



HAL
open science

Study on the Near Infrared Model Development of Mixed Liquid Samples by the Algorithm of OSC-PLS

Dong Wang, Zhihong Ma, Shengfeng Ye, Shungeng Min

► **To cite this version:**

Dong Wang, Zhihong Ma, Shengfeng Ye, Shungeng Min. Study on the Near Infrared Model Development of Mixed Liquid Samples by the Algorithm of OSC-PLS. 4th Conference on Computer and Computing Technologies in Agriculture (CCTA), Oct 2010, Nanchang, China. pp.592-597, 10.1007/978-3-642-18354-6_69 . hal-01563475

HAL Id: hal-01563475

<https://inria.hal.science/hal-01563475v1>

Submitted on 17 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Study on the Near Infrared Model Development of Mixed Liquid Samples by the Algorithm of OSC-PLS

Dong Wang^{1,2} Zhihong Ma² Shengfeng Ye¹ Shungeng Min^{*1}

1: Department of Applied Chemistry, College of Science, China Agricultural University,
Beijing 100193, P. R. China

2: Beijing Research Center for Agri-food Testing and Farmland Monitoring, Beijing Research
Center for Information Technology in Agriculture, Beijing, 100097, P. R. China
{wangd@nercita.org.cn minsng@cau.edu.cn}

Abstract. The orthogonal signal correction of Wold algorithm was introduced in this thesis, which was combined with the partial least square algorithm. Calibration model of five components of benzene, methylbenzene, chlorobenzene, benzaldehyde and acetophenone in the mixed liquid samples were developed and validated by the method of independent . The result indicated that the calibration models of the components of benzene, methylbenzene, chlorobenzene and benzaldehyde will be developed well after the 1-dimension OSC filter; while a good calibration model of the component of acetophenone will be acquired after the 2-dimension OSC filter.

Key words: Orthogonal Signal Correction, Partial Least Square, Calibration Model, Near Infrared Spectroscopy, Liquid Samples

* Supported by National Science Foundation of China, No. 20575076.

Author: Dong Wang, Ph.D., major: near-infrared spectroscopy. Email: wangd@nercita.org.cn.

Corresponding Author: Shungeng Min, professor, doctoral supervisor. Email:
minsng@cau.edu.cn

Address: Department of Applied Chemistry, College of Science, China Agricultural University,
No. 2, Yuanmingyuan West Road, Haidian District, City of Beijing 100193, P. R. China.

1 Introduction

Near-infrared (NIR) spectroscopy is a kind of non-destructive[1], rapid[2] and environmental friendly analysis method, with the characteristics of easy-acquirement optical source, abundant spectral information and strong penetrability. NIR spectroscopy analysis has been applied in the fields of quality analysis of agricultural products[3-5], petrochemical industry[6], pharmaceutical analysis[7-9] and so forth.

However, the high-strength and complicative background exists in NIR spectroscopy analysis. With the characteristics of serious overlapping band, there are non-correlative information with the target component and the information of the instruments in NIR spectra, which will influence the precision of the calibration model.

The common multi-signal calibration methods have the risk of eliminating the information correlated with the specified values from spectra, which may decrease the precision of the calibration model.

The Algorithm of Orthogonal Signal Correction (OSC) was raised by Wold[10] in 1998 firstly, which is a method of signal processing. The basic idea of OSC is that the non-correlative part of the spectral matrix (X) to the specified values matrix (Y) was eliminated by the mathematical method of orthogonality, after which, a new matrix X_{new} was acquired. The calibration model will developed by the matrix X_{new} , in order to acquire robust calibration model. Since OSC algorithm eliminated the orthogonal part of the specified values, the valuable information will be kept in spectra matrix, in addition, it may simplify the calibration model for the complicative system.

After Wold raising OSC algorithm, many scholars raised the improvement to OSC. Tom Fearn[11] improved the OSC algorithm in 2000. Johan A. Westerhuis[12] et. al. raised the Direct-OSC algorithm. Robert N. Feudale[13] et. al. raised the Piecewise OSC algorithm. OSC algorithm has been applied in the calibration of NIR data successfully at present[14, 15].

In this thesis, OSC-PLS algorithm will be applied in the calibration model of the NIR spectra of 30 mixed liquid samples. The filtering effect of different dimension of OSC was compared.

2 Experiment

2.1 Instrument and Reagent

Instrument: FT-NIR spectrometer (Spectrum One NTS, Perkin Elmer, U.S.);

Reagents: Benzene (A.R.), methylbenzene (A.R.), chlorobenzene (A.R.), benzaldehyde (A.R.), acetophenone (A.R.).

2.2 Procedure

30 mixed liquid samples, including benzene, methylbenzene, chlorobenzene, benzaldehyde and acetophenone, were made up. The information of the samples was shown in Tab. 1.

The range of NIR spectra collected was 10000 cm^{-1} - 4000 cm^{-1} . The air was regarded as reference in order to collect the background spectrum.

Tab. 1. The information of the components in the liquid mixed samples

	Benzene	Methylbenzene	Chlorobenzene	Benzaldehyde	Acetophenone
Max (%)	50.0	30.0	10.0	10.0	5.0
Min (%)	1.0	1.0	1.0	0.5	0.1
Mean (%)	9.9	19.4	5.3	4.3	2.0
Std	12.3	8.6	3.0	3.0	1.7

2.3 Data Processing

Software: Matlab v6.5, preprocessing and OSC-PLS program written by self.

Calibration method: Independent validation, of which, 6 spectra selected according to the concentration gradient were regarded as the validation set for each component; smooth by Savitzki-Golay (with the width of 5); data normalization method: SNV; OSC-PLS regression.

3 Result and Discussion

3.1 OSC Filter

Take the specified values of benzene for example, Fig. 1A is the raw spectra of the 30 mixed liquid samples in the range of 6200 cm^{-1} - 5800 cm^{-1} , which is the 1st overtone of C-H group. Centralization of the spectra was done, as is shown in Fig. 1B.

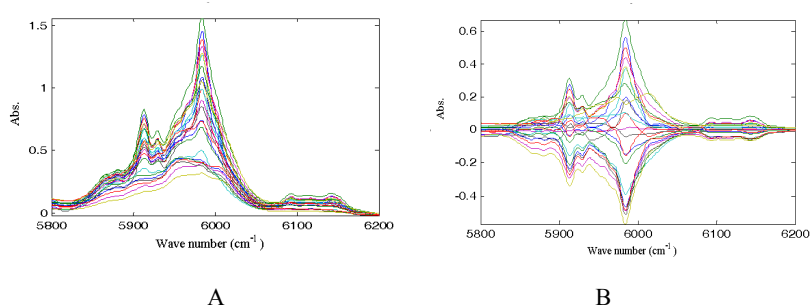


Fig. 1. The raw spectra (A) and the spectra after centralization processing (B)

After the spectra having been processed of centralization, OSC filter with 1-, 2- and 3-dimension was applied to the spectra data. The spectra after OSC filter were shown as Fig. 2.

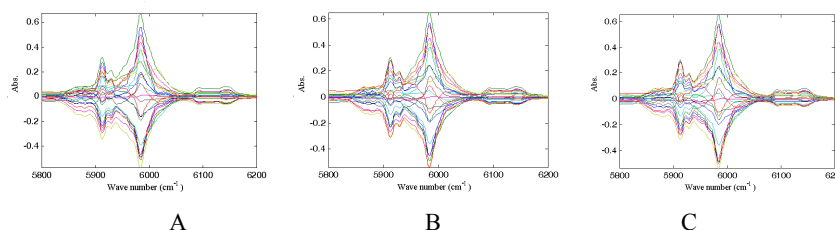


Fig. 2. The spectra processed by OSC filter with the specified values of benzene, OSC dimension: 1(A), 2(B), 3(C)

3.2 The Calibration Models of the 5 Components in the Mixed Liquid Samples

Partial Least Square (PLS) regression was applied to the specified values of benzene and the spectra filtered by 1-, 2- and 3-dimension OSC with the specified values of

benzene, the result of which was shown as Tab. 3, in which, R^2_c represents the determination coefficient of the calibration set, while R^2_v represent the determination coefficient of the validation set.

Tab. 2. The calibration result of benzene after 1-, 2-, 3-dimension OSC filter

OSC dimension	1	2	3
R^2_c (%)	99.90	99.90	99.90
R^2_v (%)	99.69	99.69	99.69
RMSEC	0.54	0.54	0.54
RMSEV	0.97	0.97	0.97
Model dimension	2	2	2

It can be seen from Tab. 2 that there is no remarkable difference among the results of 1-, 2- and 3-dimension OSC filter. The calibration after 1-dimension OSC filter had the enough precision.

Fig. 3 is the correlation of the estimated values and specified values of the calibration set (A) and the validation set (B) of benzene after 1-dimension OSC filter.

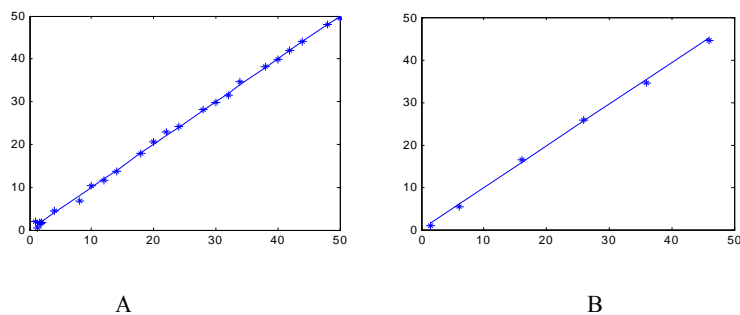


Fig. 3. The correlation of the estimated and specified values of benzene, calibration set: A, validation set: B

It can be seen from Fig. 3 that a high precision can be acquired for benzene after 1-dimension OSC filter and PLS regression.

The calibration result of the other 4 components after 1-, 2- and 3-dimension OSC filter and PLS regression were shown as Tab. 3.

Tab. 3. The calibration result after each OSC filter

N _{osc}	Methylbenzene			Chlorobenzene			Benzaldehyde			Acetophenone		
	1	2	3	1	2	3	1	2	3	1	2	3
R ² _c (%)	99.75	92.89	92.89	99.45	94.23	94.23	99.94	95.55	95.55	99.78	99.78	99.78
R ² _v (%)	99.42	97.10	97.10	96.34	91.45	91.45	84.94	78.15	78.15	97.47	97.97	97.97
RMSEC	0.52	2.65	2.65	0.23	0.74	0.74	0.09	0.66	0.66	0.09	0.09	0.09
RMSEV	0.77	1.71	1.71	0.55	0.84	0.84	1.17	1.41	1.41	0.3	0.27	0.27
N _c	4	2	2	5	4	4	8	3	3	5	5	5

In Tab. 3, N_{osc} represents the dimension of OSC filter, N_c represents the dimension of calibration model.

It can be seen from Tab. 2 and Tab. 3 that 1-dimension OSC filter is good for the components of benzene, methylbenzene, chlorobenzene and benzaldehyde since RMSEV is minimum among 1-, 2- and 3-dimension of OSC filter; while 2-dimension OSC filter is good for the component of acetophenone since RMSEV is minimum among the three dimensions of OSC filter but will not decrease when 3-dimension OSC filter being applied.

4 Conclusion

OSC-PLS algorithm was applied to benzene, methylbenzene, chlorobenzene, benzaldehyde and acetophenone in the mixed liquid samples in this thesis. The result indicated that OSC is a good filter for PLS, which can extract the useful information efficiently and acquire precise calibration model.

Acknowledgment. This thesis is supported by National Science Foundation of China, No. 20575076.

Reference

1. Guoping Wu, Bingren Xiang (吴国萍, 相秉仁): Nondestructive Determination of MDMA and MA in Ecstasy by Near Infrared Spectroscopy (近红外光谱技术应用于摇头丸中 MDMA、MA 无损定量分析的研究). *Journal of Instrumental Analysis* (分析测试学报), 26(5), pp. 689 -- 701 (2007)

2. Shengfeng Ye, Shungeng Min, Fangli Qin, Ning Li, Mingxiang Zhang (叶升锋, 闵顺耕, 覃方丽, 李宁, 张明祥): Simultaneous Determination of Glucose, Fructose and Sucrose in Aqueous Solution by Near- infrared Spectroscopy (同时测定水溶液中葡萄糖、果糖和蔗糖的近红外光谱法). *Journal of Instrumental Analysis (分析测试学报)*, 22(3), pp. 89 -- 91 (2003).
3. Cui-ling Yang, Xingzhong Zhao, Wenjie Chen, Jianhua Tian, Dianrong Li (杨翠玲, 赵兴忠, 陈文杰, 田建华, 李殿荣): Analyses of Oil Content and Erucic Acid in Small Sample of Rapeseed by Near Infrared Reflectance Spectroscopy (近红外(NIRS)技术分析小样品油菜籽芥酸和含油量的应用研究). *Journal of Instrumental Analysis (分析测试学报)*, 26(1), pp. 29 -- 33 (2007)
4. Xin Xiao, Xinhua Xie, Xingxue Mao, Wenyong Luo, Jianwei Chen, Yanzhuo Liu, Xiaofang Li (肖昕, 谢新华, 毛兴学, 罗文永, 陈建伟, 刘彦卓, 李晓方): Determination of Protein in Milled Rice by Near Infrared Transmittance Spectroscopy (用近红外透射光谱技术测定精制蛋白质含量研究). *Journal of Instrumental Analysis (分析测试学报)*, 23(4), pp. 43 -- 45 (2004)
5. Jinsong Li, Hongjun Li, Jingjing Liang, Zhifei Wang, Wei Liu, Jianqiu Hou, Jishou Zhao, Shupeng Gao (李劲松, 李红军, 梁菁菁, 王志飞, 刘巍, 侯俭秋, 赵吉寿, 高树鹏): Analysis of Ash, Total Volatile Acids and Total Volatile Bases in Tobacco with Near Infrared Spectroscopy (烟草灰分、总挥发酸和总挥发碱的近红外光谱分析). *Journal of Instrumental Analysis (分析测试学报)*, 26(5), pp. 655 -- 657 (2007)
6. Ping Qian, Guoqin Sun, Cunzhou Zhang (钱平, 孙国琴, 张存洲): A Novel Fuzzy Neural Network Method for Diesel Quantitative Analysis with Near Infrared Spectroscopy (基于近红外光谱技术的石油组分定量分析新方法). *Spectroscopy and Spectral Analysis (光谱学与光谱分析)*, 28(12), pp. 2851 -- 2854 (2008)
7. Mingyang Liu, Yu Meng, Yulin Ren, Hanqi Zhang (刘名扬, 孟昱, 任玉林, 张寒琦): Nondestructive Quantitative Analysis of Cofrel Medicines by Improved Partial Least Squares - NIR Spectroscopy (改进的偏最小二乘--近红外光谱法非破坏定量分析 Cofrel 药品). *Spectroscopy and Spectral Analysis (光谱学与光谱分析)*, 27(6), pp. 1098 -- 1101 (2007)
8. Limin Fang, Min Lin (方利民, 林敏): Prediction of Active Substance Contents in Pharmaceutical Tablet Using ICA and NIR (ICA 方法与 NIR 技术用于药片中活性成分含量的测定). *Acta Chimica Sinica (化学学报)*, 66(15), pp. 1791 -- 1795 (2008)
9. Wencui Zhao, Ying Dou, Zhen Tang, Fuqiang Liu, Mingyang Liu, Youbing Wang, Yulin Ren (赵文萃, 窦英, 汤真, 刘福强, 刘名扬, 王友兵, 任玉林): Determination of cimetidine in tablets by near-infrared spectroscopy and PLS (偏最小二乘--近红外漫反射

光谱法测定米西替丁药片). Chinese Journal of Analysis Laboratory (分析实验室), 23(10), pp. 85 -- 88 (2004)

10. Svante Wold, Henrik Antti, Fredrik Lindgren, Jerker Öhman: Orthogonal signal correction of near-infrared spectra. *Chemometrics and Intelligent Laboratory Systems*, 44, pp. 175 -- 185 (1998)
11. Tom Fearn: On orthogonal signal correction. *Chemometrics and Intelligent Laboratory Systems*, 50, pp. 47 -- 52 (2000)
12. Johan A. Westerhuis, Sijmen De Jong, Age K. Smilde: Direct orthogonal signal correction. *Chemometrics and Intelligent Laboratory Systems*, 56, pp. 13 -- 25 (2001)
13. Robert N. Feudale, Huwei Tan, Steven D. Brown. Piecewise Orthogonal Signal Correction. *Chemometrics and Intelligent Laboratory Systems*, 63, pp. 129 -- 138 (2002)
14. M. Blanco, J. Coello, I. Montoliu, M. A. Romero. Orthogonal signal correction in near infrared calibration. *Analytica Chimica Acta*, 434, pp. 125 -- 132 (2001)
15. E. Bertran, H. Iturriaga, S. MasPOCH, I. Montoliu: Effect of orthogonal signal correction on the determination of compounds with very similar near infrared spectra. *Analytica Chimica Acta*, 431, pp. 303 -- 311 (2001)