pH-static titration have been suggested. A new criterion, involved with accuracy of pH and volume measurements in pH-static titrations, is suggested. The data were obtained, according to simulating procedure based on iterative computer programs involving all attainable data related to a system in question and widely accepted physicochemical data related to the systems considered. This way, any analytical prescription performed according to titrimetric mode can be fully reproduced and none simplifying assumptions in calculations made for this purpose are required. The Ni method, confined primarily to mixtures of weak acids, has been extended to acid–base systems involving salts of different type; to apply a kind of ‘homogenisation’ in formulae related to such systems, the Simms’ constants were introduced.

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1. Introduction

More than a half of century passed after appearance of the Gran famous papers: [1,2], with formulae widely exploited later by chemists–analysts. Popularity of the formulae, presented there and elsewhere [3–5], resulted from their simplicity, effectiveness and a relatively wide range of applications. The principal idea of the Gran (I and II) methods is based on the evaluation of equivalence volume (V_{eq}) on the basis of points $\{(V_j, Y_j) j = 1, \dots, N\}$ obtained from potentiometric or pH metric titrations, $Y = E$ or pH. Although the Gran II method followed (chronologically) the Gran I method, the Gran I method can be derived from the formulae ascribed to

Gran II method; this occurrence has been taken into account in the present paper (Section 2.1 and 2.2).

From our viewpoint, the replacement of a more sophisticated formula by its ‘rough’ form (ascribed to Gran II method) done by Gran resulted from the fact that the formula derived for Gran I method has been presented in oversimplified form. This fact has lead to relatively high errors involved with V_{eq} evaluation – particularly when the volumes V_j from the nearest vicinity of V_{eq} were taken into account in calculation of V_{eq} on the basis of the original Gran I method. Otherwise, it is necessary to apply relatively small portions $\Delta V_{j,j+1} = V_{j+1} - V_j$ of titrant such that $x_j' = (V_{j+1} - V_j)/|V_{eq} - V_j| \ll 1$. However, the relative error $\delta V/\Delta V_{j,j+1}$ in volume increment assumed in the titration and the resulting relative error $\delta Y/\Delta Y_{j,j+1}$ in the Y -measurement becomes greater for small $\Delta V_{j,j+1}$ and $\Delta Y_{j,j+1}$ values when

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Nomenclature

AD	adjusting solution
AT	auxiliary titrant
D	titrand
E	electromotive force
ϕ	fraction titrated
PT	primary titrant
S/u	real value for Nernstian slope (Eq. (5)); Nernstian value for S is $RT/F \cdot \ln 10$
V	volume of titrant added
V_e	end volume
V_{eq}	equivalence volume
V_j^m	$(V_j + V_{j+1})/2$ (Eq. (25))
V_0	volume of D (in Section 3.1 and in Fig. 5)
V_D	volume of D (otherwise)

this remedy is applied; δV and δY denote the smallest difference in readout of variables V and Y .

The V_{eq} location made, according to Gran I method realises the principle of standard addition method. This extrapolative method provides more accurate results if maximal V_j value taken for calculation of V_{eq} corresponds to relatively high x_j' value. This requirement is fulfilled by the modified Gran I method that enables greater $\Delta V_{j,j+1}$ values for volume increments to be applied. The great advantage of the modified Gran I method (when compared with Gran II method) is also the possibility to obtain V_{eq} value without prior determination of the real slope of E versus pX characteristics for X-selective electrode chosen as the indicator electrode. However, the shortcomings of the Gran I method (in its primary version) decided that just the Gran II method is usually applied in practice. The difficulties arising from the slope (S) determination are frequently overcome by setting the theoretical value resulting from the Nernst formula, $S = RT/F \ln 10$; this approach is not correct, however. In this context, the modified Gran I method is the new proposal for wider application.

Another kind of linearisation provides the pH-static titration. This indicative method, reactivated lately, has been previously elaborated for titration of zinc with EDTA and NaOH, considered as primary (PT) and auxiliary (AT) titrants. We have extended the pH-static titration on more complex systems, where complexation, redox and precipitation reactions occur. The possibility of determination of two or three components from a single pH-static titration curve has been also stated. In this part, the paper provides:

- * two new methods of cyanide determination;
- * a simulated precipitation titration where three anions are determined and,
- * a valuable criterion joining an effect of buffer capacity, δV and δY with an error in titrants (PT and AT) volume increments to be evaluated.

The paper is supplemented by other linearisation methods known in literature. Some of them are generalised, derived in simpler manner or simply corrected.

2. The Gran methods

2.1. Formulation of the Gran II method

The principle of Gran II method [2] can be explained first on the basis of titration of V_0 ml of $C_0 \text{ mol l}^{-1}$ HCl with V ml of $C \text{ mol l}^{-1}$ NaOH. In this case, from charge and concentration balances and the relation $C_0 \cdot V_0 = C \cdot V_{eq}$ we get the formula:

$$(V_0 + V) \cdot ([H] - [OH]) = C \cdot (V_{eq} - V) \quad (1)$$

Then for $[H] \gg [OH]$ ('acidic branch') i.e. for $V < V_{eq}$ we have

$$G_a = (V_0 + V) \cdot 10^{-pH} = a \cdot (V_{eq} - V) \quad (a = C \cdot f_H) \quad (2)$$

and for $[H] \ll [OH]$ ('basic branch'), i.e. for $V > V_{eq}$

$$G_b = (V_0 + V) \cdot 10^{pH} = b \cdot (V - V_{eq}) \quad \left(b = \frac{C}{(K_w \cdot f_H)} \right) \quad (3)$$

This way it is assumed that pH is the function of activity (not concentration) of hydrogen ions. The expressions on the right side of Eqs. (2) and (3) are linear; it means that the expressions for G_a and G_b are linear too. The formulae (2) and (3) are the basis for the Gran II method, originated from an earlier Sørensen's [6] idea.

The formulae related to different V ranges ($V < V_{eq}$ or $V > V_{eq}$) provide an option between the points (V_j , pH_j) on the titration curve chosen for evaluation of V_{eq} . However, only the option $V < V_{eq}$ is advisable. It results from the limited pH range where glass indicator electrode appears (favourable, from analytical viewpoint) linear E versus pH relationship,

$$E = E_{0H}^* - S \cdot pH \quad (4)$$

The S changes, $S = S(pH)$, observed at higher pH values, are affected mainly by acid–base properties of $\equiv \text{Si}-\text{O}-\text{H}$ surface groups and interfering action of different cations that act as complexing species. Similar remarks refer, generally, to X indicator electrodes. For this reason, further discussion will be confined to the V -interval where $V < V_{eq}$ (back titrations will not be considered).

Within defined pX range, the voltage E in the system with the indicator electrode is expressed by linear relationship

$$E = E_{0X}^* \pm \left(\frac{S}{u} \right) \cdot pX \quad (5)$$

("+" for anions, "−" for cations) where E_{0X}^* value is assumed constant in a measuring cell considered, $pX = -\log x$, $x = f_X \cdot [X]$ is the activity of X-ions, $u = 1, 2, \dots$. For

$X = H^+(u=1)$ one gets the Eq. (4). From (2) and (4) we have $pH = (E_{0H}^* - E)/S$ and then

$$G_a^* = (V_0 + V) \cdot 10^{E/S} \\ = a^* \cdot (V_{eq} - V) \quad (a^* = C \cdot f_H \cdot 10^{E_{0H}^*/S}) \quad (6)$$

Although any of the terms a and a^* have a defined significance (Eqs. (2) and (6)), they can be chosen arbitrarily (asterisked terms refer to E -values registered); a and a^* values affect the ordinate scale and a due scaling is sometimes done in graphical procedure of V_{eq} location [7,8]. The values for a and a^* are constant if the assumptions of temperature and ionic strength (I) constancy are valid.

Referring now to the system where the precipitate **AgX** characterised by solubility product $K_{soX} = [Ag][X]$ is formed during titration of V_0 ml of $C_0 \text{ mol l}^{-1}$ NaX ($X = \text{Cl, Br, I}$) with V ml of $C \text{ mol l}^{-1}$ AgNO_3 , we get the approximate equation [8,9]

$$C(V_{eq} - V) = (V_0 + V) \cdot ([X] - [Ag]) \quad (7)$$

The approximations resulted from omission of complexes AgX_i^{+1-i} and $\text{Ag}(\text{OH})_j^{+1-j}$ ($i, j = 1, 2, \dots$) [10], see Fig. 1. At $[X] \gg [Ag]$, from (7) we get the relation

$$(V_0 + V) \cdot 10^{-pX} = a_X \cdot (V_{eq} - V) \quad (8)$$

where $a_X = C \cdot f_X$, $pX = -\log(x)$, $x = f_X \cdot [X]$ is the activity of X^{-1} ions. The pX values can be recorded with a due ion-selective X -indicator electrode. Setting $E = E_{0X}^* + S \cdot pX$ (at $u = 1$), we have the formula

$$(V_0 + V) \cdot 10^{-E/S} \\ = a^* \cdot (V_{eq} - V) \quad (a^* = C \cdot f_X \cdot 10^{E_{0X}^*/S}) \quad (9)$$

applicable when E is recorded.

The validity of approximations done in the simplified formula (7) for $X = \text{Cl}$ can be checked out on the basis of equilibrium analysis made with use of concentration, charge and electron balances and equilibrium constants. For the system where V_0 ml of $C_0 \text{ mol l}^{-1}$ NaCl is titrated with V ml of $C \text{ mol l}^{-1}$ AgNO_3 one can formulate the charge and concentration balances involving all soluble species AgCl_i^{+1-i} ($i = 1,$

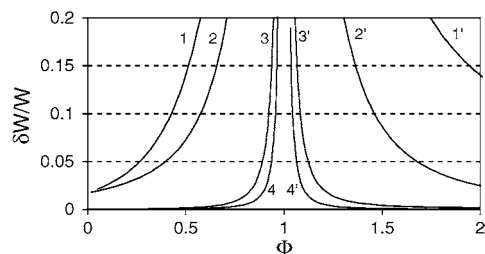


Fig. 1. Plots of $\delta W/W$ vs. Φ relationships; $W = |C(V_{eq} - V)/(V_0 + V)|$, $\delta W = |y - [Ag]|$ for $V < V_{eq}$ or $\delta W = |y + [Cl]|$ for $V > V_{eq}$, where $y = \sum_{i=2}^4 (i-1)[\text{AgCl}_i] - \sum_{j=2}^3 [\text{Ag}(\text{OH})_j]$; $C_0 = 10^{-4} \text{ mol l}^{-1}$, $C = 10^{-4} \text{ mol l}^{-1}$ (curves 1, 1'); $C_0 = 10^{-4} \text{ mol l}^{-1}$, $C = 10^{-3} \text{ mol l}^{-1}$ (curves 2, 2'); $C_0 = 10^{-3} \text{ mol l}^{-1}$, $C = 10^{-3} \text{ mol l}^{-1}$ (curves 3, 3'); $C_0 = 10^{-3} \text{ mol l}^{-1}$, $C = 10^{-2} \text{ mol l}^{-1}$ (curves 4, 4').

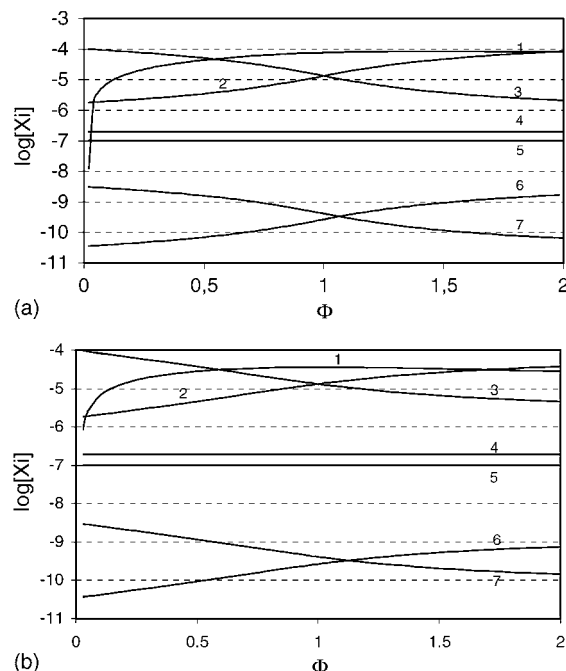


Fig. 2. Plots of $\log[X_i]$ vs. Φ relationships for different species X_i ($i = 1, \dots, 7$) at (a) $C_0 = 10^{-4} \text{ mol l}^{-1}$, $C = 10^{-3} \text{ mol l}^{-1}$ and (b) $C_0 = 10^{-4} \text{ mol l}^{-1}$, $C = 10^{-4} \text{ mol l}^{-1}$; 1 – **AgCl** (precipitate); 2 – Ag^+ ; 3 – Cl^- ; 4 – **AgCl** (soluble complex); 5 – H^+ ; 6 – **AgOH**; 7 – AgCl_2^- .

2, 3, 4; $\log K_i = 3.04, 5.24, 5.04$ and 6.14) and $\text{Ag}(\text{OH})_i^{+1-i}$ ($i = 1, 2, 3$; $\log K_i^{\text{OH}} = 2.3, 3.6$ and 4.8) and the precipitate **AgCl** ($pK_{so} = 9.75$), see Fig. 2 (plots for $\text{Ag}(\text{OH})_2^-$, $\text{Ag}(\text{OH})_3^{2-}$, AgCl_3^{2-} and AgCl_4^{3-} are beyond the frame of the figure).

The Gran methods can also be applied to complexo(nometric) titrations. Let us assume $[M] \gg \sum_j [\text{M}(\text{OH})_j]$ (it is the case frequently valid at lower pH). Then writing the concentration balances (in terms of notation applied for conditional stability constants purposes); $[M] + [\text{ML}^*] = C_0 \cdot V_0 / (V_0 + V)$, $[\text{L}^*] + [\text{ML}^*] = C \cdot V / (V_0 + V)$ and setting $C_0 \cdot V_0 = C \cdot V_{eq}$, $E = E_{0X}^* - (S/u) \cdot pM$, for $V < V_{eq}$ and $[M] \gg [\text{L}^*]$, we get the relation

$$(V_0 + V) \cdot 10^{u \cdot E/S} = a_M^* \cdot (V_{eq} - V) \quad (10)$$

applicable for measurements made with use of M -selective indicator electrode.

The formulae (2), (6), (9) and (10) were applied to evaluate V_{eq} according to Gran II method. It should be noticed that in all instances where E has been recorded, the knowledge of the true S value is required.

The equation for titration curve, related to V_0 ml $C_0 \text{ mol l}^{-1}$ HL titrated with $C \text{ mol l}^{-1}$ NaOH (termed as the Hofstee equation [11]), was transformed into the form [12]

$$V_{eq} - V = \frac{V[\text{H}]}{k_1} + (V_0 + V) \left(\frac{[\text{H}]}{k_1} + 1 \right) \frac{[\text{H}] - K_w/[\text{H}]}{C} \quad (11)$$

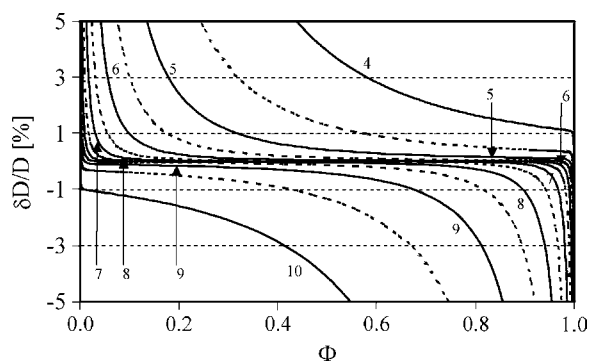


Fig. 3. The $\delta D/D$ [%] vs. Φ relationships plotted for different $pk_1 = -\log k_1$ values at $V_0 = 100$ ml $C_0 = 0.01$ mol l⁻¹ HL, $C = 0.1$ mol l⁻¹ NaOH. Number at the corresponding curve indicates pk_1 value.

Let us denote $V_{eq} - V = D$, $\delta D = (V_0 + V)([H]/k_1 + 1)/([H] - K_w/[H])/C$. On the basis of Fig. 3 one can define pk_1 for an acid HL and V -range for NaOH where the simplified relation

$$V_{eq} - V = \frac{V[H]}{k_1} \quad (12)$$

is valid within defined tolerance limits; $(\delta D)/D \ll 1$ for moderately weak acids, $5 < pk_1 < 9$ (see also [13,14]). Then Eq. (12) can be presented in the form

$$V \cdot 10^{-pH} = a \cdot (V_{eq} - V) \quad (a = f_H \cdot k_1) \quad (13)$$

adaptable for Gran II method; the titration should be made at constant ionic strength. Note that, for moderately weak acids HL, $pH = pk_1$ occurs at $\Phi \cong 0.5$. As results from Fig. 3, the application of the Gran II method requires a rejection of some points (V_j , pH_j) obtained from measurements [15].

2.2. Original and modified Gran I method

From Eq. (2) we obtain:

$$\ln 10 \cdot pH = \ln(V_0 + V) - \ln(V_{eq} - V) - \ln a \quad (14)$$

For any sequence of two points: (V_j , pH_j) and (V_{j+1} , pH_{j+1}), obtained from pH metric titration, we have

$$\ln 10 \cdot pH_j = \ln(V_0 + V_j) - \ln(V_{eq} - V_j) - \ln a$$

and

$$\ln 10 \cdot pH_{j+1} = \ln(V_0 + V_{j+1}) - \ln(V_{eq} - V_{j+1}) - \ln a$$

and then

$$\begin{aligned} \ln 10 \cdot (pH_{j+1} - pH_j) &= \ln \left(\frac{V_0 + V_{j+1}}{V_0 + V_j} \right) - \ln \left(\frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \right) \end{aligned} \quad (15)$$

Setting the identities: $V_0 + V_{j+1} = V_0 + V_j + V_{j+1} - V_j$ and $V_{eq} - V_{j+1} = V_{eq} - V_j - (V_{j+1} - V_j)$ in (15), we get:

$$\ln 10 \cdot (pH_{j+1} - pH_j) = \ln(1 + x_j) - \ln(1 - x'_j) \quad (16)$$

where

$$x_j = \frac{V_{j+1} - V_j}{V_0 + V_j} \quad \text{and} \quad x'_j = \frac{V_{j+1} - V_j}{V_{eq} - V_j} \quad (17)$$

Further transformation of (16) needs some simplifying assumptions. In the original papers, referred to Gran I method, the approximation

$$\ln(1 + x) \cong x \quad (18)$$

of the series expansion

$$f_\infty(x) = \ln(1 + x) = \sum_{j=0}^{\infty} (-1)^j \cdot \frac{x^{j+1}}{j+1} \quad (19)$$

has been factually introduced. The approximation (18) is valid for $|x| \ll 1$, whereas the modification in the Gran I method, based on the more accurate approximation [16],

$$\ln(1 + x) \cong \frac{x}{(1 + x/2)} \quad (20)$$

does not need such a stringent requirement. Note that the formula (20) can be primarily obtained from the approximation involving two first terms in the resolution (19), i.e. $\ln(1 + x) \cong x - x^2/2 = x \cdot (1 - x/2) = x \cdot (1 - x^2/4)/(1 + x/2) \cong x/(1 + x/2)$ valid at $|x| \ll 1$. From Table 1 we see that, at $x \leq 0.4$, the difference between $\ln(1 + x)$ and $x/(1 + x/2)$ is less than 1%, whereas the difference between $\ln(1 + x)$ and x (related to original version of Gran I method) is ca. 19%; at $x = 1$, the differences are ca. 4 and 44%, respectively. This means that the assumption $|x| \ll 1$ is greatly weakened in the case of the modified approach and testifies very well about the validity (robustness) of the approximation (20). A comparison of Eq. (20) ($-\delta_2 = 3.82$ at $x = 1$, Table 1) with the approximative sum $f_n(1) = \sum_{j=0}^{n-1} (-1)^j/(j+1)$ related to Eq. (19) and calculated for $x = 1$ ($\ln 2 = 0.69315$) leads to conclusion that approximation (20) is better than the expansion of $\ln(1 + x)$ into Maclaurin's series involving 18 first terms (!), as indicated in Table 2 [17]. Setting (17) and (18) in Eq. (16) we have, by turns,

$$(pH_{j+1} - pH_j) \cdot \ln 10 \cong x_j + x'_j$$

$$y_j \cong \alpha \cdot (V_{eq} - V_j) + \varepsilon_j \quad (21)$$

where

$$y_j = (V_0 + V_j)^{-1} \cdot \frac{V_{j+1} - V_j}{pH_{j+1} - pH_j} \quad \alpha = \frac{\ln 10}{V_0 + V_{eq}} \quad (22)$$

and ε_j refers to the random errors. Setting (17) and (20) in Eq. (16) we have, by turns

Table 1

Errors [%] involved with approximations (18) and (20); $\delta_k(x) = f_k(x)/\ln(1+x) - 1$; $f_1(x) = x$, $f_2(x) = x/(1+x/2)$

x	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
δ_1 (%)	2.5	4.9	9.7	14.3	18.9	23.3	27.6	31.9	36.1	40.2	44.2
$-\delta_2$ (%)	0.02	0.07	0.27	0.57	0.93	1.34	1.80	2.28	2.78	3.30	3.82

Table 2

Values for $\delta = f_n(1)/\ln 2 - 1$ (%) found for different number of terms involved in extensions for $\ln(1+x)$ in series at $x=1$; $f_n(1) = \sum_{j=0}^{n-1} (-1)^j/(j+1)$

n	1	2	...	9	10	...	18	19	...
$f_n(1)$	1	0.5	...	0.7456	0.6456	...	0.6661	0.7188	...
δ_n (%)	44.2	-27.9	...	7.6	-6.9	...	-3.9	3.7	...

$$\begin{aligned} \ln 10 \cdot (\text{pH}_{j+1} - \text{pH}_j) &= \frac{(V_{j+1} - V_j)/(V_0 + V_j)}{1 + 1/2 \cdot (V_{j+1} - V_j)/(V_0 + V_j)} \\ &+ \frac{(V_{j+1} - V_j)/(V_{\text{eq}} - V_j)}{1 - 1/2 \cdot (V_{j+1} - V_j)/(V_{\text{eq}} - V_j)} \end{aligned} \quad (23)$$

$$\ln 10 \cdot \frac{\text{pH}_{j+1} - \text{pH}_j}{V_{j+1} - V_j} = \frac{1}{V_0 + V_j^m} + \frac{1}{V_{\text{eq}} - V_j^m} \quad (24)$$

where

$$V_j^m = \frac{V_j + V_{j+1}}{2} \quad (25)$$

(m – for modified). After further transformations of (24) we get finally

$$Y_j = \alpha \cdot (V_{\text{eq}} + V_j^m) + \varepsilon_j \quad \left(\alpha = \frac{\ln 10}{V_0 + V_{\text{eq}}} \right) \quad (26)$$

where

$$Y_j = (V_0 + V_j^m)^{-1} \cdot \frac{V_{j+1} - V_j}{\text{pH}_{j+1} - \text{pH}_j} \quad (27)$$

Applying similar procedure to Eq. (13) we get, by turns,

$$\ln 10 \cdot \text{pH} = \ln V - \ln(V_{\text{eq}} - V) - \ln a$$

$$\text{pH}_j \cdot \ln 10 = \ln V_j - \ln(V_{\text{eq}} - V_j) - \ln a$$

$$\text{and } \text{pH}_{j+1} \cdot \ln 10 = \ln V_{j+1} - \ln(V_{\text{eq}} - V_{j+1}) - \ln a$$

$$(\text{pH}_{j+1} - \text{pH}_j) \cdot \ln 10 = \ln \left(\frac{V_{j+1}}{V_j} \right) - \ln \left(\frac{V_{\text{eq}} - V_{j+1}}{V_{\text{eq}} - V_j} \right) \quad (28)$$

Then setting $V_{j+1} = V_j + V_{j+1} - V_j$ and $V_{\text{eq}} - V_{j+1} = V_{\text{eq}} - V_j - (V_{j+1} - V_j)$, from (28) we have:

$$\begin{aligned} (\text{pH}_{j+1} - \text{pH}_j) \cdot \ln 10 &= \ln \left(1 + \frac{V_{j+1} - V_j}{V_j} \right) \\ &- \ln \left(1 - \frac{V_{j+1} - V_j}{V_{\text{eq}} - V_j} \right) \end{aligned}$$

$$\begin{aligned} (\text{pH}_{j+1} - \text{pH}_j) \cdot \ln 10 &= \frac{(V_{j+1} - V_j)/V_j}{1 + 1/2 \cdot (V_{j+1} - V_j)/V_j} \\ &+ \frac{(V_{j+1} - V_j)/(V_{\text{eq}} - V_j)}{1 - 1/2 \cdot (V_{j+1} - V_j)/(V_{\text{eq}} - V_j)} \end{aligned}$$

and finally

$$\begin{aligned} (V_j^m)^{-1} \cdot \frac{V_{j+1} - V_j}{\text{pH}_{j+1} - \text{pH}_j} &= \alpha \cdot (V_{\text{eq}} - V_j^m) \quad \left(\alpha = \frac{\ln 10}{V_{\text{eq}}} \right) \end{aligned} \quad (29)$$

where V_j^m is expressed by Eq. (25). Taking two successive points (V_j, E_j) and (V_{j+1}, E_{j+1}) , from Eqs. (10) and (20) we get the relation

$$\begin{aligned} Y_j &= (V_0 + V_j^m)^{-1} \cdot \frac{V_{j+1} - V_j}{E_{j+1} - E_j} \\ &= -\alpha^* \cdot (V_{\text{eq}} - V_j^m) + \varepsilon_j \quad \left(\alpha^* = \ln 10 \cdot \frac{u/S}{V_0 + V_{\text{eq}}} \right) \end{aligned} \quad (30)$$

Eqs. (29) and (30) and the related formulae derived from the other ones (Eqs. (6), (9) and (10)) with use of the approximation (20) applied are not ‘loaded’ by coarse errors and simplifications met in the original paper [18].

Eq. (30) can be rewritten into the form $Y_j = a - b \cdot V_j^m + \varepsilon_j$, where $a = -\alpha^* V_{\text{eq}}$, $b = -\alpha^*$. The parameters a and b are determined according to the least squares method and then $V_{\text{eq}} = a/b$ is calculated.

2.3. Calculations of V_{eq} according to least squares method

Eq. (26) can be rewritten into the form of linear regression equation

$$Y_j = \beta - \alpha \cdot V_j^m + \varepsilon_j \quad (j = 1, \dots, N) \quad (31)$$

where: $\beta = \alpha \cdot V_{\text{eq}}$, N is the number of experimental points (V_j, pH_j) . The parameters α and β in (31) can be obtained

according to the least squares method, i.e. the sum of squares

$$SS = \sum_{j=1}^N (Y_j - \beta + \alpha \cdot V_j^m)^2 \quad (32)$$

is minimised; then $V_{eq} = \beta/\alpha$. Moreover, greater portions of titrant can be applied (a relative error in evaluation of successive portions is thus diminished) in the procedure of evaluation of the V_{eq} value.

Similar approach to the subject in question has been applied for determination of molar concentrations C_{02} and C_{03} of Fe(II) and Fe(III), respectively, in V_0 ml of the sample titrated with $C \text{ mol l}^{-1}$ KMnO_4 were determined (speciation) from a single potentiometric titration, using the formulae [19]:

$$C_{02} = 2.5 \cdot \frac{C}{V_0} \cdot \left\{ \left[\left(\frac{Q}{R} \right)^2 + 4 \cdot \frac{P}{R} \right]^{1/2} + \frac{Q}{R} \right\}$$

and

$$C_{03} = 2.5 \cdot \frac{C}{V_0} \cdot \left\{ \left[\left(\frac{Q}{R} \right)^2 + 4 \cdot \frac{P}{R} \right]^{1/2} - \frac{Q}{R} \right\} \quad (33)$$

The values for Q/R and P/R are determined according to least squares method applied to the regression equation (see Eq. (25))

$$\frac{V_{j+1} - V_j}{E_{j+1} - E_j} = P + Q \cdot V_j^m - R \cdot (V_j^m)^2 + \varepsilon_j \quad (34)$$

2.4. General remarks on the Gran methods

On the basis of the formulae derived above, one can summarise serious limitations inherent in the original Gran I method and some drawbacks of the Gran II method. In this context, the advantages of the modified Gran I method will be emphasised.

The Gran methods should be considered as a particular case of the standard addition method. In this respect, let us remember that the inequalities: $|x_j| \ll 1$ and $|x'_j| \ll 1$ were necessarily required in the original Gran I method applied for the dataset (V_j, pH_j) or (V_j, E_j) taken for calculations; it justified the approximation (18) applied in there. In practice, the inequality $|x_j| \ll 1$ is always fulfilled in sufficient degree whereas the inequality $|x'_j| \ll 1$ is valid if the volumes V_j too close to V_{eq} are omitted in calculation of the V_{eq} value, see Fig. 4; otherwise, the original Gran I method gives biased results for V_{eq} . Probably, for this reason, the Gran II method (not the original Gran I method) has been usually applied in the related papers; some of them concern alkalinity measurements, e.g. [20,21]. It should also be noticed that the approximation (18) has not been specified explicitly in the original paper [1] and elsewhere. The approximation (20) offers far better

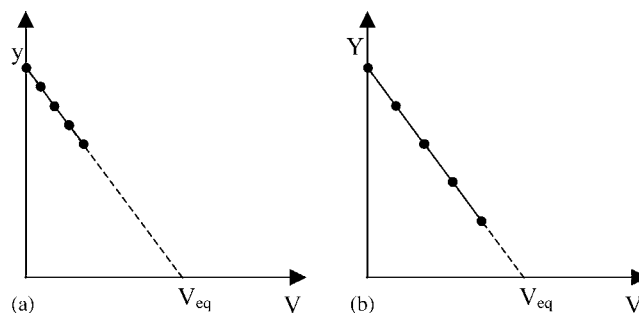


Fig. 4. Graphical depiction of differences between (a) original and (b) modified Gran I method.

results for V_{eq} , not loaded by a great systematic error. The error $|\delta_2|$ related to $x'_j = 1$, i.e. $V_{eq} - V'_j = V_{j+1} - V_j$, is smaller than $|\delta_2|$ calculated at $x'_j = 0.1$ on the basis of the simplified formula (18), see Table 1.

The principal idea of the Gran I method (not its realisation) offers some advantages over Gran II method, especially when E (Eq. (5)) is registered. The Gran II method requires exact S value to be determined for an indicator electrode used in potentiometric titrations, see Eqs. (6), (9) and (10). The real S value differs, as a rule, from the $(RT/F) \cdot \ln 10$ value calculated from the Nernst equation, as has been clearly indicated e.g. in ref. [9]. Such a necessity does not take place when the Gran I method, particularly in its modified form (Eq. (30)), is applied.

Another approaches to the Gran I method were also done. For example, the $(\text{pH}_{j+1} - \text{pH}_j)/(V_{j+1} - V_j)$ versus $V_m^* = (V_j + V_{j+1})/2$ relationship proposed in another Gran paper [5] is inappropriate in context with Eqs. (26), (29) and (30). This inapplicability is evident in the light of preliminaries done in the introductory part of this paper [5], where the correction for volume change during the titration is indispensable. In this respect, the problem is somewhat similar to one considered in the papers [9,16], where the regression equation

$$\left(1 + \frac{V}{V_0}\right)^3 \cdot E = \sum_{i=0}^3 A_i \cdot V^i$$

derived from the related balances, has been applied. In this context, small volume increments $V_{j+1} - V_j$ of titrant were required, e.g. in the Yan method [14,22], based on the formula

$$E = \sum_{i=0}^3 A'_i \cdot V^i$$

Prone to error approach in the subject in question was also done in ref. [18], where the changes in volume of the system, affected by the titrant addition, were neglected.

The difficulties arising when Gran II method is applied to potentiometric titrations caused that this method appears to be useful mainly in pH metric titrations, where determination of S value is not needed. Particularly, the systems with

a weak monoprotic acid HL involved have been considered in numerous papers, quoted extensively in [5,14,16,23]. For example, the system obtained by titration of V_0 ml of (standardised, $C_0 \text{ mol l}^{-1}$) HL with V ml of $C \text{ mol l}^{-1}$ solution of the same acid (HL, sample tested) is described by equation

$$y = \left([\text{H}] - \frac{K_w}{[\text{H}]} \right) (V_0 + V) \left(\frac{[\text{H}]}{k_1} + 1 \right) = C_0 \cdot V_0 + C \cdot V \quad (35)$$

The auxiliary variable y is the linear function of V , with C as the slope in co-ordinates (V, y) [24,25]. A particular case, $y = C \cdot V$ ($C_0 = 0$ in Eq. (35)), refers to addition of V ml of $C \text{ mol l}^{-1}$ HL (sample tested) into pure water or an inert electrolyte (e.g. KCl). The exact value for k_1 (and K_w , if the inequality $[\text{H}] \gg [\text{OH}]$ is not fulfilled) must be known beforehand and concentrations of hydrogen ions (not activities determined from pH measurements) should be considered [26]. Different rearrangements of the equation $y = C \cdot V$, considered together with Eq. (35), enable to determine k_1 and C from a more generalised straight line, $Y = a + b \cdot X$ [25], although the difficulties arising from the discrepancy between activity and concentration of hydrogen ions are still actual.

Some algorithms applied for V_{eq} evaluation, involved in the so-named Hofstee, EKVOLL and QUOTEX methods (cited in [5]), were based on the formula [27]

$$V_{\text{eq}} = V_j + \frac{V_j - V_i}{a_{ij} - 1} \quad (36)$$

derived from Eq. (11), see [14]. In order to overcome the difficulties indicated above, some empirical corrections (extension in series) were done [5].

Another approach to the Gran II method has been done in the papers [28] where V_0 ml of the titrand containing k bases $\text{B}_{(i)}$ ($C_i \text{ mol l}^{-1}$, $i=1, \dots, k$) is titrated with V ml of a strong monoprotic acid HA ($C \text{ mol l}^{-1}$). Arranging the bases in a sequence starting from the strongest up to the weakest one and denoting

$$C_i \cdot V_0 = C \cdot (V_{\text{eq}i} - V_{\text{eq}i-1}) \text{ for } i \in < 1, k >, V_{\text{eq}0} \equiv 0 \quad (37)$$

we have the balances:

$$[\text{HB}_{(i)}] + [\text{B}_{(i)}] = C \cdot \frac{V_{\text{eq}i} - V_{\text{eq}i-1}}{V_0 + V},$$

$$[\text{HB}_{(1)}] + [\text{B}_{(1)}] = C \cdot \frac{V_{\text{eq}1}}{V_0 + V} \quad (38)$$

$$[\text{A}] = \frac{C \cdot V}{V_0 + V}, \quad \sum_{i=1}^k [\text{HB}_{(i)}] = [\text{OH}] - [\text{H}] + [\text{A}]$$

In Eq. (38), $V_{\text{eq}i}$ is the total volume of the titrant added at the equivalence point related to the i th base, $\text{B}_{(i)}$. Setting $K_{\text{Bi}} = [\text{HB}_{(i)}][\text{OH}]/[\text{B}_{(i)}]$ for $\text{B}_{(i)} + \text{H}_2\text{O} = \text{HB}_{(i)} + \text{OH}^-$

and denoting $\psi_i = K_{\text{Bi}}/(K_{\text{Bi}} + [\text{OH}])$, after rearranging the terms we get, by turns,

$$\begin{aligned} \psi_1 \cdot V_{\text{eq}1} + \sum_{i=2}^k \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) \\ = \frac{([\text{OH}] - [\text{H}]) (V_0 + V)}{C} + V \\ F_1 = V_{\text{eq}1} \cdot K_{\text{B}1} - V \cdot K_{\text{B}1} \\ = ([\text{OH}] - [\text{H}]) \cdot (V_0 + V) \cdot \frac{(K_{\text{B}1} + [\text{OH}])}{C} + V \cdot [\text{OH}] \\ - \sum_{i=2}^k \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) \cdot (K_{\text{B}i} + [\text{OH}]) \quad (39) \end{aligned}$$

$$\begin{aligned} \sum_{i=1}^j \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) + \psi_j \cdot (V_{\text{eq},j} - V_{\text{eq},j-1}) \\ + \sum_{i=j+1}^k \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) \\ = ([\text{OH}] - [\text{H}]) \frac{(V_0 + V)}{C} + V \\ F_j = K_{\text{B}j} \cdot V_{\text{eq}j} - K_{\text{B}j} \cdot V = ([\text{OH}] - [\text{H}]) (V_0 + V) \\ \times \frac{(K_{\text{B}j} + [\text{OH}])}{C} + V[\text{OH}] + K_{\text{B}j} \cdot V_{\text{eq},j-1} \\ - \left[\sum_{i=1}^{j-1} \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) \right. \\ \left. + \sum_{i=j+1}^k \psi_i \cdot (V_{\text{eq},i} - V_{\text{eq},i-1}) \right] \cdot (K_{\text{B}j} + [\text{OH}]) \quad (40) \end{aligned}$$

where ψ_1 and $V_{\text{eq}1}$ (index $i=1$) refer to the strongest base $\text{B}_{(1)}$. This approach to the problem in question, expressed by Eqs. (39) and (40), has followed earlier papers [29,30]. Among others, a voluminous (complicated) approach done in the paper [29], related, among others, to polyprotic acids and its salts, can be easily simplified and generalised on more complex acid–base systems provided that the idea of Simms constants, considered e.g. in ref. [31], is applied. For example, in the system where a base L^{-n} form protonated species $\text{HL}^{+1-n}, \dots, \text{H}_q\text{L}^{+q-n}$ (e.g. $n=4$ and $q=6$ for EDTA) one can define the function $\bar{n} = \sum_{i=1}^q i \cdot [\text{H}_i\text{L}]/\sum_{i=0}^q [\text{H}_i\text{L}]$ and write the useful expressions [16] for \bar{n} or $q-\bar{n}$ in terms of Simms constants γ_j or g_j , namely:

$$\bar{n} = \sum_{i=1}^q \left(\frac{[\text{OH}]}{\gamma_i} + 1 \right)^{-1}$$

$$q - \bar{n} = \sum_{i=1}^q \left(\frac{[H]}{g_i} + 1 \right)^{-1}$$

where $g_i = K_w/\gamma_i$.

2.5. Verification of titrimetric data

It is expected that the values obtained for V_{eq} need some verification. As the verification criterion, some analytical or physicochemical data were already applied. For example, the solubility product (K_{so}) for **AgCl** and E_0^* values were evaluated from results of potentiometric titration of Cl^- ions with $AgNO_3$ solution [12]. In other instances, the concentration of complexing agent, considered as an internal standard, has been applied as a criterion of reliability of results obtained for stability constants of complexes. A special case of correlation analysis has been applied for this purpose that enables unbiased a priori values for equilibrium constants to be obtained on the basis of biased results found in separate titrations [32–35].

The Gran methods are among linearisation methods best known in literature devoted to location of equivalence volume (V_{eq}) in titrimetric methods of analysis. These methods are less affected by kinetic phenomena occurred at electrodes and in the bulk solution than those based on the inflection point location, characterised by lowest standard deviation [13] and the greatest informative content [36,37]. The reliable results are obtained if the titrations are carried out in *quasistatic* manner; otherwise, biased results are obtained.

3. Other linearisation methods

Similar advantageous properties can be ascribed to other, more contemporary linearisation methods. For example, the pH-static titration method, reactivated lately by Macca [38,39] for simplest complexometric titrations, can be extended on other areas of titrimetric analyses performed in more complex systems. Some examples of a more rigorous approach to the problem in question will be presented below. Among others, an example of multicomponent analysis will be considered.

Further part of the paper provides a more generalised approach to the method elaborated recently by Ni [40,41]. The approach refers to more complex systems with extended class of acids and salts involved.

3.1. pH-static titration

3.1.1. Principle of the method

The analytical procedure known as pH-static titration is based on several steps involving:

- preparation of V_D ml of titrand (D);
- pH adjusting of D to a pre-assumed pH_0 value by addition of an adjusting (AD) solution (acid or base);

- alternate addition of small portions ΔV_{Pj} ml of the primary titrant (PT) followed, repeatedly, by titration ΔV_{Aj} ml of auxiliary titrant (AT).

V_X ml of a sample containing $C^*_X \text{ mol l}^{-1}$ X is treated with V_B ml of $C^*_B \text{ mol l}^{-1}$ solution of a buffering species (B) (and other species, if necessary) and filled up to the mark (V_F ml) with distilled water. Then V_D ml of the titrand D containing X and B, with molar concentrations $C_X = C_X^* \cdot V_X/V_F$ and $C_B = C_B^* \cdot V_B/V_F$, is treated with ΔV_{AD} ml of AD solution that adjusts its pH to a pre-assumed pH_0 value. The volume $V_D + \Delta V_{AD}$ ml of D + AD solution, with $pH = pH_0$ value, is treated first with a portion ΔV_{P1} ml of $C_P \text{ mol l}^{-1}$ PT and the pH_0 value is restored by titration with ΔV_{A1} ml of $C_A \text{ mol l}^{-1}$ AT; this procedure is repeated $N-1$ times. A flow diagram for pH-static titration of cyanide (see Section 3.1.2.1), considered as an example, is depicted in Fig. 5. The summary volumes of PT and AT added at j th

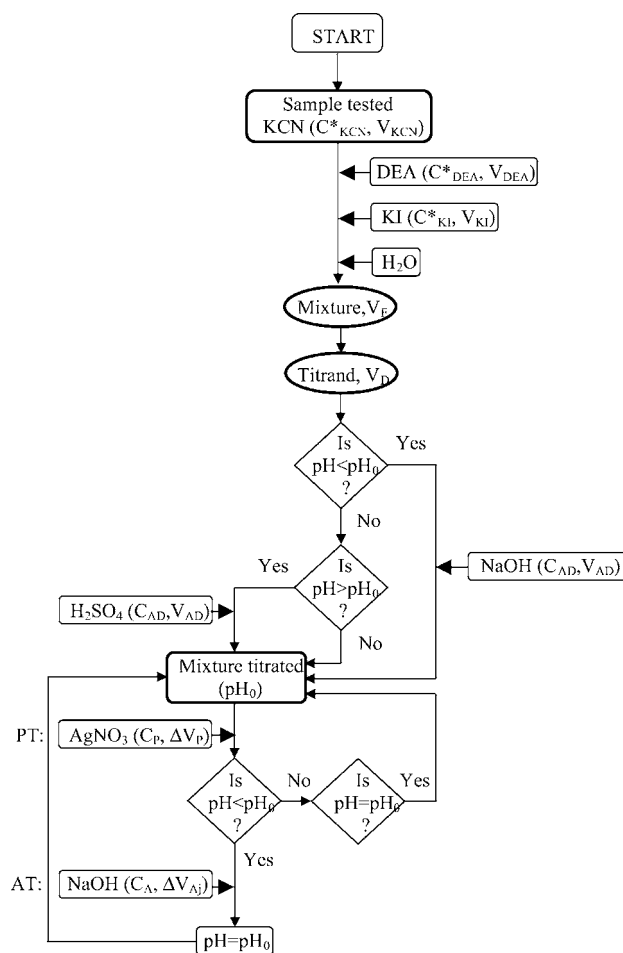


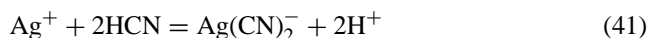
Fig. 5. Flow diagram for pH-static titration, related to the (modified) Liebig–Deniges method (Section 3.1.2.1); $C_{KCN} = C_{KCN}^* \cdot V_{KCN}/V_F$, $C_{DEA} = C_{DEA}^* \cdot V_{DEA}/V_F$, $C_{KI} = C_{KI}^* \cdot V_{KI}/V_F$ concentrations of KCN, DEA and KI in D; NaOH or H_2SO_4 used as AD; $AgNO_3$ as PT, NaOH as AT. For further details see text.

point $((V_{Pj}, V_{Aj}) | j = 1, \dots, N)$ are:

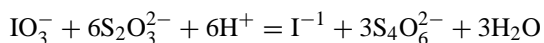
$$V_{Pj} = \sum_{i=1}^j \Delta V_{Pi} \quad \text{and} \quad V_{Aj} = \sum_{i=1}^j \Delta V_{Ai}$$

The points are arranged along a broken line (curve) plotted on a plane with co-ordinates (V_P, V_A) . In mono-component analyses, the curve consists of (or contains) two rectilinear parts intersecting at the point whose abscissa corresponds to the equivalence (eq) volume, $V_P \cong V_{eq}$. The shape of the pH-static titration curves thus obtained resemble the ones obtained in corrected (dilution effect) spectrophotometric, conductometric, thermometric (enthalpimetric), radiometric titrations and in titrations made according to surface acoustic wave (SAW) method [42]. All the titrations provide a kind of indicative method of V_{eq} location [43], in contradistinction to the Gran (I and II) extrapolative methods. As a rule, in the pH-static titration it is assumed that $\Delta V_{Pi} = \Delta V_{P1}$, i.e. $V_{Pj} = j \cdot \Delta V_{P1}$ for $j = 1, \dots, N$ and, moreover, $V_{eq} \approx V_{PN}/2$, i.e. V_{eq} is not far from the value $N/2 \cdot \Delta V_{P1}$.

The pH-static titrations are adaptable to the systems where protons are evolved or consumed as a result of PT addition into the system considered. For example, protons are evolved in reactions:



related to the systems considered in Section 3.1.2.1 and 3.1.2.3. Protons are consumed e.g. in the reaction



where $\text{Na}_2\text{S}_2\text{O}_3$ acts as a strong base [44,45].

3.1.2. Examples of pH-static titration

To illustrate some possibilities of pH-static titration, two methods of cyanide determination and one multicomponent analysis will be presented. The titration curves and the plots representing pH changes during pH-static titration specified below were plotted on the basis of calculations made according to iteration procedure applied for simulated titrations presented elsewhere [44–48].

3.1.2.1. pH-static titration of cyanide, according to the modified Liebig–Deniges method. In pH-static modification of the Liebig–Deniges method of cyanide titration with AgNO_3 solution, **AgI** (not metastable **AgCN**) is precipitated in close vicinity of the equivalence point ($\phi_{eq} = 0.5$). The point where the precipitation starts, depends on the pH_0 value assumed for the titrand containing the cyanide and diethanolamine (DEA); other silver precipitates are not formed in there. The resulting curve of pH-static titration of $\text{KCN} + \text{DEA} + \text{H}_2\text{SO}_4$ system and the error of cyanide analysis depend on the conditions assumed in the analysis (Table 3). DEA (not NH_3 , as done in the original version of the Liebig–Deniges method) enables additional errors resulting from the volatility of ammonia to

Table 3

pH_0 and the related $\phi = \phi_e$ values corresponding to the points where the solubility product (K_{so}^*) for **AgI** is crossed in conventional (column A) and pH-static (column B) titrations

pH_0	ϕ_e	
	A	B
7.5	0.1641	0.4473
8.0	0.4212	0.4820
8.5	0.4903	0.4936
9.0	0.4968	0.4973
9.5	0.4983	0.4985
10.0	0.4988	0.4988
10.5	0.4989	0.4990

In (A), 50 ml of the solution containing KCN (0.002 mol l^{-1}) + DEA (0.02 mol l^{-1}) + KI (0.002 mol l^{-1}) was adjusted with H_2SO_4 (0.1 mol l^{-1}) to the pre-assumed pH_0 value and then titrated with 0.01 mol l^{-1} AgNO_3 . In (B), the solution with the adjusted pH_0 value has been titrated with 0.01 mol l^{-1} AgNO_3 (as PT) and 0.01 mol l^{-1} NaOH (as AT) added sequentially and alternately.

be avoided (b.p. $115\text{--}120^\circ\text{C}$ for DEA). H_2SO_4 moderates pH_0 value of the titrand.

The pH-static titration curves plotted at different pH_0 values and different concentrations of KCN are presented in Figs. 6 and 7 together with detailed description of the related systems.

3.1.2.2. pH-static titration of cyanide with nickel salt. Another option of cyanide determination is the application of nickel salt as the titrant; Ni^{+2} ions form with cyanide ions a stable complex $\text{Ni}(\text{CN})_4^{2-}$ ($\log K_4 = 31.1$) accompanied by other soluble species $\text{Ni}(\text{CN})_i^{+2-i}$ ($i = 1, 2, 3$; $\log K_i = 7.0, 14.0, 22.0$). In order to avoid the precipitation of **Ni(CN)₂** ($\text{p}K_{so} = 8.8$ for $K_{so} = [\text{Ni}^{+2}][\text{CN}^{-1}]^2$) or **Ni(OH)₂** ($\text{p}K_{so1} = 14.7$), a due excess of 5-sulphosalicylic acid as the complexing and buffering ($\text{p}K_3 = 11.6$) agent has been introduced during the titrand (D) preparation. Then

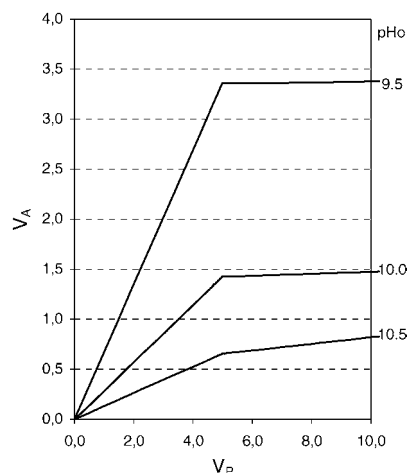


Fig. 6. The pH-static titration curves at indicated pH_0 values; PT = AgNO_3 (0.01 mol l^{-1}), AT = NaOH (0.01 mol l^{-1}); AD = NaOH (0.1 mol l^{-1}) or H_2SO_4 (0.1 mol l^{-1}); D = titrand ($V_D = 50 \text{ ml}$) containing KCN (0.002 mol l^{-1}), DEA (diethanolamine) (0.002 mol l^{-1}), KI (0.002 mol l^{-1}).

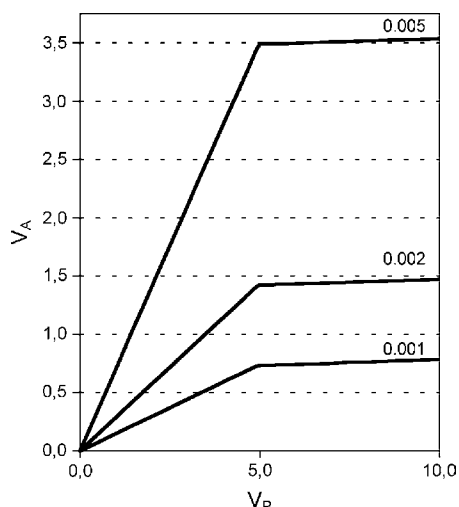


Fig. 7. The pH-static titration curves at $\text{pH}_0 = 10.0$, $C_P/C_{\text{KCN}} = 5$ and indicated C_{KCN} values; PT = AgNO_3 ($C_P \text{ mol l}^{-1}$), AT = NaOH (0.01 mol l^{-1}), AD = H_2SO_4 (0.1 mol l^{-1}); D = titrand ($V_D = 50 \text{ ml}$) containing KCN ($C_{\text{KCN}} \text{ mol l}^{-1}$), TEA (triethanolamine) (0.001 mol l^{-1}), KI (0.02 mol l^{-1}).

$V_D = 50 \text{ ml}$ of D (NaCN (0.004 mol l^{-1}) + 5-sulphosalicylic acid (0.1 mol l^{-1})) (the latter as the buffer-forming substance) was pre-adjusted to the desired pH value with 1 mol l^{-1} NaOH solution and titrated with 0.01 mol l^{-1} NiSO_4 as PT and 0.01 mol l^{-1} NaOH as AT. The resulting titration curves, presented in Fig. 8, are adaptable for location of the end point in the determination of cyanide. The shape of the curves is different from ones presented in Figs. 6 and 7 and elsewhere [38,39]. This method provides an alternative for the spectrophotometric method [49] where (unstable in alkaline media) murexide has been used as indicator.

3.1.2.3. Multicomponent analysis. The pH-static titration can be adaptable for multicomponent analysis, as well. As an

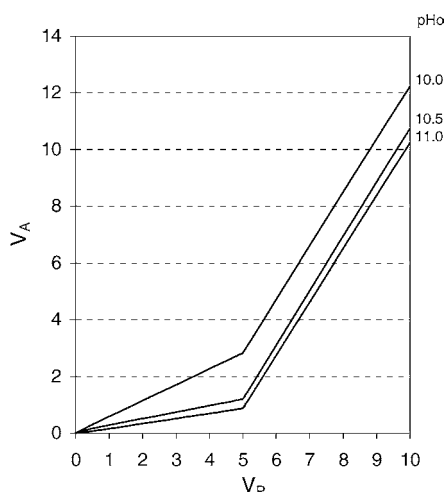


Fig. 8. The ('bared') pH-static titration curves at indicated pH_0 values; PT = NiSO_4 (0.01 mol l^{-1}), AT = NaOH (0.01 mol l^{-1}); AD = NaOH (1.0 mol l^{-1}); D = titrand ($V_D = 50 \text{ ml}$) containing NaCN (0.004 mol l^{-1}), 5-sulphosalicylic acid (0.1 mol l^{-1}).

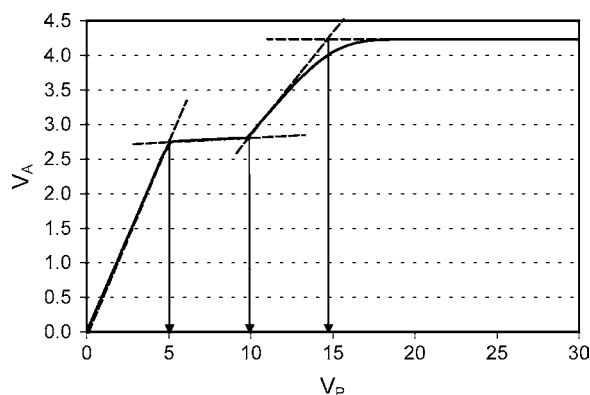


Fig. 9. Plots of pH-static titration in the system specified in the text (Section 3.1.2.3).

example, let us consider 50 ml of titrand (D) containing CaCl_2 (0.001 mol l^{-1}) + H_2S (0.003 mol l^{-1}) + H_3PO_4 (0.003 mol l^{-1}) + H_2SO_4 (0.003 mol l^{-1}) + H_2CO_3 (0.003 mol l^{-1}) + CH_3COOH (0.002 mol l^{-1}) + CH_3COONa (0.001 mol l^{-1}) adjusted to $\text{pH}_0 = 2.50$ with $\Delta V_{\text{AD}} = 3.213 \text{ ml}$ of 0.1 mol l^{-1} NaOH as AD. Then the D+AD system has been titrated alternately with 0.03 mol l^{-1} $\text{Pb}(\text{NO}_3)_2$ as PT and 0.1 mol l^{-1} NaOH as AT. The pH-static titration curve presented in Fig. 9 indicates three successive breaking points where precipitation of (1) **PbS** ($\text{pK}_{\text{so1}} = 27.5$), (2) **PbSO₄** ($\text{pK}_{\text{so2}} = 8.0$) and (3) **PbHPO₄** ($\text{pK}_{\text{so3}} = 11.36$) is terminated. The solubility product for **PbCO₃** ($\text{pK}_{\text{so4}} = 13.14$) has not been crossed.

3.1.3. An effect of buffer capacity

As has been stated above, the buffer with moderate buffer capacity is needed in pH-static titration. It enables to keep moderate ΔpH_j values affected by addition of ΔV_{Pj} ml of PT. In order to specify this statement, we refer first to more general, quantitative considerations.

Let δV be the volume corresponding to an elementary change (resolution) in pH, δpH , indicated by digital pH meter. Applying the notations as in Fig. 10, one can formulate

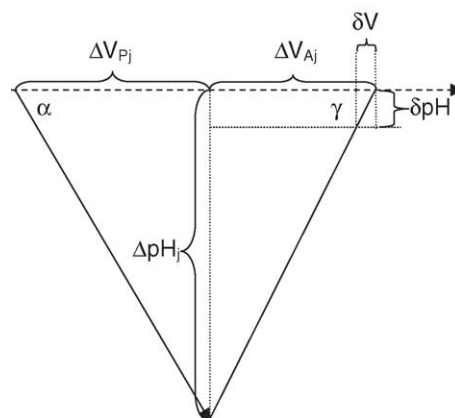


Fig. 10. Presentation of symbols applied in derivation of the formula (46).

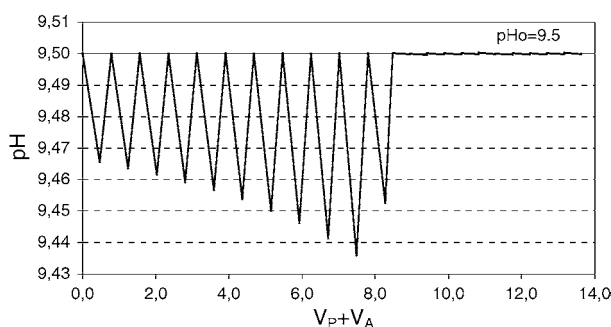


Fig. 11. The pH changes (ΔpH_j) in pH-static titrations for D + AD system specified in Fig. 6 at $pH_0 = 9.50$.

the relationships:

$$tg\alpha = \frac{\Delta V_{A1}}{\Delta V_{P1}} = \frac{\Delta V_{Aj}}{\Delta V_{Pj}} = \frac{V_{Aj}}{V_{Pj}} \quad (43)$$

$$tg\gamma_j = \frac{\Delta pH_j}{\Delta V_{Aj}} = \left(\frac{\delta pH}{\delta V} \right)_j \quad (44)$$

Then we get, by turns,

$$\Delta V_{Aj} = \Delta V_{Pj} \cdot \frac{V_{Aj}}{V_{Pj}} \quad (45)$$

$$\delta V_{ji} = \delta pH_j \cdot \frac{\Delta V_{Pj}}{\Delta pH_j} \cdot tg\alpha_i \quad (46)$$

The pH changes affected by addition of PT and AT into the system presented in Sections 2.1.2.1–2.1.2.3 are plotted in Figs. 11–13.

Referring to Fig. 11, we have $\Delta V_{Aj} = \Delta V_{A1} = 0.466$ ml, $\Delta pH_j = 0.034 \div 0.064$, $tg\alpha_1 = 3.356/5.0 = 0.671$ at $pH_0 = 9.5$. Then at $\delta pH = 0.001$, we get $\delta V_j = 4.9$ – 9.1 μ l. In other words, δV_j μ l of AT makes an elementary pH change, $\delta pH = 0.001$. In this case, it suggests the AT titration with precision better than $(0.0091/0.466) \cdot 100\% = 2\%$. It explains also the necessity to use buffers with moderate buffer capacity.

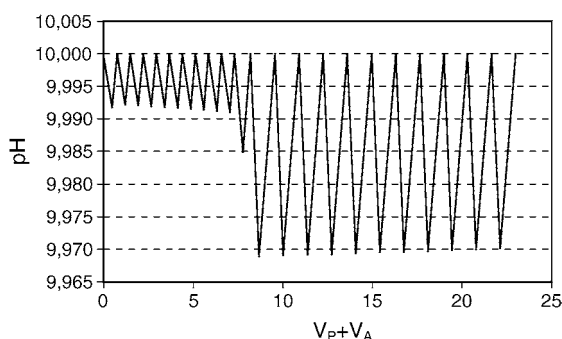


Fig. 12. The pH changes (ΔpH_j) in pH-static titrations for D + AD system specified in Fig. 8 at indicated $pH_0 = 10.00$.

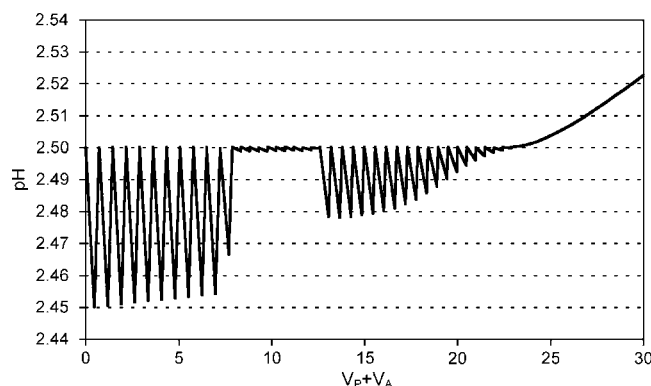


Fig. 13. The pH changes (ΔpH_j) in pH-static titrations for D + AD system specified in part 3.1.2.3 at $pH_0 = 2.5$.

3.2. The Ni method

3.2.1. Acid–base titration

Further example provides a titrimetric analysis of an acid–base system represented by V_0 ml of the a mixture containing weak acids and its salts, denoted by $M_{ki}H_{ni-ki}L^{(i)}$ ($ki=0, \dots, ni$; $i=1, \dots, P$) with molar concentrations C_i mol l⁻¹ and a strong monoprotic acid HB (C_0 mol l⁻¹). After addition of V ml of C mol l⁻¹ KOH, from the balances:

$$\sum_{l=0}^{qi} [H_l L^{(i)}] = \frac{C_i V_0}{V_0 + V};$$

$$[M] = \sum_{l=0}^{qi} ki \cdot \frac{C_{0i} V_0}{V_0 + V}; [B] = \frac{C_0 V_0}{V_0 + V};$$

$$[K] = \frac{CV}{V_0 + V}$$

$$[H] - [OH] + [M] + [K] - [B] = \sum_{i=1}^P \sum_{l=0}^{qi} (ni - l) [H_l L^{(i)}]$$

and applying the identity $ni - ki - \underline{ni} \equiv (qi - \underline{ni}) - (qi + ki - \underline{ni})$, we get the function similar to one quoted by Ni [41]

$$V = \theta_0 \cdot C^* + \sum_{i=1}^P \theta_i \cdot C_i + \theta_{P+1} \quad (47)$$

where:

$$\theta_0 = \frac{V_0}{C + \beta}$$

$$\beta = \frac{h}{f} - K_w \cdot \frac{f}{h}$$

$$C^* = C_0 - \sum_{i=1}^P (qi + ki - ni) \cdot C_i$$

$$\theta_i = V_0 \cdot \frac{qi - \bar{n}i}{C + \beta} \quad (i = 1, \dots, P) \quad (48)$$

$$\theta_{P+1} = -V_0 \cdot \frac{\beta}{C + \beta}$$

$$\bar{n}i = \frac{\sum_{l=1}^{qi} l[H_l^{(i)}]}{\sum_{l=0}^{qi} [H_l L^{(i)}]} = \frac{\sum_{l=1}^{qi} lK_{il}[H]^i}{\sum_{l=1}^{qi} K_{il}[H]^i}$$

$$[H_l L^{(i)}] = K_{il}[H]^l [L^{(i)}], K_w = [H][OH]$$

The mixture of acid–base systems can be ‘homogenised’. It means that an acid–base system consisting the species $H_l L^{(i)}$ ($l = 0, \dots, qi$) of a polyprotic acid $H_{ni} L^{(i)}$ can be considered as a sum of monoprotic acids $H L^{(i,k)}$ ($k = 1, \dots, qi$) with the same concentration (C_i) and dissociation constants expressed by Simms constants g_{ik} [31] involved in the relation

$$qi - \bar{n}i = \sum_{k=1}^{qi} \left(1 + \frac{h}{g_{ik}}\right)^{-1} \quad (49)$$

specified in Eq. (48). It means that all terms on the right side of Eq. (49) are expressed as a function of $pH = -\log h$. Then denoting $\theta_{0j} = \theta_0(pH_j)$, $\theta_{ij} = \theta_i(pH_j)$, $\theta_{P+1,j} = \theta_{P+1}(pH_j)$ for the points (V_j , pH_j), ($j = 1, \dots, N$) of pH metric titration, we get the relation

$$V_j = \theta_0 \cdot C^* + \sum_{i=1}^P \theta_i \cdot C_i + \theta_{P+1} + \varepsilon_j \quad (50)$$

where ε_j is considered as a random error at i th point (V_j , pH_j). When compared with the original approach done in [40], where a mixture of acids with $qi = ni$ has been considered ($ki = 0$), the Eq. (50) refers to a more generalised case. The strong acid (HB) introduced into the system titrated with KOH enables all acid–base species to be determined; it refers particularly to the titration of sulphate determined in multicomponent solution with initial $pH \gg 1.8$ ($pk_2 = 1.8$ for HSO_4^{-1}). The presence of HB enables to involve the case of a titrand where the salts of $H_{ni+k} L^{(i)} B_k$ type (e.g. NH_4Cl) are also considered ($k = 1, \dots, qi - ni$).

The relationship (50) resembles the equation for the second Beer’s law, with nonzero intercept. Assuming that m different pH_j values were chosen ($j = 1, \dots, m$), one can rewrite it in the matrix form

$$V = AC + \varepsilon \quad (51)$$

where $V = [V_1, \dots, V_N]^T$, $C = [C^*, C_1, \dots, C_P, 1]^T$, $\varepsilon = [\varepsilon_1, \dots, \varepsilon_m]^T$ is the vector of random errors and $A = A_{N,p+2} = [a_{ij}]$ is the matrix with N rows and $p+2$ columns involving all internal complexity of acid–base systems. However, in contradistinction to the Beer’s formula, the nature of the complexity involved in a_{ij} terms can be easily explained. The Beer’s formula does not explain the complexity and shape of absorption of UV–vis spectra. The form of Eq. (51) enables

to apply some chemometric procedures based on matrix algebra. Among others, the multivariate calibration methods: classical least squares (CLS), principal component regression (PCR) and partial least squares (PLS) methods were applied for results obtained from titration of synthetic, 3–5 component mixtures of acids titrated with standardised NaOH solution.

3.2.2. Precipitation titration

Halide and thiocyanate ions $X^{(i)}$ are often determined according to potentiometric titration made with use of silver indicator electrode. Referring to the case where V_0 ml of the solution containing P different kinds of anions $X^{(i)}$ with concentrations $C_i \text{ mol l}^{-1}$ ($i = 1, \dots, P$) is titrated with V ml of $C \text{ mol l}^{-1}$ $AgNO_3$, then assuming formation of complexes $AgX_j^{(i)}$ ($j = 1, \dots, ni$) and neglecting the hydroxo-complexes $Ag(OH)_k^{+1-k}$ ($i = 1, 2, 3$), $[Ag] \gg \sum_{k=1}^3 [Ag(OH)_k]$, we get the concentration balances:

$$\frac{CV}{V_0 + V} = [Ag] + \sum_{i=1}^P \sum_{j=1}^{ni} [AgX_j^{(i)}],$$

$$\frac{C_i V_0}{V_0 + V} = [X^{(i)}] + \sum_{j=1}^{ni} j \cdot [AgX_j^{(i)}]$$

and then, by turns:

$$y = \frac{V_0}{V_0 + V} \cdot \sum_{i=1}^P C_i - \frac{CV}{V_0 + V}$$

$$V = \sum_{i=0}^P \kappa_i \cdot C_i \quad (52)$$

where $C_0 \equiv 1$, $\kappa_i = V_0/(C+y)$ for $i = 1, \dots, P$, $\kappa_0 = -\kappa_i \cdot y$, $y = \sum_{i=1}^P [X^{(i)}] - [Ag] + \sum_{i=1}^P \sum_{j=1}^{ni} (j-1) K_{ij} [Ag][X^{(i)}]^j$, $K_{ij} = [AgX_j^{(i)}][Ag]^{-1}[X^{(i)}]^{-j}$. The potential of silver indicator electrode, $E = A + S \log [Ag]$ is related to concentration of $[X^{(i)}] = K_{soi}/[Ag]$ of the species $X^{(i)}$ precipitated at defined stage of the titration ($K_{soi} = [Ag][X^{(i)}]$ is the solubility product of the precipitate $AgX^{(i)}$). As previously, the modified linear form (52) is obtained [41].

4. Final comments

The paper provides extended and modified versions of some linearisation approaches known hitherto in titrimetric methods of analysis.

First, the explicit derivation of the modified formulae (represented by Eqs. (26), (29) and (30)) is presented; it has not been done in the earlier author’s paper [16]. The approximation done on the basis of Eq. (20) is extensively discussed, see Tables 1 and 2. It has been proven that application of the

modified Gran I (not Gran II) method is a valuable and accurate tool in all potentiometric titrations where E is registered. Some sources of serious errors resulting from other, earlier approaches (refs. [5,12]) are also indicated. A quadratic form of some regression Eq. (34) involved with Gran I method is also recalled [19]. A close relation of the Gran methods with extrapolative standard addition procedures is also indicated, see e.g. Fig. 4.

In further parts of the paper, a brief derivation of formulae (39), (40) is done; it replaces an awkward approach done in ref. [29]. Some further suggestions, based on application of Simms constants (that enable to consider a q-protic acid as a sum of q monoprotic acids) are also done.

The pH-static titration as a particular case of indicative methods has been extended by us on other areas of titrimetric analyses, related to electrolytic systems of any degree of complexity. In this paper, two titrimetric methods of cyanide analysis, one based on the modified Liebig–Deniges method and one with nickel salt applied, were proposed. The latter method is an alternative to the spectrophotometric method proposed lately [49]. What is more, the pH-static titration has been extended on multicomponent analyses, represented by the system described in Section 3.1.2.3 and illustrated by Fig. 9; nb. earlier papers concerned only one-component analyses. A role of a buffer capacity in conjunction with complexing properties of buffer components is also considered (Section 3.1.3) and exemplified in Figs. 11–13.

A more generalised approach has been also applied to the Ni method suggested recently. The method applied primarily to the systems of polyprotic acids only has been extended on the systems with salts involved. Moreover, application of Simms constants suggested enables to ‘homogenise’ the description (formulation) of acid–base systems considered.

The Gran methods, implying a linearisation of the titration curve and its graphical or numerical evaluation, are still popular among chemists–analysts. Nowadays, the Gran methods are widely used in the studies of hydrolysis, dissociation and complex formation reactions [50,51]. The software involving the Gran methods and instruments (automatic titrators), with build-in program for determination of the equivalence point, are available commercially [52]. Moreover, further modifications done there, also in the last years, proved its vivacity. The actuality of the Gran method is also expressed by the number of more than 700 references found in Internet under the conjunction of terms: Gran methods and titration.

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