RESEARCH LETTER

Introducing Doolittle multivariate calibration algorithm for infrared spectrometric determination of STTP, SS, and SC in Iranian washing powder

Mohammad Hossein Ahmadi Azghandi* and Mohammad Reza Khanmohammadi

Chemistry Department, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

(Received 28 June 2011; final version received 4 November 2011)

The basic principle of Doolittle multivariate calibration algorithm (DMCA) was investigated and used for simultaneous quantitative determination of sodium tripolyphosphate (STPP), sodium sulfate (SS), and sodium carbonate (SC) in commercial washing powders with serious overlapping. The process of the Doolittle decomposition algorithm (DDA) is implemented by lower and upper (LU) triangular matrix decomposition which is robust and convenient. Then it was applied to overcome the problem of overlapping spectra of different components in the detergent washing powder. The root mean square error of prediction (RMSEP) for DMCA is 0.084 which confirms the improvement in accuracy, in comparison with K-Matrix (KM) (RMSEP = 0.118). It was demonstrated that DDA can avoid matrix inverting, reduce the orders of matrices, and needs a little time for analysis. Therefore, it has bright prospects in chemometrics and it is feasible that the Doolittle algorithm could be applied to the practical determinations in real samples with spectral overlapping.

Keywords: detergent powder; infrared spectroscopy; chemometrics; Doolittle algorithm

Introduction

Modern detergents contain several chemical ingredients in different proportions and are complex mixtures to reflect the demands of modern day living in the new millennium. Detergent washing powders involve more than 25 different ingredients such as surfactants, builders (sodium tripolyphosphate [STPP], sodium carbonate [SC], sodium silicate, zeolite), bleaches (perborates, tetra acetyl ethylene diamine, percarbonates), enzymes, and auxiliaries (optical brighteners, fragrance, sodium sulfate [SS]) (1). With the growth in complexity of detergent formulations and lack of robust analytical methods, demand for new determination methods has increased in recent years (2). STPP is a builder used in detergent powders’ formulation for many years; as is the mixture of STPP with SS which is often used as a builder in cheaper products. SC is called washing soda or sal soda and is effective in oil, grease, and alcohol stain removal (3). There are some conventional analytical methods for analysis of washing powder samples, for example extraction by ethanol or classical wet chemistry methods (4). 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 (5). There are several multivariate calibration methods to extract the spectral data for each compound in a mixture with similar spectral characteristics. Partial least-squares (PLS) is a usual tool for multivariate calibration because of the quality of the obtained calibration models, the ease of its application, and the availability of software (6). PLS is based on linear relationship between response and intensity of absorption bands (7), but this algorithm involves matrix inverting operation and also application of this technique has been restricted with few deviations from linearity.

Doolittle decomposition algorithm (DDA) is a very simple, accurate, and stable numerical analysis algorithm with an easy computational procedure. This algorithm can avoid matrix inverting operation, which is often involved in chemometrics such as K-Matrix (KM), P-Matrix, and PLS methods; reduce the orders of matrices; speed up the operation of matrices; and raise the efficiency of computation (8–11). However, according to our survey, there are few documents reporting the application of Doolittle algorithm in chemical researches (12). In this study, Doolittle algorithm has been developed for simultaneous determination of SS, SC, and STPP in a commercial detergent powder samples by using ATR-FTIR spectroscopy and evaluating the results.
obtained by multivariate KM and DDA. More reliable results were obtained by DDA algorithm, and the introduction of the Doolittle algorithm will offer more convenience for the solution of a series of chemometrics issues.

Results and discussion

**ATR-FTIR spectra and evaluation of Doolittle analysis**

A suitable solvent dissolves the analytical samples without reacting and has the least interference at the spectral region of the analyte. The ATR-FTIR spectra of STPP, SS, and SC using water as the reference (Figure 1) showed severe overlapping in their absorbance bands, and the univariate analysis method cannot be applied to overcome this overlapping and be used to carry out a simultaneous determination of these three components. To evaluate the DDA performance, standard and predicted sample solutions were analyzed. Twenty-five samples of this solution set (sample no. 1–25 in Table 1) were chosen as standard and the 10 other (sample no. 26–35) were used as predicted samples. The compositions of the samples used in calibration and predication sets are summarized in Table 1. In the first 14 samples, collinearity could be observed between components’ concentration. This set had been prepared according to the formulation of most washing powders produced by Iranian detergent manufacturers. The other 11 samples were prepared using a fractional factorial design at five concentration levels in order to obtain accurate results in the prediction ability of the method for real samples. Finally, the combination of these two sets made it possible to achieve the aim of method. The ATR-FTIR spectra of 25 standard samples in the spectral region of 800–1500 cm$^{-1}$ are shown in Figure 2. The maximum absorbance was observed around 1100 cm$^{-1}$ spectral region.

**The process of solving the concentration matrix by Doolittle**

The calibration concentration matrix $C_{25 \times 3}$ was gained according to the concentration ratios given in Table 1.

The absorbance matrix $A_{25 \times 86}$ was obtained from the spectral data of 25 calibration samples. According to Lambert–Beer law

$$C_{25 \times 3} B_{3 \times 86} = A_{25 \times 86}$$

thus

$$C_{3 \times 25}^T C_{25 \times 3} B_{3 \times 86} = C_{3 \times 25}^T A_{25 \times 86}$$

the process of triangle decomposition of matrix, is

$$C_{3 \times 25}^T C_{25 \times 3} = LU$$

Solving the following equation

$$LY = C_{3 \times 25}^T A_{25 \times 86}$$

$Y$ is turn out; with another equation

$$UB = Y$$

the sensitivity coefficient matrix $B$ is obtained.

Through calculating the matrix $B$ gotten previously and the absorbency matrix $A_{10 \times 86}$ of the real samples, the matrix $C_{10 \times 3}$ of the concentrations of real samples is obtained. The process is as follows. The number of rows of the real samples matrix is the number of unknown samples and the number of columns of the real samples matrix is the number of components. The absorbance matrix $A_{10 \times 86}$ of 10 real samples was obtained from the spectra data of

![Figure 1. ATR-FTIR spectra of standard samples with water background (obtained in 750–2000 cm$^{-1}$).](image-url)
the samples. The number of rows of the absorbance matrix is the number of unknown samples and the number of columns of the absorbency matrix is the number of wavelengths. \( B \) is the sensitivity coefficient matrix. Again, according to Lambert–Beer Law

\[
C_{10 \times 3} B_{3 \times 86} = A_{10 \times 86}
\]

thus

\[
C_{10 \times 3} B_{3 \times 86}^{T} B_{86 \times 3}^{T} = A_{10 \times 86} B_{86 \times 3}^{T}
\]

the process of triangle decomposition of matrix is

\[
B_{3 \times 86}^{T} B_{86 \times 3} = MN
\]

Solving the following equation

\[
YN = A_{10 \times 86} B_{86 \times 3}^{T}
\]

\( Y \) is turn out, with another equation

\[
CM = Y
\]

the concentration matrix \( C_{10 \times 3} \) of real samples could be gained.

**Comparing Doolittle and KM**

The spectral data were also processed by KM which has been used widely in multi-calibration in chemometrics. Table 2 shows the results of Doolittle algorithm and KM. The general applicability of the proposed method and prediction samples was tested and evaluated by calculating two statistical parameters, the square of the correlation coefficient \( (R^2) \) and root mean square error prediction (RMSEP; Table 3). It is demonstrated that the error of Doolittle multivariate calibration is less small. It is more worthwhile to mention that Doolittle algorithm can avoid matrix inversion and improve sensitivity by reducing the orders of matrixes, speeding up the operation of matrixes and raising the efficiency of computation especially when carrying out a great amount of calculation. Doolittle multivariate calibration is superior to and more convenient than other calibrations.

**Recovery study**

Washing powders are complex formulations containing not only STPP, SS, and SC but also several other ingredients. Nine synthetic mixture samples, which also contain carboxy methyl cellulose (CMC), sodium silicate, and sodium hydroxide besides the three proposed components, were analyzed and the recovery percentages were calculated. The results are shown in Table 4. The recovery established by Doolittle multivariate calibration algorithm (DMCA) were: 95.306–110.200%, 97.568–110.307%, and 94.090–105.494% for STPP, SS, and SC, respectively. The good agreement between the obtained results (using DDA), and the known values is an indication of the successful applicability of the proposed method for simultaneous determination of STPP, SS, and SC in complex samples.

Also, the precision of the method was tested by calculating the standard deviation (SD) and relative standard deviation (RSD) of the results obtained for sample nos. 1, 3, 7, and 9 of Table 4 (see Table 5).
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, and the data treatment was done with MATLAB for windows (Mathworks, Version 7.4).

Chemical reagents

STPP, SS, SC, and NaOH were of analytical grade and were acquired from Merck. Liquid sodium silicate with a purity of 45.5% and CMC with a purity of 65% 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 and predicting samples, 35 aqueous solutions of STPP, SS, and SC were prepared in a 100 ml beaker, by distilled water. The concentration range for STPP, SS, and SC was 0.2579–2.89, 0.20–2.49, and 0.2912–1.2010 g/100 g for STPP, SC, and SS, respectively (water as the reference).

For each of these real samples, after grinding and homogenizing, 1.000 g was used for analysis. Each weighed sample was diluted to a final weight of 25 g with distilled water. 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 background, obtained under the same experimental conditions as the samples and standards (Figure 1). According to our previous experiences, the ATR-FTIR spectra of standard samples were obtained in 750–2000 cm⁻¹ spectral region (5).

Principles of Doolittle multivariate calibration

Doolittle algorithm

Doolittle algorithm is a mathematical method based on decomposition of matrix $A$ (a nonsingular matrix)

$A = X \cdot Y^T$

Table 2. Quantitative analysis of STPP, SS, and SC applied in prediction (samples no. 26–35) set by DMCA and KM models (g per 100 g).

| Method | STPP | SS  | SC  |
|--------|------|-----|-----|
| 1      | KM   | 0.344 | 1.460 | 0.982 |
|        | DMCA | 0.335 | 1.497 | 1.084 |
|        | References | 0.350 | 1.479 | 1.000 |
| 2      | KM   | 0.350 | 1.749 | 0.974 |
|        | DMCA | 0.327 | 1.945 | 0.792 |
|        | References | 0.330 | 2.000 | 0.800 |
| 3      | KM   | 0.332 | 1.979 | 0.815 |
|        | DMCA | 0.312 | 1.997 | 0.786 |
|        | References | 0.310 | 2.010 | 0.800 |
| 4      | KM   | 2.406 | 1.825 | 0.876 |
|        | DMCA | 2.210 | 2.041 | 1.162 |
|        | References | 2.350 | 2.000 | 1.110 |
| 5      | KM   | 0.516 | 0.916 | 1.188 |
|        | DMCA | 0.567 | 0.935 | 1.356 |
|        | References | 0.560 | 0.930 | 1.320 |
| 6      | KM   | 1.514 | 1.322 | 0.817 |
|        | DMCA | 1.476 | 1.293 | 0.786 |
|        | References | 1.550 | 1.300 | 0.797 |
| 7      | KM   | 2.008 | 0.999 | 1.022 |
|        | DMCA | 2.068 | 1.027 | 1.102 |
|        | References | 2.080 | 1.030 | 1.120 |
| 8      | KM   | 1.104 | 1.333 | 0.655 |
|        | DMCA | 1.041 | 1.278 | 0.690 |
|        | References | 1.050 | 1.280 | 0.710 |
| 9      | KM   | 1.204 | 1.089 | 0.817 |
|        | DMCA | 1.331 | 1.118 | 0.804 |
|        | References | 1.280 | 1.120 | 0.800 |
| 10     | KM   | 1.671 | 1.006 | 1.586 |
|        | DMCA | 1.647 | 0.960 | 1.322 |
|        | References | 1.710 | 0.98 | 1.400 |

Note: STPP, Sodium tripolyphosphate; SS, sodium sulfate; SC, sodium carbonate; DMCA, Doolittle multivariate calibration algorithm; KM, K-Matrix.
The second step

\[ u_{2j} = a_{2j} - l_{21} \times u_{1j}, \quad (j = 2, 3, \ldots, n) \]

\[ l_{22} = (a_{i2} - l_{12} \times u_{12})/u_{22}, \quad (i = 3, \ldots, n) \]

and so on, until the \((k-1)\)th step

The \(k\)th step

\[ u_{kj} = a_{kj} - (l_{k1} \times u_{1j} + \ldots + l_{k,k-1} \times u_{k-1,j}), \quad (j = k, k+1, \ldots, n) \]

\[ l_{kk} = (a_{kk} - l_{k1} \times u_{1k} - \ldots - l_{k,k-1} \times u_{k-1,k})/u_{kk}, \quad (i = k + 1, \ldots, n) \]

The \(n\)th step

\[ u_{nn} = a_{nn} - (l_{n1} \times u_{1n} + \ldots + l_{n,n-1} \times u_{n-1,n}) \]

The solution of equation \((A \cdot x = b)\) can be obtained by solving \(L \cdot y = b\) and \(U \cdot x = y\).

### Conclusion

A new method based on mid-IR reflectance spectroscopy was proposed for the nondestructive quantitative determination of SS, SC, and STPP, with the Doolittle multivariate calibration being compared to PLS. Doolittle multivariate calibration improved the sensitivity of the results by the triangle decomposing of the matrices and avoiding matrix inverting. The investigations demonstrated that the Doolittle multivariate calibration results are more robust. Therefore, the Doolittle algorithm is sufficient in multivariate calibration and shows good capability in analyzing the mixed systems with noticeable spectral overlapping. Obviously, Doolittle multivariate calibration will have a bright prospect in analyzing systems which are difficult to separate. While such a calibration
method is still based on linear model and the system has its linear range, for non-linear systems, it cannot provide satisfactory results.

References

(1) Hoyt, J.L.; Sones, E.L.; Sooter, A.J. *Separation and Quantitative Determination of Active Ingredients in Detergent Formulations*; Continental Oil Company, Research and Development Department: Ponca City, Oklahoma, 2000; p 74601.

(2) Wilsch-Irrgans, A.; Sanli, O.; Harer, J.; Jauman, G. *Tenside. Surf. Det.* 2003, 40, 187.

(3) Henry Hancox, MD. A Case of Death from the Absorption of Washing Soda. *The Lancet Journal*. 1854, 64, 434–435.

(4) ASTM Method D501–89, Standard Test Method for Sampling and Chemical Analysis of Alkaline Detergents. American Society for Testing and Material, Philadelphia, PA, 2005.

(5) Khanmohammadi, M.R.; Ashori, A.; Kargosha, K.; Bagheri Garmarudi, A. *J. Surfact. Deterg*. 2007, 10, 81–86.

(6) Franco, V.G.; Per’In, J.C.; Mantovani, V.E.; Goicoechea, H.C. Monitoring Substrate and Products in a Bioprocess with FTIR Spectroscopy Coupled to Artificial Neural Networks Enhanced with a Genetic-Algorithm-Based Method for Wavelength Selection. *Talanta*. 2006, 68, 1005–1012.

(7) Hemmateenejad, B.; Miri, R.; Akhonda, R.; Shamsipur, M. *Chemom. Intell. Lab. Syst.* 2002, 64, 91–99.

(8) Ding, Y.P. *Anal. Sci.* 2005, 21, 327–330.

(9) Chen, N.Y.; Ding, Y.P.; Li, G.Z.; Ye, C.Z. *Comput. Appl. Chem. 2002*, 19, 717.

(10) Brown, C.W.; Lynch, P.F.; Obermks, R.J. *Anal. Chem. 1982*, 54, 1472–1479.

(11) Li, Q.Y.; Wang, N.C.; Yi, D.Y. *Modern Numerical Analysis*; Science Publication: Beijing, 1995; pp 170–185.

(12) Ding, Y.P.; Mu, T.; Wu, Q. *Chemom. Intell. Lab. Syst.* 2007, 88, 167–169.

(13) Qamber, I.S. *Relia. Eng. Syst. Saf.* 1999, 64, 359.

(14) Abbasbandy, S.; Ezzati, R.; Jafarian, A. *J. Comput. Math. Comput. Appl. Math. 2006*, 172, 633.

(15) Kurdi, A.A.; Kincaid, D.R. *J. Comput. Math. Comput. Appl. Math. 2006*, 185, 391.

(16) Kaya, D.; Wright, K. *J. Comput. Math. Comput. Appl. 2005*, 163, 179.

(17) Mittal, R.C.; Al-Kurdi, A. *J. Comput. Math. Appl. 2002*, 43, 131–155.

(18) Agensin, K.E. *Numerical Analysis Introduction*; Shanghai Science and Technology Publication: Shanghai, 1986.

Table 5. Precision for synthetic mixtures ($n=3$).

| Sample | STPP     | SS       | SC       |
|--------|----------|----------|----------|
|        | SD     | Percentage of RSD | SD     | Percentage of RSD | SD     | Percentage of RSD |
| 1      | 0.005  | 1.009     | 0.008   | 0.771     | 0.006  | 0.982     |
| 3      | 0.003  | 0.592     | 0.004   | 0.275     | 0.006  | 0.491     |
| 7      | 0.008  | 0.782     | 0.006   | 0.389     | 0.010  | 1.039     |
| 9      | 0.006  | 0.363     | 0.005   | 0.493     | 0.004  | 0.630     |

Note: STPP, Sodium tripolyphosphate; SS, sodium sulfate; SC, sodium carbonate; SD, standard deviation; RSD, relative standard deviation.