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New methods applicable for calibration of indicator electrodes

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ABSTRACT

The new methods applicable for calibration of indicator electrodes, based on standard addition and standard subtraction methods, are suggested. Some of the methods enable the slope of an indicator electrode and equivalence volume V_{eq} to be determined simultaneously from a single set of potentiometric titration data. Some other methods known hitherto were also taken into account. A new model, based on a standard addition method, applicable also in nonlinear range for the ISE slope (S) is suggested, and its applicability was confirmed experimentally in calibration of calcium ISE.

1. Introduction

The calibration of indicator electrodes is of primary importance in potentiometry [1]. Potentiometric methods applying indicator electrodes offer several advantages over other methods of analysis. They are non-destructive, can easily be automated, and little or no sample preparation is required. This problem was raised recently [2,3], in context with redox indicator electrodes. The theoretical basis for these methods, involved with redox and non-redox systems, were reviewed elsewhere [4,5]. The new proposals for calibration of redox electrodes, based principally on the modified Gran (I and II) methods, were also suggested [2,3,6,7]. Although the original Gran II method (abbr. G(II)) [8] has been employed more extensively than the original Gran I method (abbr. G(I)) [9], the possibilities and advantages offered by the modified Gran I method appeared to be valuable as well [2,3,7].

This paper provides further modifications in the multiple standard addition (MSA) and multiple standard subtraction (MSS) methods, completing earlier approaches, presented in [10] and later [2,3,6,7]. A typical example of MSS is provided by G(I) and G(II) methods. The MSA appears to be a useful, complementary technique towards MSS. In MSA and MSS, the real slope (S) of an indicator electrode and equivalence volume (V_{eq}) are determined simultaneously, from the single titration curve, and resolved with use of the least squares (LS) method [11,12], or an iterative computer program, as presented elsewhere [2–7]. The next modification applies a transformation suggested by Li [13], designed for simultaneous determination of V_{eq} and S; in these modifications, an iterative computer program is needed. In the last part of the paper, a two-parametric function is applied for modeling the parameters for fluoride ISE and calcium ISE, also in the concentration range where the assumption of the S constancy is not valid.

2. Some calibration methods

In MSA, V mL of titrant (T) with C mol/L A (as the standard species) is added into V_0 mL of titrand (D), with C_0 mol/L A (as the analyte) and potential E is registered in the system with indicator electrode reversible towards A. In MSS, the A concentration in D is decreased by addition of C mol/L standard solution of B ($\neq$ A) that reacts with A, e.g. B = MnO_4^- reacts with A = Fe(II) species in acidic (H_2SO_4) media [2,3].

In potentiometry, MSA and MSS are applicable in the cases where a signal (potential, E) registered in the measuring device is selective towards an analyte A, i.e. a change in the signal readout, affected by standard addition, can be ascribed only to A.

2.1. Standard addition methods

The standard addition methods are realized in single (SSA), double (DSA) or multiple (MSA) versions. Some modifications of the

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Nomenclature

A	analyte
B	reagent in MSS
C	concentration (mol/L) of A or B in T
C_0	concentration (mol/L) of A in D
D	titrand
E	potential (mV)
LS	least squares method
MSA	multiple standard addition
MSS	multiple standard subtraction
S	slope
T	titrant
V	volume [mL] of T
V_0	volume [mL] of D
V_{eq}	equivalence volume [mL]

methods applied hitherto for calibration of redox indicator electrodes [2,3] were also suggested.

2.1.1. *Single and double addition*

In SSA, the potential is measured for the sample itself and after addition of V mL of the standard solution. In the simplest case we write

$$E = P + S\ \log\frac{C_0V_0 + CV}{V_0 + V} \tag{1}$$

and for $V = V_1 = 0$, $E_1 = P + S\log C_0$, where $S > 0$ for cationic ISE, $S < 0$ for anionic ISE; P involves all constant parameters referred to the electrode system. Then we get

$$C_0 = C\frac{V/V_0}{(1 + V/V_0)\times 10^{\Delta E/S} - 1} \tag{2}$$

The SSA needs the preliminary knowledge of the S value. This necessity is omitted in DSA (DKAM [14]), where three E-readings are made: for the sample itself, of volume V_0 with unknown concentration C_0 of an analyte A, and after additions of two consecutive portions, ΔV_i $(i = 1, 2)$, of the stock solution of A, with known concentration C. If $\Delta V_1 + \Delta V_2 \ll V_0$, we have [14]

$$\frac{\log(1 + (\Delta C_1 + \Delta C_2)/C_0)}{\log(1 + \Delta C_1/C_0)} - \frac{E_3 - E_1}{E_2 - E_1} = 0 \tag{3}$$

where $\Delta C_i = C\cdot\Delta V_i/V_0$ $(i = 1, 2)$, E_1 refer to the sample tested. Eq. (3) is resolvable for C_0 with use of any iterative computer program [15] or simply, according to a common zeroing procedure. The errors involved with DKAM were considered in [16].

2.1.2. *Multiple addition*

The MSA method is based on addition of N successive portions of the standard solution. As in SSA and DKA methods, the first potential readout, E_1, refers to $V_1 = 0$. The set of experimental points $\{(V_j, E_j)\ |\ j = 1, \ldots, N\}$, where $V_{j+1} - V_j = \Delta V = \text{const.}$ is the basis for calculation of [17]

$$C_0 = \frac{(N-1)C\Delta V}{3V_0}\frac{\sum(2N - 3j + 2)y_j}{\sum(2j - N - 1)y_j} \tag{4}$$

where

$$y_j = (V_0 + (j-1)\Delta V)\times 10^{E_j/S} \tag{5}$$

(see Appendix 1). An increasing of the number (N) of experimental points $\{(V_j, E_j)\ |\ j = 1, \ldots, N\}$ within a given concentration range makes a growth in precision of the fit, in principle. Nevertheless, in (5) it is assumed that S is known beforehand. Such a case occurs also in the formula referred to the G(II) method [8], considered as the standard subtraction method, where the Nernstian slope

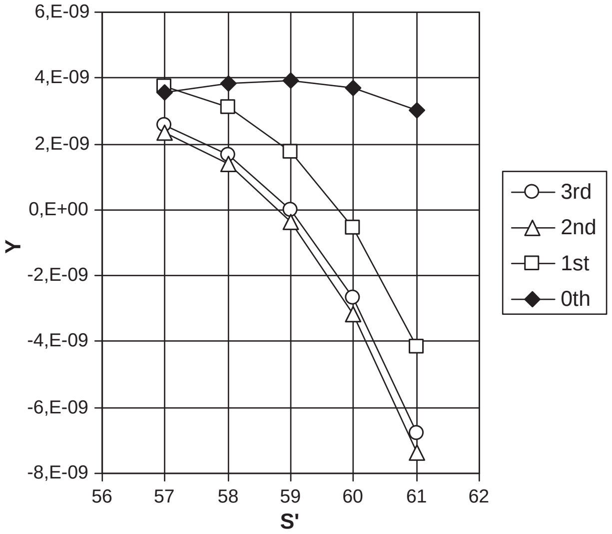

Fig. 1. The plots of simulated functions (12), obtained for different pre-assumed S' values from the set of points $\{(V_j,\ E_j)|j = 1, \ldots, N\}$, where $E_j = 400 + 59\log[V_j/(10 - V_j)]$, $V_j \in \langle 3.0,\ 9.5\rangle$, $\Delta V = 0.25$ and E_j rounded to 3rd, 2nd, 1st, and 0th decimal point, at error-free V_j-values [19].

$$S_0 = \frac{RT}{zF}\ln 10 \tag{6}$$

equal $S_0 = 59.16/z$ mV at 25 °C, was commonly applied; $z = \pm 1, \pm 2, \ldots$ However, such an approach may provide, in some instances, inadmissibly high systematic errors of analyses [3]; those related to G(I) method [9], were indicated in Ref. [7].

2.2. *Simultaneous determination of S and V_{eq}*

2.2.1. *Ivaska method*

The principle of the Ivaska method [18] was intended to be applied to the function

$$y = V \times 10^{-E/S} = \Gamma_2(V_{eq} - V) \quad (\Gamma_2 = \text{constant}) \tag{7}$$

applicable, e.g. for potentiometric titration of Fe(II) species with permanganate in acidic (H_2SO_4) media, made according to G(II) method [3] and valid at $V < V_{eq}$, where V_{eq} is the equivalence volume in the titration. Applying it to the set of N points $\{(V_j, E_j)\ |\ j = 1, \ldots, N\}$, registered at $V_{j+1} - V_j = \Delta V = \text{const}$, the S-value is considered as the real root of the equation $Y = Y(S) = 0$, referred to the nonlinear function

$$Y = Y(S) = y_1 - 2\sum_{j=2}^{N-1}(-1)^j y_j + y_N \tag{8}$$

where

$$y_j = V_j \times 10^{-E_j/S} \tag{9}$$

One should notice that the primary Ivaska method [18] has been applied to the function $y = (V_0 + V) \times 10^{E/S}$, compare with (7).

As results from Fig. 1, the zeroing procedure applied to Eq. (8) could provide a pre-assumed/expected S-value (here: $S = 59$ mV) only under assumption that all experimental points (V_j, E_j) are registered with high accuracy for E_j, ca. ±0.01 mV or better, at error-free V_j values. However, such accuracies are not attainable in real potentiometric titrations; $\Delta E = \pm 0.01$ mV refers to $\Delta pA = \Delta E/S \approx \pm 0.00017$ for monovalent ions. One should be

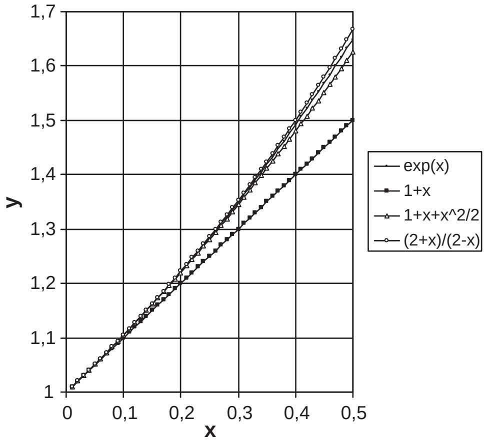

Fig. 2. Comparison of the plots for $y=y_1(x)=e^x$ with its approximations: $y=y_2(x)=1+x$, $y=y_3(x)=1+x+x^2/2$, and $y=y_4(x)=(2+x)/(2-x)$.

noticed that the line (8) referred to 0th approximation assumed for E_j values (mV) does not intersect the line $Y=0$.

2.2.2. Modifications of Li method

The primary form of Li method [13] is involved with application of the identity

$$\frac{1}{S} \equiv \frac{1}{S^\bullet} + \left(\frac{1}{S} - \frac{1}{S^\bullet}\right) = \frac{1}{S^\bullet} + \frac{1}{\eta} \tag{10}$$

where

$$\eta = \frac{S^\bullet S}{S^\bullet - S} \tag{11}$$

where $S^\bullet$ is the pre-assumed (arbitrarily chosen) value for the slope of the indicator electrode. On the basis of experimental data $\{(V_j, E_j) \mid j=1,\ldots,N\}$ and Eqs. (7), (10) and (11), one can suggest two modifications of the Li method (see Appendix 2). The first modification, is based on searching the V_{eq} and η values minimizing the sum of squares

$$SS = \sum_{j=1}^{N-1}\left(\frac{V_{eq}-V_{j+1}}{V_{eq}-V_j}\left(1+\frac{q_j}{\eta}\right) - \psi_j\right)^2 \tag{12}$$

where

$$\psi_j = \frac{V_{j+1}}{V_j}10^{-(E_{j+1}-E_j)/S^\bullet}, \quad q_j = \ln 10(E_{j+1}-E_j) \tag{13}$$

In (12), the approximation

$$e^x \cong 1 + x \tag{14}$$

where $x=q_j/\eta$, has been applied. In the second (more accurate) modification, an approximation [7,10]

$$e^x \cong 1 + x + \frac{x^2}{2} = 1 + x\left(1+\frac{x}{2}\right) \cong 1 + \frac{x}{1-x/2} = \frac{2+x}{2-x} \tag{15}$$

has been suggested, see Fig. 2. In this option, V_{eq} and η values minimize the sum of squares

$$SS = \sum_{j=1}^{N-1}\left(\frac{V_{eq}-V_{j+1}}{V_{eq}-V_j}\frac{2\eta+q_j}{2\eta-q_j} - \psi_j\right)^2 \tag{16}$$

Minimization of the functions: (12) and (16) is realized according to iterative computer programs. After searching the η value, the true S-value is found from the relation

$$S = \frac{S^\bullet \times \eta}{S^\bullet + \eta} \tag{17}$$

obtained from Eq. (11).

The approximation (14) was applied by Li [13]. However, the values

$$q'_j = \ln 10(E_{j+1} - E_1) \tag{18}$$

involving the potential changes referred to the first point (V_1, E_1); this provides a serious limitation in the Li method, where only a few first points $\{(V_j, E_j) \mid j=1,\ldots,N\}$, where $|E_N - E_1|/\eta \ll 1$, can be applied in the calculations. In order to extend the potential range for calculation purposes, the pre-assumed $S^\bullet$ value should be put closely to the true S value. In such a case, η assumes higher values, that enables the inequality $|E_N - E_1|/\eta \ll 1$ to be fulfilled within a wider ΔE range; e.g. at $S^\bullet = 59.16$ mV and $S=55$ mV, from (11) we get $\eta=782$. The change $\Delta E = E_{j+1}-E_j = 10$ mV in E-value gives $\Delta E/\eta = 0.0128$. Then we have

$$10^{0.0128} = e^{\ln 10\times 0.0128} = e^{0.0294} = 1 + 0.0294 + 0.0004 + \cdots \tag{19}$$

Instead of (18), the q_j values, related to successive portions $V_{j+1} - V_j$ of titrant (Eq. (13)) were applied in both modifications. Moreover, referring again to Fig. 2, we see that $y_4(x)$ fits $y_1(x)$ much better than $y_2(x)$, within defined x-range. It must be noticed, however, that the approximation of the function $y_1(x)$ by another approximating function is not required if an iterative computer program be applied.

2.3. The new calibration methods

2.3.1. Method I

This method enables to calculate the slope value at prior knowledge of C_0 and C values

$$S_j = \theta_j \frac{C_0V_0 + CV_j^*}{C - C_0} \tag{20}$$

at each experimental point from the set $\{(V_j, E_j), j=1,\ldots,N\}$, where:

$$\theta_j = \frac{V_0 + V_j^*}{V_0}\frac{E_{j+1}-E_j}{V_{j+1}-V_j}\ln 10 \tag{21}$$

$$V_j^* = \frac{V_j + V_{j+1}}{2} \tag{22}$$

(see Appendix 3). Note that $\theta_j > 0$ for cationic ISE, $\theta_j < 0$ for anionic ISE, and then $S_j \approx -S_0$ for fluoride ISE, $S_j \approx S_0/2$ for calcium ISE. Then we calculate

$$S = \frac{1}{N}\sum_{j=1}^{N} S_j \tag{23}$$

2.3.2. Method II

In this method, V_{eq} and S are calculated from the formulae:

$$V_{eq} = \frac{\sum(V_j^*)^2\sum y_j - \sum V_j{}^*\sum y_j\cdot V_j^*}{\sum V_j^*\sum y_j - N\sum y_jV_j^*} \tag{24}$$

$$S = \ln 10 \times \frac{N\sum(V_j{}^*)^2 - (\sum V_j{}^*)^2}{\sum(V_j^*)^2\sum y_j - \sum V_j^*\sum y_jV_j^*} \tag{25}$$

where $\sum = \sum_{j-1}^{N-1}$, and N is the number of experimental points taken for calculations.

2.3.3. Method III

To describe quantitatively a nonlinear $E = E(\mathrm{pA})$ relationship, the function

$$E = P - \frac{S}{1+10^{p\mathrm{A}-p\mathrm{D}}}p\mathrm{A} \tag{26}$$

is suggested, where P, S and pD are constant parameters, $\mathrm{pA} = -\log[\mathrm{A}]$; $[\mathrm{A}] = (C_0V_0 + CV)/(V_0 + V)$ for addition of V mL of C mol/L A into V_0 mL C_0 mol/L A according to SAM; $\mathrm{A} = \mathrm{F}^-$, Ca^{2+}. Note that the fraction

$$\frac{S}{1+10^{p\mathrm{A}-p\mathrm{D}}} \tag{27}$$

equals S for $p\mathrm{A} \ll p\mathrm{D}$.

The points $\{(p\mathrm{A}_j,\ E_j)\ |\ j = 1,\ldots,N\}$ should involve the nonlinearity region of E vs. pA dependence. On the other side, this set of points should involve a subset covering the linearity range. Otherwise, the S value obtained from calculations may differ significantly from the one expected on the basis of Eq. (5).

In order to omit P on the first stage of the calculation procedure, let us take $(p\mathrm{A}_i, E_i)$ as the reference point. From (26) we have

$$E_i = P - \frac{S}{1+10^{p\mathrm{A}_i-p\mathrm{D}}}p\mathrm{A}_i \tag{26a}$$

and then

$$E - E_i = \frac{S}{1+10^{p\mathrm{A}_i-p\mathrm{D}}}p\mathrm{A}_i - \frac{S}{1+10^{p\mathrm{A}-p\mathrm{D}}}p\mathrm{A} \tag{28}$$

Denoting $(S(i), p\mathrm{D}(i))$ as the values for $(S, p\mathrm{D})$ pair obtained at the reference point $(p\mathrm{A}_i, E_i)$ according to a procedure specified below, one can rewrite (28) into the form

$$E - E_i = \frac{S(i)}{1+10^{p\mathrm{A}_i-p\mathrm{D}(i)}}\mathrm{pA}_i - \frac{S(i)}{1+10^{p\mathrm{A}-p\mathrm{D}(i)}}p\mathrm{A} \tag{28a}$$

At $(p\mathrm{A}, E) = (p\mathrm{A}_j, E_j)$ we get the regression equation

$$E_j - E_i = \frac{S(i)}{1+10^{p\mathrm{A}_i-p\mathrm{D}(i)}}p\mathrm{A}_i - \frac{S(i)}{1+10^{p\mathrm{A}_j-p\mathrm{D}(i)}}p\mathrm{A}_j + \varepsilon_{ij} \tag{28b}$$

and then the sum of squares

$$\begin{aligned}\mathrm{SS}(i) &= \sum_{j=1}^{N}\varepsilon_{ij}{}^2 \\ &= \sum_{j=1}^{N}\left(E_j - E_i - S(i)\left(\frac{p\mathrm{A}_i}{1+10^{p\mathrm{A}_i-p\mathrm{D}(i)}} - \frac{p\mathrm{A}_j}{1+10^{p\mathrm{A}_j-p\mathrm{D}(i)}}\right)\right)^2\end{aligned} \tag{29}$$

is formulated. At any i value ($i = N, N-1, \ldots, 2, 1$), the (S(i), pD(i)) values, where SS(i) = min, are calculated.

Minimization of (29) proceeds according to iteration procedure, realized with use of the computer program. The (reverse) sequence of the points results from the fact that the experimental points referred to lower [A], i.e. higher pX values, appear more "scattered" E-values; the point $(p\mathrm{A}_N, E_N)$ refers here to the lowest pA-value. Moreover, the procedure applied avoids the consequences of a choice of only one reference point, that may appear to be a "non-representative" against other points. The pairs $(S(i), p\mathrm{D}(i))$ of the optimized parameters are then arranged in sequence: $(S(N), p\mathrm{D}(N))$, $(S(N-1), p\mathrm{D}(N-1)), \ldots, (S(1), p\mathrm{D}(1))$. Then, for $n \le N$ first points of this sequence, the values:

$$S = S_n = \frac{1}{n}\sum_{i=N}^{N-n+1} S(i), \quad \mathrm{pD}_n = \frac{1}{n}\sum_{i=N}^{N-n+1} \mathrm{pD}(i) \tag{30}$$

are calculated for different n, and then a convergence of S_n and pD_n values can be considered. The P value can be calculated from the formula

$$P = P_n = \frac{1}{n}\sum_{j=N}^{N-n+1}\left(E_j + \frac{S_n p\mathrm{X}_j}{1+10^{p\mathrm{X}_j-p\mathrm{D}_n}}\right) \tag{31}$$

obtained on the basis of Eq. (26). In experimental part, the $(S, p\mathrm{D}, P) = (S_N, \mathrm{pD}_N, P_N)$ values, obtained at $n = N$, are calculated.

The standard deviations (s) were referred to particular results, not to their mean values; namely

$$s = \sqrt{s^2}, \quad \text{where} \quad s^2 = (n-2)^{-1}\sum_{j=N}^{N-n+1}(\varphi_j - \varphi(p\mathrm{X}_j))^2 \tag{32}$$

where $\varphi = P, S, p\mathrm{D}$.

In this paper, potentiometric titrations were made for calibration of platinum, fluoride and calcium indicator electrodes. Calibrations of fluoride and calcium ISE's were made according to MSA. The MSS was applied for calibration of Pt electrode used in the redox titration. Different calibration methods specified above were tested.

3. Experimental

3.1. Apparatus and reagents

Redox titrations were made in thermostated (25.0 ± 0.1 °C) system, with use of Pt indicator electrode (Radiometer P 101) and calomel (Metrel 40563) reference electrode. Before the use, the Pt electrode was cleaned in ultrasound bath.

The measurements made with use of calcium and fluoride ISE's (Eutech Instruments) were carried out on a Cerko Lab System potentiometer (resolution ±0.03 mV) equipped with a self-constructed measuring cell, a magnetic stirrer, in a temperature-controlled (resistance sensor Pt 1000, ±0.1 °C) closed system, protected against an effect of carbon dioxide.

Preparations of $(\mathrm{NH_4})_2\mathrm{Fe(SO_4)_2}\cdot 6\mathrm{H_2O}$, $\mathrm{KMnO_4}$, $\mathrm{CaCl_2}\cdot 5\mathrm{H_2O}$, NaF, KCl, $\mathrm{H_2SO_4}$, $\mathrm{CH_3COOH}$ and $\mathrm{CH_3COONa}$ (all of p.a. purity grade, >99.5%) were purchased from MERCK. Freshly prepared, doubly distilled water with conductivity approx. 0.18 μS/cm, was used for preparation of stock solutions: NaF (1.0×10^{-3} mol/L) and $\mathrm{CaCl_2}$ (5.0×10^{-3} mol/L) and acetate buffer (pH 5.0), obtained by mixing 5.9 ml of 0.2 mol/L acetic acid and 14.1 mL of 0.2 mol/L sodium acetate.

3.2. Procedures

The Pt electrode was applied for titration of $V_0 = 50$ mL of $C_0 = 0.01$ mol/L $(\mathrm{NH_4})_2\mathrm{Fe(SO_4)_2}\cdot 6\mathrm{H_2O} + \mathrm{H_2SO_4}$ (1.0 mol/L) as D with V mL of $C = 0.02$ mol/L $\mathrm{KMnO_4}$ as T, added in portions $\Delta V = 0.25$ mL. The results obtained in these titrations were applied to: method II (Section 2.3.2), the Ivaska method (Section 2.2.1), the modified forms of the Li method (Section 2.2.2), and to the method based on calculation of the linear correlation coefficient (R) [3] value.

Working solutions used for the fluoride and calcium ISE calibration were prepared in volumetric flasks ($V_f = 25.0$ mL), as indicated in Table 1. After introducing the corresponding stock solutions and buffer or KCl solution, the flasks were filled up to the mark with distilled water. Then $V_0 = 2.000$ mL of D was titrated with V mL of the corresponding T. The (D, T) pairs No. 1, 3, 4 were applied to calibration according to method III (Section 2.3.3). The (D, T) pair No. 2 was applied to the method I (Section 2.3.1).

Table 1
Composition of (D, T) pairs of solutions (indicated by rows 1–4) prepared in $V_f = 25.0$ mL flasks.

No.	Stock solution	C_0 (mol/L) in D	C (mol/L) in T	Acetate buffer (mL)		KCl conc. (mol/L)	
				D	T	D	T
1	NaF	5.0×10^{-6}	5.0×10^{-4}	10	10	0	0
2	$CaCl_2$	5.0×10^{-6}	5.0×10^{-4}	0	0	0.1	0.1

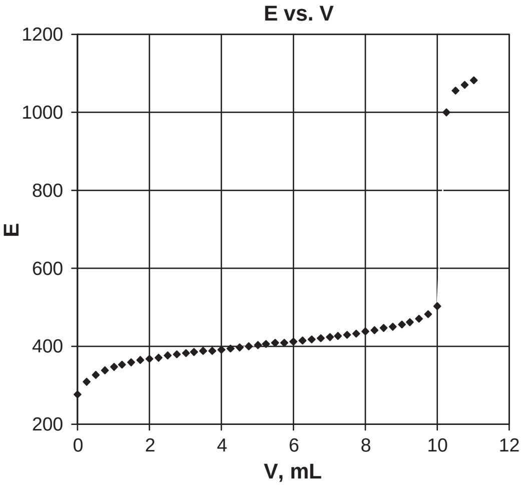

Fig. 3. The experimental points $\{(V_j, E_j) \mid j = 1, \ldots, N\}$ obtained from potentiometric titration of $(NH_4)_2Fe(SO_4)_2$ (0.01000 mol/L) with $KMnO_4$ (0.02000 mol/L) in acidic (H_2SO_4, 1.0 mol/L) medium.

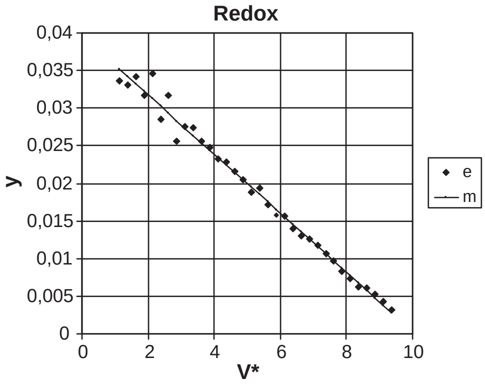

Fig. 4. The points $\{(V_j{}^*, y_j) \mid j = 1, \ldots, N\}$ and the $y = y(V^*)$ line, see Table 2, No. 1; e–experimental points (in converted scale), m–approximating line obtained according to LS method.

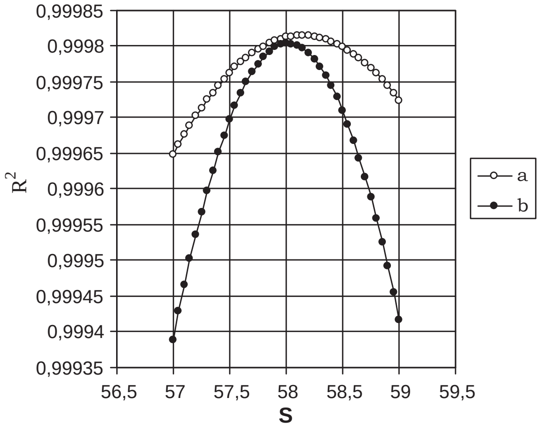

Fig. 5. The R^2 (Eq. (33)) vs. S' values pre-assumed for S in Eq. (11).

4. Results and discussion

Three titrations of Fe(II) with potassium permanganate in acidic (H_2SO_4) media (MSS method) were made under identical *a priori* conditions. The curve of titration no. 1 (Table 2) is presented in Fig. 3. On the stage of data handling, the points $\{(V_j, E_j)\}$ were converted into $\{(V_j^*, y_j)\}$, see Eqs. (22) and (4.4) and Fig. 4. Several first points (V_j^*, y_j) were considered as more scattered, also in repeated titrations (for unknown reasons), and then omitted from calculations. The set of points in No. 1a is the subset of points in No. 1. The titrations No. 2 and 3 were also done for confined set of points, as in No. 1a. The line $y = 0.039391 - 0.003859V^*$ (4.5) in Fig. 4 refers to No. 1 in Table 2. The values for V_{eq} (Eq. (24)) are not far from the expected value 10.000 mL, and the values for S (Eq. (25)) are similar. It should be noted that some preliminary tests aiming to overcome the dissipation effect at the first titration points, were also done.

The Li method, expressed by the formulae (12) and (16), has been applied for the results obtained in the first titration (Table 2, No. 1 and 1a). The results obtained for V_{eq} (Table 3) are nearly identical, but biased with positive error ca. 2%. The S-values obtained according to this method are somewhat greater than those presented in Table 2.

The data in Table 2 were also considered from the viewpoint of the Ivaska method [18]. None of the series of experimental data, when applied to Eq. (8), gave the results required, however, as expected from Fig. 1, i.e. the related curves $Y = Y(S)$ (Eq. (8)) do not intersect the line $Y = 0$; it refers both to the points taken from V-intervals: $\langle 1.0, 9.5\rangle$ and $\langle 3.0, 9.5\rangle$. The remark involved with Fig. 1 was then confirmed.

The results presented in Fig. 5 (Table 2, No. 1, 1a) were also taken for evaluation of S on the basis of the linear correlation coefficient (R) value [3], related to Eq. (7). Setting different values S' for S in Eq. (7), and applying it to the points $\{(V_j, y_j) \mid j = 1, \ldots, N\}$, one can find

Table 2
The results of repeated titrations, obtained on the basis of (24) and (25) for $(NH_4)_2Fe(SO_4)_2 + H_2SO_4/KMnO_4$ system.

No.	N	$\langle V_1, V_N\rangle$	a	b	V_{eq} (mL)	S (mV)
1	34	⟨1.0, 9.5⟩	0.03939	0.003859	10.091	58.18
1a	27	⟨3.0, 9.5⟩	0.04037	0.004024	10.032	58.04
2	27	⟨3.0, 9.5⟩	0.03925	0.003902	10.060	58.66
3	27	⟨3.0, 9.5⟩	0.03918	0.003892	10.066	58.78

N–number of experimental points involved in calculations; $\langle V_1, V_N\rangle$–volume (mL) interval for T considered in calculations; $\Delta V = 0.25$ mL.

Table 3
The results obtained according to the modified Li methods from the points presented in Fig. 3.

No.	S'	Eq. (12)			Eq. (16)		
		V_{eq}	η	S	V_{eq}	η	S
1	60	10.225	8823	59.59	10.217	8753	59.59
1a	65	10.231	717	59.60	10.217	713	59.57

the S value corresponding to the R^2 value closest to 1, where

$$R^2 = \frac{\left(\sum(V_j-\bar{V})(y_j-\bar{y})\right)^2}{\sum(V_j-\bar{V})^2\sum(y_j-\bar{y})^2} \qquad (33)$$

see Eq. (13). The curves in Fig. 5 refer to V-intervals: (a) $\langle 3.0, 9.5\rangle$, (b) $\langle 1.0, 9.5\rangle$, $\Delta V = 0.25$. The S values thus obtained are: 58.0 for (a) and 58.15 for (b). The S-values are close to ones presented in Table 2. The related V_{eq} values found according to LS applied to Eq. (7) are: 10.080 mL for (a) and 10.058 mL for (b).

The formula (20), was applied to MSA realized with use of fluoride ISE, in acetate buffer media (see Table 1, No. 2). In the titration, $V_0 = 2$ mL of $C_0 = 5 \times 10^{-6}$ mol/L NaF + acetate buffer was titrated with V mL of $C = 5 \times 10^{-4}$ mol/L NaF+ acetate buffer (pH 5.0) in D and T. The curve (Fig. 6a) was also tested according to formulae (29)–(31) and the following data were obtained: $P = P_N = -149.5 \pm 1.1$ mV; $S = S_N = 60.59 \pm 0.30$; $p\text{D} > 10$. High value for pD testifies on account of the opinion that the related curve can be considered as the straight line (Fig. 6b). All points $\{(V_j, E_j) \mid j = 1, \ldots, N\}$ in Fig. 6a were taken for calculations realized according to method I. The results obtained from Eq. (20) are presented in Fig. 6c. Mean value $S = 1/59\sum_{i=1}^{59} S_i = 59.75$ mV (Eq. (23)) differs by 0.84 from 60.59.

Within the pH-range assumed, the validity of approximation $[\text{A}] = C_\text{A}$ is required; e.g. at pH ca. 5, in the D + T system tested with use of fluoride ISE, we have $[\text{HF}]/[\text{F}^-] = 10^{3.17-p\text{H}} \ll 1$ [20], and then the approximation $[\text{F}^-] = C_\text{F}$ is valid.

The $S(i)$ values, obtained according to the method I, are strongly affected by small random (local) fluctuations of E-values registered at particular points (V_j, E_j). However, a large number of the points $\{(i, S(i))\ (i = 1, \ldots, N)\}$ provides quite accurate mean S-values, even for larger scattering of the points along the ordinate axis than one presented in Fig. 7. This fact was already confirmed [3] in the tests made with use of generator of normally distributed random numbers [14,21].

Method III was applied for determination of parameters: P, S and pD referred to titration in the system No. 4 in Table 1. The results obtained are presented in Fig. 7. Mean values for P, S and pD were there as follows: $P = P_N = 441.56 \pm 0.62$; $S = S_N = 27.80 \pm 0.15$; $p\text{D} = p\text{D}_\text{N} = 6.378 \pm 0.008$ (see Eqs. (29)–(31). An effect of the starting point (V_i, E_i) applied in Eq. (28) is not distinctly marked. The approximating function (24) fits the (converted) experimental points very well (Fig. 7b).

It should be noticed that $S(i)$, pD(i) and $P(i)$ cover a narrow range of the related values, obtained at different, pre-assumed starting points (V_j, E_j). It testifies on account of the opinion that the method III can be perceived as one providing more stable values of the related parameters in Eq. (26). Higher/lower $S(i)$ value corresponds to lower/higher $p\text{D}(i)$ value, at any point $(p\text{A}_i, E_i)$, see Fig. 7.

The pD value obtained for calcium ISE can be referred to ones provided by manufacturers and found in earlier literature. It is particularly stated that the linearity range covers the pCa-interval of 0–6.3 [22,23] or 0–5.3 [24], although earlier literature stated on the linearity up to $p\text{Ca} = 8$ and curvilinear range up to $p\text{Ca} = 11$, at 0.1 mol/L ionic strength [25].

5. Final comments

In this paper, several calibration methods referred to fluoride and calcium ISE's and redox indicator electrodes are suggested and tested in potentiometric titrations, realized according to multiple standard subtraction (MSS) or multiple standard addition (MSA) methods. The MSS was referred to calibration of platinum electrode, based on the titration of Fe(II) species with permanganate in acidic (H_2SO_4) media [2], whereas the MSA was applied for calibration of the ISE's, both in linear and nonlinear ranges.

Method I is based on calculation of $S(i)$ values at particular points $i = 1, \ldots, N$ (Eq. (20)) of the titration made according to MSA method, referred to the system with fluoride ISE, in its linear range, at equal TISAB concentrations in D and T. Although the S_j values are scattered, the mean S-value (Eq. (23)) is located close to the one obtained according to a method [2] based on calculation of R^2 for linear correlation coefficient (R) value (Eq. (33)). The R^2 value closest to 1 indicates the real S-value.

Method II has been applied to simultaneous determination of S and V_{eq} according to MSS. The results obtained for S and V_{eq} (Table 2) are close to ones obtained on the basis of Fig. 5.

When applying Eq. (26) for nonlinear range of an ISE, the set of points $\{(p\text{A}_j, E_j) \mid j = 1, \ldots, N\}$ should involve the points both from nonlinear and linear pA ranges of the function $E = E(p\text{A})$. If this set refers only to higher pA values, the $|S|$ value in Eq. (26) may appear to be distinctly smaller than $|S_0|$ value calculated from Eq. (6). To cover more wider pA interval, with more dense first points $(p\text{A}_1, E_1)$,

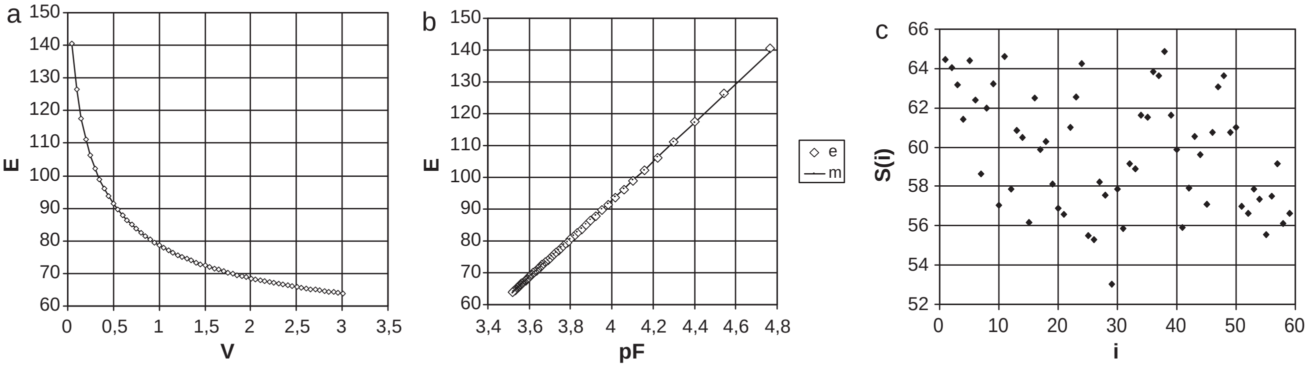

Fig. 6. The (a) E vs. V, (b) E vs. $p\text{F} = -\log[\text{F}^-]$, (c) $S(i)$ vs. i (Eq. (31)) relationships found for D + T system specified in Table 1, No. 2.

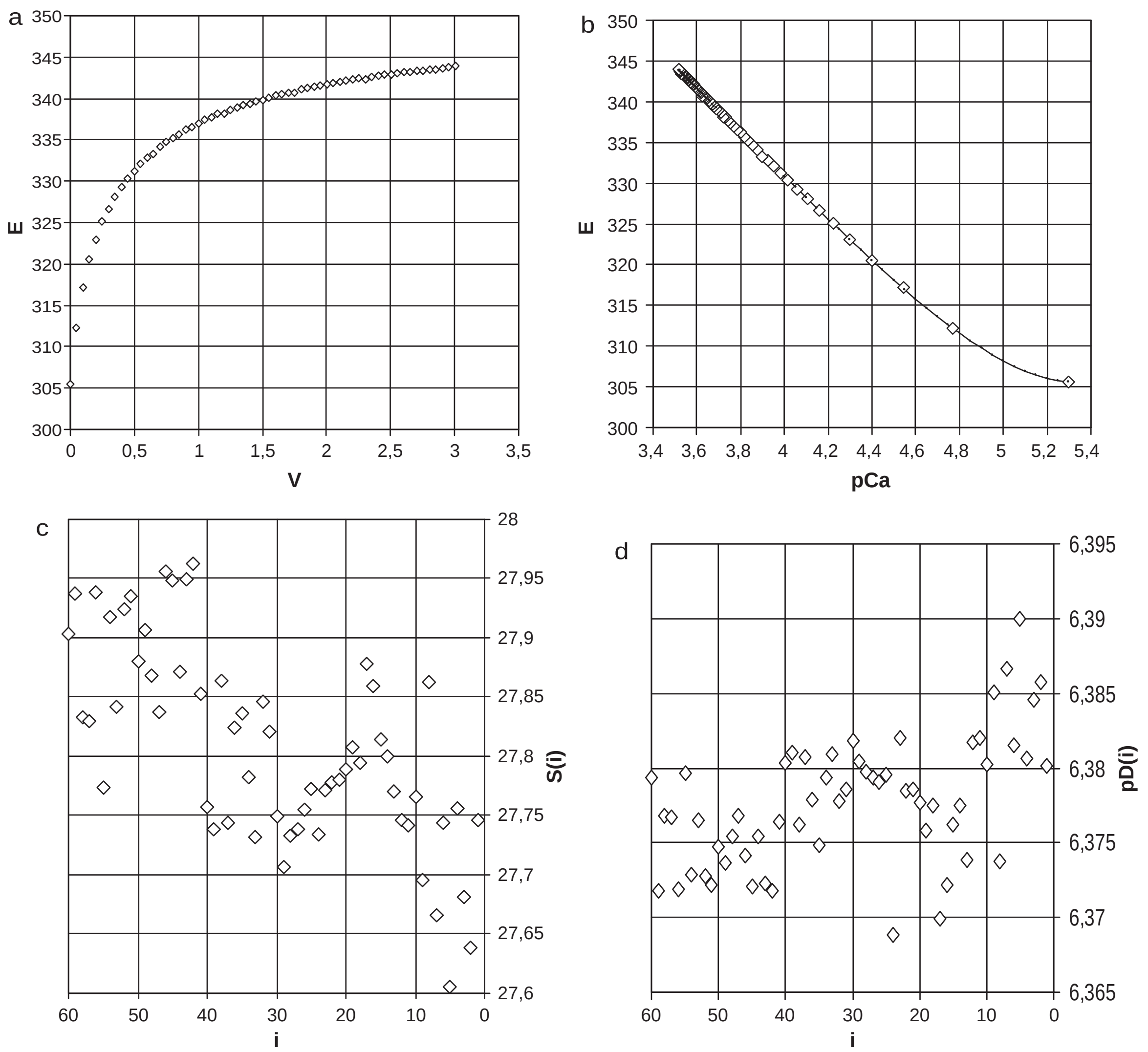

Fig. 7. The plots for calcium ISE in 0.1 mol/L KCl medium. The points (◇): (a) $\{(V(j), E(j))\,|\,j=1,\ldots,N\}$, (b) $\{(\mathrm{pCa}(j), E(j))\,|\,j=1,\ldots,N\}$, (c) $\{(i, R(i))\,|\,i=1,\ldots,N\}$, (d) $\{(i, \mathrm{pD}(i))\,|\,i=1,\ldots,N\}$, plotted for calcium ISE; $V_0=2, C_0=5\times10^{-6}$, $C=5\times10^{-4}$, $N=60$, 25.0 °C, and (b) the related approximating line (Eq. (26)) plotted at mean values for: $P=441.556$, $S=27.798$, pD = 6.378.

(pA_2, E_2), …, two (or three) D + T systems, e.g. with (C_0, C) = (10^{-6}, 10^{-5}), (10^{-6}, 10^{-4}), (10^{-5}, 10^{-3}) should be applied. All the titrations should be made at identical a priori conditions (*ceteris paribus*: temperature, concentration of buffering or basal electrolyte, pH) and the collected results $\{(V_j, E_j)\,|\,j=1,\ldots,N\}$ are taken for calculations. At high pC value, the first points are disturbed rarely or do not refer to low pA values, where the nonlinear course of the curve (26) occurred. One can also apply $C_0=0$. The results are more stable in presence of basal/buffering electrolyte.

It was also stated that the Ivaska method [18] is not adaptable for handling the data obtained according to the MSS method. Two modifications of the original Li method [13] enabled to overcome the shortages inherent in the original version of this method. However, the results for S and V_{eq} are punitive, when compared with ones obtained according to other methods considered in this paper (when referred to S) and expected from preliminary tests (V_{eq}).

Appendix 1. Derivation of Eq. (4)

Eq. (1) can be rewritten into the form

$$\frac{E}{S} + \log(V_0+V) = \frac{P}{S} + \log(C_0V_0 + CV)$$

Applying the identity $x \equiv \log(10^x)$, we have

$$y = (V_0+V)10^{E/S} = (C_0V_0+CV)10^{P/S}$$

$$y_j = (V_0+V_j)10^{E_j/S} = a_0 + a_1 \times V_j + \varepsilon_j \qquad (1.1)$$

where $a_0 = C_0V_0 \times 10^{P/S}$, $a_1 = C \times 10^{P/S}$ are calculated from (1.1) according to LS. Then

$$C_0 = C_X = \frac{C}{V_0}\frac{a_0}{a_1} = \frac{C}{V_0}\,\frac{\sum y_j \sum V_j^2 - \sum y_jV_j \sum V_j}{N\sum y_jV_j - \sum y_j \sum V_j} \qquad (1.2)$$

where $\sum = \sum_{j=1}^{N}$. If $V_{j+1} - V_j = \Delta V$, then $V_j = (j-1)\Delta V$ and from (1.2) we get Eqs. (4) and (5).

Appendix 2. Derivation of equations (12) and (16)

Applying the function (7) for two consecutive points (V_j, E_j) and (V_{j+1}, E_{j+1}), we get

$$\frac{V_{j+1}}{V_j}10^{-(E_{j+1}-E_j)/S} = \frac{V_{\mathrm{eq}} - V_{j+1}}{V_{\mathrm{eq}} - V_j} \qquad (2.1)$$

Then, applying (10) and (11), we have

$$\psi_j = \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} e^{q_j/\eta} \tag{2.2}$$

where ψ_j and q_j are specified in Eq. (13). Applying in (2.2) the approximation (14), where $x = q_j/\eta$, gives the regression equation

$$\psi_j = \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \left(1 + \frac{q_j}{\eta}\right) + \varepsilon_j \tag{2.3}$$

and then Eq. (12). Applying (15) in (2.2), on similar way we get Eq. (16).

Appendix 3. Derivation of Eqs. (20) and (21)

Applying Eq. (1) for two consecutive points, (V_j, E_j) and (V_{j+1}, E_{j+1}), we have, by turns:

$$E_j = P + S \log \frac{C_0V_0 + CV_j}{V_0 + V_j}, \quad E_{j+1} = P + S \log \frac{C_0V_0 + CV_{j+1}}{V_0 + V_{j+1}}$$

$$(E_{j+1} - E_j)\frac{\ln 10}{S} = \ln\left(1 + \frac{C(V_{j+1} - V_j)}{C_0V_0 + CV_j}\right) - \ln\left(1 + \frac{V_{j+1} - V_j}{V_0 + V_j}\right) \tag{3.1}$$

Then using the approximation [6,10]

$$\ln(1 + x) = \frac{x}{1 + (x/2)} \tag{3.2}$$

in (3.1), we have, by turns,

$$(E_{j+1} - E_j)\frac{\ln 10}{S} = \frac{C(V_{j+1} - V_j)/(C_0V_0 + CV_j)}{1 + (1/2)(C(V_{j+1} - V_j)/(C_0V_0 + CV_j))} - \frac{(V_{j+1} - V_j)/(V_0 + V_j)}{1 + (1/2)((V_{j+1} - V_j)/(V_0 + V_j))}$$

$$(E_{j+1} - E_j)\frac{\ln 10}{S} = \frac{C(V_{j+1} - V_j)}{C_0V_0 + CV_j^*} - \frac{V_{j+1} - V_j}{V_0 + V_j^*}$$

$$\frac{V_0 + V_j^*}{V_0}\frac{E_{j+1} - E_j}{V_{j+1} - V_j}\frac{\ln 10}{S} = \frac{C - C_0}{C_0V_0 + CV_j^*} \tag{3.3}$$

Eq. (3.3) gives (20) and (21).

One can also assume that only C is known beforehand. Rewriting (3.3) into the regression equation

$$y_j = a - b\theta_j + \varepsilon_j \tag{3.4}$$

where $y_j = C\theta_jV_j^*$, $S(C - C_0) = a$, $C_0V_0 = b$, one can calculate a and b according to LS method, and then

$$C_0 = \frac{b}{V_0}, \quad S = \frac{a}{C - C_0} = \frac{aV_0}{CV_0 - b} \tag{3.5}$$

Appendix 4. Derivation of equations (24) and (25)

From (2.1) we have, by turns,

$$\ln\frac{V_{j+1}}{V_j} - \ln 10(E_{j+1} - E_j)\frac{1}{S} = \ln\frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \tag{4.1}$$

$$\ln\left(1 + \frac{V_{j+1} - V_j}{V_j}\right) - \ln 10(E_{j+1} - E_j)\frac{1}{S} = \ln\left(1 - \frac{V_{j+1} - V_j}{V_{eq} - V_j}\right) \tag{4.2}$$

Then applying (3.2) in (4.2), we get, by turns

$$\frac{(V_{j+1} - V_j)/V_j}{1 + (1/2)(V_{j+1} - V_j)/V_j} - \ln 10(E_{j+1} - E_j)\frac{1}{S} = -\frac{(V_{j+1} - V_j)/(V_{eq} - V_j)}{1 - (1/2)(V_{j+1} - V_j)/(V_{eq} - V_j)}$$

$$\frac{V_{j+1} - V_j}{V_j^*} + \frac{V_{j+1} - V_j}{V_{eq} - V_j^*} = \ln 10(E_{j+1} - E_j)\frac{1}{S}$$

$$\frac{1}{V_j^*}\frac{V_{j+1} - V_j}{E_{j+1} - E_j} = \frac{\ln 10}{S}\frac{V_{eq} - V_j^*}{V_{eq}} \tag{4.3}$$

where $V_j{}^*$ is expressed by Eq. (22). Denoting

$$y_j = \frac{1}{V_j^*}\frac{V_{j+1} - V_j}{E_{j+1} - E_j}; \quad a = \frac{\ln 10}{S}; \quad b = \frac{\ln 10}{SV_{eq}} \tag{4.4}$$

from (4.3) we get the regression equation:

$$y_j = a - bV_j^* + \varepsilon_j \tag{4.5}$$

where a and b are found according to LS method. Then we calculate: $V_{eq} = a/b$ (Eq. (24)) and S (Eq. (25)).

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