Numerical analysis of the Gran methods
A comparative study

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ABSTRACT

The paper concerns mainly the modified Gran methods, considered as extrapolative standard addition methods. Particularly, the approximation:

$$\ln(1 + x_1) - \ln(1 - x_2) \cong \frac{1}{1/x_1 + 1/\xi} + \frac{1}{1/x_2 - 1/\xi}$$

where $\xi \cong 2$, is applied for the needs of the modified Gran I methods, in accurate and simplified versions, denoted as MG(I)A and MG(I)S methods. These methods are compared with Gran II methods, in original (G(II)) and modified accurate (MG(II)A) versions. All the methods were tested with use of results obtained from simulated potentiometric titrations. The effects involved with a pre-assumed slope ϑ^*-value for a redox indicator electrode and in errors in potential (E) and volume (V) readouts on the error in equivalence volume (V_{eq}) value thus determined is considered. It is recognized that MG(I)A and MG(II)A appear to be the best methods applicable for V_{eq} determination among ones considered hitherto. Moreover, the MG(I)S method is the best choice for determination of the true slope ϑ-value for the redox indicator electrode.

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1. Introduction

Any titration aims to estimate the equivalence volume V_{eq}, i.e. the volume of titrant (T) containing the number of mmoles of a reagent equivalent (eq) to the number of mmoles of analyte contained in the titrand (solution titrated, D). Accuracy and precision of the results for V_{eq}, obtained from potentiometric titration, depends on: (a) the composition and physicochemical nature of D + T system; (b) the kinetics of reactions occurred in this system; (c) the time elapsed between addition of successive portions of T; (d) the divergence $|\vartheta - \vartheta_0|$ between true ϑ and Nernstian ϑ_0 (=RT/F ln 10 = 59.1 mV at 298 K) slopes or the

divergence $|\vartheta - \vartheta^*|$ between true and pre-assumed (ϑ^*) slopes for the indicator electrode; (e) the precision of volume V and potential E (or pH) readouts during the titration; (f) the model applied for V_{eq} determination, and (g) the set of points $\{(V_j, E_j) \mid j = 1, \ldots, N\}$ taken for V_{eq} determination.

The mathematical models introduced in the original Gran methods, particularly Gran I (G(I)) method [1], do not provide accurate results for V_{eq}; the errors involved in G(I) may exceed tens percents, as indicated in [2]. Also the original Gran II (G(II)) [3] method may not provide accurate results in the titrations where voltage (emf, E) is measured as the function of volume V of T added into D. The matter lies in the divergence (ranging

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Abbreviations: a, parameter in Eq. (15); C, concentration of reagent in T; C_0, concentration of analyte in D; D, titrand; E, voltage; G(I) and G(II), original Gran I and Gran II methods; MG(I)S and MG(I)A, modified Gran I methods in simplified and accurate versions, resp.; MG(II)A, modified form of G(II) method; T, titrant; ϑ, ϑ^* ϑ_0, true, pre-assumed and Nernstian slopes, resp.; V, volume of T added; V_0, volume of D; V_{eq}, equivalence volume; V_{eq0} (=10 mL), theoretical V_{eq} value; z, see Eq. (44).

several percents [4]) between true and Nernstian slopes of the indicator electrode and in some difficulties encountered in calibration of this electrode. Namely, concentrations of ions in the standard samples prepared for calibration purposes, are known beforehand whereas activities of the ions are measured.

The G(I) method offers an important idea, however. It is the possibility to perform the potentiometric titrations without prior knowledge of ϑ – provided that ϑ is constant within defined V-range covered in the Gran methods, where the validity of assumption $\vartheta = \vartheta(V) = \text{const}$ is increased – in contradistinction to the methods based on the inflection point location; a dramatic change of the analyte concentration occurs in the vicinity of this point.

Such advantages of G(I) method were exploited in the modified Gran I methods [2,4,5], hereafter referred to as simplified (MG(I)S) and accurate (MG(I)A) methods. The difference between simplified (S) and accurate (A) versions of the Gran I methods is explained in Section 3.

The present paper provides a comparative study of MG(I)S and MG(I)A methods with G(II) method and its accurate version (MG(II)A). This study needs some objectiveness, not affected by non-controllable effects encountered in real titrations that can dim the picture needed for right interpretation. Moreover, the fundamental assumption concerning quasi-static course of potentiometric titration is illusive (highly doubtful) in many instances. One can indicate numerous papers where the automatic titrations designed for G(I) or G(II) methods were performed within 1–5 min, although it is well known that the potentiometric titration does not tolerate such haste. If the titration is performed rapidly, the electrode system does not follow the changes occurred in the bulk solution and its indications are delayed. This way, under comparable conditions of analysis imposed and maintained, one can obtain (at the very most) reproducible, but not accurate results.

The objectivity and usefulness of results obtained from simulated titration for practical purposes is based on the general principles:

1. Firmly established theoretical basis for resolution of complex electrolytic systems.
2. Useful computer programs.
3. Reliability of physicochemical data (standard potentials, equilibrium constants of complexes, etc.) values.

- Ad.1: The first requirement is ensured by the generalised approach to electrolytic systems (GATES) [6], with the generalised electron balance (GEB) [7–9] concept involved. The GATES is adaptable for resolution of thermodynamic (equilibrium and metastable) systems of any degree of complexity; none simplifying assumptions are needed, see e.g. [10]. Application of GATES provides the reference levels for real analytical systems, where some effects involved with kinetics and transportation (diffusion) phenomena occurred at the electrodes. The GATES makes possible to exhibit some important details, of qualitative and quantitative nature, invisible in real experiment, e.g. speciation.
- Ad.2: The starting values for (V, E)-pairs were obtained on the basis of calculations made with use of MATLAB itera-

tive computer program applied to the set of charge, electron and concentration balances and interrelations resulting from expressions for the corresponding equilibrium constants taken from [11]. These data were 'corrupted', to some degree assumed, with use of a generator of random numbers applied for V and E values. The points $\{(V_i, E_i) \mid i = 1, \ldots, N\}$ thus obtained were taken for calculations.
- Ad.3: The third requirement is fulfilled, among others, for 1° manganometric and 2° cerometric titrations of ferrous ions, where equilibria are established rapidly in the bulk solution. This way, we provide an approach to a more general problem involved with optimisation *a priori* in redox systems, realised according to GATES principle.

2. General formulation of the systems

Let us introduce the expression for the fraction titrated [12]:

$$\phi = \frac{CV}{C_0 V_0} \tag{1}$$

From (1) and relations (9A) and (10A) (see Appendix B), we have

$$\phi = \frac{V}{V_{eq}} \tag{2}$$

for Fe(II)–Ce(IV) system, and

$$5\phi = \frac{V}{V_{eq}} \tag{3}$$

for Fe(II)–KMnO$_4$ system.

In further parts of the paper we assume: $V_0 = 100$ mL, $C_0 = 0.01$ mol/L and $C = 0.1$ mol/L for Fe(II)–Ce(IV) system and $V_0 = 100$ mL, $C_0 = 0.01$ mol/L and $C = 0.02$ mol/L for Fe(II)–KMnO$_4$ system. In both instances $V_{eq} = V_{eq0} = 10.000$ mL.

Inserting (1) into (6A) and (8A) (Appendices A and B), then applying the simplifications done on the basis of Fig. 1a and b, for $\phi < \phi_{eq}$ we have

$$[Fe^{2+}] + [FeSO_4] = C_0 V_0 \frac{1 - \phi}{V_0 + V} \tag{4}$$

for Fe(II)–Ce(IV) system, or

$$[Fe^{2+}] + [FeSO_4] = C_0 V_0 \frac{1 - 5\phi}{V_0 + V} \tag{5}$$

for Fe(II)–KMnO$_4$ system. The balance (3A) (Appendix A) can be simplified into the form:

$$[Fe^{2+}] + [FeSO_4] + [Fe^{3+}] + [FeSO_4^+] + [Fe(SO_4)_2^-] = \frac{C_0 V_0}{V_0 + V} \tag{6}$$

valid for both systems. The extensive simplification done within $\phi < \phi_{eq}$ testifies in favor of notations (6A) and (8A).

Inserting the expressions for equilibrium constants of the corresponding complexes [11]:

$$[FeSO_4] = 10^{2.3}[Fe^{2+}][SO_4^{2-}], \quad [FeSO_4^+] = 10^{4.18}[Fe^{3+}][SO_4^{2-}],$$

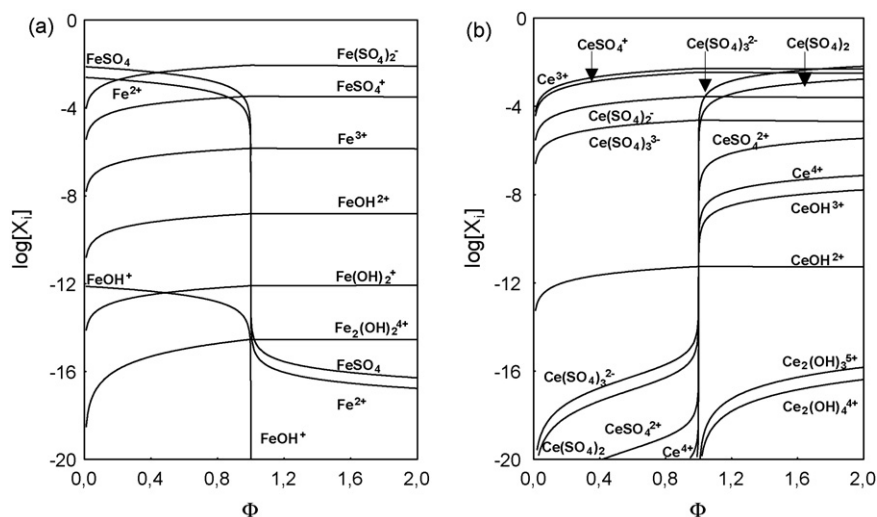$$[Fe(SO_4)_2^-] = 10^{7.4}[Fe^{3+}][SO_4^{2-}]^2 \tag{7}$$

Fig. 1 – Speciation curves for (a) Fe(II,III) and (b) Ce(III,IV) species in Fe(II)–Ce(IV) system where $V_0 = 100$, $C_0 = 0.01$, $C_{a0} = 1.0$, $C = 0.1$, and $C_a = 0.5$; plotted on the basis of equilibrium data quoted in [11].

and applying (2) and (3), from (4) to (6) we have, by turns,

$$b_2[Fe^{2+}] = \left(1 - \frac{V}{V_{eq}}\right)\frac{C_0 V_0}{V_0 + V} \tag{8}$$

$$b_2[Fe^{2+}] + b_3[Fe^{3+}] = \frac{C_0 V_0}{V_0 + V} \tag{9}$$

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{b_2}{b_3}\frac{V/V_{eq}}{1 - V/V_{eq}} \tag{10}$$

where $b_2 = 1 + 10^{2.3}[SO_4^{2-}]$, $b_3 = 1 + 10^{4.8}[SO_4^{2-}] + 10^{7.4}[SO_4^{2-}]^2$. From the relation:

$$E = E_0 + a_0 \ln\frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{11}$$

and (10) we get

$$E = E_0 + a_0\theta + a_0 \ln\frac{V}{V_{eq}} - a_0 \ln\left(1 - \frac{V}{V_{eq}}\right) \tag{12}$$

where

$$a_0 = \frac{RT}{F} = \frac{\vartheta_0}{\ln 10} \tag{13}$$

$$\theta = \ln\frac{b_3}{b_2} \tag{14}$$

and ϑ_0 is the Nernstian slope of indicator electrode; $E_0 = 0.771$ V is the standard redox potential in the related system with normal hydrogen electrode as the reference electrode. Referring to real systems and denoting by ϑ the true slope of an indi-
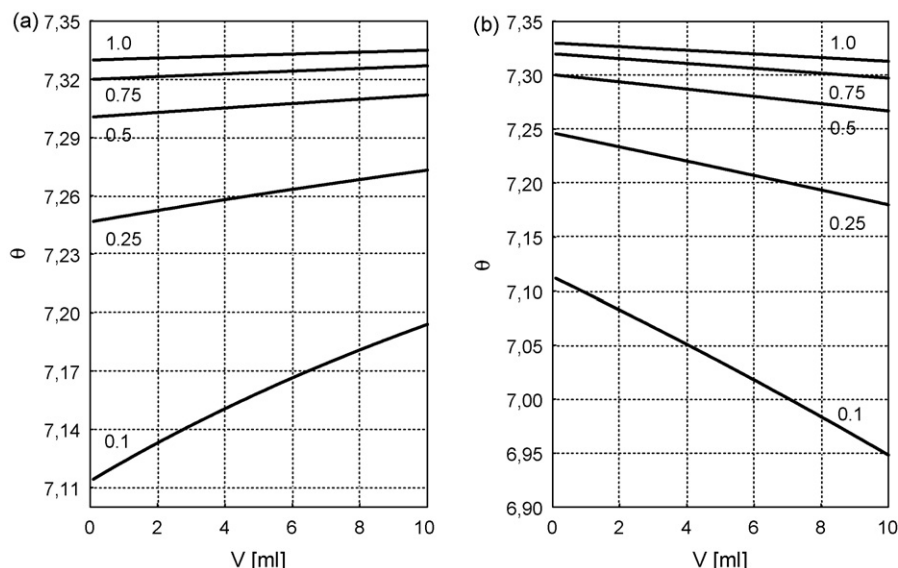

Fig. 2 – The θ vs. V relationship for the system: (a) Fe(II)–Ce(IV) at $C_0 = 0.01$, $C = 0.1$, $C_a = 0.5$; (b) Fe(II)–KMnO$_4$ at $C_0 = 0.01$, $C = 0.02$; the C_{a0} values (mol/L) are indicated at the corresponding curves.

cator electrode in the system with other reference electrode, one can rewrite (12) into the form:

$$E = \omega - a\theta + a\ln\frac{V}{V_{eq}} - a\ln\left(1 - \frac{V}{V_{eq}}\right) \tag{15}$$

where

$$a = \frac{\vartheta}{\ln 10}, \quad \text{i.e.} \quad \vartheta = a\ln 10 \tag{16}$$

and ω are assumed constant. The ω-value involves standard potential of the reference electrode, together with concentration of its internal electrolyte. Eq. (15) is valid, independently on ϕ_{eq} value, i.e. stoichiometry.

From Fig. 2a and b it results that the θ vs. V relationship is quasi-linear, i.e. one can assume that

$$\theta = \alpha + \beta V \tag{17}$$

where α, β are constant; moreover, $\beta > 0$ in Fig. 2a and $\beta < 0$ in Fig. 2b. One should notice that $\beta \ll 1$, especially for higher C_{a0} values, ca. 1 mol/L, where the linearity (17) is more enhanced.

For two successive points: (V_j, E_j), (V_{j+1}, E_{j+1}), referred to potentiometric titration of D with T, from (17) and (15) we get, by turns,

$$\theta_{j+1} - \theta_j = \beta(V_{j+1} - V_j) \tag{18}$$

$$E_{j+1} - E_j = -a\beta(V_{j+1} - V_j) + a\ln\frac{V_{j+1}}{V_j} - a\ln\left(\frac{V_{eq} - V_{j+1}}{V_{eq} - V_j}\right)$$
$$= -a\beta(V_{j+1} - V_j) + a(\ln(1 + x_{1j}) - \ln(1 - x_{2j})) \tag{19}$$

where

$$x_{1j} = \frac{V_{j+1} - V_j}{V_j}, \qquad x_{2j} = \frac{V_{j+1} - V_j}{V_{eq} - V_j} \tag{20}$$

One can apply the approximation [5]:

$$\ln(1 \pm x_{ij}) \cong \pm\frac{x_{ij}}{1 \pm x_{ij}/2} \equiv \pm\left(\frac{1}{x_{ij}} \pm \frac{1}{2}\right)^{-1} \quad (i = 1, 2) \tag{21}$$

for positive (discrete) x_{ij} values, and write

$$\ln(1 + x_{1j}) - \ln(1 - x_{2j}) \cong \left(\frac{1}{x_{1j}} + \frac{1}{2}\right)^{-1} + \left(\frac{1}{x_{2j}} - \frac{1}{2}\right)^{-1} \tag{22a}$$

$$= 4\frac{x_{1j} + x_{2j}}{(2 + x_{1j})(2 - x_{2j})} = \frac{(V_{j+1} - V_j)V_{eq}}{V_j^*(V_{eq} - V_j^*)} \tag{22b}$$

where

$$V_j^* = \frac{V_j + V_{j+1}}{2} \tag{23}$$

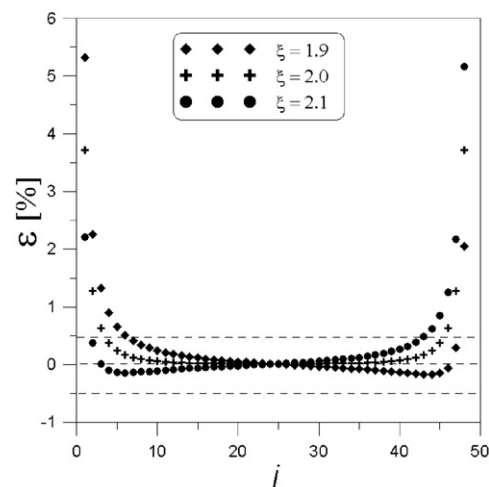The possibility of further improvement in the approximation has also been considered. For this purpose, the number ξ

Fig. 3 – The $\varepsilon = \varepsilon(j, \xi)$ vs. j relationships plotted for different ξ-values on the basis of Eq. (27).

has been inserted for 2 in the approximation (22a), i.e.

$$y(j, \xi) = \left(\frac{1}{x_{1j}} + \frac{1}{\xi}\right)^{-1} + \left(\frac{1}{x_{2j}} - \frac{1}{\xi}\right)^{-1} \tag{24a}$$

$$= \xi^2 \frac{x_{1j} + x_{2j}}{(\xi + x_{1j})(\xi - x_{2j})} \tag{24b}$$

Let us take $V_{j+1} - V_j = \Delta V = 0.2\,\text{mL}$ for successive portions of titrant T, i.e. $V_j = j\,\Delta V$. From (20) we have: $x_{1j} = 1/j$, $x_{2j} = \Delta V/(V_{eq0} - j\,\Delta V) = 0.02/(1 - 0.02j)$ for $V_{eq0} = 10\,\text{mL}$. Setting it into (22a) and (24a), we get

$$y_{exact}(j) = \ln(1 + x_{1j}) - \ln(1 - x_{2j})$$
$$= \ln\left(1 + \frac{1}{j}\right) - \ln\left(1 - \frac{0.02}{1 - 0.02j}\right) \tag{25}$$

$$y_{appr}(j, \xi) = \left(j + \frac{1}{\xi}\right)^{-1} + \left(50 - j - \frac{1}{\xi}\right)^{-1} \tag{26}$$

The errors resulting from the approximation (22a), expressed by the formula:

$$\varepsilon = \varepsilon(j, \xi) = \frac{y_{exact}(j) - y_{appr}(j, \xi)}{y_{exact}(j)} \times 100\% \tag{27}$$

and referred to different ξ and j values, are small and do not exceed $|\varepsilon| = 0.5\%$ for $5 \leq j \leq 45$ at $\xi = 2.0$ (Fig. 3); the approximation for $\xi = 2$ seems to be the best one.

From (15) and (17) one obtains, by turns,

$$\ln\frac{V}{V_{eq} - V} = \alpha - \frac{\omega}{a} + \frac{E}{a} + \beta V$$

$$V \times 10^{-E/\vartheta} = G_2(V_{eq} - V)\exp(\beta V) \tag{28}$$

where $\ln G_2 = \alpha - \omega/a$. Note that $\exp(\pm E/a) \equiv 10^{\pm E/\vartheta}$.

3. The Gran I methods

From (19) and (22b) we get the equation:

$$\frac{E_{j+1} - E_j}{V_{j+1} - V_j} = -a\beta + \frac{a}{V_j^*} + \frac{a}{V_{eq} - V_j^*} + \varepsilon_j \qquad (29)$$

that is the basis for the modified Gran I method in accurate (A) version, MG(I)A; ε_j, random error. Setting $\beta = 0$, i.e. assuming $\theta = $ const (this assumption is more acceptable for higher C_{a0} values), we get

$$\frac{1}{V_j^*} \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = G_1(V_{eq} - V_j^*) + \varepsilon_j \qquad (30)$$

where

$$G_1 = \frac{1}{aV_{eq}} = \frac{\ln 10}{\vartheta V_{eq}} \qquad (31)$$

Eq. (30) is the basis for the modified Gran I method in its simplified version denoted as MG(I)S.

One can also refer to the Gran I method in its original form, G(I). For this purpose, one should apply the approximation:

$$\ln(1 \pm x_{ij}) \cong \pm x_{ij} \qquad (32)$$

not expressed explicitly in [1]; equivalently, $x_{ij} \ll 2$ in (22b). Then we have

$$\ln(1 + x_{1j}) - \ln(1 - x_{2j}) = x_{1j} + x_{2j} = \frac{(V_{j+1} - V_j)V_{eq}}{V_j(V_{eq} - V_j)} \qquad (33)$$

Assuming $\beta = 0$ in (19) and setting (33). We obtain the equation referred to G(I) method:

$$\frac{1}{V_j} \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = G_1(V_{eq} - V_j) + \varepsilon_j \qquad (34)$$

Comparing Eqs. (30) and (34) we see that V_j^* (Eq. (23)) is put for V_j; G_1 in (34) is expressed by Eq. (31). As will be seen below, this substitution dramatically improves the accuracy of results obtained for V_{eq} according to MG(I)S method, in comparison with G(I) method. Moreover, MG(I)S appears to be the accurate method of ϑ determination for redox indicator electrodes.

4. The Gran II methods

Assuming $|\beta|V_{eq} \ll 1$, one can apply the approximation:

$$\exp(\beta V) = 1 + \beta V \qquad (35)$$

Setting (35) in (28) we obtain, at $V = V_j$ ($j = 1, \ldots, N$):

$$V_j \times 10^{-E_j/\vartheta} = B_2 V_j^2 - B_1 V_j + B_0 + \varepsilon_j \qquad (36)$$

where $B_2 = -G_2\beta$, $B_1 = G_2(1 - \beta V_{eq})$, $B_0 = G_2 V_{eq}$. Then we have, by turns,

$$\beta = -V_{eq}\frac{B_2}{B_0}$$
$$\frac{B_1}{B_0} = \frac{1}{V_{eq}} - \beta \qquad (37)$$
$$B_2 V_{eq}^2 - B_1 V_{eq} + B_0 = 0$$

$$V_{eq} = \frac{B_1 - (B_1 - 4B_0 B_2)^{1/2}}{2B_2} \qquad (38)$$

Eqs. (36) and (38) refer to the modified Gran II method in its accurate version denoted as MG(II)A method. Moreover, from (37) one can check whether the assumption (35) is valid for $V < V_{eq}$, $|\beta|V_{eq} = V_{eq}^2 abs(B_2/B_0)$. It refers to the general case, where the shape (also: growth or decrease) of θ vs. V relationship is unknown a priori, compare with Fig. 2a and b.

For $\beta = 0$, at $V = V_j$ one gets the relation:

$$V_j \times 10^{-E_j/\vartheta} = G_2(V_{eq} - V_j) + \varepsilon_j \qquad (39)$$

referred to the original Gran II method, i.e. G(II).

5. The principle of calculations in redox systems

The results $\{(V_{i0}, E_{i0})|i = 1,2, \ldots\}$ were obtained from calculations made according to iterative computer program MATLAB, with use of an algorithm involving all (qualitative and quantitative) physicochemical knowledge about the system in question [6]. The algorithm involved the set of balances and all interrelations between concentrations, expressed by the corresponding equilibrium constants: stability constants of proto-, hydroxo- and sulphate complexes and standard potentials. The results were 'corrupted' with use of a generator of random errors, providing the data $\{(V_i, E_i)|i = 1,2, \ldots\}$, affected by random errors with pre-assumed standard deviations: for volume V of titrant added (σ_V) and for potential E measured (σ_E). The subset of the selected data $\{(V_j, E_j)|j = 1,2, \ldots, N\}$ chosen for calculations covers the j-interval $<j_{inf}, j_{sup}>$, where $j = 1$ refers to j_{inf} and j_{sup} refers to $j = N$. This subset has been applied for calculation of parameters according to least squares method for MG(I)S, G(II), G(II)A methods whereas the parameters: V_{eq}, β and a in Eq. (29), referred to MG(I)A method, can be calculated according to an iterative procedure applied for non-linear equations, or a combination of the least squares method and iterative procedure (see Section 8.2). The value for a thus obtained can be considered as the basis for determination of the true slope (ϑ) value (Eq. (16)).

For example, Eq. (30) can be written as follows:

$$Y_j = P_1 - G_1 V_j^* + \varepsilon_j \qquad (40)$$

where

$$Y_j = \frac{1}{V_j^*} \cdot \frac{V_{j+1} - V_j}{E_{j+1} - E_j} \qquad (41)$$

The external parameters: P_1 (=$G_1 V_{eq}$) and G_1 found according to least squares method are the basis for calculation of V_{eq} value:

$$V_{eq} = \frac{P_1}{G_1} \qquad (42)$$

Then applying (31), we calculate:

$$\vartheta = \frac{\ln 10}{P_1} \qquad (43)$$

As we see, in MG(I)S method we are not forced to apply a pre-determined slope value. This remark concerns also G(I) and MG(I)A methods. In G(I) method, great error in V_{eq} value affects the error in ϑ-value. The V_{eq} and ϑ-values are then correlated and this fact will be raised in Section 10.

6. Generation of the data

The new formulae, related to the modified Gran I method, will also be presented and applied for results of simulated titrations, obtained with use of the iterative computer program MATLAB and the generator of pseudo-random numbers, specified in [13]. This way, one can obtain objective and reproducible data, where some effects (not controllable in experimental titrations) can be introduced and followed consciously.

In further parts of the paper, the calculations are exemplified by Fe(II)–KMnO$_4$ system where V_{j0} mL of $C = 0.02$ mol/L of KMnO$_4$ is added, in portions $\Delta V = V_{j+1} - V_j = 1$ mL, into $V_0 = 100$ mL of the solution containing FeSO$_4$ ($C_0 = 0.01$ mol/L) + H$_2$SO$_4$ ($C_{a0} = 1.0$ mol/L) and the related E_{j0} values are registered in simulated potentiometric titration. The calculations were referred to the V-interval ⟨1, 9⟩ and different values assumed for ϑ^* [mV]: 54.5, 57.0, 59.1 (i.e. Nernstian value at 25 °C) and 61.0. Then the values (V_{j0}, E_{j0}) were corrupted by random errors, δV and δE, characterized by normal distributions with standard deviations for σ_V [mL]: 0, 0.005, 0.010, 0.020 and σ_E [mV]: 0, 0.1, 0.2, 0.5 and 1.0. The corrupted data are considered as the sum of exact values and random errors, i.e. $V_j = V_{j0} + \delta V_j$, $E_j = E_{j0} + \delta E_j$.

The data $\{(V_j, E_j)|j = 1, \ldots, N\}$, $N = 9$, applied in calculations were taken from the j-interval $\langle j_{inf}, j_{sup} \rangle = \langle 1, 9 \rangle$, i.e. the points cover the V-interval <1.0, 9.0> with the step $\Delta V = 1.0$ mL. The error (z) in V_{eq} value, calculated from the formula:

$$z = \left(\frac{1}{N} \sum_{j=1}^{N} \delta_j^2 \right)^{1/2} \quad (\%) \qquad (44)$$

where

$$\delta_j = 100 \times \frac{V_{eqj} - V_{eq0}}{V_{eq0}} \quad (\%) \qquad (45)$$

involves both relative systematic error $\Delta_1 = \overline{V_{eq}}/V_{eq0} - 1$ and relative standard deviation $\Delta_2 = s_{Veq}/V_{eq0}$, where

$$\Delta_2 = \frac{\left((N-1)^{-1} \sum_{j=1}^{N} (V_{eqj} - \overline{V_{eq}})^2 \right)^{1/2}}{V_{eq0}} \qquad (46)$$

and $\overline{V_{eq}} = 1/N \sum_{j=1}^{N} V_{eqj}$; then $z = 100 \times (\Delta_1^2 + (1 - 1/N)\Delta_2^2)^{1/2}$. The 'weights' of accuracy and precision are nearly equal, especially for higher N-values.

7. Generation of random errors

Normal distribution was assumed for random errors in V and E values. The errors were generated with use of random error generator (RND) with uniform distribution in the interval (0, 1). The numbers with normal distribution were obtained according to formula [14]:

$$X = \left(\frac{12}{m} \right)^{1/2} \left(\sum_{i=1}^{m} R_i - \frac{m}{2} \right) \qquad (47)$$

where R_i the values for random variable R with uniform distribution in the interval (0, 1), $\delta V = \sigma_V X$ and $\delta E = \sigma_E X$. The value $m = 30$ has been taken for calculations. The numbers for X (Eq. (47)) have the expected zero value and unitary standard deviation. The histogram in Fig. 4 has been obtained after generating 1000 numbers with expected zero value and standard deviation $\sigma = 0.01$. As we see, the histogram agrees very well with the related Gauss' curve.
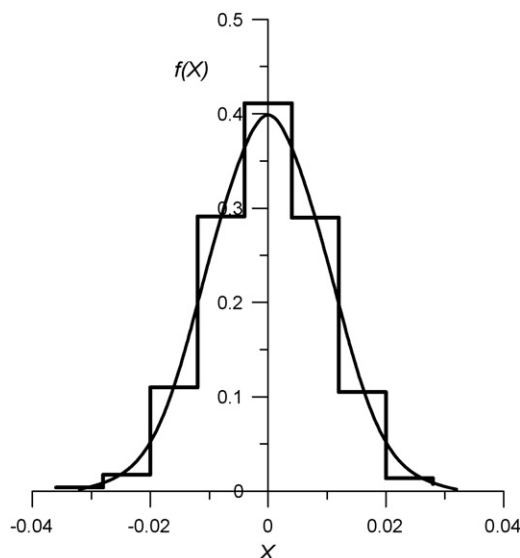

Fig. 4 – Histogram and the related Gauss' curve.

8. Examples

8.1. Simplified modification of Gran I method

The pairs (V_j, E_j), generated at defined σ_V, σ_E and $\vartheta^* = \vartheta_0$ values assumed, were the basis for determination of parameters P_1 and G_1 in Eq. (40), according to the least squares method. On this basis, the V_{eq} and ϑ-values were determined. The errors z (Eq. (44)) related to different $(\sigma_V, \sigma_E, \vartheta^*)$ values pre-assumed in calculations according to MG(I)S method are presented in Fig. 5. As we see, within defined range of the variables assumed, the error is affected significantly by σ_E value and does not depend on the ϑ^*-value taken in calculations made for generation of $\{(V_j, E_j)|j = 1, \ldots, N\}$ data.

The solid line $Y = 0.0378 - 0.00373V^*$ in Fig. 6 has been determined from the data depicted there as points $(V_j^*,$
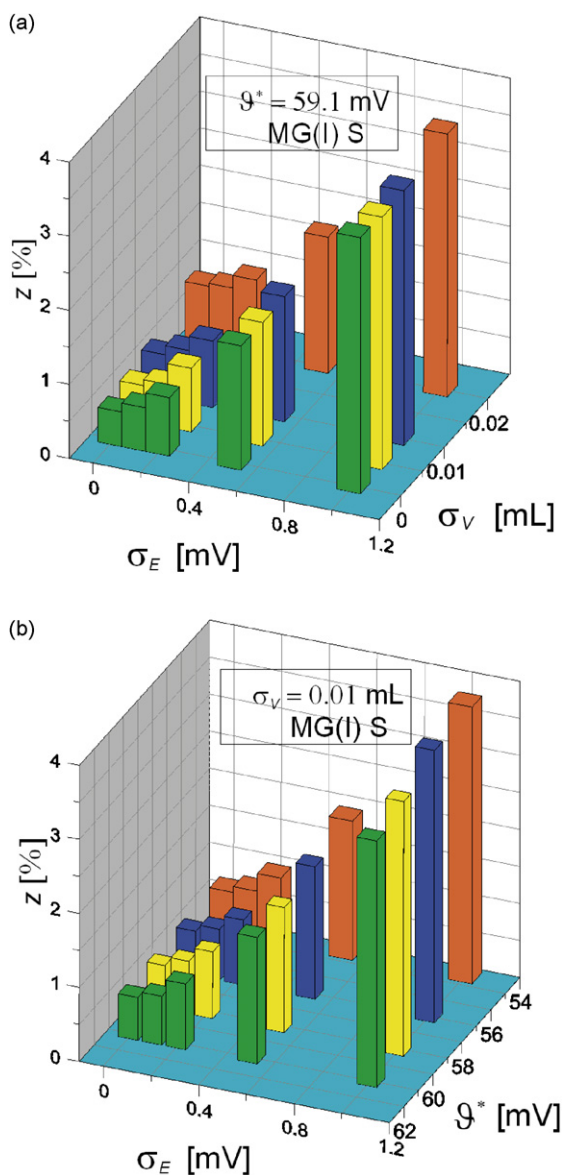

Fig. 6 – The y vs. V^* relationship (Eq. (40)) found at $\vartheta^* = \vartheta_0 = 59.1\,\text{mV}$, $\sigma_V = 0.005\,\text{mL}$, $\sigma_E = 0.2\,\text{mV}$.

Y_j), see Eqs. (40) and (41). Then from Eq. (42) one can calculate $V_{eq} = 0.0378/0.00373 = 10.13\,\text{mL}$ that differs from $V_{eq0} = 10.00\,\text{mL}$ by 1.3%; $a = 1/P_1 = 26.45$ is comparable with theoretical value $59.1/\ln 10 = 25.67$.

8.2. Accurate modification of Gran I method

In this case, the least squares method cannot be applied immediately for resolution of parameters in Eq. (29), referred to MG(I)A method. Instead, one can apply a modified form of the iterative procedure, based on non-gradient minimization method of a golden section search [15]. For this purpose, we introduce the new variables:

$$u_j = \frac{1}{V_j^*} + \frac{1}{V_{eq} - V_j^*} \tag{48}$$

$$y_j = \frac{E_{j+1} - E_j}{V_{j+1} - V_j} \tag{49}$$

The u_j value can be calculated for any pre-assumed V_{eq} value. After rewriting Eq. (29) into the linear form:

$$y_j = d + au_j + \varepsilon_j \tag{50}$$

one can search the parameters d and a according to least squares method:

$$SS = \sum_{j=1}^{N} \varepsilon_j^2 = \sum_{j=1}^{N} (y_j - d - au_j)^2 \tag{51}$$

for any pre-assumed V_{eq} value. Then the searched V_{eq} value is calculated, together with a and d, at the point where the function (51) attains minimal value:

$$SS = SS(V_{eq}) = \min \tag{52}$$

The principle of this method is illustrated in Fig. 7a and b. Fig. 7a explains the successive steps of searching the minimal

Fig. 5 – The z values (Eq. (44)) found for MG(I)S (a) at $\vartheta^* = \vartheta_0 = 59.1$ and different σ_V and σ_E, and (b) at $\sigma_V = 0.01$ and different σ_E and ϑ^* values.
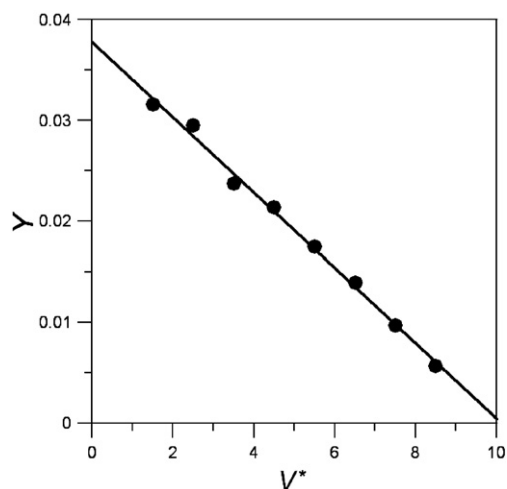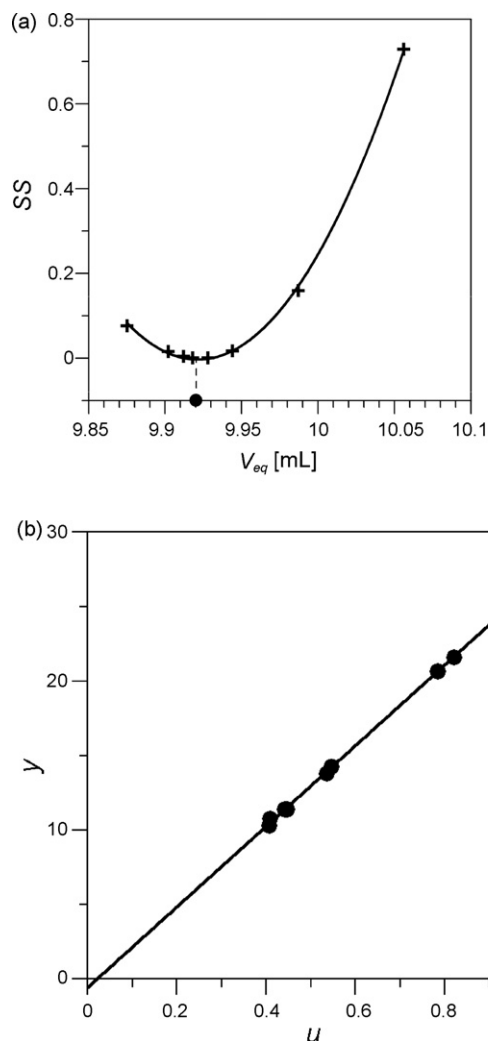
Fig. 7 – The MG(I)A method: (a) searching the V_{eq} value, and (b) the points (u_j, y_j) obtained on the basis of Eq. (50) for $\vartheta^* = \vartheta_0 = 59.1$ mV, $\sigma_V = 0.005$ mL, $\sigma_E = 0.2$ mV.

Fig. 8 – The z values (Eq. (44)) found for MG(I)A: (a) at $\vartheta^* = \vartheta_0 = 59.1$ and different σ_V and σ_E, and (b) at $\sigma_V = 0.01$ and different σ_E and ϑ^* values.

value for SS; min(SS) is attained here at $V_{eq} = 9.92$ mL. At this point, the line $y = -0.60 + 27.15u$ is obtained on the basis of the points depicted in Fig. 7b; hence $a = 27.15$.

The errors z (Eq. (44)) related to different $(\sigma_V, \sigma_E, \vartheta^*)$ values pre-assumed in calculations according to MG(I)A method are presented in Fig. 8. As in Fig. 5, within defined range of the variables assumed, the error is affected significantly by σ_E value and does not depend on the ϑ^*-value taken in calculations made for generation of (V_j, E_j) data. Nonetheless, the errors for z are smaller than ones involved in MG(I)S method. The effect of σ_V on z is more expressed at lower σ_E values. At higher σ_E, the z values are not affected significantly by σ_V value.

9. The effects of σ_V, σ_E and ϑ values in the Gran II methods

The results presented in Fig. 9 were obtained under assumption that the pre-assumed ϑ^*-value [mV], taken from the set: 54.5, 57.0, 59.1, 61.0 (see Section 7), has been applied
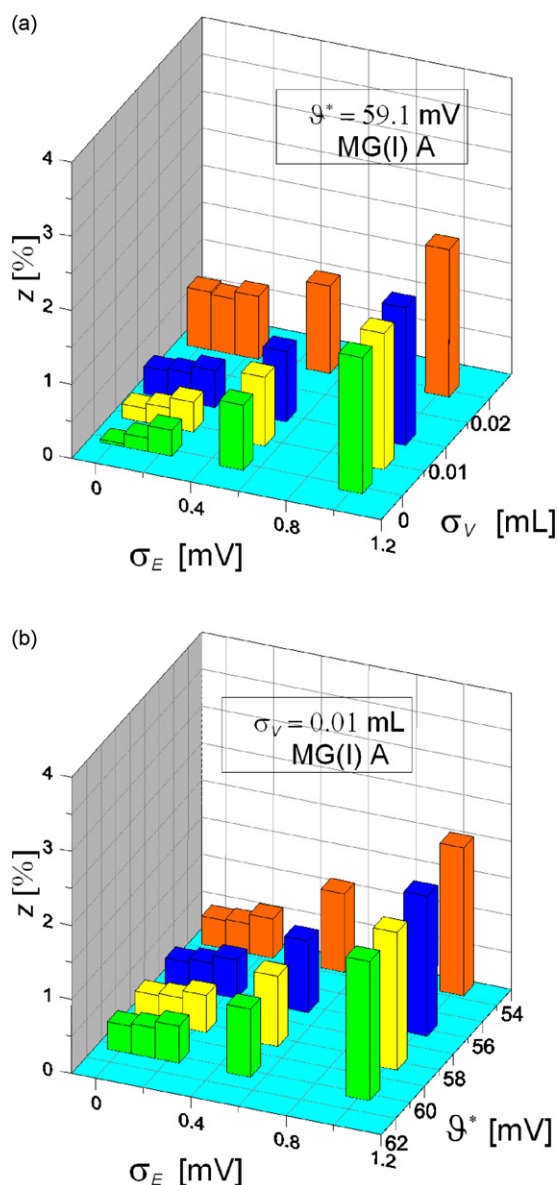
in the related algorithm and V_{eq} is calculated on the basis of equations: (36) or (39), where the value $\vartheta^* = \vartheta_0 = 59.1$ mV is introduced. As results from Fig. 9a related to G(II) method, this substitution leads to high errors of analyses and the discrepancy (z) rises with growth of difference between true ϑ and Nernstian (ϑ_0) values. The error z (Eq. (44)) is small if the electrode is characterized by the Nernstian slope. One can also state that the error in G(II) method is small only in the case where the ϑ-value is known (determined) adequately.

The MG(II)A method (Eqs. (36) and (38)) improves the results dramatically (Fig. 9b). The expected errors are much lower than ones presented in Fig. 9a. The error z is not affected significantly by the true ϑ-value of an indicator electrode.
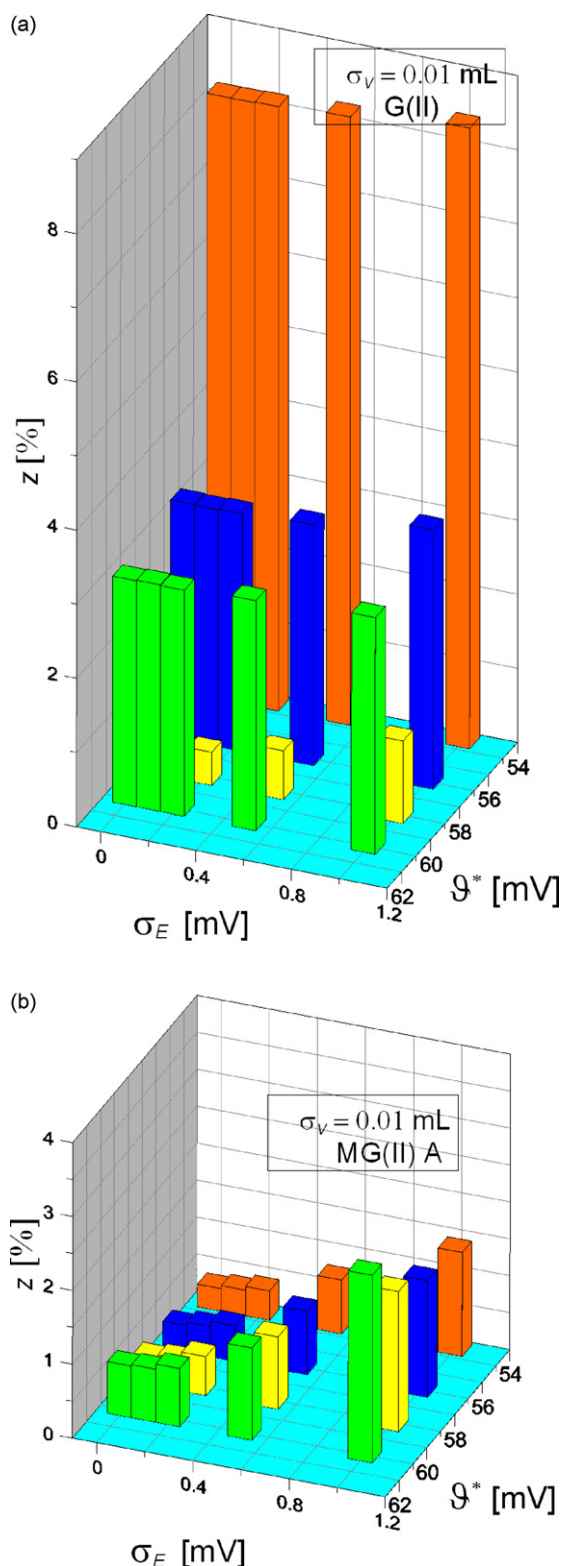
(a)

(b)

Fig. 9 – The z values (see Eq. (44)) found at $\sigma_V = 0.01$ mL and different ϑ^* and σ_E values for (a) G(II) and (b) MG(II)A.

10.   Determination of the true slope ϑ-value

As was stated above, the modified Gran I methods enable also to define the true ϑ-value. The accuracy of ϑ determination will be then considered from the viewpoint of MG(I)S and MG(I)A methods.

As in [16], a correlation between errors in V_{eq} calculation and true slope ϑ-values has been stated. This time, we aimed to apply this correlation for evaluation of the unloaded estimator for ϑ, $\vartheta(0) = \vartheta(\delta = 0)$ assuming that the true value for $V_{eq} = V_{eq0}$ (=10 mL) and then δ_j value (Eq. (45)) are known beforehand. In experimental calibration, it needs an application of standard titrand (D) and titrant (T) solutions.

The calculations presented below were done for two ϑ^*-values: 54.5 and 59.1 mV at $\sigma_V = 0.02$ mL, $\sigma_E = 1.0$ mV (i.e. the σ_E value taken there is relatively high). In each case, 100 values for (δ_j, ϑ_j) pairs (Figs. 10 and 11) were generated.

The MG(I)S method provides accurate results for $\vartheta = \vartheta(0)$ values, calculated at $\delta = 0$: $\vartheta(0) = 59.0$ (against $\vartheta^* = \vartheta_0 = 59.1$) and $\vartheta(0) = 54.8$ (against $\vartheta^* = 54.5$). It was also stated that the ϑ-values
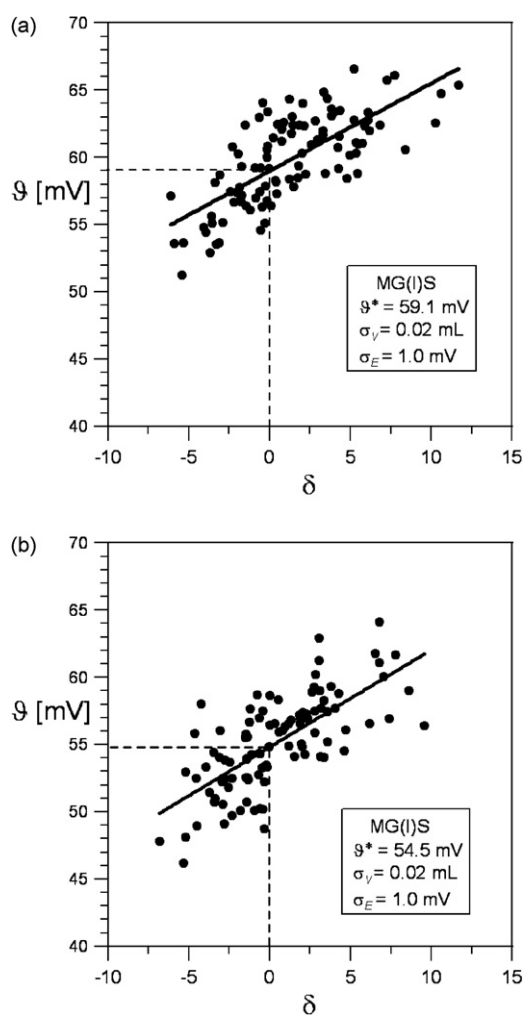

(a)

(b)

Fig. 10 – The correlations found for MG(I)S method at (a) $\vartheta^* = \vartheta_0 = 59.1$ (correlation line: $\vartheta = 59.0 + 0.652\delta$) and (b) $\vartheta^* = 54.5$ (correlation line: $\vartheta = 54.8 + 0.723\delta$).
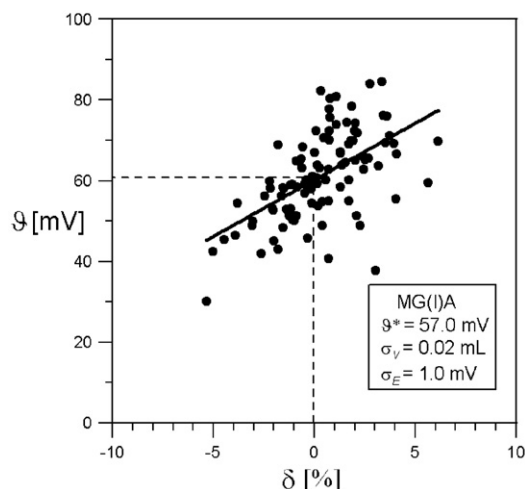
Fig. 11 – The correlation line $\vartheta = 60.2 + 2.8\delta$ found for MG(I)A method at $\vartheta^* = 57.0$.
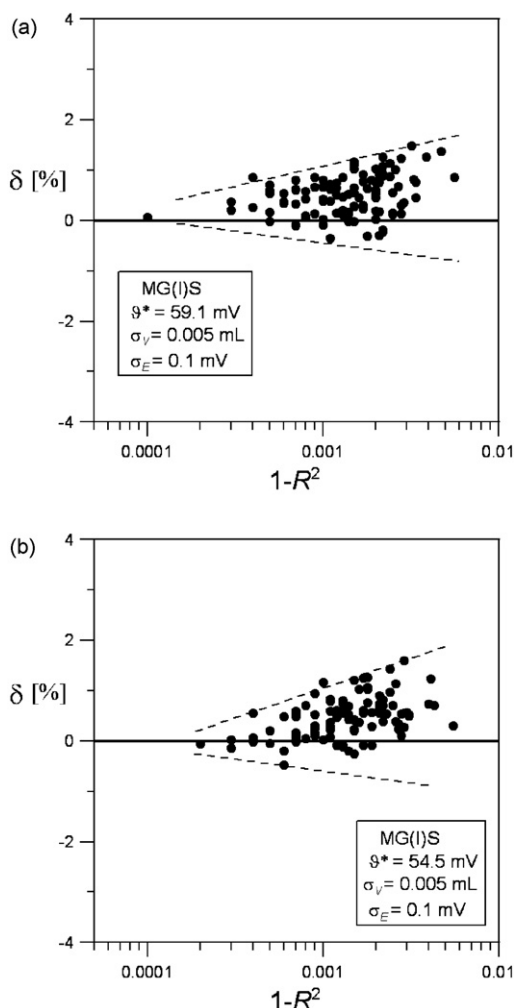

Fig. 12 – The δ vs. $1 - R^2$ relationships referred to MG(I)S method at (a) $\vartheta^* = \vartheta_0 = 59.1$ and (b) $\vartheta^* = 54.5$.

obtained in the more accurate (against V_{eq}) MG(I)A method provides worse results for $\vartheta(0)$ value. For example, the value $\vartheta(0) = 60.2$ obtained in Fig. 11 differs significantly from $\vartheta^* = 57.0$. Such regularities were stated in repeated calculations, also in ones done for other ϑ-values.

As results from Figs. 10 and 11, the dispersion of the points (δ_j, ϑ_j) is great (low R^2 value for correlation coefficient R), although the general tendency provides quite accurate results in the case of MG(I)S method. One can also state that the worse δ value (Eq. (45)) corresponds to lesser R^2 value, see Fig. 12.

11. Conclusions

Except some Michałowski's papers, the Gran methods were not applied hitherto, in mature form, for handling the results obtained from titration in redox systems. The present paper provides an example of such a treatment. The appropriate example concerns the well-known potentiometric titration of ferrous ions with permanganate.

The Gran I method, reactivated in the modified form by Michałowski, was presented in two: simplified and accurate versions, denoted as MG(I)S and MG(I)A. One should remember that in the modified Gran I methods, the approximation expressed by Eq. (22a) has been introduced for $\xi = 2$. Moreover, in MG(I)S, the assumption $\beta = 0$ ($\theta = \text{const}$) has been done.

The Gran II method has been presented in its original form G(II) and in its accurate version, MG(II)A.

Generally, MG(I)A (Fig. 8) provides more accurate results for V_{eq} than MG(I)S (Fig. 5). The σ_V affects insignificantly the z value (Eq. (44)), see Figs. 5 and 8, within the scope assumed for σ_V. The z value is affected strongly by σ_E value. At defined σ_V ($=0.01$ mL in Fig. 5), the z value is independent on the ϑ-value taken for calculation of $\{(V_{j0}, E_{j0})|j = 1, \ldots, N\}$, see Section 8. Again, the z values in MG(I)A are smaller than in MG(I)S, independently on the ϑ-value; $(\sigma_V, \sigma_E) = (0, 0)$ refers to the error-free data, i.e. the value for z is found from the points $\{(V_{j0}, E_{j0})|j = 1, \ldots, N\}$ calculated at defined ϑ^*-value. Relatively small value for z obtained at $(\sigma_V, \sigma_E) = (0, 0)$ testifies very well about the adequacy of the model applied in MG(I)A method.

In the Gran I methods, it is more advantageous to apply greater volume increments, ΔV, of titrant added. The main reasons are: (1°) shortening the period of titration and (2°) the error involved with determination of $\Delta E/\Delta V$ value. Firstly, the time consumed for titration is approximately proportional to the number (N) of titration points applied in calculations. Secondly, from the relation:

$$\frac{E_{j+1} - E_j + \delta E}{V_{j+1} - V_j + \delta V} = y_j \frac{1 + \delta E/(E_{j+1} - E_j)}{1 + \delta V/(V_{j+1} - V_j)} \leq |y_j|$$

$$\times \left(\frac{|\delta E|}{|E_{j+1} - E_j|} + \frac{|\delta V|}{|V_{j+1} - V_j|} \right) \tag{53}$$

it results that higher errors occur when $|V_{j+1} - V_j|$ is comparable with $|\delta V|$ and then $|E_{j+1} - E_j|$ is comparable with $|\delta E|$. For this purpose, greater ΔV value, $\Delta V = 1$ mL, has been taken in

all calculations; it also makes shorter the time designed for titration.

The Gran II method in its original form, denoted as G(II), provides the results for V_{eq} that depend strongly on the ϑ^*-value taken in the related formula (Eq. (39)). Great discrepancies between true and Nernstian slope values provide greater errors in z value, see Fig. 9a. The results are less affected by σ_E value in G(II).

The Gran II method in its accurate version, MG(II)A, based on Eqs. (36) and (38), provides far better results for V_{eq} than ones obtained in G(II) method. What is more, the results obtained there are comparable with ones obtained in MG(I)A method and, practically, do not depend on the true value of the indicator electrode. Summarizing, the MG(II)A and MG(I)A methods are recommended for V_{eq} calculation purposes.

Another matter concerns the calculation of the true (unbiased) slope $\vartheta = \vartheta(0)$ value, needed in G(II) and MG(II)A methods. It can be accomplished with use of standard titrand (D) and titrant (T) solutions and the calculation procedure based on results of titrations and MG(I)S method used for calculation purposes; MG(I)A provides less accurate results for ϑ, although it gives more accurate results for V_{eq} than MG(I)S method. In our further tests it was stated [17] that the accurate ϑ-value is obtainable after four to five titrations made according to MG(I)S method in the system of standardized D + T solutions. It should be remembered that serious difficulties and time-consuming troubles are involved with calibration of indicator electrodes.

This way, the paper provides also the new manner of the electrode calibration. In this case, one can apply some standard solutions that enabled to get correct ϑ-value on the basis of the correlation analysis, analogous to one described in Refs. [16,18–23].

The problem of Gran method application for electrode calibration is not a new one. However, it was considered for glass electrodes only [24,25], with use of the primary form of the formula referred to the G(II) method [26,27]. The present paper provides the approach to calibration, based on MG(I)S method, adaptable for indicator electrodes used in redox titrations.

The physicochemical knowledge on the system considered is well established; the related equilibrium constants involved are known from the related tables. The calculation procedure applied for this purpose is based on the generalised approach to electrolytic systems (GATES) elaborated by Michałowski [6] for equilibrium and metastable electrolytic systems of any degree of complexity, where all physicochemical knowledge can be involved and none simplifying assumptions are needed.

In this paper, the numerical data were obtained according to iterative procedure offered by MATLAB; other computer programs (FORTRAN, PASCAL, DELPHI, C, C++) can also be applied for this purpose. A kind of drift involved in calculation (not in titrimetric) procedure has been realised in the formulae based on the assumption $\theta = \text{const}$ ($\beta = 0$), Eqs. (14) and (17).

The algorithms in the models applied involve all physicochemical knowledge on the systems in question. However, the results for V_{eq} and ϑ do not involve numerical values for the related equilibrium constants (E_{0i}, K_{ij}). This means that the analytical data are not affected by accuracy of E_{0i} and K_{ij} deter-

mination. It is another advantage of the methods proposed in this paper.

Appendix A. Fe(II)–Ce(IV) system

Let us consider V_0 mL of titrand D, containing FeSO$_4$ (C_0) + H$_2$SO$_4$ (C_{a0}), titrated with V mL of Ce(SO$_4$)$_2$ (C) + H$_2$SO$_4$ (C_a) solution as titrant T. The set of the related equations consists of five balances:

- electron balance

$$
\begin{aligned}
&(Z_{Fe} - 2)\,([Fe^{2+}] + [FeOH^+] + [FeSO_4]) + (Z_{Fe} - 3)\,([Fe^{3+}] \\
&\quad + [FeOH^{2+}] + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}] + [FeSO_4^+] \\
&\quad + [Fe(SO_4)_2^-]) + (Z_{Ce} - 3)\,([Ce^{3+}] + [CeOH^{2+}] + [CeSO_4^+] \\
&\quad + [Ce(SO_4)_2^-] + [Ce(SO_4)_3^{3-}]) + (Z_{Ce} - 4)\,([Ce^{4+}] \\
&\quad + [CeOH^{3+}] + 2[Ce_2(OH)_3^{5+}] + 2[Ce_2(OH)_4^{4+}] \\
&\quad + [CeSO_4^{2+}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{2-}]) \\
&\quad - ((Z_{Fe} - 2)C_0V_0 + (Z_{Ce} - 4)CV)/(V_0 + V) = 0
\end{aligned} \tag{1A}
$$

- charge balance

$$
\begin{aligned}
&2[Fe^{2+}] + [FeOH^+] + 3[Fe^{3+}] + 2[FeOH^{2+}] + [Fe(OH)_2^+] \\
&\quad + 4[Fe_2(OH)_2^{4+}] + [FeSO_4^+] - [Fe(SO_4)_2^-] + 3[Ce^{3+}] \\
&\quad + 2[CeOH^{2+}] + [CeSO_4^+] - [Ce(SO_4)_2^-] - 3[Ce(SO_4)_3^{3-}] \\
&\quad + 4[Ce^{4+}] + 3[CeOH^{3+}] + 5[Ce_2(OH)_3^{5+}] + 4[Ce_2(OH)_4^{4+}] \\
&\quad + 2[CeSO_4^{2+}] - 2[Ce(SO_4)_3^{2-}] - [HSO_4^-] - 2[SO_4^{2-}] \\
&\quad + [H^+] - [OH^-] = 0
\end{aligned} \tag{2A}
$$

- concentration balances

$$
\begin{aligned}
&[Fe^{2+}] + [FeOH^+] + [FeSO_4] + [Fe^{3+}] + [FeOH^{2+}] \\
&\quad + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}] + [FeSO_4^+] + [Fe(SO_4)_2^-] \\
&\quad - C_0V_0/(V_0 + V) = 0
\end{aligned} \tag{3A}
$$

$$
\begin{aligned}
&[Ce^{3+}] + [CeOH^{2+}] + [CeSO_4^+] + [Ce(SO_4)_2^-] \\
&\quad + [Ce(SO_4)_3^{3-}] + [Ce^{4+}] + [CeOH^{3+}] + 2[Ce_2(OH)_3^{5+}] \\
&\quad + 2[Ce_2(OH)_4^{4+}] + [CeSO_4^{2+}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{2-}] \\
&\quad - CV/(V_0 + V) = 0
\end{aligned} \tag{4A}
$$

$$
\begin{aligned}
&[FeSO_4] + [FeSO_4^+] + 2[Fe(SO_4)_2^-] + [CeSO_4^+] \\
&\quad + 2[Ce(SO_4)_2^-] + 3[Ce(SO_4)_3^{3-}] + [CeSO_4^{2+}] \\
&\quad + 2[Ce(SO_4)_2] + 3[Ce(SO_4)_3^{2-}] + [HSO_4^-] + [SO_4^{2-}] \\
&\quad - (C_0V_0 + C_{a0}V_0 + 2CV + C_aV)/(V_0 + V) = 0
\end{aligned} \tag{5A}
$$

where $Z_{Fe} = 26$ and $Z_{Ce} = 58$ in (1A) are atomic numbers for Fe and Ce. It will be advisable to combine (1A) with (3A) and (4A). Multiplying the sides of Eqs. (3A) and (4A) by $-(Z_{Fe} - 3)$ and $-(Z_{Ce} - 3)$, respectively, adding the resulting equations to (1A), and cancelling similar terms, one obtains the useful linear combination:

$$
\begin{aligned}
&[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - ([Ce^{+4}] + [CeOH^{+3}] \\
&\quad + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] \\
&\quad + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) \\
&\quad = (C_0V_0 - CV)/(V_0 + V)C_0V_0((1 - \phi)/(V_0 + V))
\end{aligned} \tag{6A}
$$

Appendix B. Fe(II)–KMnO$_4$ system

Let us consider V_0 mL of titrand D, containing FeSO$_4$ (C_0) + H$_2$SO$_4$ (C_{a0}), titrated with V mL of C mol/l KMnO$_4$ solution as titrant T. The set of the related equations consists of five balances. Adding the sides of electron balance:

$$
\begin{aligned}
&(Z_{Fe}-2)([Fe^{2+}] + [FeOH^+] + [FeSO_4]) + (Z_{Fe}-3)([Fe^{3+}] \\
&\quad + [FeOH^{2+}] + [Fe(OH)_2^+] + 2[Fe_2(OH)_2^{4+}] + [FeSO_4^+] \\
&\quad + [Fe(SO_4)_2^-]) + (Z_{Mn} - 2)([Mn^{2+}] + [MnOH^+] + [MnSO_4]) \\
&\quad + (Z_{Mn} - 3)([Mn^{3+}] + [MnOH^{2+}]) + (Z_{Mn} - 6)[MnO_4^{2-}] \\
&\quad + (Z_{Mn} - 7)[MnO_4^-] - ((Z_{Fe} - 2)C_0V_0 \\
&\quad + (Z_{Mn} - 7)CV)/(V_0 + V) = 0
\end{aligned} \tag{7A}
$$

($Z_{Mn} = 25$ for Mn) and concentration balances for Fe (multiplied by $-(Z_{Fe} - 3)$) and Mn (multiplied by $-(Z_{Mn} - 2)$), after cancellations we get

$$
\begin{aligned}
&[Fe^{2+}] + [FeOH^+] + [FeSO_4] - (5[MnO_4^-] + 4[MnO_4^{2-}] + [Mn^{3+}] \\
&\quad + [MnOH^{2+}]) = \frac{C_0V_0 - 5CV}{V_0 + V} = C_0V_0\frac{1 - 5\phi}{V_0 + V}
\end{aligned} \tag{8A}
$$

The choice of linear combinations resulted from the fact that, at $\phi < \phi_{eq}$, the expressions in parentheses on the left sides of Eqs. (6A) and (8A) can be omitted as a whole (see Fig. 1a and b), where

$$
\phi_{eq} = \frac{CV_{eq}}{C_0V_0} = 1 \tag{9A}
$$

for Fe(II)–Ce(IV) system, or

$$
\phi_{eq} = \frac{CV_{eq\,0}}{C_0V_0} = \frac{1}{5} \tag{10A}
$$

for Fe(II)–KMnO$_4$ system.

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