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A ROBUST LEAST SQUARE METHOD FOR CALIBRATION OF PRECISE OPTICAL ABSORPTION GAS ANALYZERS

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Abstract – Basing on the results of the described comparison the conception is built concerning the modulating functions method robustness in the case of calibration curve reconstruction problem using nonlinear model (1). Efficiency of the mentioned method expands the usability of quite monotonous nonlinear models like (1) for calibration curve parameters determination in a wide groupe of problems of calibration curve reconstruction on the base of an output of precise optical absorption gas analyzers.

Keywords: least square method, precise gas analyzers

As it was stated in [1] a calibration curve of a two-channel differential optical absorption gas-analyser could be presented in form:

$$f_0(x) = a_0 + \int_{\lambda \ge 0} z_\lambda(x)\Gamma\{d\lambda\} \tag{1}$$

where $x \ge 0$ - concentration values of a target component in a binary mixture, a_0–some constant, $\Gamma\{...\}$–some measure, and function $z_\lambda(x)$ is defined as follows

$$z_\lambda(x) = \frac{1 - e^{-\lambda x}}{\lambda} \tag{2}$$

Roughly speaking, a calibration curve function (1) is an infinite weighted sum of members (2) with various λ and a constant a_0. The whole class of functions of the type (1) is parameterised with a constant a_0 and a measure Γ. These functions have completely monotonic derivatives for $x \geq 0$.

We will use a specific subclass of functions (1) as models for calibration curves. If measure in (1) is atomic, then Lebesgue integral in (1) is transformed into finite sum of members (2) in atomic points λ_j

$$f(x) = a + bx + \sum_{j=1}^{k} c_j \frac{1 - e^{-\lambda_j x}}{\lambda_j} \tag{3}$$

where a, $b>0$, $c_j>0$, $\lambda_j>0$ –are some constant coefficients.

Functions of type (3) are parameterised with finite number of parameters and have several nice properties. First, if function (3) interpolates some set of points (x_i, y_i), $y_i=f(x_i)$, then it serves as an upper (or low) bound in between x_i and x_{i+1} for all functions of class (1) interpolating the same points. Second, function (3) explicitly provides separate linear and non-linear parts (it is equal to $f(x)=a + bx$, for c_j=0), and non-linear part remains continuous at $x \to 0$ here. Third, model (3) exactly matches to the physical model of a differential optical absorption gas-analyser, and due to this fact it allows to build a very robust method of a calibration curve reconstruction [1,2].

Let we have a number of measured calibration points (x_i, y_i). Parameters a, b, c_j, λ_j for the model (3) can be estimated with iterative least-square algorithm briefly described below.

A problem of finding of the local minima for functional

$$\phi = \sum_{i=1}^{n} (y_i - f(x_i))^2 \tag{4}$$

where y_i – observed values of response, $f(x_i)$ – calculated according (3), n – number of observations) may be easily solved for a, b, c_j when some values of λ_j are fixed. For this (linear regression) step we use a very stable variant of Householder reflections with limitations. After finding optimal a, b, c_j we use a variant of a gradient method to calculate new λ_j values. This two-step procedure continues until model stabilization.

Theoretically, these two-step iterations are steady to choice of initial λ_j values. But an essential part of the algorithm is a procedure used to calculate initial values for λ_j before the first iteration. This step is critical to provide solution stability and fast convergence of a method. We use here a modified variant of a method of modulating functions [3] to obtain initial values for λ_j. The method does not require explicit solution extreme problem to find a global minimum of functional (3), but is reduced to numerical integration and a search root of algebraic polynomial.

Brief description of the method is given therein after.

It is noted that function (3) derivative is a mixture of the exponents:

$$y'(x) = f^{'}(x) = b + \sum_{j=k}^{k} c_j e^{-\lambda_j x} \tag{5}$$

By change of variables:

$$x = \alpha\theta + \beta \quad \alpha = \frac{x_n - x_1}{2} \quad \beta = \frac{x_n + x_1}{2} \tag{6}$$

where x_i and x_n are point and extremity of measurement range, the equation (5) is resulted to kind:

$$y(\alpha\theta + \beta) = b + \sum_{j=1}^{k} \rho_j e^{-\mu_j \theta} \tag{7}$$

where $\rho_j = c_j e^{-\lambda_i \beta}$, $\mu_i = \lambda_j \alpha$, $\lambda_j > 0$, $\mu_j > 0$, $-1 \le \Theta \le 1$

The estimation of coefficients μ_i is realised by analysis of algebraic polynomial $q(\mu)$ in degree k which has roots $-\mu_j$

$$\begin{aligned} q(\mu) &= \prod_{j=1}^{k} (\mu + \mu_j) = \\ &= \mu^k + a_{k-1}\mu^{k-1} + \ldots + a_1\mu + a_0 = 0 \end{aligned} \tag{8}$$

where the coefficients $a_k = 1$, a_{k-1}, ... a_1, a_0 – positive numbers. A calculation of the coefficients could be made using method of modulating functions, by numerical integration and solving of linear regression problem on a_k. Afterwards the roots μ_j of algebraic polynomial (8) may be calculated, and initial values of λ_j by formulas (6)-(7) may be obtained.

Numerical experiments were made on modelled data files in order to compare above mentioned method with the traditional methods of non-linear programming (Nelder-Meed method and Box method with restrictions to λ_i coefficient values, STATISTICA package v.5.5). These methods proved unsteady with respect to choice initial coefficients values, while supposed algorithm resulted in steady estimations. Availability of the method to be robust in respect to choice initial parameters enhances an attraction of completely monotonic non-linear models of type (3) for construction of the calibration curve of a differential optical absorption gas-analyser.

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