Short communication

A non-linearity criterion applied to the calibration curve method involved with ion-selective electrodes

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ABSTRACT

Some rational functions of the Padé type, $y = y(x; n,m)$, were applied to the calibration curve method (CCM), and compared with a parabolic function. The functions were tested on the results obtained from calibration of ion-selective electrodes: NH_4-ISE, Ca-ISE, and F-ISE. A validity of the functions $y = y(x; 2,1)$, $y = y(x; 1,1)$, and $y = y(x; 2,0)$ (parabolic) was compared. A uniform, integral criterion of nonlinearity of calibration curves is suggested. This uniformity is based on normalization of the approximating functions within the frames of a unit area.

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1. Introduction

In the calibration curve method (CCM), commonly considered as the preliminary step in different methods of chemical analysis, the linear functions are usually applied. The degree of linearity of such lines is expressed by the coefficient of determination R^2 (squared linear correlation coefficient, R) value [1]. When referred to nonlinear relationships, except the nonlinear correlation coefficient [2], there are no valuable manners of such an evaluation; it particularly refers to curvilinear relationships approximated by rational functions of the Padé type [3–5], expressed as the ratio of two polynomial functions $P_n(x)$ and $Q_m(x)$, of nth and mth degree, respectively [6]

$$y = y(x; n, m) = \frac{P_n(x)}{Q_m(x)} \qquad (1)$$

The Padé approximants still attract attention of physicists and mathematicians; an extensive list of the related papers is provided in [7]. It was found that various experimental data can be elegantly modeled with use of rational functions [8–14].

The functions of the Padé type appeared to be a valuable tool for modeling the titration curves referred to complex acid–base systems; see [15,16] and other references cited therein, or to a complex redox system [17]. There were shown that rational functions provide much better approximation than polynomial functions with the same number of parameters involved, expressed in terms of natural or converted variables [18–22]. This method is computationally efficient and manifests a high robustness [6,23]. The Padé approximants are now employed in diverse contexts, indicated in [24].

This paper refers to the normalization of calibration curves applied for determination of some ions: NH_4^+, Ca^{2+} and F^-, with use of ion-selective electrodes (ISEs), within defined ranges of concentrations of particular ions. Nonlinearity of the curves within these ranges is measured according to an integral criterion of nonlinearity, with use of rational and parabolic functions. Applicability of particular functions for modeling purposes has also been taken into account.

2. Some rational functions and normalization principle

Let us refer first to the rational function (A-model)

$$y = \frac{a_0 + a_1 \cdot x + a_2 \cdot x^2}{1 + a_3 \cdot x} \qquad (2)$$

Nomenclature		ISE	Ion-selective electrode
		LSM	Least squares method
CCM	Calibration curve method	T	Titrant
D	Titrand		

i.e., $n=2$ and $m=1$ in Eq. (1). On this basis, one can also consider some simplified forms of Eq. (2), referred to the options: $a_2=0$ (B-model), or $a_3=0$ (C-model). In particular, for the C-model we get the parabolic function

$$y = a_0 + a_1 \cdot x + a_2 \cdot x^2 \tag{3}$$

where $Q_m = Q_0 = 1$. Function (2) and its simplified forms will be applied for CCM purposes.

Let us take the set of experimental data $\{(x_j, y_j) \mid j = 1,...,N\}$, where $x_1 < x_2 < ... < x_N$. Denoting $\Delta x = x_N - x_1$ and $\Delta y = y_N - y_1$, for the monotonic function ($y_j \langle y_{j+1}$ or $y_j \rangle y_{j+1}$ at $j = 1,..., N-1$), we introduce the variables u and v through the relations:

$$x = x_1 + u \cdot \Delta x \text{ and } y = y_1 + v \cdot \Delta y \tag{4}$$

Applying them to function (2), after a lengthy but straightforward algebra, we get the relation for the A-model (see Appendix A)

$$v = v(u) = \frac{\alpha \cdot u + \beta \cdot u^2}{1 + \gamma \cdot u} \tag{5}$$

where

$$\alpha = \frac{(a_1 + 2a_2 \cdot x_1 - a_3 y_1)}{1 + a_3 x_1} \cdot \frac{\Delta x}{\Delta y} \tag{6}$$

$$\beta = \frac{a_2}{1 + a_3 x_1} \cdot \frac{(\Delta x)^2}{\Delta y} \tag{7}$$

$$\gamma = \frac{a_3}{1 + a_3 x_1} \cdot \Delta x \tag{8}$$

Note that $v(0) = 0$. At $(u, v) = (1, 1)$, we have the relation

$$\alpha + \beta = 1 + \gamma, \text{ i.e. } \gamma = \alpha + \beta - 1 \tag{9}$$

The parameters $a_0, ..., a_3$ in Eqs. (6)–(8) are obtained according to the least squares method (LSM) applied to the regression equation

$$y_j = a_0 + a_1 \cdot x_j + a_2 \cdot x_j^2 - a_3 \cdot x_j \cdot y_j + \varepsilon_j \tag{10}$$

derived from Eq. (2). Note that the formulas (6)–(8) do not involve a_0, and the value $s = \Delta y / \Delta x$, inherent in α and β (Eqs. (6) and (7)), is the mean slope of the curve $y = y(x)$ (Eq. (2)) within the $\langle x_1, x_N \rangle$ interval. For the models B ($a_2 = 0$), C ($a_3 = 0$), we have (B) $\beta = 0$, (C) $\gamma = 0$ respectively. In these cases, Eq. (5) simplifies into the relations [25,26]:

$$\text{B} \quad v = \frac{\alpha \cdot u}{1 + \gamma \cdot u} \quad \text{(where } \gamma = \alpha - 1\text{)} \tag{11}$$

$$\text{(C)} \quad v = \alpha \cdot u + \beta \cdot u^2 \quad \text{(where } \beta = 1 - \alpha\text{)} \tag{12}$$

The relations, Eq. (5) with Eq. (9), Eq. (11) and Eq. (12), are in close relevance to the homotopy problem [27,28].

On the basis of formula (5) or its simpler forms, referred to the models, B and C, any set of experimental points $\{(x_j, y_j) \mid j = 1,...,N\}$ in the CCM can be presented within the frames of coordinates (u, v), where $u \in \langle 0, 1 \rangle$ and $v \in \langle 0, 1 \rangle$; see Fig. 1. In all instances, the curve $v = v(u)$ links the points $(0, 0)$ and $(1, 1)$ on the (u, v) plane. A reference is the linear function $y = a_0 + a_1 \cdot x$ ($a_2 = a_3 = 0$ in Eq. (2)), where we get the straight line

$$v = u \tag{13}$$

connecting the points $(0, 0)$ and $(1, 1)$ on the (u, v) plane.

In order to use the formulas $v = v(u)$, applicable for calculations made according to tables with elementary integrals, one can apply some transformations of Eqs. (5), (11) and (12); namely, we have (see Appendix A) for the A-model

$$v = \frac{\alpha \cdot u + \beta \cdot u^2}{1 + \gamma \cdot u} = \frac{\beta}{\gamma} \cdot u + \frac{\alpha \cdot \gamma - \beta}{\gamma^2} - \frac{\alpha \cdot \gamma - \beta}{\gamma^3} \cdot \frac{d}{du} \ln\left(u + \frac{1}{\gamma}\right) \tag{14}$$

Putting $\beta = 0$ in Eq. (14) we have

$$v = \frac{\alpha \cdot u}{1 + \gamma \cdot u} = \frac{\alpha}{\gamma} - \frac{\alpha}{\gamma^2} \cdot \frac{d}{du} \ln\left(u + \frac{1}{\gamma}\right) \tag{15}$$

for the B-model. Eq. (12), referred to the C-model, needs none preparatory transformation.

3. The integral criterion of nonlinearity

The area between the lines, $v = v(u)$ and $v = u$, plotted in normalized coordinates (u, v), is the measure of nonlinearity of any monotonic relationship obtained on the basis of experimental points $(x_j, y_j) \mid j = 1,...,N$; see Fig. 1. This area is expressed as follows:

$$\Omega = \int_0^1 |v - u| \cdot du = \begin{cases} \frac{1}{2} - \int_0^1 v \cdot du & \text{for } u \geq v \\ \int_0^1 v \cdot du - \frac{1}{2} & \text{for } v \geq u \end{cases} \tag{16}$$

Then from Eqs. (12), (14) and (15) we get

$$\theta_A = \int_0^1 v \cdot du = \frac{\beta}{2\gamma} + \frac{(\alpha-1)(\alpha+\beta)}{\gamma^2} \cdot \left(1 - \frac{1}{\gamma} \cdot \ln|\alpha + \beta|\right)$$
$$\text{for the A-model, } \gamma = \alpha + \beta - 1 \tag{17}$$

$$\theta_B = \int_0^1 v \cdot du = \frac{\alpha}{\alpha - 1} - \frac{\alpha}{(\alpha - 1)^2} \cdot \ln|\alpha| \text{ for the B - model} \tag{18}$$

$$\theta_C = \int_0^1 v \cdot du = \frac{\alpha + 2}{6} \text{ for the C-model} \tag{19}$$

respectively. Then for $u \geq v$ we get

$$\Omega_A = \tfrac{1}{2} - \theta_A, \ \Omega_B = \tfrac{1}{2} - \theta_B \text{ and } \Omega_C = \tfrac{1}{2} - \theta_C$$
$$\text{(see Eq. (16)).} \tag{20}$$

4. Experimental part

4.1. Apparatus and reagents

All the calibration experiments were made according to potentiometric titration mode, with use of ion-selective (1°) ammonium (NH$_4$-ISE), (2°) calcium (Ca-ISE), and (3°) fluoride (F-ISE) electrodes, purchased in Eutech Instruments. Titrand D and titrant T were freshly prepared in flasks (25 mL) where stock solutions of the corresponding reagents, NH$_4$Cl, CaCl$_2$, NaF, KCl, CH$_3$COOH, and CH$_3$COONa, each of pa purity, were introduced and filled up to the mark with water. Doubly distilled water, with conductivity approximately 0.18 μS/cm, was used for preparation of the solutions and dilutions. In 2°, concentration of KCl (0.1 mol/L) was the same in D and T. In 3°, D and T contained 10 mL of acetate buffer