Second-order advantage obtained from standard addition first-order instrumental data and multivariate curve resolution - alternating least-squares. Calculation of the feasible bands of results.

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Abstract

In order to achieve the second-order advantage, two-way data per sample are usually required, e.g., kinetic spectrophotometric data. In this study, instead of monitoring the time evolution of spectra (collecting kinetic-spectrophotometric data) replicate spectra are used to build a spectrophotometric data matrix which is rank deficient. Augmentation of these data with standard addition data [or standard sample(s)] will break the rank deficiency. making the quantification of the analyte of interest possible. These data correspond to the kinetics of all sample constituents being identical when employing second-order kinetic-spectroscopic measurements. The MCR-ALS algorithm has been applied for the resolution and quantitation of the analyte in both simulated and experimental data sets. In order to evaluate the rotational ambiguity in the retrieved solutions, the algorithm MCR-BANDS has been employed. The reliability of the quantitative results significantly depends on the amount of spectral overlap in the spectral region of occurrence of the compound of interest and the remaining constituents. The ability of the proposed algorithm to quantitate the analyte is illustrated both with simulated data systems as well as with binary experimental mixtures.

Keywords: Second-order advantage; First-order data; Standard addition; MCR-ALS; Feasible solutions

Introduction

The problem of the appearance of measurement interferences is common in chemical analysis. In most cases, analysts have to deal with natural samples which are far from simplicity, such as biological matrices, pharmaceuticals and environmental specimens. To cope with these issues, many sophisticated instrumentations which provide multidimensional (multi-way) data have been developed. Multi-way data are second-order (matrices), third-order (three-mode arrays), etc. for a single sample, which can be organized in a three- or four-way array , respectively, for a group of samples. One data mode refers to the compositional variation of the system and the other ones are related to the variation in the collected responses in the instrumental modes. When the number of data modes increases, different data-processing and mathematical algorithms are required for the convenient study of this body of information [1]. A calibration model obtained from multi-way measurements allows one not only to mark new samples containing components which do not take part in the calibration data set, but also to quantitate the analyte of interest without knowledge of the interfering chemical components that may be present in complex chemical matrices [2-7], a property known as the second-order advantage [8]. However, univariate calibration, which employs a single data per sample or a vector data for a sample set, is not able to detect a sample containing interference components. This would be possible with first-order calibration (vector data per sample and two-way data for a sample set), which can distinguish such a sample as an outlier, because it cannot be adequately modeled with a given calibration data set, a concept which is the inherent advantage of the first-order calibration methods [8]. This means that first-order calibration may compensate for interferences only if they are included in the calibration set. In other words, the standards employed to construct a first-order calibration model are themselves real samples. This explains why a large number of

samples is needed in first-order calibration in comparison with second-order calibration, which can be performed using a few standards (in an extreme case, with only a single calibration sample). On the other hand, second-order data are provided by advanced hyphenated instrumentations such as two-dimensional NMR, capillary electrophoresis or chromatographic systems coupled to mass spectroscopy or diode-array detectors, whereas first-order instrumental data can be measured using fairly simple equipments employing spectroscopic, chromatographic and voltammetric tools.

Analyte quantitation from first-order multivariate data in the presence of unexpected components (second-order advantage) is a very recent subject and to the best of our knowledge only a few reports exist in the literature [9-13]. It has been shown that the correlation-constrained MCR-ALS version facilitates the analyte quantitation in the presence of unexpected interferences using first-order data [9-13]. MCR-ALS with the proposed correlation constraint has been applied to resolution and quantification of mixtures of metal ions with overlapping voltammetric peaks [9], determination of the major components in complex mixtures using first-order spectrophotometric data [10,11], quantification of industrial mixtures from the vinyl acetate monomer process using near infrared spectroscopic data and a quantitative self modeling curve resolution (SMCR) methodology, and urinary quantification of nicotine in the presence of metabolite cotinine and the alkaloid anabasine using surface enhanced Raman spectroscopy [13]. In this latter case, standard addition in combination with the MCR–ALS method has been employed to deal with matrix effects and non-calibrated interferences in the quantification of nicotine present in human urine.

In the presence of analyte-background interactions, chemical analysis can be further complicated by matrix effects [14]. When the sensitivity of the calibration depends on the matrix composition, quantitative predictions using pure standards may be expected to be biased. This problem can only be solved by the standard addition method.

A proper calibration model should reflect the complexity of the matrix composition, otherwise poor predictions may result when using calibration curves obtained from pure standards [15].

Kinetic-spectroscopic second-order data have been employed recently for analyte quantitation in the presence of uncalibrated interferences, achieving the second-order advantage [16]. In some particular kinetic-spectral experiments, the kinetics of all sample constituents are identical, so the selectivity in the time direction is zero. In this case, the second-order advantage can be achieved, however, by augmenting the data matrices in the direction of time, creating selectivity in the augmented direction and using extended MCR-ALS with correspondence (also called sample selectivity) restrictions [16].

In the present study, which was inspired by the Ref. 16, we aimed to avoid the time-consuming kinetic experiments and gain the second-order advantage using only spectra (first-order data) and its replicates.

Usually, in order to achieve the secondorder advantage two-way data, e.g., kinetic spectrophotometric data are required. In this study, instead of monitoring the spectra versus time (collecting kinetic-spectrophotometric data) spectral replicates are used to build a replicatedspectrophotometric data matrix. These data are rank deficient. Augmentation of these data with standard addition data [or standard sample(s)] will break the rank deficiency problem and make the quantification of the analyte of interest possible. These data are the same as if the kinetics of all sample constituents were identical employing the second-order kinetic-spectroscopic measurements.

In this work it will be shown that it is not necessary, in principle, to perform kinetic experiments, and that by using only spectra (first-order data), creating a data matrix (not an augmented data matrix) with the spectra of the calibration samples and the test sample containing interferences quantitation of the analyte is possible, achieving the second-order advantage. This activity is relevant, because: (1) the second-order advantage obtained from first-order data is a very recent subject, with only few published

works in the entire literature, so researchers are is unaware of this possibility (indeed the very expression "second-order advantage with first-order data" appears self-contradictory), and (2) experimental time and effort may be saved by avoiding the kinetic experiments and using only spectra.

In order to quantitate the analyte of interest using these data, augmentation with one or a few external standard test samples or standard addition samples are required. In this work we used the standard addition method, which allows to overcome matrix effects . This means that when each sample arrives at the laboratory, the experimentalist has to perform several measurements and experimental sample preparation activities. Although with external calibration, calibration only needs to be performed once, the standard addition method is unavoidable when it is necessary to overcome matrix effects .

Conventional standard addition in conjunction with the MCR-ALS approach has been employed to quantitate the analyte of interest in the presence of unexpected interference components. Avoiding tedious procedures of complex sample pretreatments, minimizing analyte loss and increasing precision in the results are the advantages provided by the standard addition method. Finally, in order to evaluate the extent of rotational ambiguity in the retrieved solutions, the algorithm MCR-BANDS has been applied. The calibration curves were built, similarly to the traditional standard addition method, using the recovered concentration profiles as a function of standard concentrations. In order to demonstrate the applicability of the proposed method, several simulated examples and a number of synthetic binary mixtures were analyzed using the proposed algorithm.

1. Experimental procedure

1.1. Reagents

All experiments were performed with analytical reagent grade chemicals. Malachite green (MG), crystal violet (CV), paracetamol (PC), ibuprofen (IB), HCl and methanol were obtained from Merck (Darmstadt, Germany) and used without any purification. To perform binary mixture analysis, individual standard solutions of MG and CV (20 µg mL^{-1}) were prepared by dissolving appropriate amounts in distilled water. Also, standard solutions of 100 µg mL^{-1} each of PC and IB were prepared by dissolving the compounds in a 0.1 mol L^{-1} HCl-methanol (1:3) mixture. Different aliquots of the standard solutions of MG and CV, and also of PC and IB within the linear calibration range were transferred into 10 mL voltammetric flasks and completed to the volume with distilled water and a 0.1 mol L^{-1} HCl-methanol (1:3) mixture, respectively.

1.2. Apparatus

A model $T80^{+}$ UV-Vis double-beam spectrophotometer with a PG mode (China) with 1-cm quartz cells (volume 5 mL) was employed for spectrophotometric measurements.

2. Theoretical background and algorithm

Multivariate curve resolution techniques are powerful approaches promoted to tackle many chemical problems that could not be solved otherwise. The common purpose of all multivariate resolution methods is to transform the raw experimental measurements

into useful information. To do so, neither the number nor the nature of the pure components in a studied analytical system need to be known in advance. Any information available about the system may be used, but it is not strictly required [17-21]. MCR-ALS uses an alternative approach to iteratively find the concentration profiles and instrumental responses. In comparison with other multivariate methods such as principle component analysis (PCA) and partial least-squares (PLS), MCR-ALS is intended for the simultaneous recovery of qualitative information about the analyte and possible unknown interferences. Bilinear decomposition of the initial mixture data matrix **D** into the product of concentration profiles (**C**) and pure spectra ($\mathbf{S}^T$) according to Beer's law can be expressed as:

$$D = C S^T + E = \sum_{i=1}^{N} c_i s_i^T + E = D^* + E \qquad (1)$$

where **E** is the residual data matrix not explained by the model, which should ideally be close to the experimental error, and $\mathbf{D}^*$ is the noiseless approximation to the data matrix. The iterative ALS optimization procedure to find the matrices of concentration profiles and pure spectra, which optimally fits the experimental data matrix **D**, starts with initial estimates of either **C** or $\mathbf{S}^T$ profiles. During the optimization, several constraints may be applied depending on the characteristics of the system under study [17,22-24]. Initial estimates can be obtained using chemometric methods such as Evolving Factor Analysis [25], SIMPLISMA [26] or orthogonal projection approach (OPA) [27] to select purest variables that are most dissimilar to each other. Decomposition of the **D** matrix is accomplished by the iterative optimization of equations (2) and (3) under appropriately chosen constraints:

$$\min_{S^T} \left\| D_{PCA} - \hat{C}\,\hat{S}^T \right\| \qquad (2)$$

$$\min_{C} \left\| D_{PCA} - \hat{C}\,\hat{S}^{T} \right\| \qquad (3)$$

This means that at each iterative cycle, the **C** and $\mathbf{S}^{\mathbf{T}}$ matrices that minimize the error are found. Calculations continue until convergence is fulfilled.

It is well known that the main source of uncertainty associated with the solutions obtained by MCR methods (like for any other factor analysis-based methods) are the ambiguities of the recovered profiles. When ambiguity exists, a band of feasible solutions instead of a unique profile will be obtained for a compound. If no restrictions are imposed to Eq. (1), an infinite number of possible solutions will fit to the equation from a mathematical standpoint; however, they will be completely different from a physical standpoint. Ambiguities (intensity and rotational) can be mathematically represented by the following equation:

$$D^{*} = C_{old}\, S_{old}^{T} = (C_{old} T^{-1})\,(T S_{old}^{T}) = C_{new}\, S_{new}^{T} \qquad (4)$$

where **T** is any non-singular invertible matrix which is responsible for rotation in Eq. (4). Imposing appropriate constraints can considerably reduce the number of possible solutions or the number of possible **T** matrices.

Since several different degrees of overlap will be applied to the simulated sytems in this paper, to calculate the degree of spectral overlap between the compound of interest and interference the following expression was used:

$$S_{12} = \frac{\left\| \mathbf{s}_1^{T}\, \mathbf{s}_2 \right\|}{\left\| \mathbf{s}_1 \right\| \left\| \mathbf{s}_2 \right\|} \qquad (5)$$

where $\mathbf{s}_1$ and $\mathbf{s}_2$ are the spectra related to the analyte and interference, respectively.

In order to evaluate the accuracy of the proposed method, the prediction error of analyte concentrations in the mixtures was calculated as the relative standard error (R.S.E.) of the prediction concentrations:

$$\text{R.S.E. (\%)} = \left(\frac{\sum_{j=1}^{N}(\hat{C}_j - C_j)^2}{\sum_{j=1}^{N}(C_j)^2}\right)^{1/2} \times 100 \qquad (6)$$

where N is the number of samples, C_j the real concentration of the component in the jth mixture and $\hat{C}_j$ is the estimated concentration.

Relative error of prediction (REP) for quantitative measurements in analyte concentrations was calculated according the following equation:

$$\text{REP (\%)} = \frac{(C_{found} - C_{true})}{C_{true}} \times 100 \qquad (7)$$

where C_{true} is considered the known concentration value for analyte and C_{found} is the prediction concentration.

2.1. Algorithm of the proposed method

A graphical description of the proposed algorithm is presented in Fig. 1, and further expanded below.

i) Construction of a data matrix

Absorbance for a series of samples prepared according to the standard addition method was measured within a given wavelength range and a data vector (spectrum) was

obtained (first-order data). Each of these vectors provides the spectrum of a mixed sample. Then, the row data vector for every standard added sample was arranged repeatedly below each other (arbitrarily, 5 replications per any sample) and a two-way data matrix was created. This kind of data arrangement may be considered as a second-order kinetic-spectroscopic data matrix where the kinetic mode (row direction) represents an invariant reaction rate during the time. A particular case occurs when the kinetics of all sample constituents are identical, and as a consequence there is no selectivity in the time mode.

ii) Column-wise augmentation of the standard addition data matrices

By successive standard addition of an analyte, the concentrations of the remaining components (interferences) remain constant and introduce linear dependency between interference concentrations in the samples. This theoretically leads to rank deficiency. A data matrix is rank-deficient when the number of significant contributions to the data variance (mathematical rank) is lower than the real number of chemical components existed in the system (chemical rank). It is possible to break the linear dependency by augmenting the data matrices in the rank deficient direction. This was carried out by organizing the individual data matrices corresponding to each standard added sample under the data vector for an unknown sample (column-wise augmentation). Then, the number of components was simply estimated by singular value decomposition of augmented matrices, which implies the presence of two components including the analyte of interest and the interference(s).

iii) MCR-ALS analysis

The iterative ALS optimization starts with the initial estimates of either **C** or $\mathbf{S}^{\mathbf{T}}$. In general, the use of chemically meaningful estimates is an essential factor that can help not only to rapid convergence of the results but also to decrease the ambiguity of the solutions. In our work, to provide a suitable initial estimate, pure components spectra were employed. The purest spectrum of the analyte was obtained using pure standard. In order to obtain the purest spectrum of the interferences, the pure analyte spectrum was subtracted from that of the mixed sample (the first column of the standard added data matrix). If the contributions of the analyte of interest, considered being present in the real sample, completely removed from the total signal for the mixture, the remaining will be mainly corresponded to the interference(s). It is noteworthy to mention that, when an initial estimation from SIMPLISMA was used to initialize the MCR-ALS algorithm, provided the analyte was present in the primary real sample, incorrect results for the analyte concentration (zero concentration) were obtained. This may be explained by the fact that SIMPLISMA works selecting in a sequential way the variables that have less information in common with the previously selected ones [26,28]. MCR-ALS was implemented on the augmented data matrix comprising an unknown sample and those of the standard addition:

$$D_{aug} = C_{aug} S^T + E_{aug} \qquad (8)$$

where the augmented data matrix (D_{aug}) is of size $I \times J$ (I is the number of standard added samples repeated X times next to each other and J is the number of wavelengths), the columns indicate the concentration variations in the standard added samples and the rows involve the pure component absorption spectra. Bilinear decomposition of the data matrix D_{aug} into the matrix of concentration profiles C_{aug} (size $I \times N$) and pure spectra S^T (size $N \times J$), where N represents the number of components, achieved according to the

MCR-ALS approach. It was assumed that the column vector space (sample) would be unshared, but the row space (spectra) would be common. According to the nature and structure of the data, non-negativity for both concentration and spectral profiles and equality for the analyte spectrum were imposed as suitable constraints. The latter constraint was chosen since one typically has prior information about the pure component signals of the components of interest while that of the interferences display intrinsic variability in unknown samples. The number of iterative cycles was set in a way that convergence was fulfilled in each case.

iv) Evaluation of rotational ambiguity

After the MCR-ALS decomposition, the extent of rotational ambiguity remaining in the retrieved profiles was investigated. Concentration and spectral profiles as the initial input values were submitted to the MCR-BANDS program. During the optimization, the constraints implemented in the previous MCR-ALS procedure were selected. Optimization was carried out and maximum and minimum band boundaries of concentration and spectral profiles were obtained. The differences between the maximum and minimum component relative contribution optimization function ($\mathbf{f_n^{max} - f_n^{min}}$) were calculated as a criterion of the rotational ambiguity for the analyte concentration profiles [29,30].

v) Quantitative analysis

The calibration curves were built, similarly to the conventional standard addition method. The relative concentration values in matrix **C** to each addition were plotted *versus* the standard concentration. Extrapolation of the calibration curve, i.e., the

intercept of the calibration line with the abscissa, gave the concentration of analyte in the sample.

Figure 1

3. Data and modeling

3.1. Simulated data

In order to evaluate the performance of the proposed algorithm, it was employed to analyze simulated data systems. Four data sets with different degrees of spectral overlap were prepared. The spectrum for the analyte was intentionally constructed so that the degrees of spectral overlap gradually increased from data set 1 to data set 4, as presented in Fig. 2 (A-D). Spectral overlap for the simulated data sets 1, 2, 3 and 4 were calculated 0.23, 0.61, 0.87 and 0.76, respectively, using Eq. (5). For every sample, several successive additions of the analyte were done, while concentrations of the other two components (interferences) were kept constant in all the samples according to the standard addition model. The data sets were generated from noiseless UV-vis spectral and concentration profiles. To built up a data matrix, the spectrum (row vcector) corresponding to each standard added sample was repeated five times (this number is optional) below each other. Simulated spectral profiles, concentration profiles and the constructed data matrix are shown in Fig. 3 (A), (B) and (C), respectively. Each sample contained two chemical components, and one was considered the analyte of interest. The constructed data matrix was used for subsequent calculations.

Figure 2

Figure 3

3.2. Binary synthetic mixture analysis

To demonstrate the analytical applicability of the proposed method, binary mixtures of MG and CV, which were assumed alternatively as the analyte and the unknown interference, and also of PC in the presence of IB as an interference were created. The absorption spectra of the mixture samples were recorded within the wavelength range of 350-700 nm for MG and CV, and 200-310 nm for PC and IB with the increment of 1 nm against the appropriate solvent blank. The data wer processed as the simulated data sets, with the spectrum corresponding to each standard added sample repeated five times below each other.

4.3. Software

All simulations and initial estimates prior to MCR-ALS algorithm were carried out using MATLAB (version 7.10.0 R2010a) computer environment. Data processing was done in Microsoft Excel for Windows. MCR-ALS was performed with the graphical user-friendly interface provided by R. Tauler [31]. Calculations related to rotational ambiguities were implemented using MCR-BANDS graphical user interface [29]. Programs were freely downloaded from the MCR-ALS webpage [32].

4. Results and discussion

4.1. Simulated data

As illustrated in the previous section, four data sets with different degrees of spectral overlap were simulated and analyzed. For data set 1, eight successive additions of the analyte were made and a data matrix of size 40 (5 replications per any sample × 8 standard addition mode) × 201 (number of wavelengths) was obtained. MCR-ALS decomposition of the data matrix was done using the initial estimate explained in the third step of the proposed algorithm. A set of solutions **C** (40 × 2) and $\mathbf{S^T}$ (2 × 201) were obtained and used as initial inputs for the MCR-BANDS program. In both procedures, non-negativity constraints for concentration and spectral profiles, and equality constraint for the analyte spectrum were imposed. In each case, one of the standard added data matrices was removed (five out of fifty) and the new data matrix was analyzed. Quantitative analysis was performed for every sample as illustrated in the fifth step of the proposed algorithm. In Table 1 (upper part), the obtained results for data set 1 are given.

Table 1

MCR-BANDS results for three samples with the simulated concentrations of 0, 0.3 and 0.6 (in arbitrary units) for the analyte and constant concentration of 1 for both interferences are shown in Fig. 4. Maximum and minimum band boundaries for the analyte concentration profiles imply the range of feasible solutions ($\mathbf{f_n^{max}}$ and $\mathbf{f_n^{min}}$) where the maximum band boundaries (continuous blue line) coincide with the red dotted line of the initial profiles. As can be seen from Fig.4, with increasing the analyte concentration, the range of feasible concentration profiles also increases, while the lower concentration level (minimum band boundary) remains invariant and equals to zero concentration. Therefore, the upper level (maximum band boundary) defines the analyte concentration. Extrapolation of the standard addition calibration curve for the upper boundary determines the analyte concentration in each sample. Excellent recoveries were obtained which indicate that the results are accurate.

Figure 4

Likewise, other three data sets were built up and analyzed with MCR-ALS and MCR-BANDS programs. Table 1 (lower part) and Table 2 collect the results for all data sets 2, 3 and 4, respectively. In each case, relative standard error (R.S.E.), quantitation error and also the differences between the maximum and minimum optimization function values are calculated. As was the case for data set 1, the lower concentration level was invariant and equal to zero concentration and, then, extrapolation of the standard addition calibration curve for the upper level ascertained the analyte concentrations in samples.

Table 2

From the obtained results for the analyte quantitation in four simulated data systems it can be concluded that with increasing the degrees of spectral overlap between the analyte and interferences, the value of relative error in the predicted concentrations for the upper boundary increases, whereas for the lower one it is always -100%. For data set 1, the proposed method yields excellent recoveries. This may be due to the fact that the degree of spectral overlap between the analyte and interferences is small (0.23 as calculated from the Eq. 5). In the case of data sets 2 and 3, with degrees of overlap 0.61 and 0.87, respectively, satisfactory quantitation results are also obtained. However, analysis of data set 4 led to apparently worse recoveries. In fact, the the latter data set provides the opportunity to test an extreme spectral overlap effect, where the spectrum for the compound of interest is completely embedded in the sample background and there is no selective region for it. This may be ascribed to the fact that the analyte spectrum becomes mixed up with those of the interferences and the analyte contribution is not

totally removed from the rest of the mixture. As a consequence, the proposed method overestimates the concentration of the analyte.

4.2. Experimental example

In order to illustrate the proposed algorithm with experimental examples, quantitation of MG and CV, which were assumed alternately as an analyte and unknown interference, and also PC in the presence of IB as interference in binary mixtures were performed.

4.2.1. Malachite green and crystal violet determination

Beer's law was obeyed in the concentration range 0.2 – 1.5 μg mL^{-1} for MG and CV using standard solution. As Fig. 5 shows, the absorption spectra of MG and CV overlapped in the wavelength region of 450-650 nm. The degree of spectral overlap was calculated 0.53. Quantitation analysis of this binary system was carried out through nine successive additions of the analyte, while the concentration of CV and MG, assumed as interference components, respectively, were fixed at 1 μg mL^{-1}in all samples. A two-way data matrix of size 45 × 351 (5 replications per any sample × 9 standard addition mode and 351 wavelengths) was constructed. The number of components, estimated using singular value decomposition, was two, as expected. Initial estimation obtained from subtraction of the pure analyte spectrum from the first column of the standard added data matrix was used. Under the enforcement of non-negativity constraints for concentration and spectral profiles and equality constraint for analyte spectrum, MCR-ALS decomposition was implemented. MCR-BANDS retrieved profiles for the determination

of MG which are shown in Figure 6. As for the simulated data, one of the standard added data matrices was left out in each case, and the new data matrix was analyzed. It should be noted that the lower concentration level was zero and the upper level determined the analyte concentration in samples. Extrapolation of the standard addition calibration curve for the upper level specified the analyte concentration in each sample. Table 3 gives the recovery and relative standard error of prediction for the determination of MG and CV. Comparing the prediction performance of the proposed method for both examples indicates that good recoveries are obtained for MG, which is in excellent agreement with the actual content. This could have been expected, because the extent of the selective spectral region for MG is wider compared to that of the CV.

Figure 5

Figure 6

Table 3

4.2.2. Paracetamol determination

Beer's law was obeyed in the concentration range of 0.6-11 μg mL^{-1} for PC in 0.1 mol L^{-1} HCl-methanol (1:3) mixture. As Fig. 7 shows, the absorption spectra of PC and IB overlapped in the wavelength region of 200-240 nm. In this case, the degree of spectral overlap is 0.61. Quantitation analysis of PC was done by five successive addition of the analyte, while the concentration of IB, as interference, was fixed at 5 μg mL^{-1}in all samples. A two-way data matrix of size 35 × 111 (5 replications per any sample × 7 standard addition mode and 111 wavelengths) was constructed. The data matrix was analyzed as before, and good quantification results were obtained, which are presented in

Table 4. It should be noted that the differences observed in standard error of prediction values for both experimental systems were explained by the lower degree of spectral overlap between MG and CV compared to PC and IB.

Figure 7

Table 4

5. Conclusion

The main objective of this study was to investigate the possibility of achieving the second-order advantage from first-order spectrophotometric data when the kinetics of all sample constituents are identical. Standard addition in combination with the MCR–ALS method was applied as an alternative to circumvent the matrix effect and quantitation of the analyte in the presence of unknown interference components. It has been demonstrated that using second-order instrumental data in such particular cases does not offer any further advantage. Despite a band boundary of feasible solutions for analyte concentration profiles recovered from MCR-ALS, the maximum band boundary determines the analyte concentrations, provided the minimum one is always invariant and equals to zero concentration. It may be noted that successful analyte quantitation in the presence of interference components (second-order advantage) based on the proposed method, depends significantly on the degree of selectivity in the columns of the standard added data matrix. The degree of selectivity, in turn, depends on the amount of overlap in the region of occurrence for the compound of interest with the rest of constituents. With increasing degrees of spectral overlap between the analyte and interferences, the uncertainty for the maximum band boundary also increases. This study showed that the

proposed algorithm succeeded in the analyte quantitation in interfering systems, where there is at least a minimum selective spectral region for the analyte.

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