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A novel second-order standard addition analytical method based on data processing with multidimensional partial least-squares and residual bilinearization

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ABSTRACT

In the presence of analyte–background interactions and a significant background signal, both second-order multivariate calibration and standard addition are required for successful analyte quantitation achieving the second-order advantage. This report discusses a modified second-order standard addition method, in which the test data matrix is subtracted from the standard addition matrices, and quantitation proceeds via the classical external calibration procedure. It is shown that this novel data processing method allows one to apply not only parallel factor analysis (PARAFAC) and multivariate curve resolution-alternating least-squares (MCR-ALS), but also the recently introduced and more flexible partial least-squares (PLS) models coupled to residual bilinearization (RBL). In particular, the multidimensional variant N-PLS/RBL is shown to produce the best analytical results. The comparison is carried out with the aid of a set of simulated data, as well as two experimental data sets: one aimed at the determination of salicylate in human serum in the presence of naproxen as an additional interferent, and the second one devoted to the analysis of danofloxacin in human serum in the presence of salicylate.

1. Introduction

Calibration by standard addition is employed to cope with background effects, which are usually due to a change in analyte response brought about by interactions with the background, i.e., a change in the slope of the univariate signal–concentration relationship. Univariate standard addition is designed to circumvent this phenomenon [1]. More generally, an interfering background signal may be overlapped with that from the analyte. This problem can only be solved by univariate standard addition when the background response arises from the chemical treatment of the sample rather than from the sample itself. This allows one to adequately subtract it from the analyte signal (for example, by carrying out two standard additions on different sample amounts, or by combining standard addition with Youden calibration) [2]. This latter situation is not the most common one, however, and does not include the analysis of natural or biological samples containing a variety of responsive non-analytes. A background signal stemming from responsive non-analytes constitutes an interference in univariate analysis, and cannot be corrected by means of standard addition.

In the first-order multivariate calibration scenario, a generalized version of univariate standard addition method (the so-called GSAM) is available [3,4], which implies measuring first-order data (i.e., spectra) for various overlapping analytes embedded in a sample background. Generalized standard addition not only demands knowledge of the number and identity of the analytes, but also that standards of each of them are available, in order to be added in perfectly known amounts to each sample. The limitations of this method regarding the background effects are analogous to those for the univariate standard addition mode.

The presence of a responsive background, which does also affect the analyte response in a sample (for example, through inner filter effects or analyte–background interactions such as complex formation or protein binding) requires second-order standard addition for analyte quantitation [5]. This ubiquitous analytical problem can also be solved by second-order external calibration in the presence of background, provided the latter is available to be spiked with the analyte [6]. In general, however, this approach is not experimentally feasible.

Only a few references exist in the literature on this interesting standard addition multi-way research field [7–11]. The algorithm of choice for obtaining the second-order advantage from standard addition data is parallel factor analysis (PARAFAC) [12], although a recent report prefers the PARALIND variant [9] (a PARAFAC version adapted to linearly dependent systems, as described in Ref.

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[13]). This is because of the presence of linear dependencies in standard addition data when more than one interferent occurs in the test sample. In certain cases, standard addition PARAFAC could not be employed because of serious profile overlapping in one of the data dimensions, in which case multivariate curve resolution-alternating least-squares (MCR-ALS) [14] was successfully applied [11]. It should be noticed that linear dependency is a general phenomenon, which is not only present in standard addition data, but also in pH-gradient [14] or kinetic-modulated spectral experiments [15,16].

Recently, attention has been focused on alternative second-order multivariate calibration algorithms achieving the second-order advantage, which are based on powerful latent-structured methodologies. Pertinent examples are unfolded partial least-squares/residual bilinearization (U-PLS/RBL) [17] and multidimensional partial least-squares/residual bilinearization (N-PLS/RBL) [18]. These methods cannot be directly applied in the standard addition mode, because they include a calibration step in which nominal analyte concentrations are required, and these are neither available for test samples nor for those obtained after the addition of standards. This is somewhat deceptive, since PLS-based methods are more flexible and have been recently shown to provide better figures of merit than their competitors [6,19–22]. In some cases, they have even been found to be the only possible choice among the available second-order methodologies [19].

Interestingly, these second-order PLS/RBL methods can be applied to standard addition data, provided a recently discussed modification is incorporated, which consists of subtracting the test data matrix from the standard addition matrices, with quantitation proceeding by a classical external calibration procedure [11]. The purpose of the present work is to compare the performances of these new standard addition U-PLS/RBL and N-PLS/RBL algorithms with those based on PARAFAC, PARALIND and MCR-ALS analyses. Both simulated and experimental results indicate similar prediction abilities of the new models, suggesting that the methods herein described deserve to be added to the analyst resources for tacking complex samples with both a responsive background and analyte–background interactions.

2. Experimental

2.1. Equipment

Fluorescence excitation–emission matrices were measured with a PerkinElmer LS 55 luminescence spectrometer equipped with a xenon discharge lamp (equivalent to 20 kW for 8 μs duration) and connected to a PC microcomputer, using 1.00 cm quartz cells. Instrumental parameters were: excitation and emission slits, 5 nm, photomultiplier voltage 650, scan rate 1500 nm min^{-1}. For the experimental system 1 (analyte salicylate in serum in the presence of naproxen), excitation was scanned in the range 260–320 nm (each 0.5 nm), and emission in the range 330–494 nm (each 2 nm), producing matrices of size 121×83 data points. For the experimental system 2 (analyte danofloxacin in serum in the presence of salicylate), the corresponding ranges were 272–321 nm (each 0.5 nm) and 400–500 nm (each 2 nm) respectively, yielding matrices of size 99×51.

Data were saved in ASCII format, and transferred to a PC Sempron AMD microcomputer for subsequent manipulation by the multivariate programs.

2.2. Reagents

All chemicals used were of analytical reagent grade. For the experimental system 1, the following solutions were employed: NH_3 0.1 mol L^{-1}, prepared from commercial NH_3 (Merck, Darmstadt, Germany), stock solutions of sodium salicylate 1000 mg L^{-1} (Merck, Darmstadt, Germany) and of sodium naproxenate 1000 mg L^{-1} (Sigma, St. Louis, MO, USA), both prepared weighting the required amount of the corresponding compounds and dissolving it in doubly distilled water.

For the experimental system 2, a sodium acetate/acetic acid buffer (1.00 mol L^{-1}, pH 4.00) was used. Stock solutions of danofloxacin 100 mg L^{-1} (Riedel-de Haën, Sigma–Aldrich, Steinheim, Germany) in acetic acid 5×10^{-2} M, sodium salicylate 1000 mg L^{-1} (Merck, Darmstadt, Germany) were also prepared, weighting the required amount of the corresponding compound and dissolving it in doubly distilled water.

2.3. Procedure

For the determination of salicylate in serum in the presence of naproxen, appropriate aliquots of the corresponding stock solutions and 4.00 μL of serum were placed in a 2.00 mL volumetric flask and completion to the mark was achieved with NH_3 0.1 mol L^{-1}. The solution was placed in the measuring cell and the fluorescence excitation–emission matrix was measured. Three successive additions of analyte stock solution (1.4 μL) were then carried out, in such a way that the analyte concentrations were respectively increased by (1) 0.07, 0.14 and 0.21 mg L^{-1} for salicylate (concentration changes by dilution were considered negligible). After each addition, the samples were homogenized. The final concentration ranges for the analyzed drug was as follows (values refer to the measuring cell): salicylate, from 0.00 to 0.60 mg L^{-1}. We estimate the uncertainties in all these analyte concentrations to be of the order of ± 0.01 mg L^{-1}. The degree of serum dilution (1:500) was such that the maximum serum concentration of the studied drug was 300 mg L^{-1} for the salicylate, and ca. 100 mg L^{-1} for naproxen. All these concentration ranges are within the therapeutic values of the studied drugs in human serum.

For the determination of danofloxacin in serum in the presence of salicylate, appropriate aliquots of the corresponding stock solutions, 200 μL of acetic/acetate buffer and 13 μL of serum were placed in a 2.00 mL volumetric flask and completion to the mark was achieved with distilled water. The solution was placed in the cuvette and the matrix was measured. Three successive additions of analyte stock solution (1.0 μL) were then carried out, in such a way that the analyte concentrations were respectively increased by (1) 5.0, 10.0 and 15.0 ng L^{-1} for danofloxacin (concentration changes by dilution were considered negligible). After each addition, the samples were homogenized. The final concentration ranges for the analyzed drug was as follows (values refer to the measuring cell): danofloxacin, from 0.00 to 55.0 ng L^{-1}. We estimate the uncertainties in all these analyte concentrations to be of the order of ± 0.01 mg L^{-1}. The degree of serum dilution (1:150) was such that the maximum serum concentration of the studied drug was 5.00 mg L^{-1} for danofloxacin and ca. 200 mg L^{-1} for salicylate. All these concentration ranges are within the therapeutic values of the studied drugs in human serum.

3. Simulations

Data were simulated for multi-component mixtures having a single analyte and two potential interferents appearing in the test samples, and for the corresponding standard additions of pure analyte at known concentrations. Noiseless profiles for the analyte and for the potential interferents are shown in Fig. 1A and B in both data dimensions, leading to data matrices of size 50×40 data points. Using the analyte profiles shown in Fig. 1, 1000 test samples were created in which the analyte was considered to be present at concentrations which were taken at random from the range 0–1. These test samples did also contain both potential interferents, at con-