ISSN : 0974-7419 Volume 10 Issue 12

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 10(12), 2011 [831-834]

Cholesky multivariate decomposition algorithm for infrared spectrometric determination of active components in laundry detergent powder

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Received: 4th August, 2011 ; Accepted: 4th September, 2011

ABSTRACT

A new calibration method based on of Cholesky decomposition (CD) has been introduced. It is the decomposition of a positive-definite matrix into the product of a lower triangular matrix and its conjugate transpose. This approach has been utilized to overcome the problem of serious spectral overlapping during the infrared spectrometric determination of sodium tripolyphosphate, sodium sulfate and sodium carbonate in laundry detergent powders. Comparing the root mean square error of prediction in Cholesky method and those obtained by partial least squares regression, it was concluded that Cholesky algorithm would offer more reliable prediction efficiency. It is also mentionable that Cholesky is a rapid data processing technique which speeds reduces the order of matrices.

INTRODUCTION

Cholesky decomposition is a very simple, accurate and stable numerical analysis algorithm with an easy computational procedure. Decomposition algorithms avoid matrix inversion operation, which is often involved in chemometrics approaches such as K-Matrix (KM), P-Matrix (PM) and partial least squares (PLS), reduces the orders of matrices, speeds up the operation procedure and improves the computation efficiency[5, 6].

Cholesky decomposition is also used use in econometrics, decomposing the covariance matrix for a set of residuals in the context of a vector auto regression. This sort of analysis was pioneered by Christopher Sims during 1980 decade and quickly became popular.

However, according to the literature survey, there is no document reporting the application of Cholesky algorithm in chemical analysis.

With growth in complexity of detergent formulations and lack of robust analytical methods, demand for new determination methods increase in recent years. Sodium tripolyphosphate is a builder used in detergent powders' formulation for many years, also the mixture of STPP with sodium sulfate (SS) is often used as a builder in cheaper products. Sodium carbonate is called washing soda or sal soda which would be effective in oil, grease, and alcohol stain removal. There are some conventional analytical methods for analysis of a washing powder samples e.g. extraction by ethanol or classical wet chemistry methods. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry has been introduced as an efficient technique with high signal-to-noise ratio for quantitative determination of ingredients of washing powder samples[7-9].

In this research, Cholesky model has been developed for simultaneous determination of sodium Sulfate

(SS), sodium Carbonate (SC) and Sodium Tripolyphosphate (STPP) in laundry detergent powder samples by using ATR-FTIR spectroscopy. The obtained results have also been compared to those of K-matrix and Cholesky decomposition algorithm.

EXPERIMENTAL

Apparatus and Software

A FTIR spectrometer (Magna 550, Nicolet, Madison,WI, USA) equipped with a DTGS detector, an Ever-Glo source and a CsI beam splitter was applied. The ATR- FTIR spectra were obtained by a 45° ZnSe cell. The data obtained from WINFIRST software were exported in ASCII format, the data treatment was done with MATLAB for windows (Mathworks, Version 7.4).

Chemical reagents

SS, SC and STPP were of analytical grade and were purchased from Merck. Liquid sodium silicate 45.5%, carboxy methyl cellulose (CMC) 65% and LABS 95.8% were supplied by Clariant and Tolypers Co., respectively. Distilled water was used as the solvent during the procedure.

FTIR spectrometry

In order to provide the standard samples, 25 aqueous solutions of STPP, SS and SC were prepared in a 100 mL beaker, by distilled water. The concentration range for STPP, SC ands SS was 0.2579-2.8913, 0.2029-2.4935 and 0.2912-1.2010 (g per 100 g). Different amounts of other ingredients of Iranian washing powders (CMC, Sodium silicate and sodium hydroxide) were also added to each mixture. Some detergent powder real samples were also prepared by the same procedure. Spectra of standard solution and real sample with air background do not contain any useful information in IR signals, thus the spectrum of distilled water was set as the background, obtained under the same experimental conditions as the samples and standards. According to our previous experiences, the ATR-FTIR spectra of standard samples, obtained in 750–2000 cm–1 spectral region[7].

Theory of Cholesky algorithm

Cholesky is a mathematical algorithm based on decomposition of matrix A (a positive definite matrix) into a lower triangular matrix L and its transpose, L^T

The decomposition process is as[10-11]

The matrix $A \varepsilon R^{n\times n}$ is positive definite or $|\mathbf{A}| \neq 0$) can be expressed as:

$$A = LL^T \qquad L = \begin{pmatrix} l_{11} & 0 & \dots & 0 \\ l_{21} & l_{22} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ l_{n1} & \dots & \dots & l_{nn} \end{pmatrix}$$

The corresponding Cholesky factor L (sometimes called the matrix square root) always exists and is unique. Matrices of this sort arise in many econometric contexts, making the Cholesky decomposition a very useful computational tool. For example, it can be used to solve the normal equations of least squares to produce coefficient estimates in multiple regression analysis. In this case, the place of A is occupied by the matrix of squares and cross-products of the regressors, X^TX. Given the Cholesky decomposition of A, the set of linear equations $Ax = b$ in the unknown vector x may be written as $LL^Tx = b$[12]. Writing y for $L^Tx = b$, we get $Ly = b$ which may be solved for y, then $y = L^Tx$ is solved for x. Algorithms for computing the decomposition are based on the following relationships between the elements a_{ij} of A and the elements l_{ij} of L:

Element l_{ij} can be computed if we know the elements to the left and above. Thus, in order to have the general symmetric matrix A as LL^T, from the first column, we have:

$$l_{1,1} = \text{sqrt}(a_{1,1})$$

$$l_{2,1} = a_{2,1} / l_{1,1}$$

$$l_{3,1} = a_{3,1} / l_{1,1}$$

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$$l_{n,1} = a_{n,1} / l_{1,1}$$

Having calculated these values from the entries of the matrix A, we may go to the second column, and we note that, because we have already solved for the entries of the form $l_{n,1}$, we may continue to solve:

$$l_{2,2} = \text{sqrt}(a_{2,2} - l_{2,1}^2)$$

$$l_{3,2} = (a_{3,2} - l_{2,1}l_{3,1}) / l_{2,2}$$

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$$l_{n,2} = (a_{n,2} - l_{2,1}l_{n,1}) / l_{2,2}$$

and thus, finally we may solve for the last entry $l_{n,n}$:

$$l_{n,n} = \text{sqrt}(an, n - l_{n,1}^2 - l_{n,2}^2 - \quad .... \quad - l_{n,n-1}^2)$$

The solution of equation $Ax = b$ can be obtained by solving $Ly = b$ and $L^T x = y$.

RESULTS AND DISCUSSION

The process of solving the concentration matrix by Cholesky

The calibration concentration matrix $C_{25\times3}$ was gained according to the concentration ratios given in TABLE 1. The absorbance matrix $A_{25\times86}$ was obtained from the spectral data of 25 calibration samples. According to Lambert-Beer law

$$C_{25\times3}B_{3\times86} = A_{25\times86}$$

thus

$$C_{3\times25}^T C_{25\times3} B_{3\times86} = C_{3\times25}^T A_{25\times86}$$

the process of decomposition of matrix, is

$$C_{3\times25}^T C_{25\times3} = LL^T$$

Solving the following equation

$$\mathbf{LY = C_{3\times25}^T A_{25\times86}}$$

Y is turn out; with another equation

$$L^T B = Y$$

then, the sensitivity coefficient matrix B is obtained.

Through calculating the matrix B gotten previously and the absorbance matrix of the real samples ($A_{10\times86}$), the concentration matrix ($C_{10\times3}$) of real samples is obtained. In this procedure, the absorbance matrix of 10 real samples ($A_{10\times86}$) was obtained from the spectral data. The number of the rows of the absorbance matrix is the number of the unknown samples and the number of the columns of the absorbency matrix is the number of wavelengths. Again, according to Lambert-Beer Law

$$C_{10\times3}B_{3\times86} = A_{10\times86}$$

thus

$$C_{10\times3}B_{3\times86}B^T_{86\times3} = A_{10\times86}B^T_{86\times3}$$

the process of decomposition of matrix, is

$$B_{3\times86}B^T_{86\times3} = L\,L^T$$

Solving the following equation

$$C_{10\times3}\,L\,L^T = A_{10\times86}B^T_{86\times3}$$

Y is turn out, with another equation

$$Y\,L^T = A_{10\times86}B^T_{86\times3}$$

the concentration matrix $C_{10\times3}$ of real samples could be gained.

$$C\,L = Y$$

the concentration matrix $C_{10\times3}$ of real samples could be gained.

Comparing Cholesky decomposition and K-matrix

As partial least square has been used widely in multi-calibration in chemometrics, result of Cholesky compare with K-matrix result. TABLE 1 shows the results of Cholesky algorithm and K-matrix. Also, the statistical parameters are shown in TABLE 2. It is observed that Cholesky is more superior and convenient than K-matrix calibration.

CONCLUSIONS

A new algorithm was proposed for the quantitative determination of SS, SC and STPP with the Cholesky multivariate calibration, being compared to partial least square based on Mid-IR reflectance spectrometry. The concentration predicated for SS, SC and STPP component showed that sensitivity in Cholesky multivariate calibration is improved. Also, it was demonstrated that Cholesky can avoid matrix inverting, reduce the orders of matrices and needs a little time for analysis. Furthermore, computing the Cholesky decomposition is more efficient and numerically more stable than computing

TABLE 1 : Quantitative analysis of detergent powder real samples by DMCA and K-matrix models (g per 100 g)

	Method	STPP	SS	SC
1	K-matrix	15.64	39.66	5.54
	Cholesky method	15.23	40.61	6.11
	References	15.00	41.00	6.20
2	K-matrix	14.20	36.66	7.54
	Cholesky method	14.47	40.75	6.24
	References	14.60	41.90	6.30
3	K-matrix	15.34	40.96	7.03
	Cholesky method	14.42	41.34	6.78
	References	14.30	41.60	6.90
4	K-matrix	16.71	40.87	5.78
	Cholesky method	16.08	40.63	5.34
	References	17.10	39.80	5.10
5	K-matrix	16.69	38.71	4.58
	Cholesky method	16.51	42.64	5.96
	References	16.30	42.40	5.80
6	K-matrix	20.19	30.56	8.82
	Cholesky method	20.86	30.84	8.97
	References	21.90	31.00	9.80
7	K-matrix	19.37	31.17	7.89
	Cholesky method	19.59	30.62	8.27
	References	19.70	30.70	8.40
8	K-matrix	19.31	30.87	7.12
	Cholesky method	19.84	31.76	7.59
	References	20.00	31.80	7.80
9	K-matrix	23.14	31.35	6.65
	Cholesky method	22.88	30.07	7.24
	References	22.00	30.10	7.20
10	K-matrix	20.33	29.56	6.13
	Cholesky method	20.81	29.78	6.33
	References	21.60	30.40	6.70

TABLE 2 : Statistical parameters of the applied models

Calibration model		R^2	RMSEP
K-Matrix	STPP	0.962	0.118
	SC	0.835	0.110
	SS	0.873	0.011
Cholesky decomposition	STPP	0.947	0. 141
	SC	0.967	0.035
	SS	0.992	0.009

any decomposition method. So it has bright prospects in chemometrics and it is feasible that the Cholesky Algorithm could be applied to the practical determinations in real samples with spectral overlapping.

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