Journal of Chemistry and Applied Chemical Engineering

Research Article

A SCITECHNOL JOURNAL

A Uniform Nonlinearity Criterion Resulting from Normalization of Nonlinear Models Applied for Calibration Curve and Standard Addition Methods

Anna Maria Michałowska-Kaczmarczyk[1], Aneta Spórna-Kucab[2] and Tadeusz Michałowski[2]*

Abstract

It is proved that the shape of equations obtained after transformation of real (x, y) into normalised (u, v) variables enables to present polynomial and rational functions in a unified form. In terms of normalised variables, the equations applicable for calibration curves are analogous to ones obtained for standard addition method. It enables to apply a common criterion adaptable for both methods of chemical analysis.

Keywords

Chemical analysis; Standard addition; Calibration; Non-linear models

Abbreviations: CCM: Calibration Curve Method; LSM: Least Squares Method; SAM: Standard Addition Method

Introduction

The instruments used in chemical laboratories require prior calibration before they are used to produce relevant analytical data. Calibration [1-8] is defined as the sequence of operations that enables to establish, under specified conditions, the functional relationship between values of the measurable signal y (output quantity, e.g. absorbance) indicated by a measuring device and the corresponding values of variable x (input quantity or property, e.g. concentration) realised by standards of an analyte X, under defined conditions assumed. If the calibration is performed incorrectly, the results of analyses will be unreliable [1,5].

We consider polynomial and rational, monotonically increasing functions y=y(x), i.e., dy/dx>0 within defined x-range. For the monotonic function y=y(x), there is an inverse relation x=x(y) within the specified y-range. The model y=y(x) will be applied to the set of arranged experimental data (x_j, y_j), j=1, ..., N, where $y_j \leq y_{j+1}$ at $x_j \leq x_{j+1}$.

The linear relationship y=a+b·x is applicable only within a limited

*Corresponding author: Tadeusz Michałowski, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland, Tel: +48126282035; E-mail: michalot@o2.pl

(narrowed down) range for x. For a more extended range of the variable x, the non-linear (parabolic, hyperbolic) models seem to be more adaptable. They are represented by equations:

$$y = a_0 + a_1 \cdot x + a_2 \cdot x^2 \tag{1}$$

$$y = \frac{c_0 + c_1 \cdot x}{1 + c_2 \cdot x} \tag{2}$$

for parabola (1), and hyperbola (2). Equation 2 is a particular case of rational function [9,10]

$$y = y(x, \mathbf{a}, \mathbf{b}, n, m) = \frac{\sum_{i=0}^{n} a_i \cdot x^i}{1 + \sum_{j=1}^{m} b_j \cdot x^j} \tag{3}$$

where $\mathbf{a}=[a_0, ..., a_n]^T$, $\mathbf{b}=[b_1, ..., b_m]^T$, $a_i, b_j \in R$. A particular case are there the functions of the Padé type [11-14]; some of them (with m=n+1) were applied [15] to semi-empirical modelling purposes. In a common opinion, rational functions have greater approximative power than polynomial functions – in the sense that, with the same number of parameters involved, they enable to get better approximation. The modified rational function (3) where $a_0=0$, i.e.,

$$y = y(x, \mathbf{a}, \mathbf{b}, n, m) = \frac{\sum_{i=1}^{n} a_i \cdot x^i}{1 + \sum_{j=1}^{m} b_j \cdot x^j} \tag{4}$$

is applicable for standard addition method [16,17].

Equations (1) and (2) assume linear form at $a_2 = c_2 = 0$. The model (2) and its simpler form, with c0 = 0, proved to be applicable in analyses made with use of AAS method [9] and in potentiometric acid-base titration curves, where generalised Simms constants [15,18,19] are involved.

Numerous examples testifying in favour of hyperbolic approximations are provided in [20-24] where the approximation

$$\ln(1 + x) \cong \frac{x}{1 + x / 2} \tag{5}$$

has been applied against the approximation

$$\ln(1 + x) \cong x \tag{6}$$

referred to the Gran I method, and the approximation $\ln(1+x) \cong x - x^2/2$. The validity of the approximations is clearly visible in Table 1, [22]. The divergences are, for example: 0.02% in Equation 6 and 2.5% in Equation 7 at x=0.05; 0.27% in Equation 6 and 9.8% in Equation 7 at x=0.20; 3.8% in Equation 6, and 44% in Equation 7 at x=1.00.

Standard addition method (SAM)

Let us introduce a new variable z, involved in relation

$$x=x_0+z \tag{7}$$

where x_0 is the initial concentration of an analyte X in the sample tested. Let y_0 be the signal related to $x=x_0$ (i.e., $z=z_0=0$) and N be the number of standard additions, i.e., N+1 experimental points $\{(z_j, y_j) \mid j=0,1, ..., N\}$ are registered.

From Equation (1) we get

Table 1: The *ln*(1+x) values and their approximations.

1	x	0.05000	0.10000	0.20000	0.25000	0.50000	0.75000	1.00000
2	ln(1+x)	0.04879	0.09531	0.18232	0.22314	0.40547	0.55962	0.69315
3	$x - x^2/2$	0.04875	0.09500	0.18000	0.21875	0.37500	0.46875	0.50000
4	$x/(1+x/2)$	0.04878	0.09524	0.18182	0.22222	0.40000	0.54545	0.66667

$$y = y_0 + a_1^* \cdot z + a_2 \cdot z^2 \qquad (8)$$

where:

$$y_0 = a_0 + a_1 \cdot x_0 + a_2 \cdot x_0^2 \qquad (9)$$

$$y_0 = a_0 + a_1 \cdot x_0 + a_2 \cdot x_0^2 \qquad (10)$$

$$a_1^* = a_1 + 2 \cdot a_2 \cdot x_0 \rightarrow a_1 = a_1^* - 2 \cdot a_2 \cdot x_0 \qquad (11)$$

At $a_0 = 0$ in Equation (9), from Equations (9)–(11) we have, by turns:

$$a_2 \cdot x_0^2 - a_1^* \cdot x_0 + y_0 = 0 \qquad (12)$$

$$X_0 = 0.5 \times (a_1^* - \sqrt{(a_1^*)^2 - 4 \times a_2 \times y_0}) / a_2 \qquad (13)$$

where y_0, a_1^* and a_2 are determined from Equation (8), according to LSM.

From Equation (2) we have, by turns,

$$y = \frac{c_0 + c_1 \cdot (x_0 + z)}{1 + c_2 \cdot (x_0 + z)} \rightarrow y\left(1 + c_2 \cdot x_0 + c_2 \cdot z\right) = c_0 + c_1 \cdot x_0 + c_1 \cdot z \rightarrow$$

$$y\left(1 + c_2^* \cdot z\right) = y_0 + \frac{c_1}{1 + c_2 \cdot x_0} \cdot z \rightarrow$$

$$y\left(1 + c_2^* \cdot z\right) = y_0 + y_0 \cdot c_2^* \cdot z + \frac{c_1}{1 + c_2 \cdot x_0} \cdot z - y_0 \cdot c_2^* \cdot z \rightarrow$$

$$y(1 + c_2^* \cdot z) = y_0 + y_0 \cdot c_2^* \cdot z + \left(\frac{c_1}{1 + c_2 \cdot x_0} - y_0 \cdot c_2^*\right) \cdot z \rightarrow$$

$$y = y_0 + \frac{c_1^* \cdot z}{1 + c_2^* \cdot z} \qquad (14)$$

where:

$$y_0 = \frac{c_0 + c_1 \cdot x_0}{1 + c_2 \cdot x_0} \; ; \; c_1^* = \frac{c_1 - c_0 \cdot c_2}{(1 + c_2 \cdot x_0)^2} \; ; \; c_2^* = \frac{c_2}{1 + c_2 \cdot x_0} \qquad (15)$$

Before application of the LSM, Equation (14) should be rewritten into the form

$$y = y_0 + d_1 \cdot z - c_2^* \cdot y \cdot z \qquad (16)$$

where:

$$d_1 = c_1^* + c_2^* \cdot y_0 \qquad (17)$$

At $c_0 = 0$, from Equation (15) we have, by turns,

$$\frac{y_0}{c_1^*} = x_0 \cdot (1 + c_2 \cdot x_0) = x_0 \cdot \left(1 + \frac{c_2^*}{1 - c_2^* \cdot x_0} x_0\right) = \frac{x_0}{1 - c_2^* \cdot x_0} \rightarrow$$

$$y_0 = x_0 \cdot (c_1^* + c_2^* \cdot y_0) \qquad (18)$$

and then from Equations (17) and (18) we have

$$x_0 = \frac{y_0}{d_1} \qquad (19)$$

Uniformity of Non-Linear Models

In order to compare the models applied within different ranges of concentrations and/or signals y registered, a uniformity (normality) procedure is necessary, i.e., both variables (x and y) should be normalised. Taking into account that nonlinear models are considered within different areas of chemical analysis, the resulting models should also be independent on the instrumental method applied for analytical purposes. The sensitivity of the method should also be considered. All the requirements are fulfilled when the normalised variables are introduced. The normalising procedure consists of two steps: (1°) calculation of parameters of the regression equation in its initial or transformed forms and (2°) formulation of the comparative criterion of fit of the modelling functions, in terms of normalised variables. The parameters of the functions are obtained by the least squares method (LSM). The functions considered will be related to the calibration curve and standard addition methods.

CCM

Let $x_1, ..., x_N$ be the set of N ordered reference values and $y_1, ..., y_N$ be their respective test values. Then for the arranged set of over-determined experimental data (x_j, y_j), j=1,...,N $(x_j \le x_{j+1}, y_j \le y_{j+1})$, we introduce the relations:

$$u = (x - x_1)/(x_N - x_1) = (x - x_1)/\Delta x \qquad \rightarrow x = x_1 + u \cdot \Delta x \qquad (20)$$

$$v = (y - y_1)/(y_N - y_1) = (y - y_1)/\Delta y \qquad \rightarrow y = y_1 + v \cdot \Delta y \qquad (21)$$

where $u \in <0,1>$, $v \in <0,1>$. Applying Equations (20) and (21) in Equations (1) and (2), we get the formulas:

$$v = \alpha \cdot u + (1 - \alpha) \cdot u^2 \qquad (22)$$

$$v = \frac{\gamma \cdot u}{1 + (\gamma - 1) \cdot u} \qquad (23)$$

where: $v = 0$ for $u = 0$, and $v = 1$ for $u = 1$

$$\alpha = (a_1 + 2 \cdot a_2 \cdot x_1)/s$$

$$\gamma = [(c_1 - c_0 \cdot c_2)/(1 + c_2 \cdot x_1)^2]/s$$

and $s = \Delta y/\Delta x$ is the mean sensitivity of the CCM; the s value is affected – to some degree – by the range $<x_1, x_N>$ of the variable x chosen to plot the related calibration curve. The straight line connecting the points (0, 0) and (1, 1) in the co-ordinates (u, v) has the form

$$v = u \qquad (24)$$

SAM

Introducing:

$$v^* = (y - y_0)/(y_N - y_0) = (y - y_0)/\Delta y^* \quad \rightarrow \quad y = y_0 + v^* \cdot \Delta y^* \qquad (25)$$

$$w^* = (z - z_0)/(z_N - z_0) = z/z_N = z/\Delta z^* \rightarrow z = w^* \cdot \Delta z^* \text{ (at } z_0 = 0) \qquad (26)$$

into Equations (1) and (2), we have, in terms of normalised variables (w^*, v^*):

$$v^* = \alpha^* \cdot w^* + (1 - \alpha^*) \cdot (w^*)^2 \qquad (27)$$

where $v^*=0$ at $w^*=0$ and $v^*=1$ at $w^*=1$. Applying Equations (25) and (26) in Equation 14, we have

$$v^* \cdot \Delta y^* = \frac{c_1^* \cdot w^* \cdot \Delta z^*}{1 + c_2^* \cdot w^* \cdot \Delta z^*} \rightarrow v^* = \frac{c_1^*/s^* \cdot w^*}{1 + c_2^* \cdot \Delta z^* \cdot w^*} = \frac{\gamma^* \cdot w^*}{1 + \gamma_1^* \cdot w^*} \quad (28)$$

Assuming that the curve passes through the points $(w^*, v^*) = (0, 0)$ and $(1,1)$, we get $\gamma_1^* = \gamma^* - 1$, and then we have the relation

$$v^* = \frac{\gamma^* \cdot w^*}{1 + (\gamma^* - 1) \cdot w^*} \quad (29)$$

where: $\alpha^* = a_1^*/s^*$, $\gamma^* = c_1^*/s^* = [(c_1 - c_0 \cdot c_2)/(1 + c_2 \cdot x_0)^2]/s^*$ and $s^* = \Delta y^*/\Delta z^*$.

Some remarks

Note that the formulas for SAM with asterisked data (α^*, γ^*, s^*, w^* and v^*) involve x_0, not x_1. The x_1 enters the formulas for α, γ, s, u and v, referred to CCM. Similarities between the formulas: (22) and (27) or (23) and (29) are the basis for application of identical criteria for CCM and SAM; these formulas are in close relevance to the homotopy problem [25], considered within topology.

Applying equidistant values for z_j, i.e., $z_{j+1} - z_j = \Delta z$ for $j=0, ..., N-1$, we get $z_j = (j/N) \cdot \Delta z^*$. Similarly, at $x_{j+1} - x_j = \Delta x$, for $j=1, ..., N-1$, we have $x_j = x_1 + (j-1)/(N-1) \cdot \Delta x$. Then the external parameters of the corresponding regression equations can be calculated with use of the following formulas:

$$\sum_{j=1}^{N} j = \frac{N(N+1)}{6} = \sigma_1; \sum_{j=1}^{N} j^2 = \frac{N(N+1)(2N+1)}{6} = \sigma_2;$$
$$\sum_{j=1}^{N} j^3 = (s_1)^2; \sum_{j=1}^{N} j^4 = s_2 \cdot \frac{(3N^2 + 3N - 1)}{5} \quad (30)$$

A nonlinearity criterion of the model

As the criterion of the nonlinearity one can assume the area between the lines (5)–(7) and straight line (Equation 8) in the normalised variables (u, v) [9] (Figure 1). This integral criterion is expressed by

$$F_1 = \int_0^1 \{[\alpha \cdot u + (1-\alpha) \cdot u^2] - u\} \cdot du = \frac{\alpha - 1}{6} \quad (31)$$

$$F_2 = \int_0^1 \{\frac{\gamma \cdot u}{1 + (\gamma - 1) \cdot u} - u\} \cdot du = \frac{\gamma \cdot (\gamma - 1 - \ln\gamma)}{(\gamma - 1)^2} - \frac{1}{2} \quad (32)$$

When referring to standard addition, the parameters α, β, γ should be replaced by α^*, β^*, γ^*. Setting $\ln\gamma = \ln(1+\gamma-1)$ and applying the approximation (5), from Equation (32) we get

$$F_2 \cong \frac{\gamma - 1}{2 \cdot (\gamma + 1)} \quad (33)$$

The area between the line $v=v(u)$ and the line $v=u$, plotted in the normalized coordinates (u, v), is the measure of nonlinearity of any monotonic relationship obtained on the basis of experimental points $(x_j, y_j)|j=1, ..., N\}$, compare with Figure 1. This area is expressed as follows

$$\Omega = \int_0^1 |v - u| \cdot du \quad (34)$$

More complex rational functions $y=y(x)$ (Equations 3 and 4) were also considered in references [9,16,17], e.g. the function

$$y = \frac{a_0 + a_1 \cdot x + a_2 \cdot x^2}{1 + a_3 \cdot x + a_4 \cdot x^2} \quad (35)$$

is expressed, in normalized variables, by the relation $v=v(u)$

$$v = \frac{\alpha \cdot u + \beta \cdot u^2}{1 + \gamma \cdot u + \eta \cdot u^2} = \frac{\beta}{\eta} + \frac{\beta}{2\eta} \cdot \left(\frac{\alpha}{\beta} - \frac{\gamma}{\eta}\right) \cdot \frac{d}{du} \ln\left(u^2 + \frac{\gamma}{\eta} \cdot u + \frac{1}{\eta}\right)$$
$$- \frac{\beta}{\eta^2} \cdot \left(\frac{\gamma}{2} \cdot \left(\frac{\alpha}{\beta} - \frac{\gamma}{\eta}\right) + 1\right) \cdot \frac{1}{u^2 + \frac{\gamma}{\eta} \cdot u + \frac{1}{\eta}} \quad (36)$$

$$v = \frac{\alpha \cdot u + \beta \cdot u^2}{1 + \gamma \cdot u + (\alpha + \beta - 1 - \gamma) \cdot u^2} \quad (37)$$

For the function (36), illustrated by Figure 1, we have $v \geq u$ within $u \in < 0, 1 >$.

From the tables of elementary integrals [26,27] we find, among others,

$$\int \frac{1}{a\xi^2 + b\xi + c} \cdot d\xi = \begin{cases} \frac{2}{\sqrt{-\Delta}} \cdot \tan^{-1} \frac{2\xi + b}{\sqrt{-\Delta}} & \text{for } \Delta < 0 \\ \frac{-2}{2a\xi + b} & \text{for } \Delta = 0 \\ \frac{1}{\sqrt{\Delta}} \cdot \ln\left|\frac{2a\xi + b - \sqrt{\Delta}}{2a\xi + b + \sqrt{\Delta}}\right| & \text{for } \Delta > 0 \end{cases} \quad (38)$$

with $\Delta = b^2 - 4ac$. Setting $a=1$, $b=\gamma/\eta$, $c=1/\eta$ and $\xi=u$ in Equation (38), we get [9]

$$\Psi(\Delta) = \int_0^1 \frac{1}{u^2 + \frac{\gamma}{\eta}u + \frac{1}{\eta}} \cdot du = \begin{cases} \frac{2}{\sqrt{-\Delta}} \cdot \left(\tan^{-1}\frac{2\eta + \gamma}{\eta \cdot \sqrt{-\Delta}} - \tan^{-1}\frac{\gamma}{\eta \cdot \sqrt{-\Delta}}\right) & \text{for } \Delta < 0 \\ 2\eta \cdot \left(\frac{1}{\gamma} - \frac{1}{2\eta + \gamma}\right) & \text{for } \Delta = 0 \\ \frac{1}{\sqrt{\Delta}} \cdot \ln\left|\frac{2\eta + \gamma - \eta \cdot \sqrt{\Delta}}{2\eta + \gamma + \eta \cdot \sqrt{\Delta}} \cdot \frac{\gamma + \eta \cdot \sqrt{\Delta}}{\gamma - \eta \cdot \sqrt{\Delta}}\right| & \text{for } \Delta > 0 \end{cases} \quad (39)$$
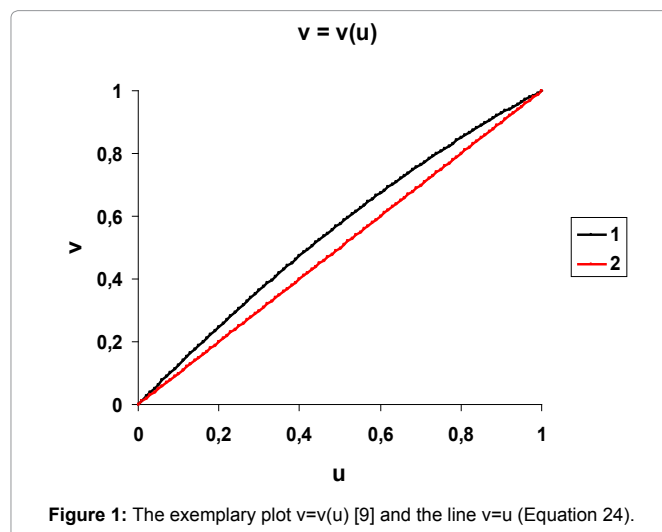
where

Figure 1: The exemplary plot $v=v(u)$ [9] and the line $v=u$ (Equation 24).

$$\Delta = \left(\frac{\gamma}{\eta}\right)^2 - \frac{4}{\eta} \qquad (40)$$

In particular, for $\Delta < 0$ we get the Ω value (Equation 34)

$$\Omega = \frac{\beta}{\eta} - \frac{1}{2} + \frac{\beta}{2\eta} \cdot \left(\frac{\alpha}{\beta} - \frac{\gamma}{\eta}\right) \cdot \left(\ln\left(1 + \frac{\gamma}{\eta} + \frac{1}{\eta}\right) + \ln\eta\right)$$
$$- \frac{\beta}{\eta^2} \cdot \left(\frac{\gamma}{2} \cdot \left(\frac{á}{\beta} - \frac{\gamma}{\eta}\right) + 1\right) \cdot \Psi(\Delta) \qquad (41)$$

Final Comments

Calibration is one of the basic activities realized within any analytical measurement. On the step of calibration, the functional relationship between the y-values indicated by measuring instrument and concentrations x of the standard samples (s) is established under strictly defined conditions of the calibration procedure.

In univariate calibration, with x as an independent variable, the linear regression is most frequently used and abused [28]. In some instances, however, a nonlinear model expressing a functional relationship y=y(x) between variables x and y within defined x-range provides better description of a relationship between x and y, under specified conditions. To obtain a valid model, the analyst must also subjectively decide on the boundaries of the system and on the attributes to be quantified in the model.

The calibration enables, among others, to estimate the real value x_0 of the measurand from the experimental value obtained in the measurement. The calibration provides an empirical relationship between the measured values.

The nonlinear modelling is done both for analytical and physicochemical purposes [2,29]. The success of calibration (accuracy, precision) depends on interrelations within the "triplet": dataset $\{(x_j, y_j)|j=1, ..., N\}$, model y=y(x) and the analytical method applied. When applying the least squares method to linear regression, it is assumed that each data–point in a given x–range has a constant absolute variation (homoscedasticity). If y=y(x) is not a linear model with respect to changes in analyte concentration, i.e., y(x) cannot be sufficiently modelled by a first order polynomial, a nonlinear calibration model must be employed [29]. The nonlinear model is also necessary when the unknown sample contains some species affecting the y value; otherwise, the prediction will be inaccurate [30]. An accurate, univariate calibration is prohibited, in most cases, by matrix effects. In such instances, an issue is the standard addition method.

The uncertainty (errors) may also be the physical modifications (changes) taking place between the calibration and the measurement process using this curve. For example, if the temperature of the samples is not equal to the calibration temperature, then the results may be wrong. In flame AAS (FAAS), the change of temperature influences the surface tension of the liquid sample, and thus on the efficiency of nebulization preceding the sample atomization. The composition of the reference samples must be similar to the composition of the samples tested. This applies, in particular, to the sample matrix and the size of particles contained therein [31]. For example, analysis of blood serum samples for pesticide or drug residues should not be based on calibration curves based on measurement of signals for aqueous solutions of the respective reference substances [32]. Because the serum blood composition is not reproducible in calibration solutions, another method is required [33], especially the standard addition method.

In this work we have shown that for CCM, as an extrapolation method and for SAM, as the interpolation method, we obtain formally identical functional relations in a normalized, dimensionless system of coordinates. Hence results the possibility of applying a unified criterion of nonlinearity of the appropriate results of analysis. This criterion is independent of the scale and range of concentrations covered by the measurements, and the indications and sensitivity of the measuring devices.

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Author Affiliation   Top

[1]*Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland*

[2]*Department of Analytical Chemistry, Technical University of Cracow, 31-155 Cracow, Poland*