

Accommodating of resolved chemical kinetic model of uncalibrated interferences during multivariate calibration models

Hamid Abdollahi^a and Tahereh Heidari^b

^aFaculty of Chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran

^bDepartment of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

The simultaneous determination of several analytes based on kinetic spectrophotometric method is usually performed by chemometrics method, especially in cases where the analytes react with a common reagent. One of the most serious problems with multivariate calibration methods is the lack of possibility to handle interferences which are not present during calibration [1]. If the kinetic profile of the unmodeled component can be obtained and mathematically added in variable amounts to the original calibration spectra, then a new synthetic multivariate calibration model can be generated from the augmented data to accommodate the presence of the unmodeled source of spectral. In this study a new simple method is proposed for estimation of kinetic model of an unknown interferent by estimation of its rate constant. This algorithm is based on similarity of kinetic mechanism of the analyt and interference, exponentially decaying contribution profiles or (pseudo) first order kinetic. In the proposed method, no chemical and spectral information about interference is necessary. The applicability of the proposed method was examined for analysis of simulated and experimental outlier prediction set from first-order kinetic reactions data. The satisfactory results were obtained using partial least square regression calibration model. The method was successfully applied for determination of semicarbazide in the synthetic prediction samples and spiked tap water containing hydrazine as unmodeled interferent. The accuracy and precision of the results are all satisfactory, and show the applicability of the method for real and complex samples.

References

- [1] K.S. Booksh, B.R. Kowalski, Anal. Chem. 66 (1994) 782A.

Accommodating of resolved acid-base titration model of uncalibrated interferences during multivariate calibration models

Hamid Abdollahi^a and Tahereh Heidari^b

^aFaculty of Chemistry, Institute for Advanced Studies in Basic Sciences, Zanjan, Iran

^bDepartment of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

Multivariate calibration methods are used for the determination of mixtures of acids (or bases) with similar pK by potentiometric titration. The linear titration equations of mixtures of acids are derived and the obtained potentiometric data are processed by multivariate calibration approaches such as partial least squares. The most serious problem with multivariate calibration methods is the lack of possibility to handle interferences which are not present during calibration [1]. If acid-base titration model of the unmodeled component can be obtained and mathematically added in variable amounts to the original calibration spectra, then a new synthetic multivariate calibration model can be generated from the augmented data to accommodate the presence of the unmodeled source of spectral. In this study a new simple method is proposed for estimation of acid-base titration model of unknown interferent by estimation of its pK. In the proposed method, no chemical information about interference is necessary. The practical utility of this method was demonstrated for the analysis of simulated and experimental outlier prediction set and acceptable results were obtained using partial least square regression calibration model. The effects of differences in pKa on accuracy were studied in detail. Synthetic mixtures of benzoic acid (analyte) and acetic acid or salicylic acid or 2-chlorobenzoic acid (unknown interferent) were analyzed by the proposed method and acceptable results were obtained. The satisfactory results were obtained for determination of benzoic acid in white vinegar samples. The accuracy and precision of the results are all satisfactory, and show the applicability of the method for real and complex samples.

References

- [1] K.S. Booksh, B.R. Kowalski, Anal. Chem. 66 (1994) 782A.

Analysis of sunset yellow in adulterated saffron from solvent components gradual change-visible spectra data processed by Rank Annihilation Factor Analysis

Tahere Heidari^{a*}, Elahe Bidad^b

^aDepartment of Chemistry, Faculty of Science, Ferdowsi University, Mashhad, Iran

^bFaculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Second-order calibration is used for second-order data. Such data are produced by instruments that give a matrix of responses for a single measured standard or unknown sample. This allows determination of analyte of interest in the presence of uncalibrated sample constituents, a property known as the second-order advantage. It was discovered that a second order spectra data matrix of sunset yellow produced from the solvent components gradual change-visible absorption spectra can be expressed as the combination of two bilinear data matrices. Based on this discovery, a new method for the determination of sunset yellow in gray systems using second order calibration algorithms has been developed. The second order calibration algorithm was based on the rank annihilation factor analysis (RAFA). In the method described here, the components of the solvent were changed gradually by adding dioxan into water, the absorption spectra of sunset yellow and saffron samples in a series of water-dioxan mixed solvents with various dioxan volume fractions were recorded, and then the second order data were obtained from the solvent components gradual change-visible absorption spectra. Thus, the concentration of sunset yellow in adulterated saffron samples could be determined from the spectra matrices using second order calibration algorithms. This method is simple, convenient and dependable. The method has been successfully used to determine sunset yellow in saffron samples with satisfactory results.

References

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Evaluation of chemical hydride generation for simultaneous spectrophotometric determination of arsenic and antimony using partial least squares multivariate calibration

Tahereh Heidari and Marziyeh Solimani

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

Hydride generation spectrophotometric methods using NaBH_4 - acid reduction is well known techniques for analysis of arsenic and antimony [1]. A batch chemical hydride generation system was developed for the simultaneous spectrophotometric determination of inorganic As(III) and Sb(III) by silver