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Short communication

Application of rational functions for the standard addition method

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ABSTRACT

Some rational functions are considered as the basis for calculation of unknown concentration (x_0) of an analyte X determined according to the standard addition method (SAM). The correction for dilution of the sample tested during addition of successive increments of standard(ised) solution of X is involved in the related algorithm applied for calculation of the x_0 value. The formulae derived were put in context with experimental data, obtained according to the AAS method from Cu-measurements in samples obtained by digestion of an ash obtained from incinerated sludge. It was stated that the use of rational functions for modeling purposes strengthens the robustness of the results thus obtained.

1. Introduction

The standard addition method (SAM) is commonly used to determine the concentration x of an analyte X in a complex matrix such as biological fluids, soil samples, sludges, etc., whose constituents are not known before the analysis. In such samples, containing complex (not reproducible) matrices [1–7], application of a common calibration curve method (CCM) would be involved with a systematic error, resulting from the matrix effect. On the analysis step, some of the components may affect the signal, y, ascribed to X, causing inaccuracy in the evaluated concentration of X in the sample analyzed.

SAM is applicable in all instances where a change in the response of the measuring system, caused by addition of the standard solution, can be attributed solely to the analyte X, i.e., the analyte sensor used in SAM is fully selective against this analyte in a sample tested [8]. It is not the case in the generalized standard addition method (GSAM) [1], where multiple linear regression is designed for analysis of multicomponent samples, and some polynomial functions are applied.

Better approximation is offered by nonlinear functions. In particular, the rational functions of variable x

$$y = y(x) = \frac{P_n(x)}{Q_m(x)} \tag{1}$$

named as Padé approximants [9–11], and defined as a ratio of two polynomial functions: $P_n(x)$ and $Q_m(x)$ of n-th and m-th degree, respectively, give much better approximation than truncated Taylor/Maclaurin's series with the same number of parameters [12–15]. Other types of rational functions were applied in [16,17].

In this paper, we refer to particular cases of a rational function

$$y = \frac{a_1 x + a_2 x^2}{1 + \sum_{k=1}^{m} a_{2+k} x^k} \tag{2}$$

exemplified by the relations

$$y = \frac{a_1 x + a_2 x^2}{1 + a_3 x + a_4 x^2} \tag{3}$$

$$y = \frac{a_1 x + a_2 x^2}{1 + a_3 x} \tag{4}$$

The functions (3) and (4) will be put in context with parabolic function

$$y = a_1 x + a_2 x^2 \tag{5}$$

In further parts of the paper, the function (3) is termed as the model A; the simplified forms of (3) are named as model B ($a_4=0$, Eq. (4)), and model C ($a_3=a_4=0$, Eq. 5). All the functions (2)–(5) fulfill the general requirement $y(0)=0$ put on the functions applied for SAM purposes.

The functions (3)–(5) will be applied for calculation of unknown concentration, x_0 [mg/L X], of an analyte X in the sample tested, according to SAM. All the calculations made in this paper were performed with use of the least squares method (LSM).

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List of symbols

D	stock solution (as titrand);
ΔV	basic volume [mL] increment
LSM	least squares method
$r=$	$\Delta V/V_0$
SAM	standard addition method
V	volume [mL] of T
V_0	volume [mL] of D
T	working standard solution of X (as titrant)
X	analyte
x_0	unknown concentration [mg/L] of X in D
x_S	known concentration [mg/L X] of X in T.

2. Derivation of the formulae

The SAM realized in this paper is based on addition of different portions of working standard solution T (x_S mg/L X) of X into V_0 mL of the series of identical stock solutions D containing X of unknown concentration x_0 mg/L X. If $x_S > x_0$, a growth in total concentration x [mg/L] of X resulted from this procedure is expressed by a variable z in the relation

$$x = x_0 + z \quad (i.e.,\ x_j = x_0 + z_j,\ j = 0, \ldots, N) \tag{6}$$

Let $y_0 = y(x_0)$ be a signal corresponding to $x = x_0$ (i.e., $z = z_0 = 0$), and N is the number of the standard additions of T into $N+1$ cylinders, numbered as 0, 1,…,N. A volume $j\Delta V$ mL ($j = 0,\ldots,N$) of T is added into j-th cylinder with V_0 mL of D, where ΔV [mL] is the basic increment of T, identical for all solutions in the series of $N+1$ solutions. The T is obtained beforehand by a proper dilution of the primary standard solution with water. For each of the D+T solutions thus obtained, the experimental points $\{(x_j, y_j)|j = 0,1,\ldots, N\}$ are obtained; for example, in the AAS method, absorbance (A) is measured, $y_j = A_j$. The change in concentration of X in j-th cylinder, resulting from addition of $V_j = j\Delta V$ of T equals to

$$z_j = \frac{x_0 V_0 + x_S j\Delta V}{V_0 + j\Delta V} - x_0 = (x_S - x_0)\delta_j \tag{7}$$

where

$$\delta_j = j\Delta V/(V_0 + j\Delta V) = jr/(1 + jr) \tag{8}$$

$$r = \frac{\Delta V}{V_0} \tag{9}$$

The additivity in volumes of D and T is assumed in (7). From Eqs. (6) and (7) we get $z_{j+1} - z_j = x_{j+1} - x_j$

$$x_{j+1} - x_j = \frac{(x_S - x_0)r}{(1 + jr)(1 + (j+1)r)} \tag{10}$$

As we see, $x_{j+1} > x_j$ at $x_S > x_0$. If $(2N+1)\cdot r \ll 1$, one can rewrite (10) in approximated form

$$x_{j+1} - x_j \cong (x_S - x_0)r(1 - (2j+1)r) \tag{11}$$

Further approximation leads to $x_{j+1} - x_j \cong (x_S - x_0)r$.

From Eqs. (5) and (6) we get, by turns,

$$y = a_1(x_0 + z) + a_2(x_0 + z)^2 \tag{12}$$

$$y = a_1 x_0 + a_2 {x_0}^2 + (a_1 + 2a_2 x_0)z + a_2 z \tag{13}$$

From Eqs. (13) and (7) we have

$$y = a_1 x_0 + a_2 {x_0}^2 + (a_1 + 2a_2 x_0)(x_S - x_0)\delta + a_2(x_S - x_0)^2\delta^2 \tag{14}$$

where Δ is the dilution factor. Denoting

$$a_1 x_0 + a_2 {x_0}^2 = b_0 \tag{15}$$

$$(a_1 + 2a_2 x_0)(x_S - x_0) = b_1 \leftrightarrow a_1 x_0 + 2a_2 {x_0}^2 = \frac{b_1 x_0}{x_S - x_0} \tag{16}$$

$$a_2(x_S - x_0)^2 = b_2 \leftrightarrow a_2 = \frac{b_2}{(x_S - x_0)^2} \tag{17}$$

we get, by turns,

$$a_2 {x_0}^2 = \frac{b_1 x_0}{x_S - x_0} - b_0 \tag{18}$$

$$\frac{b_2}{(x_S - x_0)^2}{x_0}^2 = \frac{b_1 x_0}{x_S - x_0} - b_0$$

$$d_2 {x_0}^2 - d_1 x_S x_0 + b_0 {x_S}^2 = 0$$

where

$$d_2 = b_0 + b_1 + b_2,\ d_1 = 2b_0 + b_1 \tag{19}$$

From Eqs. (14)–(17) we have

$$y = b_0 + b_1\delta + b_2\delta^2 \tag{20}$$

Eq. (20) can be rewritten in the form of regression equation

$$y_j = b_0 + b_1\delta_j + b_2{\delta_j}^2 + \varepsilon_j \tag{21}$$

where δ_j is defined by Eq. (8). On the basis of experimental points $\{(\delta_j, y_j)|j = 0,\ldots,N\}$ obtained according to an analytical method, we calculate b_0, b_1 and b_2, and then d_2 and d_1 values (Eq. (19)). From Eq. (18) we calculate the desired x_0 value

$$x_0 = \frac{x_S}{2d_2}\left(d_1 - \sqrt{{d_1}^2 - 4b_0 d_2}\right) \tag{22}$$

Similar procedure can be applied for more complex, rational functions. In particular, from Eq. (3) we get the regression equation

$$y_j = b_0 + b_1\delta_j + b_2{\delta_j}^2 + b_{11}y_j\delta_j + b_{12}y_j{\delta_j}^2 + \varepsilon_j \tag{23}$$

resolvable according to LSM, on the basis of the points $\{(\delta_j, y_j)|\ j = 0, \ldots, N\}$. The parameters: b_0, b_1, b_2, b_{11}, b_{12} in Eq. (23) are involved in the relations

$$a_1 x_0 + a_2 {x_0}^2 = b_0(1 + a_3 x_0 + a_4 {x_0}^2) \tag{24}$$

$$a_1 x_0 + 2a_2 {x_0}^2 = \frac{b_1 x_0(1 + a_3 x_0 + a_4 {x_0}^2)}{x_S - x_0} \tag{25}$$

$$a_2 = \frac{b_2(1 + a_3 x_0 + a_4 {x_0}^2)}{(x_S - x_0)^2} \tag{26}$$

$$b_{11} = -\frac{(a_3 + 2a_4 x_0)(x_S - x_0)}{1 + a_3 x_0 + a_4 {x_0}^2} \tag{27}$$

$$b_{12} = -\frac{a_4(x_S - x_0)^2}{1 + a_3 x_0 + a_4 x_0^2} \tag{28}$$

From Eqs. (24)–(26) we get again the formula for x_0, formally identical with Eq. (22). However, the d_1 and d_2 values (Eq. (19)) are calculated here for b_0, b_1 and b_2 obtained from (23), according to LSM. Analogous remarks refer to Eq. (4), where b_0, b_1 and b_2, used in Eqs. (19) and (22), are obtained according to LSM, applied to regression equation

$$y_j = b_0 + b_1\delta_j + b_2{\delta_j}^2 + b_{11}y_j\delta_j + \varepsilon_j \tag{29}$$

The regression equation referred to the function (2) has the form

$$y_j = b_0 + b_1\delta_j + b_2{\delta_j}^2 + \sum_{k=1}^{m} b_{1k} y_j {\delta_j}^k + \varepsilon_j \tag{30}$$

The requirement $y(0)=0$ is necessary in the models applied for SAM purposes. For example, the function $y = a_0 + a_1x + a_2x^2$ put for Eq. (5) gives the regression equation

$$y_j - a_0 = b_0 + b_1\delta_j + b_2{\delta_j}^2 + \varepsilon_j \tag{31}$$

with undefined *a priori* a_0 value.

3. Experimental part

Applicability of the proposed SAM is illustrated by measurements of Cu contents in an ash, resulting from burning of sewage sludge at 950 °C. The ash came from combustion of sewage sludge from wastewater treatment plants belonging to KP SA Tyskie Princes Brewery working in the anaerobic reactors BIOPAQ-IC. The components obtained by digestion of the ash in concentrated nitric acid were considered as a matrix in the analysis performed according to the SAM principles and realized with use of the AAS method.

3.1. Apparatus, reagents and procedure

The analyses were made on the apparatus AAS Analyst 300 Perkin-Elmer. The Cu determinations were carried out at a wavelength of 324.8 nm, and 0.7 nm aperture. Gas flow was set at 2 dm^3/min for acetylene (analytical purity $\geq$99.996%, pressure 83–96 kPa) and 10 dm^3/min air (350–450 kPa).

Certified standard solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1000 ± 2 mg Cu/L) in 0.5 mol/L HNO_3 purchased in Merck, and doubly distilled water was applied for preparation of stock and standard solutions. Concentrated HNO_3 (65% m/m, pa, POCh) was applied for the ash dissolution. An appropriate standard glassware was used for measuring and storage of the solutions.

The stock solution, containing 1.90 mg/L Cu, was obtained by digestion of 2.0011 g of the ash in 300 mL of the concentrated HNO_3 solution and boiling within 20 min. After introducing 1.90 mL of the standard copper nitrate solution, the mixture was cooled, then filtered into 1000 mL measuring flask and the solution was filled up to the mark with water and mixed. The Cu-contents in the stock solution was chosen on the basis of presumptive composition of other environmental samples of this kind, analyzed in our laboratory.

The working standard solutions, with Cu concentrations (x_S) equal 100 mg/L (in option 1) and 25.0 mg/L (in option 2), were obtained by pipetting the defined portions of the standard solution and dilution with water in volumetric flasks.

Table 1
Absorbances (A_i, $i=1,\ldots,10$) measured according to SAM principle (option 1), and concentrations (x_0, mg/L Cu) calculated from Eq. (22), on the basis of Eqs. (23),(29) and (31), respectively; $N=10$, $V_0=30$, $\Delta V=0.15$.

j	$j\Delta V$	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	Mean A
0	0	0.154	0.152	0.153	0.152	0.154	0.153	0.153	0.153	0.153	0.152	0.153
1	0.15	0.191	0.190	0.192	0.191	0.190	0.192	0.191	0.190	0.191	0.190	0.191
2	0.30	0.230	0.231	0.231	0.230	0.233	0.231	0.229	0.229	0.230	0.231	0.231
3	0.45	0.268	0.264	0.265	0.265	0.266	0.266	0.264	0.266	0.264	0.264	0.265
4	0.60	0.306	0.304	0.306	0.305	0.304	0.307	0.306	0.306	0.305	0.304	0.305
5	0.75	0.342	0.342	0.342	0.341	0.343	0.341	0.341	0.342	0.342	0.342	0.342
6	0.90	0.379	0.378	0.380	0.376	0.381	0.378	0.377	0.377	0.380	0.378	0.378
7	1.05	0.411	0.415	0.415	0.414	0.413	0.413	0.413	0.413	0.413	0.415	0.414
8	1.20	0.445	0.446	0.443	0.444	0.445	0.445	0.445	0.443	0.445	0.446	0.445
9	1.35	0.472	0.471	0.468	0.470	0.468	0.471	0.471	0.472	0.470	0.471	0.470
10	1.50	0.504	0.505	0.507	0.507	0.505	0.509	0.509	0.508	0.506	0.505	0.507
Cu contents, x_0 [mg/L], found from absorbance (AAS) measurements												Mean Cu
Model A		1.890	1.852	1.891	1.861	1.890	1.870	1.935	1.895	1.912	1.852	1.892
Model B		1.936	1.938	1.965	1.944	1.970	1.956	1.966	1.948	1.965	1.938	1.957
Model C		1.745	1.714	1.738	1.760	1.725	1.786	1.791	1.766	1.738	1.714	1.756

Table 2
Absorbances (A_i, $i=1,\ldots,10$) measured according to SAM principle (option 2), and concentrations (x_0, mg/L Cu) calculated from Eq. (22), on the basis of Eqs. (23),(29) and (31), respectively; $N=10$, $V_0=30$, $\Delta V=0.90$.

j	$j\Delta V$	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	Mean A
0	0	0.153	0.151	0.151	0.153	0.154	0.154	0.153	0.153	0.152	0.153	0.153
1	0.90	0.203	0.203	0.203	0.204	0.205	0.203	0.204	0.204	0.204	0.206	0.204
2	1.80	0.256	0.254	0.254	0.256	0.259	0.256	0.255	0.256	0.256	0.256	0.256
3	2.70	0.307	0.306	0.306	0.308	0.309	0.309	0.305	0.307	0.305	0.305	0.307
4	3.60	0.349	0.352	0.353	0.356	0.358	0.352	0.351	0.352	0.352	0.352	0.353
5	4.50	0.396	0.395	0.395	0.397	0.399	0.397	0.394	0.398	0.398	0.397	0.397
6	5.40	0.430	0.431	0.431	0.433	0.435	0.429	0.429	0.432	0.429	0.431	0.431
7	6.30	0.473	0.472	0.472	0.474	0.476	0.473	0.471	0.474	0.473	0.472	0.473
8	7.20	0.501	0.505	0.505	0.508	0.511	0.504	0.503	0.504	0.506	0.506	0.505
9	8.10	0.528	0.532	0.532	0.534	0.538	0.531	0.530	0.537	0.532	0.529	0.532
10	9.00	0.559	0.558	0.558	0.560	0.562	0.559	0.556	0.559	0.566	0.561	0.560
Cu contents, x_0 [mg/L], found from absorbance (AAS) measurements												Mean Cu
Model A		1.865	1.902	1.890	1.907	1.894	1.869	1.946	1.922	1.848	1.885	1.885
Model B		1.912	1.854	1.852	1.870	1.869	1.914	1.907	1.886	1.902	1.914	1.889
Model C		1.696	1.654	1.649	1.656	1.662	1.696	1.705	1.683	1.727	1.713	1.686

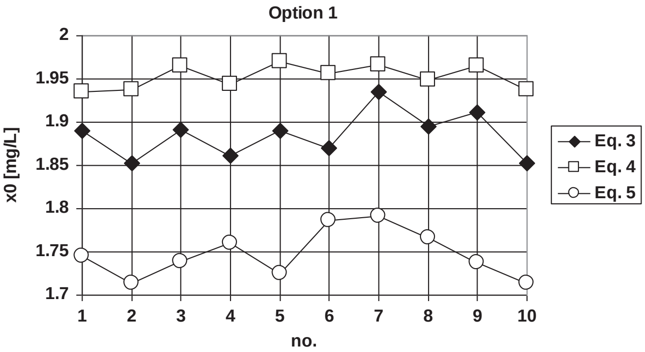

Fig. 1. The x_0 values calculated from Eq. (22) on the basis of Eqs. (23), (29) and (31), for subsequent absorbance readouts in option 1.

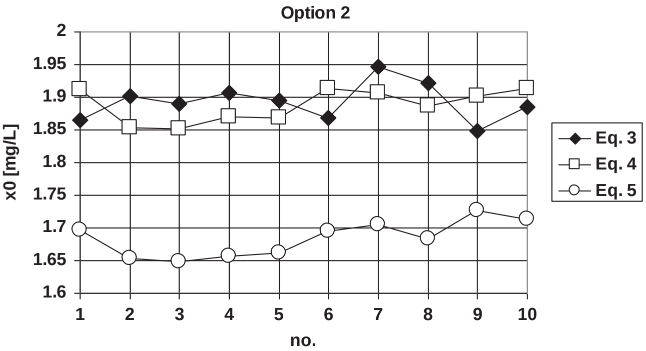

Fig. 2. The x_0 values calculated from Eq. (22) on the basis of Eqs. (23), (29) and (31), for subsequent absorbance readouts in option 2.

Three series of stock solutions, corresponding to the options 1 and 2, were prepared. Within the options, 11 samples, with aliquots $V_0=30$ mL of the stock solution contained in cylinders, were treated with $i\cdot0.15$ mL (option 1) or $i\cdot0.90$ mL (option 2) ($i=0,1,\ldots,10$) of the related working standard solution; the working standard solutions were not added into the first samples in each series. After addition of the working standard solutions, the volume of the solution in 11-th cylinder was equal (1) 31.50 mL and (2) 39 mL, i.e., the relative growth in volume was equal (1) 5%, and (2) 30%, respectively.

3.2. *Results of measurements and discussion*

For each sample, 10 absorbance measurements were done. The result of each measurement was the average of three readouts taken every 5 s. The results thus obtained are collected in Table 1 (option 1), and Table 2 (option 2), together with the results for x_0 (Eq. (22)) obtained according to regression Eqs. (23), (29) and (31) and presented in Figs. 1 and 2.

The results obtained confirm an applicability of the models A and B, and inadequacy of the model C, suggested e.g. in [5]. The results for x_0 obtained according to model C are significantly lower than those obtained from models A and B; the values for x_0 equal ca. 1.90 mg/L or more were expected here. The results for x_0 obtained from models A and B are close to this limit, which implies that the ash contained no copper. Moreover, the model B turned out to be sufficient in these studies, whereas the model C (and linear model, as well) are unsuitable for this purpose. The Student's t-test [18] indicated that, for experimental data presented in Tables 1 and 2, the differences between mean x_0-values obtained from models A, B, C in option 1 are significant on 95% confidence level. In option 2, only the differences between x_0-values obtained from models A and B are insignificant.

In SAM, it is usually assumed that the volume of the solution tested is not significantly changed as a result of addition of successive portions of a standard solution. In the analyses presented in this paper, the effect of dilution of the stock solution in options 1 and 2 had no significant effect on x_0 values when the models A and B are applied.

The error associated with model C increases in option 2, where the non-additivity of D and T volumes in mixture D+T and resulting change in the matrix composition are greater than in option 1. However, the use of model A or model B gives, also in the option 2, the x_0 values close to the expected value. This clearly testifies in favor of robustness of the models A and B.

4. Final comments

In univariate calibration, with concentration x as an independent variable, the linear regression is most frequently used and abused [19]. In many instances, however, a nonlinear model expressing a functional relationship $y=y(x)$ between variables x and y, within defined range of variable x, provides more accurate fit between these variables, under specified conditions.

The nonlinear modeling, designed both for analytical and physicochemical purposes [20,21], confirms the statement that “the success of calibration (accuracy, precision) depends on the interrelations within the “triplet”: (i) dataset, (ii) model, and (iii) the analytical method applied [22]. 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, a nonlinear calibration model must be employed [21]. The nonlinear model is also necessary when the unknown sample contains some species affecting the y-value; otherwise, the prediction will be inaccurate [23]. In most cases, an accurate, univariate calibration is prohibited by matrix effects. In such instances, an issue is the standard addition method.

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