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A new strategy for solving matrix effect in multivariate calibration standard addition data using combination of H-point curve isolation and H-point standard addition methods

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ABSTRACT

This work presents a new and simple strategy for solving matrix effects using combination of H-point curve isolation method (HPCIM) and H-point standard addition method (HPSAM). The method uses spectrophotometric multivariate calibration data constructed by successive standard addition of an analyte into an unknown matrix. By successive standard addition of the analyte, the concentrations of remaining components (interferents) remain constant and therefore give constant cumulative spectrum for interferents in the unknown mixture. The proposed method firstly extracts such spectrum using H-point curve isolation method and then applies the obtained cumulative interferents spectrum for determination of analyte by H-point standard addition method. In order to evaluate the applicability of the method a simulated as well as several experimental data sets were tested. The method was then applied to the determination of paracetamol in pharmaceutical tablets and copper in urine samples and in a copper alloy.

1. Introduction

When a multivariate calibration model is used, it is usually required that there is (are) no new constituent(s) in the samples being analyzed. If there are new constituents, a recalibration including this new constituent will be necessary in order to be able to predict accurately, but this will be possible only if the interference(s) can be identified. In case of multiway data, it is possible to handle unknown interferences as a part of the calibration. Several methods for doing so have been developed; most notably partial least squares [1,2], rank annihilation method [3,4] and Kalman filtering [5,6], MCR-ALS [7,8], generalized rank annihilation method [3] PARAFAC [9] and more recently PARALIND [10] have been proposed to resolve this problem. All of these methods except partial least square and Kalman filtering require three-way data to resolution procedure and are based on second-order advantage.

Chemical analysis can be further complicated by matrix effects [12]. When the sensitivity of the response depends on the matrix composition, quantitative predictions based on pure standards may be affected by differences in the sensitivity of the response of the analyte in the presence and in the

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absence of chemical matrix of the sample. The standard addition method can be used to compensate such matrix effects. Standard addition can compensate non-spectral interferences and certain types of spectral interferences (e.g. non-analyte absorption), which enhance or depress the analytical signal of the analyte concentration.

In 1988, H-point standard addition method (HPSAM) was presented based on the principle of dual-wavelength spectrophotometry and the standard addition method [11–13]. The greatest advantage of HPSAM is that it can remove the presence of an interference and reagent blank [14]. In order to apply HPSAM to resolve mixtures, the interferent(s) species should be known. Two methods namely generalized H-point standard addition method (GHPSAM) [15–17] and H-point curve isolation method (HPCIM) [18] were proposed to solve this problem.

Curve resolution procedure for isolating the spectra of unknown interferent(s) from the sample spectrum in order to determine analyte based on the H-point standard addition method and *K*-ratio-HPSAM was proposed [19–21]. Safavi et al. developed combination of HPCIM and HPSAM methods for spectral deconvolution of solute–miceller systems [22]. Recently, Abdollahi and Zeinali used H-point curve isolation and H-point standard addition methods for spectrophotometric studies of complex formation equilibria [23].

In the present work we used combination of HPCIM and HPSAM for solving matrix effects and hence the determination of an analyte in the presence of unknown interferent(s). Only multivariate calibration spectrophotometric data constructed by standard addition has been used.

It should be noted that in many practical situations the endogenous and spiked analyte interact with the matrix in the same manner and also the matrix interaction is not a function of (spiked) analyte concentration. In order to cancel contribution of analyte spectrum on sample spectrum, and obtain cumulative spectrum of interferents, usually pure analyte spectrum is used. But it is well known that the absorption properties of a matrix surrounding an analyte influence the absorption spectrum of analyte [24] e.g. cause wavelength shifting in the spectrum of analyte. Therefore, application of pure analyte spectrum for obtaining cumulative spectrum of interferents can cause significant errors in the predicted concentration values. Hence, for removing this source of error in the results the matrix effect on the absorption spectrum of analyte (e.g. shifting in wavelength) should be considered.

In order to compensate the matrix effects on absorption properties of analyte (wavelength shifting), the exact spectrum of analyte could be obtained by standard addition of analyte into the sample. The spectrum of unknown sample before and after standard addition was recorded. The exact analyte spectrum was then obtained by subtraction (from a few repeated experiments) and can then be used successfully to perform HPCIM. Finally, the created cumulative spectrum of interferent(s) using HPCIM can be applied for the determination of analyte in the presence of unknown interferents using HPSAM. In order to evaluate the applicability of the proposed method, several model data sets as well as an experimental data set were tested. Also, the results of this method were compared with those obtained by using the pure analyte spectrum instead. The results from experimental data set relating to the spectrophotometric determination of ascorbic acid (ASC), acetylsalicylic acid (ASA) and paracetamol (PAR) in synthetic mixtures were presented. The method was successfully applied to the determination of paracetamol in pharmaceutical tablets and copper in urine sample and in a copper alloy.

2. Methods

2.1. HPCIM for extracting the spectra of interferents in an unknown mixture

H-Point curve isolation method can be used for obtaining the pure interferent spectrum, which is the sum of interferents spectra. We will use the term interferent, instead of the sum of interferents for simplicity. Consider that the total absorbance of solution is defined by the following equation:

$$S_i = A_i + I_i \tag{1}$$

where subscript *i* refers to wavelength ($i = 1, 2, 3, \ldots, p$) and S, A and *I* are sample absorbance, analyte absorbance and interferent absorbance, respectively (*S*, *A* and *I* are $p \times n$ matrices). By standard addition of known amounts of analyte into sample solution, the new values will be obtained:

$$S_{i,k} = A_i + I_i + A_{i,k} \tag{2}$$

$$\vdots$$

$$S_{i,l} = A_i + I_i + A_{i,l} \tag{3}$$

$$S_{i,n} = A_i + I_i + A_{i,n} \tag{4}$$

where, because of standard addition of analyte into sample solution, $A_{i,k}$, $A_{i,l}$ and $A_{i,n}$ are added values to initial absorbance value. Hence, we have an $p \times n$ matrix *S* which contains all of standard addition spectra (S_i). Subtracting Eqs. (2)–(4) from Eq. (1) gives the analyte spectra (real spectra of analyte in the solution, S_{me}).

The average vector of these values, results as analyte spectrum, as below:

$$A_i = \frac{\sum_{m=k}^{n} (S_{me,i,k} - S_i)}{n} \tag{5}$$

A_i is the real analyte spectrum in the solution. As A_i is obtained by standard addition method, matrix effects occurred on it and therefore it may be different from spectrum of pure analyte in pure solvent (without matrix effects).

The reference wavelength is selected over the wavelength range of the spectrum created by Eq. (5). Then the $K_{i,ref}$ is defined as:

$$K_{i,ref} = \frac{A_{A,ref}}{A_i} \tag{6}$$

As Eq. (6) shows $K_{i,ref}$ is a vector that is obtained by dividing the absorbance at reference wavelength($A_{A,ref}$) to the absorbance at other wavelengths.

If we use the analyte spectrum and select reference wavelength from this spectrum, the analyte contribution to the