

Second-Order Standard Addition Method Based on Alternating Trilinear Decomposition

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In this study, a second-order standard addition method based on alternating trilinear decomposition (ATLD-SOSAM) was developed. It was applied to second-order HPLC-DAD data and compared to methods employing direct trilinear decomposition (DTLD) and PARAFAC. The results show that ATLD-SOSAM is slightly superior to both DTLD-SOSAM and PARAFAC-SOSAM.

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The standard addition method (SAM) as a means of overcoming matrix or background effects is usually applied to zeroth-order instrumentation (instruments that return only a scalar quantity per sample analyzed).¹ For a successful calibration, SAM requires two assumptions be fulfilled: (1) there is a linear change in the instrument response with increasing analyte concentration; (2) for zero concentration of an analyte the instrument response must be zero. A plot of the instrument response (ordinate) against the amount of standard added (abscissa) estimates the analyte concentration in the sample by fitting a line to the data and finding the intercept of the line on the abscissa.

The generalized standard addition method (GSAM)^{2,3} is an extension of SAM to first-order instruments (instruments that return a vector of data per sample, *e.g.*, a diode array spectrometer). GSAM requires that the response profiles of the sought-for analyte be different from each other and any spectroscopically interfering species. This relaxes the constraint that the analytical method must be fully selective to the analyte of interest. However, a reliable analysis requires the absence of any unaccountable source of instrumental signal beyond the calibration framework. That is, in the absence of all species included in the calibration model, the instrument response is zero at all channels. Therefore, Booksh *et al.* have extended SAM to second-order instrumentation (instruments that return a matrix of data per sample, *e.g.*, HPLC-DAD).⁴ As pointed out in ref. 5, ideally, a second-order calibration can be performed in the presence of interfering species unaccounted by the calibration model. However, if the interfering species change the instrument response of the analyte (in scale or shape), standard additions must be employed to ensure an accurate analyte concentration estimation.⁴ Booksh *et al.* presented a second-order standard addition method (SOSAM) using direct trilinear decomposition (DTLD). The present authors have developed a method called the alternating trilinear decomposition (ATLD).⁶ In this study, the SOSAM based on the ATLD algorithm was applied to second-order HPLC-DAD data and compared with methods employing DTLD and PARAFAC.

Theory

Second order data

Second-order tensor data are usually generated from hyphenated instruments, such as HPLC-DAD or an excitation-emission fluorescence spectroscope. They should obey the following trilinear model (see Fig. 1):

$$x_{ijk} = \sum_{n=1}^N a_{in} b_{jn} c_{kn} + e_{ijk} \quad (1)$$

($i=1, \dots, I; j=1, \dots, J; k=1, \dots, K$),

where N denotes the number of factors, or the total number of existing species, including sought-for component(s) as well as unexpected interferant(s) usually accounted as a part of the analytical background; x_{ijk} is the element (i, j, k) of the three-way response array \mathbf{X} of size $I \times J \times K$; a_{in} is the element (i, n) of an $I \times N$ matrix \mathbf{A} of relative concentrations of N species in I samples after the ($i-1$)th standard is added; b_{jn} is the element (j, n) of a $J \times N$ matrix \mathbf{B} of relative sensitivity coefficients of N species at J wavelengths; c_{kn} is the element (k, n) of a $K \times N$ matrix \mathbf{C} of elution profiles of N species; and e_{ijk} is the i, j, k th residual element of an $I \times J \times K$ three-way residual array \mathbf{E} . In subsequent discussions the matrices \mathbf{A} , \mathbf{B} , \mathbf{C} will be called the relative concentration matrix, the relative spectrum matrix, and the relative chromatogram matrix, respectively.

Matrix effects occur when two or more sample components, particularly when an analyte and an interferant interact with each other, such that the analytical signal of the analyte depends on the concentration of the interferant in the sample. These interactions can cause changes in the sensitivity of the hyphenated instrument or changes in the intrinsic instrumental profiles. Since it is often impractical to quantitatively isolate the analyte from all other compounds in the sample, one method to solve the problem of matrix effects is to keep the interferant concentration constant in all calibration and unknown samples. This can be accomplished by the method of standard additions in zeroth-, first- and second-order analyses. In particular, SOSAM can be used to overcome the problem of matrix effects and simultaneously determinate several components even in the presence of unexpected interferant(s).

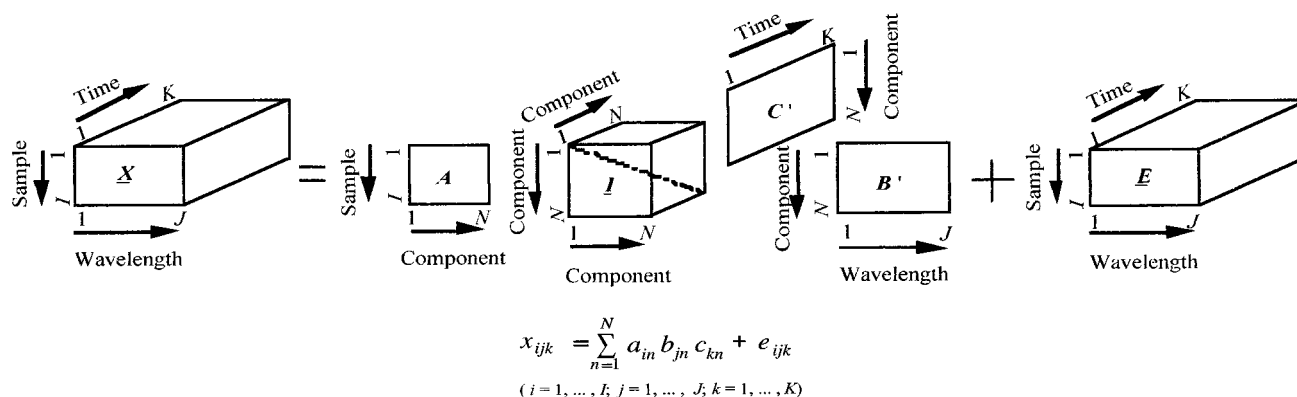
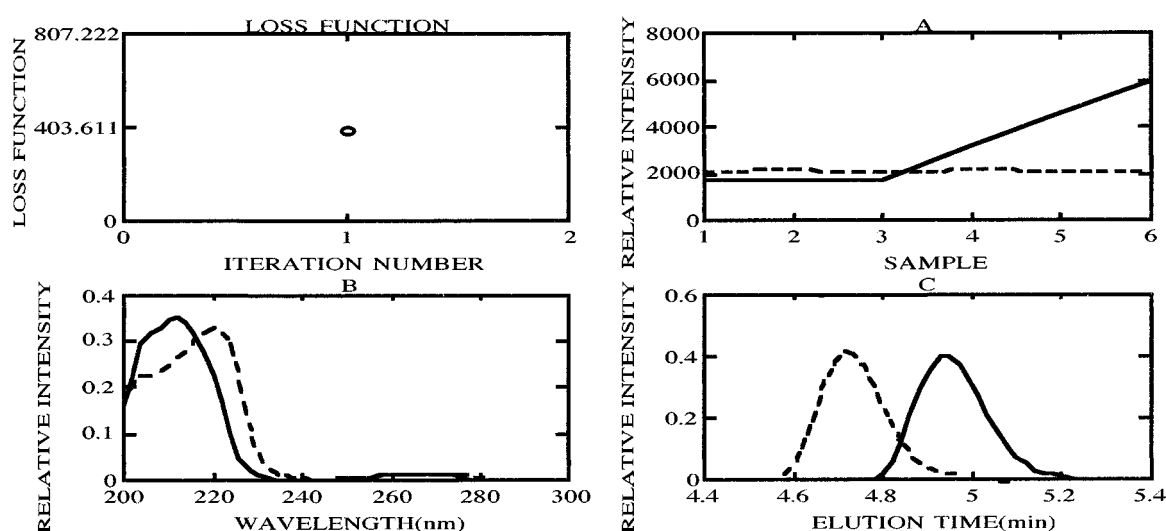


Fig. 1 Trilinear model for the second-order standard addition method.

Fig. 2 Results obtained for HPLC-DAD experimental data using the 2-factor DTLTD-SOSAM method. The average predicted concentration of *o*-chlorotoluene (---) in samples #1 to #3 was 26.37 ± 0.3 mg/n and their average recovery was $117.7 \pm 1.3\%$.

The second-order standard addition method

SOSAM comprises three major steps: (1) decomposition of the three-way response data array X with an appropriate number of factors; (2) location of the column of N relative concentration estimates corresponding to the analyte of interest; (3) finding the original relative concentration of each component of interest by regression from the corresponding added standard concentrations.

(1) Decomposition of the three-way response data array X

Decomposition of the three-way data arrays has been reviewed extensively.⁷ DTLTD has been used with SOSAM to provide a non-iterative eigenproblem-based solution for the decomposition of X . Theoretically, PARAFAC can also be used to decompose a three-way data array. In this study, ATLD, similar to DTLTD, decomposes X into the product of three matrices (A , B and C) with a residual E . All of these three matrices have N columns.

(2) Location of the corresponding column of the sought-for analyte

Based on the similarities in obtaining the (relative) spectra and the (relative) time profiles to those of the sought-for analyte, the column corresponding to the sought-for analyte may be located.

(3) Regression

The regression of a_n against the standard-addition δ in SOSAM is identical to that in zeroth-order standard addition. The regression is done by using the least-squares model

$$a_n = \beta + \alpha\delta \quad (2)$$

where α and β are the slope and intercept of the least-squares fit, respectively. The estimated analyte concentration, a^* , in the original sample is

$$a^* = -\beta/\alpha \quad (3)$$

Experimental

A high performance liquid chromatography (HPLC) system, comprising an SSC-3110T pump and an SSC-3100C2 microprocessor controlling unit (Senshu Scientific Co., Ltd., Japan), with an L-column ODS (4.6 mm \times 150 mm, Chemical Inspection and Testing Institute, Japan) and a diode array detector (Shimadzu SPD-M10AV) was used for the quantitative analysis of *o*-chlorotoluene in the presence of *p*-chlorotoluene.

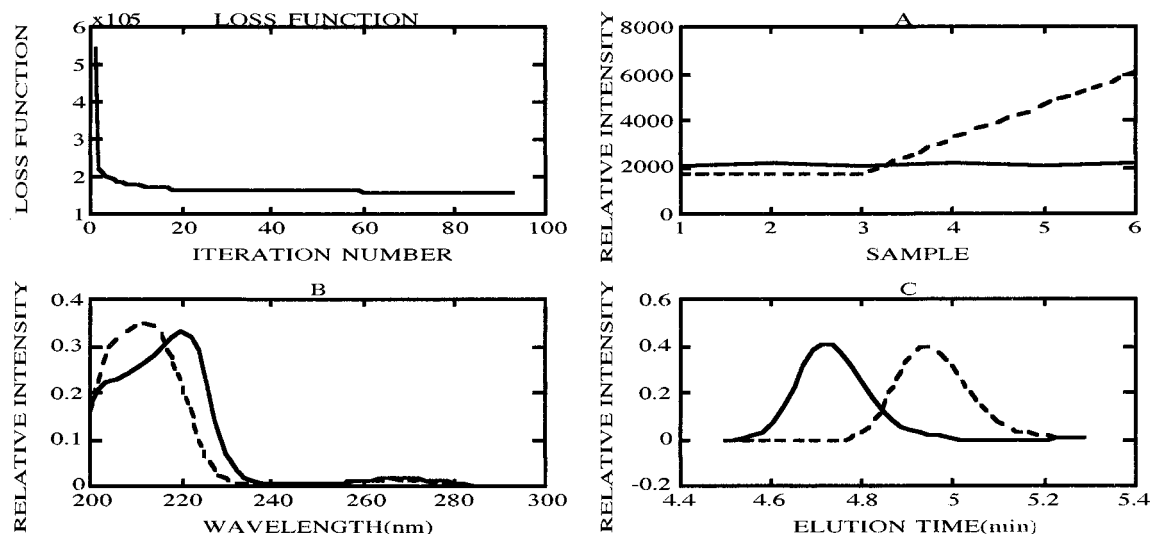


Fig. 3 Results obtained for HPLC-DAD experimental data using the 2-factor PARAFAC-SOSAM method. The average predicted concentration of *o*-chlorotoluene (---) in samples #1 to #3 was 26.44 ± 0.4 mg/ml and their average recovery was $118.0 \pm 1.8\%$.

Table 1 Compositions of six real samples

Sample No.	Concentration/ $\mu\text{g ml}^{-1}$		
	<i>p</i> -Chlorotoluene	<i>o</i> -Chlorotoluene	Chlorobenzene
#1	23.0	22.4	25.4
#2	23.0	22.4	25.4
#3	23.0	22.4	25.4
#4	23.0	22.4 + 22.4	25.4
#5	23.0	22.4 + 44.8	25.4
#6	23.0	22.4 + 67.2	25.4

Chlorobenzene was added to these samples as an internal standard of the elution time in order to keep the relative retention times obtained in a batch analysis as consistent as possible

Chlorobenzene was added to these samples as an internal retention time standard in order to correct the obtained retention time of the samples. The column temperature was controlled and kept at $25.0 \pm 0.5^\circ\text{C}$. A mixture of methanol and water (80:20, w/w) was used as the eluent. The flow rate of the eluent was 1.0 ml min^{-1} .

The two-way response data were collected with a Compaq Prolinea 4/33S personal computer with the CLASS-M10A program (Shimadzu). The reagents used were of analytical grade.

The response data used for the second-order standard addition method were taken over an elution time range of 4.50 to 5.30 min (Δt was about 0.02 min, $K=38$) and a wavelength range of 200.0 to 299.0 nm ($\Delta\lambda$ was 2 nm, $J=50$). These data were then transferred into a Macintosh computer (PowerBook 550c) and combined into a three-way response array.

Six samples (designated as #1–#6) were analyzed; the concentrations of each component are given in Table 1. Here, #1 to #3 were the same samples without any standard addition for checking the reproducibility of the analytical results; #4 to #6 were samples with added standards. A three-way data array of size $6 \times 50 \times 38$ was obtained using these samples.

The SOSAM algorithms for the trilinear decompositions based on DTLT, PARAFAC and ATLD were implemented in the MATLAB programming environment according to references 5, 8 and 6, respectively.

Table 2 Summary of the first singular values obtained from X_p^I , X_p^J , X_p^K and the determination of the number of factors

Factor No.	First singular values (percent variance, %)		
	X_p^I	X_p^J	X_p^K
1	12836(96.33)	12927(97.69)	12724(94.65)
2	2483(3.60)	1914(2.14)	2998(5.26)
3	297(0.05)	527(0.16)	331(0.06)
4	125(0.01)	50(0.00)	186(0.02)

$N^* = 2$ for PARAFAC and 2 or 3 for DTLT and ATLD

Results and Discussion

Deducing the number of factors

The rank of the three-way data array, estimated according to a method described elsewhere,⁶ is given in Table 2. It should be pointed out that for PARAFAC the number of factors chosen must be identical to the numerical rank of the three-way data array; otherwise, the obtained results would have no physical meaning. This restriction is relaxed for DTLT and ATLD, which can provide physically meaningful results when the number of factors chosen is equal to or greater than the actual rank. Without experimental errors, the optimal number of factors should be the numerical rank, rank_X . Actually, however, there usually exist experimental errors and other nonlinear factors in a trilinear model. They could lead to a small increase of the factor numbers compared to the estimated rank of the three-way data array. The selected numbers of factors were two for PARAFAC and two or three for DTLT and ATLD.

Determination of *o*-chlorotoluene

A $6 \times 50 \times 38$ three-way HPLC-DAD data array was decomposed by using the N -factor DTLT-SOSAM, PARAFAC-SOSAM and ATLD-SOSAM algorithms respectively. The three matrices, that is, the relative concentration, spectrum, time profile matrices and a loss function vector in variation with the iteration number could be obtained for each trilinear decomposition. Figures 2 to 4 show one set of the results based on using the 2-factor DTLT-SOSAM algorithm, the 2-factor PARAFAC-

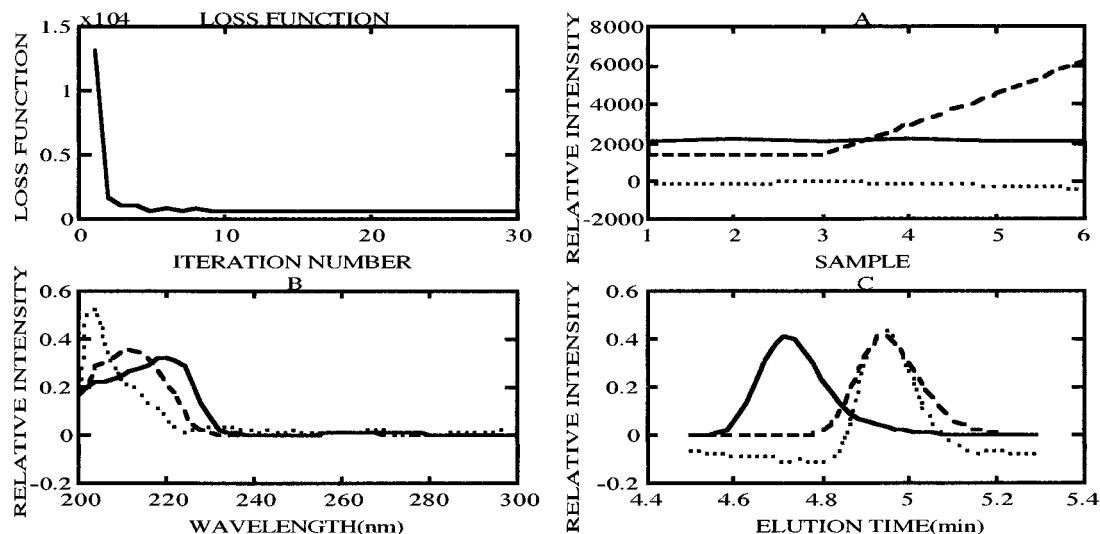


Fig. 4 Results obtained for HPLC-DAD experimental data using the 3-factor ATLD-SOSAM method. The average predicted concentration of *o*-chlorotoluene (---) in samples #1 to #3 was 20.40 ± 0.4 mg/ml and their average recovery was $91.1 \pm 1.8\%$.

SOSAM algorithm and the 3-factor ATLD-SOSAM algorithm respectively. Based on the corresponding, relative concentration matrices, the regression curves were obtained by plotting the relative concentration values corresponding to *o*-chlorotoluene vs. their added standards. The concentrations of *o*-chlorotoluene obtained using Eq.(3) from the slope and intercept were the $26.37 \mu\text{g/ml}$ for the 2-factor DTLT-SOSAM, $26.44 \mu\text{g/ml}$ for the 2-factor PARAFAC-SOSAM, $24.96 \mu\text{g/ml}$ for the 2-factor ATLD-SOSAM and $20.42 \mu\text{g/ml}$ for the 3-factor ATLD-SOSAM. Their corresponding recoveries were 117.7%, 118.0%, 111.4% and 91.2%, respectively. The results show that the ATLD-SOSAM method is slightly superior to both the DTLT-SOSAM and PARAFAC-SOSAM methods

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