Talanta 130 (2014) 307–314

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

A uniform nonlinearity criterion for rational functions applied to calibration curve and standard addition methods

Anna Maria Michałowska-Kaczmarczyk [a], Agustin G. Asuero [b], Julia Martin [b], Esteban Alonso [b], Jose Marcos Jurado [b], Tadeusz Michałowski [c,*]

[a] Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland
[b] Department of Analytical Chemistry, The University of Seville, 41012 Seville, Spain
[c] Faculty of Engineering and Chemical Technology, Technical University of Cracow, Warszawska 24, 31-155 Cracow, Poland

ARTICLE INFO

Article history:
Received 2 February 2014
Accepted 22 April 2014
Available online 10 May 2014

Keywords:
Chemical analysis
Calibration
Standard addition
Curve fitting
Rational functions

ABSTRACT

Rational functions of the Padé type are used for the calibration curve (CCM), and standard addition (SAM) methods purposes. In this paper, the related functions were applied to results obtained from the analyses of (a) nickel with use of FAAS method, (b) potassium according to FAES method, and (c) salicylic acid according to HPLC-MS/MS method. A uniform, integral criterion of nonlinearity of the curves, obtained according to CCM and SAM, is suggested. This uniformity is based on normalization of the approximating functions within the frames of a unit area.

1. Introduction

The nonlinear functions of variable x, applied for modeling made in many branches of applied sciences, are usually approximated over a limited part of its domain. Among various approximation methods, two are of particular interest: (1) the polynomial models based on Maclaurin's series expansion and (2) the model based on the rational functions called as Padé approximants [1–3], expressed by a quotient $P_n(x)/Q_m(x)$ of two polynomials $P_n(x)$ and $Q_m(x)$, with degrees m and n. The Padé function [4–6].

$$y = y_0(x; n, m) = \frac{\sum_{k=0}^{n} a_k x^k}{1 + \sum_{l=1}^{m} a_{n+l} x^l} = \frac{a_0 + \sum_{k=1}^{n} a_k x^k}{1 + \sum_{l=1}^{m} a_{n+l} x^l} \quad (1)$$

is applied for the calibration curve method (CCM). At $a_0=0$, from Eq. (1) we obtain the function

$$y = y_1(x; n, m) = \frac{\sum_{k=1}^{n} a_k x^k}{1 + \sum_{l=1}^{m} a_{n+l} x^l} \quad (2)$$

applicable for a standard addition method (SAM). As a rule, the functions (1) and (2) express the relationships between analytical signals (y) and concentrations (x) of an analyte. However, when referred to titrimetric methods of analysis, the roles of x and y are usually interchanged.

The fit of approximating functions: (1) and (2) to experimental points $\{(x_j, y_j)|j=1,\ldots,N\}$ is of primary importance in SAM and CCM. Rational function provides better approximation to experimental points $\{(x_j, y_j)|j=1,\ldots, N\}$ than polynomial functions. An illustration/proof of this property is the fit of polynomial and rational functions to the function $y = \ln(1+x) = \sum_{k=0}^{\infty}(-1)^{k+1}x^{k+1}/(k+1)$, shown in Fig. 1. Among others, the function [7]

$$y = \frac{2x}{2+x} \quad (3)$$

as a particular case of one-parametric relationship $y=y_1(x; 1,1)=ax/(1+ax)$ $(=x/(b+x), b=1/a)$, appears to be better than extension of $\ln(1+x)$ into Maclaurin's series up to 15th component [8], at $x=1$. The function (3) has been widely applied in modifications of the Gran I method [7–11]. Approximation $e^x=(2+x)/(2-x)$ was applied in [12]. More extended functions of the Padé type (Eq. (2)) were applied for modeling pH titration curves in the systems of concentrated electrolytes [13–19], where: $x=h$ – activity of H^+ ions, $pH=-\log h$, $y=W=V_0+V$; V_0 – volume of titrand (D), V – volume of titrant (T) added into D at a particular point of titration. In context with Eq. (2), it should be noted that the common titration is a kind of SAM, although T in [13–17] contained a standardized solution, together with a sample tested and a basal electrolyte. In [17–19], a function of the Padé type was presented as a sum of simple rational functions, of $a_i/(x+b_i)$ type; similar transformation (with Simms' constants involved) was used later in [20,21] for calculation of total alkalinity. Using rational functions requires nonlinear regression [4] and then analytical and physicochemical problems involved with Padé approximants were resolved there according to iterative procedures [22,23].

* Corresponding author. Tel.: +48 12 628 21 77.
E-mail address: michalot@o2.pl (T. Michałowski).

http://dx.doi.org/10.1016/j.talanta.2014.04.067
0039-9140/

Notations

CCM calibration curve method
LSM least squares method
SA salicylic acid
SAM standard addition method

As stated above, the rational functions with fewer number of coefficients give better approximation than the corresponding polynomial functions [4,24]. Rational functions are particularly applicable when strongly unsymmetrical dependences occur [25,26]. The Padé approximants are perceived as an accurate tool in some extrapolation procedures [27]; this property is particularly valuable in the context with SAM.

Rational functions were used for modeling enzyme-catalyzed reactions [28], and for ridge regression [29], where linear terms were introduced in numerator and denominator of the rational function in a kinetic model applied for esterification of ethanol with acetic acid. Another kind of rational function was applied [30] for flame atomic absorption spectrometry (FAAS) purposes. The Padé approximants were also considered as a flexible tool used for modeling adsorption data [31,32], for optimizing sugar production [26], scanning electrochemical microscopy [33], and handling the data related to mass transfer at microelectrodes [34,35].

A new formulation involved with rational functions and applied to SAM and CCM, has been presented recently [36,37]; it was proved that the functions $y=y_1(x; 2,1)$ and $y=y_1(x; 2,2)$ (see Eq. (2)) provide the results of FAAS analysis much more accurate than ones obtained with use of parabolic function [38], $y=y_1(x; 2,0)$. What is more, the functions $y=y_1(x; 2,1)$ and $y=y_1(x; 2,2)$ appeared to be robust against an effect of the matrix change, resulting from the addition of the standard solutions that changed a volume of the solution up to ca. 30% (the dilution effect was included in the model applied in [36]). This way, omission of one of the basic assumptions applied in SAM did not cause a deterioration of the accuracy of determinations, although SAM is commonly considered as a last resort rather than the method of choice [39].

In this paper, an effect of m in $y=y_0(x; 2,m)$ (see Eq. (2), $n=2$) on the fit of the related approximating functions to experimental points $(x_j, y_j)\ |j=1,\ldots,N\}$, expressed by the differences $\delta_j=y_j-y_0(x_j; 2,m)$, is indicated on an example of CCM applied for nickel determination according to FAAS method. Then nonlinear models derived for SAM were applied for results of analyses of potassium in a wine, and performed according to flame atomic emission spectrometry (FAES), widely used for determination of sodium and potassium in biological fluids [40–42]. The nonlinear model applied in SAM is referred here to the manner of preparation of analyzed samples (working solutions), different from the one applied in [36].

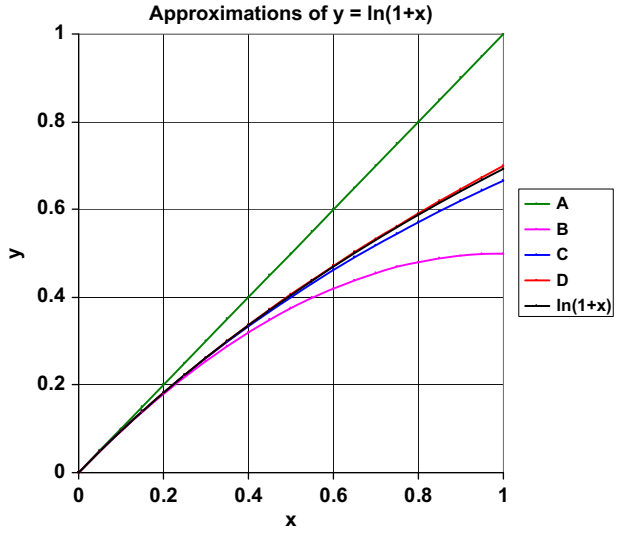

Fig. 1. Comparative plots of functions: (A) $y=x$, (B) $y=x-x^2/2$, (C) $y=2x/(2+x)$, and (D) $y=x(1+x/6)/(1+2x/3)$ (the best fit) with $y=\ln(1+x)$.

The CCM was also applied to results of determination of salicylic acid (SA) according to HPLC-MS/MS method; the quantitation is based here on comparing areas of peaks (y) obtained from mass chromatograms at different concentrations (x, mg/L) of SA, see Eq. (1). The relationships $y=y1(x; n, m)$ (Eq. (1)) were modeled here at $(n, m)=(2, 2)$, $(2, 1)$, $(1, 1)$ and $(2, 0)$, in a logarithmic scale.

Except fitting the curves obtained according to SAM and CCM, a new, integral criterion of a degree of nonlinearity of the curves fitted according to nonlinear models is suggested. For this purpose, the curves are transformed (converted) into a normalized system of variables, and put within a square with sides equal to unity. Generally, the normalization is involved here with a uniform, integral criterion of nonlinearity of curves obtained with use of different methods of analysis, within different ranges of concentrations for standard solutions, and made under different physicochemical conditions, pre-assumed in the analyses. The uniformity of normalization for CCM and SAM results from the fact that a_0, distinguishing the formulas (1) and (2), is not involved in the relations applied in the system of normalized coordinates (u, v).

All calculations made within this work were performed according to the least squares method (LSM), realized with use of Excel spreadsheet.

2. Modified standard addition method

It is assumed that N measuring flasks (V_f mL) are used. Equal volumes V_0 mL of a sample tested with unknown concentration x_0 [mg/L] of an analyte X and different volumes V_j mL ($j=1,\ldots, N$) of stock solution of X (x_S mg/L) were added into jth flask and filled up to the mark with water. Concentration of X in the jth flask is as follows:

$$x_j=\frac{x_0V_0+x_SV_j}{V_f} \tag{4}$$

Applying Eq. (4) to

$$y=y_1(x;2,2)=\frac{a_1x+a_2x^2}{1+a_3x+a_4x^2} \tag{5}$$

we get the regression equation

$$y_j=d_0+d_1V_j+d_2V_j^2+d_{11}V_jy_j+d_{21}V_j^2y_j+\varepsilon_j \tag{6}$$

where:

$$d_0=(b_1+b_2x_0V_0)x_0V_0/z;\ \ d_1=(b_1+2b_2x_0V_0)x_S/z;\ \ d_2=b_2x_S^2/z; \tag{7}$$

$$d_{11}=-(b_3+2b_4x_0V_0)x_S/z;\ \ d_{21}=-b_4x_S^2/z \tag{7a}$$

and $z=1+b_3x_0V_0+b_4x_0^2V_0^2$; $b_1=a_1/V_f$, $b_2=a_2/V_f^2$, $b_3=a_3/V_f$, $b_4=a_4/V_f^2$. Further transformations of (7) give

$$x_0=\frac{d_1x_S}{2d_2V_0}\left(1-\left(1-\frac{4d_0d_2}{d_1^2}\right)^{0.5}\right) \tag{8}$$