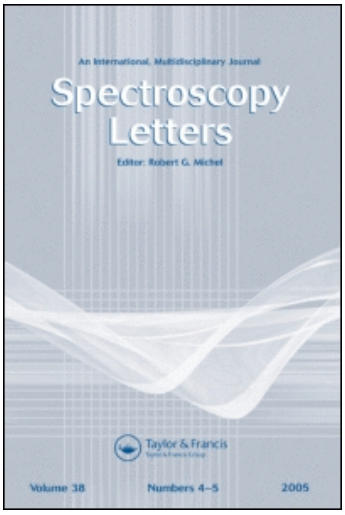

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ELIMINATION OF INTERFERENTS INFLUENCE IN SIMULTANEOUS DETERMINATION OF ORGANIC GASES USING PLS WITH FTIR SPECTROSCOPY*

Keywords: Multicomponents Analysis; Organic Compounds Analysis; FTIR; Partial Least-Squares Method; Interference

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Abstract

The most serious problem in multivariate calibration analysis is that the prediction samples may contain the interferents which are not modeled in the calibration step. Then how to detect the interferents and eliminate their influence is significantly important in order to obtain the correct compositional analysis results. The so-called residual spectra library search is supplied and an iterative loop regression algorithm to successfully correct the spectrum containing two interferents is developed in this paper. Three groups of which each sample contains no, one or two interferents are supplied to amplify the above method. The mean relative standard deviation (RSD) for the three groups are 0.163, 0.375, 0.355%, respectively. There are no

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comparable difference among these RSDs, which proves the validation of the method provided in this paper. The results specify that PLS with FTIR spectroscopy is a powerful tool to resolve both the multicomponent simultaneous determination and the identification of interferents when combined with additional diagnostic and corrected procedure.

I. INTRODUCTION

In last decade, the applications using partial least squares method (PLS) with FTIR spectroscopy has grown rapidly[1-5]. The distinctive virtue to use PLS is in that PLS has the prognostic function either by a prognostic vector[6] or by residual spectra search[7] to conclude whether the prediction samples contains constituents which are not modeled in the calibration model during the prediction step. If the prediction samples contain interferents, we should analyze the composite of the prediction samples to identify the category of the interferents. Hitherto, the composition analysis of a mixture can be accomplished by the so-called library search (LS) either with a simple curve fitting technique[8-10] or with a Mix-Match search technique[11]. After unambiguously identifying the interferents, we can eliminate the influence of the interferents by the so-called recalibration to build a new calibration model in which the interferents are included, and then predict the sample composition. However, Ruyken et al. produced a residual spectra search method to detect and identify the interferents simultaneously. They successfully detected and corrected one interferent in the simultaneous determination of two component mixtures using the PCR with FTIR spectroscopy, while "the presence of two or more interferents can be detected but not corrected with the method described "[7]. In this paper, our efforts focus on the following points: 1) to verify the validation of PLS with FTIR spectroscopy to simultaneously determine five components mixtures. 2) to detect one interferent in the prediction samples and eliminate the influence of the interferent without recalibration. 3) to develop an iterative loop algorithm to detect two interferents and correct the spectrum in the presence of these interferents.

II. THEORY

In this section we will give a brief description of the PLS principle, the detection and correction for one interferent when using PLS

calibration method. For detail, please refer to references [12,13] for PLS principle and [7] for "detection and correction for one interferent". We will describe somewhat specifically of correcting two interferents in the prediction samples. Notion used: upper case italic characters, matrices, lowercase italic characters, column vectors, a prime denotes a transposed matrix or vector.

2.1. The PLS calibration and prediction

In the calibration step, the absorbance matrix X and the concentration matrix Y are decomposed into their loadings and scores by an iterative NIPALS algorithm:

$$X = TB + E$$

$$Y = UV + F$$

$$U = TD$$

where T and U represent the scores matrix of X and Y, respectively. The B and V are the loading matrix of X and Y, respectively. The s is the significant factor number. The E and F represent the unique variation in X and Y that are not explained by determined significant factor solution. D is the regression coefficient matrix of scores U for T.

In the prediction step, the absorbance vector x_i is decomposed using the calibration model and the concentration vector y_i is formed:

$$x_i = tB$$

$$u = tD$$

$$y = uV$$

where x_i is the prediction samples vector and y_i is the solution desired. Then we got the residual spectrum vector e_i and the root-mean-square spectrum error ($RMSSPE$)

$$e_i = x_i - \sum_{s=1}^{S} t_{i,s} B_{s,k}$$

$$RMSSPE = \sqrt{\sum_{k=1}^{K} e_{i,k}^2 / K}$$

where s is the significant number and K is the number of measured wavenumbers.

2.2. The identification of interferents

$H(x, z)$ is defined to compare the similarity between the spectra x and z.

$$H(x,z)=\frac{x\ z}{\|x\|\|z\|}$$

We calculated $H(e_x,e_z)$ for all the library spectra z, where e_x and e_z are the residual spectra of sample spectrum x and library spectrum z. The z that maximizes $H(e_x,e_z)$ is the interferent in sample x[7].

2.3 The correction of one interferent

Suppose z is the interferent in the prediction sample x. From the residuals it follows that

$$e_x=\lambda^{-1}e_z$$

then λ can be calculated by

$$\lambda=\frac{RMSSPE_{(z)}}{RMSSPE_{(x)}}$$

so, the corrected spectrum can be obtained:

$$x_{corr}=x-\lambda^{-1}z$$

In theory, if the concentration of the interferent in prediction sample has been known and the Lambert-Beer law holds, the coefficient of the interferent $\lambda_{th.}$ can be calculated:

$$\lambda_{th.}=\frac{c_s}{c_l}$$

where the c_s,c_l are the concentrations of the interferent in prediction sample and spectra library, respectively.

2.4. The correction of two interferents

Suppose z_1 and z_2 are the interferents in the prediction sample x. The residual e_x can be written by analogy :

$$e_x=\lambda_1^{-1}e_{z_1}+\lambda_2^{-1}e_{z_2}$$

then λ_1 and λ_2 can be estimated:

$$\lambda_1=\frac{RMSSPE_{(z_1)}}{RMSSPE_{(x-\lambda_2^{-1}z_2)}}$$

$$\lambda_2=\frac{RMSSPE_{(z_2)}}{RMSSPE_{(x-\lambda_1^{-1}z_1)}}$$

The iterative loop equations are written in the following:

$$\lambda_1^k=\frac{RMSSPE_{(z_1)}}{RMSSPE_{(x-\lambda_2^{k-1}z_2)}}\qquad(k=1,2,3\cdots)$$

$$\lambda_2^k = \frac{RMSSPE_{(z_2)}}{RMSSPE_{(x-\lambda_1^{k-1}z_1)}} \qquad (k = 1,2,3\cdots)$$

to take the first value $\lambda_1^0 = RMSSPE_{(z_1)} / RMSSPE_{(x)}$, through the above equation we got the $\lambda_2^1, \lambda_1^1; \lambda_2^2, \lambda_1^2; \cdots; \lambda_2^k, \lambda_1^k$ values until $\left|\lambda_1^k - \lambda_1^{k-1}\right| < 10^{-3}$. Then λ_1 and λ_2 are obtained:

$$\lambda_1 = \lambda_1^k$$

$$\lambda_2 = \lambda_2^k$$

so, the corrected spectrum are calculated:

$$x_{corr} = x - \lambda_1^{-1} z_1 - \lambda_2^{-1} z_2$$

III. EXPERIMENTAL

3.1. The experimental instruments

A Nicolet 170SX FTIR Spectrometer equipped with a globar light source, TGS detector with KBr window and a KBr beamsplitter was used. The data system was a Nicolet 1280 data station with 4096 byte of RAM and a 24 Mbyte winchester disk driver.

3.2. The data collection and process

Since PLS is a full-spectrum calibration method, the spectral regions in 3160-2800 and 850-655 cm^{-1} are used for the multivariate calibration. The spectral limits are selected in order to cut off most of the contributions from water vapor(4000-3170 and 2140-1230 cm^{-1}) and carbon dioxide (2400-2230 and 735-613 cm^{-1}) and to contain as many spectra information as possible. All spectra were obtained with a resolution of 2 cm^{-1} by using 32 co-added interferograms in the frequency range from 4000-400 cm^{-1}. But the collected data for the absorbance identity is acquired at the interval of 15 cm^{-1}. The library spectra in this study consists of 31 toxic organic compounds and each compound concentration is 50 ppm. The computational program is written with Q-Basic 4.5. All the data for absorbance and concentration are not centered or normalized.

IV. RESULTS AND DISCUSSION

4.1. The choice of five components and interferents

The air toxic organic compounds whose spectra are strongly overlapped one another are selected to measure the performance of PLS

method. The chosen compounds are Ethylbenzene, Styrene, o-Xylene, m-Xylene and p-Xylene. The FTIR spectra for the five components are shown in Fig.1.A, 1.B, 1.C, 1.D and 1.E. From Fig.1, the strong overlap in the two measured wavenumber bands selected among the five components can be seen clearly. Furthermore, the five components have close boiling points, which nearly rules out the possibility to separate the components for further measurement individually. As for the interferents, they must belong to the air toxic organic compounds prescribed by EPA, and they should have obvious absorption peak in the above chosen measured wavenumber bands. The five interferents used in this paper are Acrylic acid, Acetophenone, Acrolein, Allyl chloride and Chloroprene, whose FTIR spectra for the interferents are provided in Fig.2. As a similar example of the prediction sample, a composite spectrum in Fig.1.K consisting of the above five components and two interferents which are Acrylic acid and Chloroprene as well as the spectra of the two interferents in Fig.1.F and 1.J are also supplied to manifest the overlap situation among the components and interferents.

4.2. The experimental design of the calibration, validation and prediction samples

The composite of each calibration samples is designed according to the $L_{16}(4^5)$ orthogonal experimental design in that the number of the components in the mixture is five and all the concentrations of each component in the mixture vary from 5 to 100 ppm. The four levels are 5, 20, 50 and 100 ppm, respectively. That is to say, it is a five factor four level experimental design. Five validation samples, which are similar to the calibration samples, are used to determine the significant factor number. As for the prediction samples, 15 prediction samples are divided into three groups of which each group contains five samples.

No interferents lie in the samples of the first group (Group #1) which is similar to the calibration samples. The samples in the second group (Group #2) contain one interferent each, while two interferents whose concentrations are in the same order compared with those of the prediction components are mixed in the samples of the third group (Group #3). The components and the interferents for each prediction sample are listed in Table 1.

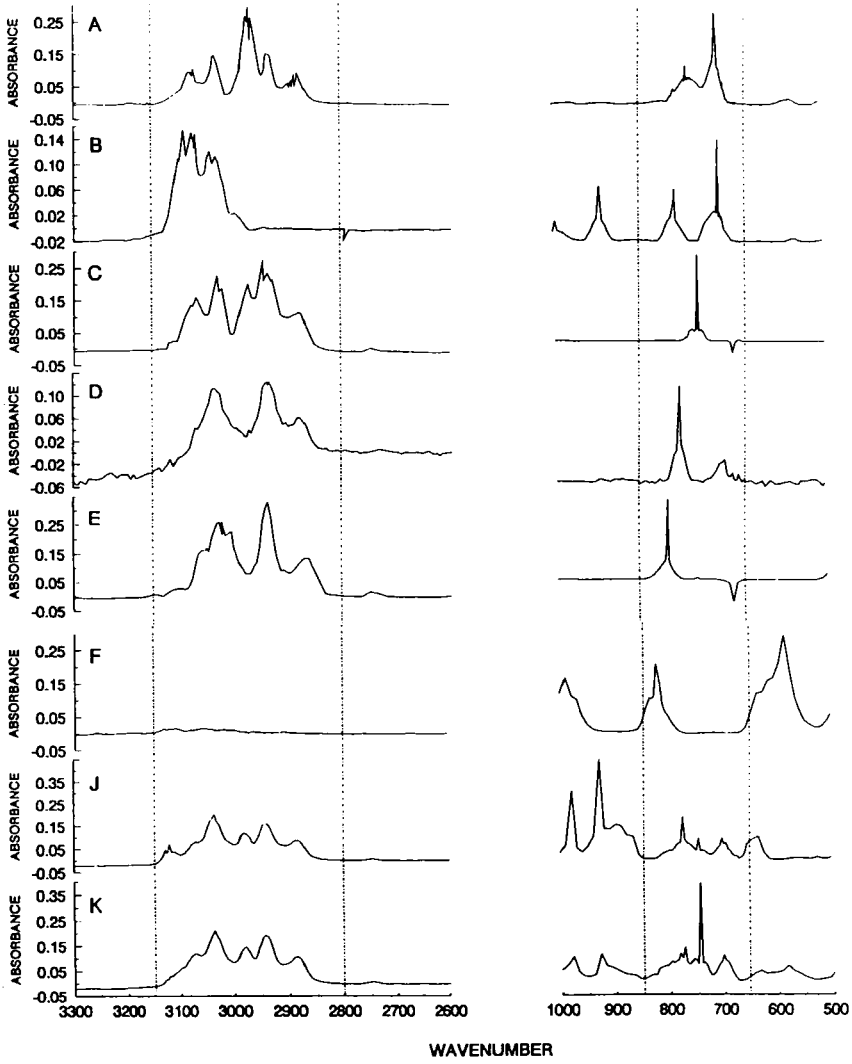

Fig. 1. The spectra of five components (500 ppm each), two interferents(500 ppm each) and their composite mixture (100 ppm for each compound).

Note: A. Ethylbenzene; B. Styrene; C. o-Xylene; D. m-Xylene; E. p-Xylene; F. Acrylic acid; J. Chloroprene.
K. The mixture of the seven compounds above.

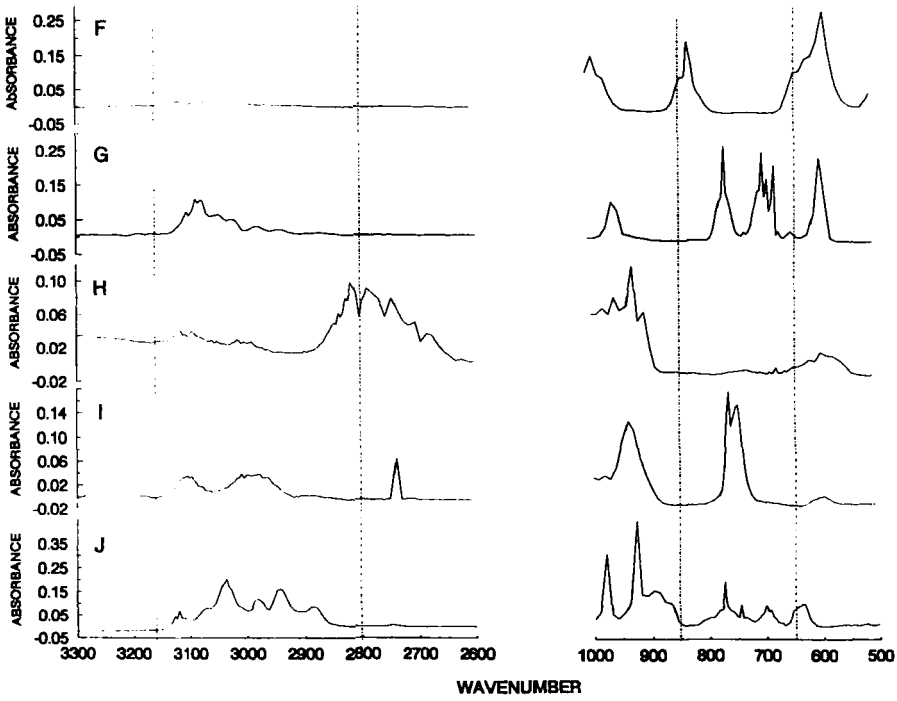

Fig.2. The spectra of five interferents (500 ppm each).
Note: F. Acrylic acid; G. Acetophenone; H. Acrolein; I. Allyl chloride; J. Chloroprene.

4.3. The significant factor number

During the calibration step, the significant factor number can be decided by three methods generally. It includes manual designation, samples validation and cross-validation methods. Although the significant factor numbers are 7, 7 and 9, respectively by the above three determination methods, no comparable difference lies in the prediction results in this study. In this paper the validation sample method is adopted to determine the significant factor number as 7 since this method needs less computation time compared with the cross-validation method and assure the reliability of the results in contrast to the manual designation method.

Table 1. The composite of the prediction samples ppm

		Components					Interferents				
Group	No.	A	B	C	D	E	F	G	H	I	J
	1	8.0	15.0	70.0	15.0	15.0	–	–	–	–	–
	2	30.0	40.0	60.0	70.0	20.0	–	–	–	–	–
#1	3	70.0	8.0	15.0	30.0	40.0	–	–	–	–	–
	4	40.0	35.0	45.0	35.0	50.0	–	–	–	–	–
	5	15.0	10.0	20.0	18.0	16.0	–	–	–	–	–
	6	55.0	35.0	45.0	65.0	25.0	50.0	–	–	–	–
	7	6.0	8.0	10.0	15.0	18.0	–	20.0	–	–	–
#2	8	8.0	15.0	70.0	15.0	15.0	–	–	50.0	–	–
	9	10.0	30.0	6.0	10.0	8.0	–	–	–	50.0	–
	10	15.0	10.0	20.0	18.0	16.0	–	–	–	–	50.0
	11	55.0	35.0	45.0	65.0	25.0	20.0	–	–	–	20.0
	12	6.0	8.0	10.0	15.0	18.0	–	20.0	20.0	–	–
#3	13	8.0	15.0	70.0	15.0	15.0	–	–	20.0	20.0	–
	14	10.0	30.0	6.0	10.0	8.0	–	–	–	20.0	20.0
	15	15.0	10.0	20.0	18.0	16.0	–	–	20.0	–	20.0

Note: A. Ethylbenzene; B. Styrene; C. o-Xylene; D. m-Xylene; E. p-Xylene; F. Acrylic acid; G. Acetophenone; H. Acrolein; I. Allyl chloride; J. Chloroprene.

4.4. The *RM SSPE* consideration

As a guideline, the threshold limit of *RM SSPE* is set at a value of 2-3 times the *RM SSPE* calculated from the validation samples. So we set the threshold limit of *RM SSPE* as 12.66×10^{-5} in this paper through the calculation. In the prediction step, if the prediction samples are similar to the calibration samples, the calculated values of *RM SSPE* should be less than the given threshold limits. Otherwise, the prediction samples probably contains the interferents which are not modeled in the calibration step. Then we eliminate the influence of the top hit interferent which is obtained from the residual library search and calculate the *RM SSPE* again. As above discussed, if the quantity of *RM SSPE* is still larger than the threshold limit, it proves that two interferents exist in the prediction samples. We should eliminate both the two interferents effect and got the new *RM SSPE* value. Then the quantity of the new *RM SSPE* should be less than the threshold limit, and

it guarantees the success of eliminating the interferents influence and then the good prediction results. If not, it shows that the prediction samples may contain more than two interferents or the interferents which are not included in the library spectra. For this situation, special method is under the investigation to deal with it. Therefore, the $RMSSPE$ is used as an important criterion to conclude the number of interferents and assure the reliability of the prediction results.

4.5. The prediction results of samples in Group #1

As we have discussed in 4.2, Group #1 has five prediction samples which are similar to the calibration samples. So the results are attained without additional calculation step. The prediction results as well as the $RMSSPE_1$ value can be seen from Table 2, where the $RMSSPE_1$ represents the $RMSSPE$ calculated from the original data sets. From Table 2, the $RMSSPE_1$ values for the five prediction samples are 2.93, 4.39, 4.40, 4.46 and 4.93×10^{-5}, respectively, which all are not larger than the threshold limit(12.66×10^{-5}). The relative standard deviations (RSD%) for the five components are 0.237, 0.116, 0.064, 0.276 and 0.122% , respectively. The average value for the above RSD% is 0.024%. It was proved that good results were acquired by PLS with FTIR spectroscopy in spite of the strong overlap among the prediction components.

4.6. The prediction results of Group #2 samples

Since one interferent lies in each prediction sample in Group #2(see Table 1), the calculation process is different from 4.5 discussed above. The $RMSSPEs$, interferent coefficient and residual library search results are listed in Tables 3 and 4, respectively, where the $RMSSPE_2$ is the one after elimination of the influence of the best top hit interferent. We demonstrate the computation process with No. 6 sample as an example. From Table 3, the $RMSSPE_1$ for No. 6 sample is 265.16×10^{-5}, which is obviously larger than the threshold limits. So we got the first five top hits shown in Table 4 by the residual spectra library search. From Table 4, the maximum of H equals to 0.9998 and the detected interferent is Acrylic acid which is indeed the constituent used as the interferent listed in Table 1. Since the coefficient of Acrylic acid λ_1 = 0.9991(seen from Table 3), which is close to the value of its theoretical value $\lambda_{th,1}$ (1.0000), it shows the sample spectrum could be correctly

Table 2. The prediction results of the five components mixtures for samples in Group #1

	Components (ppm)															
	Ethylbenzene			Styrene			o-Xylene			m-Xylene			p-Xylene			$RMSSPE_1$
No.	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	($\times 10^{-5}$)
1	8.000	7.966	-0.43	15.000	14.999	-0.01	70.000	69.967	-0.05	15.000	15.097	0.65	15.000	14.955	-0.30	2.93
2	30.000	30.083	0.28	40.000	39.972	-0.07	60.000	59.964	-0.06	70.000	69.930	-0.10	20.000	19.983	-0.08	4.39
3	70.000	69.993	-0.01	8.000	7.984	-0.20	15.000	14.985	-0.10	30.000	30.111	0.37	40.000	39.970	-0.07	4.40
4	40.000	40.039	0.10	35.000	34.954	-0.13	45.000	44.981	-0.04	35.000	34.927	-0.21	50.000	49.958	-0.08	4.46
5	15.000	14.857	-0.95	10.000	10.000	0.00	20.000	20.025	0.12	18.000	17.895	-0.58	16.000	16.032	0.20	4.93
RSD%		0.237			0.116			0.064			0.276			0.122		
Mean[a]								0.024								4.22

Note: a. The average value for RSD% and $RMSSPE_1$.

Table 3. The $RMSSPE$ and interferent coefficient for Group #2 in the PLS prediction step

Group	No.	$RMSSPE_1$ ($\times 10^{-5}$)	$RMSSPE_2$ ($\times 10^{-5}$)	λ_1	$\lambda_{\#1}$
	6	265.16	5.40	0.9991	1.0000
	7	107.70	5.18	2.5391	2.5000
#2	8	230.51	5.88	1.0172	1.0000
	9	220.02	5.31	1.0035	1.0000
	10	142.38	4.70	1.0001	1.0000
Mean	–	193.15	5.29	–	–

Threshold limit for $RMSSPE$, 12.66×10^{-5}

adjusted. That the $RMSSPE_2$ equals to 5.40×10^{-5}, which is less than the threshold limit (12.66×10^{-5}), also specifies the influence of the interferent Acrylic acid was successfully eliminated by the residual spectra search technique. Therefore, the concentrations of the five components in No. 6 sample are calculated by the corrected spectrum and the results are listed in Table 5. The relative errors (RE%) for sample No. 6 from Table 5 is very little. Similar computation and approximate results are obtained for the other four samples in Group #2. From Table 5, the RSDs for the five components in Group #2 samples are 0.361, 0.332, 0.086, 0.800 and 0.296%, respectively. The arithmetic mean value of RSD% is 0.375%. The results prove the validation of the residual spectra search technique for the sample that contains only one interferent.

4.7. The prediction results of the samples containing two interferents in Group #3

Table 6 consists of the $RMSSPE$ results and coefficients of interferents where the $RMSSPE_1$ and $RMSSPE_2$ have the same meaning as that in 4.6 and $RMSSPE_3$ represents the $RMSSPE$ calculated from the corrected spectrum after eliminating the two interferents influence. The residual library search results are listed in Table 7. As an example, No. 11 sample is used to elucidate the results. From Table 6, assumption that no interferents lies in No. 11 sample, the $RMSSPE_1=$

Table 4. The residual spectra search results for Group #2

Sample No.	Top hit No. 1		Top hit No. 2		Top hit No. 3		Top hit No. 4		Top hit No. 5	
	Name	*H*	Name	*H*	Name	*H*	Name	*H*	Name	*H*
6	Acrylic acid	0.9998	2,4,6-Tri-chlorophenol	0.5422	Methyl methacrylate	0.4602	Quinine	0.3518	Maleic anhydride	0.2730
7	Aceto-phenone	0.9988	Styrene oxide	0.6936	Allyl chloride	0.6786	o-Cresol	0.5920	Benzene	0.3131
8	Acrolein	0.9997	Acet-aldehyde	0.8224	Methanol	0.3581	Aceto-phenone	0.2589	Chloroprene	0.2573
9	Allyl chloride	0.9997	Aceto-phenone	0.6799	Styrene oxide	0.6616	o-Cresol	0.4896	Methyl chloride	0.3235
10	Chloroprene	0.9995	Benzene	0.4506	Vinyl bromide	0.3064	Acrolein	0.2647	Aceto-phenone	0.2269

Table 5. The prediction results of the five components mixtures for samples in Group #2

Sample	Components (ppm)															mean
	Ethylbenzene			Styrene			o-Xylene			m-Xylene			p-Xylene			
No.	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	RE%[a]
6	55.000	55.034	0.06	35.000	34.978	-0.06	45.000	44.991	-0.02	65.000	64.723	-0.43	25.000	25.102	0.41	0.20
7	6.000	6.004	0.07	8.000	8.095	1.18	10.000	10.011	0.11	15.000	14.994	-0.04	18.000	17.995	-0.03	0.29
8	8.000	7.958	-0.52	15.000	14.966	-0.23	70.000	70.010	0.01	15.000	14.800	-1.33	15.000	15.013	0.09	0.44
9	10.000	10.108	1.08	30.000	29.922	-0.26	6.000	5.986	-0.23	10.000	9.731	-2.69	8.000	8.009	0.11	0.87
10	15.000	15.092	0.61	10.000	10.067	0.67	20.000	19.947	-0.27	18.000	17.927	-0.39	16.000	16.032	0.20	0.43
RSD%		0.361			0.332			0.086			0.800			0.296		
Mean[b]								0.375								0.45

Note: a. The mean absolute value RE%; b. The arithmetic mean for five RSD% and mean RE%.

Table 6. The $RMSSPE$ and interferents coefficient for Group #3 in the PLS prediction step

Group	No.	$RMSSPE_1$ ($\times10^{-5}$)	$RMSSPE_2$ ($\times10^{-5}$)	$RMSSPE_3$ ($\times10^{-5}$)	λ_1	$\lambda_{th.1}$	λ_2	$\lambda_{th.2}$
	11	121.95	58.66	5.26	2.4988	2.5000	2.4995	2.5000
	12	161.96	94.74	5.98	2.4805	2.5000	2.5002	2.5000
#3	13	126.42	95.64	5.70	2.5301	2.5000	2.4928	2.5000
	14	149.17	91.83	5.62	2.5332	2.5000	2.5143	2.5000
	15	121.90	56.50	3.77	2.4886	2.5000	2.5051	2.5000
Mean	–	136.28	79.47	5.27	–	–	–	–

Threshold limit for $RMSSPE$, 12.66×10^{-5}

121.95×10^{-5} and it is larger than the threshold limit. So the top hit Acrylic acid is identified by the residual spectra library search and its influence is eliminated by the same procedure as that in 4.6. But $RMSSPE_2=58.66\times10^{-5}$, which is still larger than the threshold limit. So we call the iterative loop program to correct the spectrum by simultaneously eliminating the influence of the first top two hits, i.e., Acrylic acid and Chloroprene listed in Table 7. From Table 6, the coefficients for the above interferents λ_1, λ_2 are 2.4805 and 2.5002, which are very near to their theoretical value 2.5000, 2.5000(see $\lambda_{th.1}$ and $\lambda_{th.2}$), respectively. So the spectrum of this sample has been successfully corrected. The less value of $RMSSPE_3(5.26\times10^{-5})$ compared with the threshold limit(12.66×10^{-5}) also shows that the elimination procedure has been performed successfully. Therefore, the prediction results listed in Table 8 are calculated by the corrected spectrum. The relatively less quantities of RE% (see Table 8) specify the interferents in No. 11 are Acrylic acid and Chloroprene, which are actually the interferents used in No. 11 sample, and the influence of these two interferents are successfully eliminated. The same computation steps as those of No. 11 sample are practiced and similar results are obtained for the other four samples in Group #3. From Table 8, the RSDs for each component are 0.592, 0.212, 0.139, 0.363, 0.469%, respectively. The mean RSD is 0.355%.

Table 7. The residual spectra search results for Group #3

Sample No.	Top hit No. 1		Top hit No. 2		Top hit No. 3		Top hit No. 4		Top hit No. 5	
	Name	*H*	Name	*H*	Name	*H*	Name	*H*	Name	*H*
11	Acrylic acid	0.8843	Chloroprene	0.4951	Methyl methacrylate	0.4462	2,4,6-Tri-chlorophenol	0.3452	Vinyl bromide	0.3071
12	Aceto-phenone	0.8289	Acrolein	0.7530	Styrene oxide	0.5075	Acet-aldehyde	0.4846	Allyl chloride	0.4482
13	Acrolein	0.7138	Allyl chloride	0.6805	Aceto-phenone	0.6690	Acet-aldehyde	0.5295	Styrene oxide	0.5133
14	Chloroprene	0.8105	Allyl chloride	0.6612	Aceto-phenone	0.5748	Styrene oxide	0.5312	o-Cresol	0.4648
15	Acrolein	0.8926	Chloroprene	0.6648	Acet-aldehyde	0.6155	Aceto-phenone	0.3139	Benzene	0.2464

Table 8. The prediction results of the five components mixtures for samples in Group #3

Sample	Components (ppm)															mean
	Ethylbenzene			Styrene			o-Xylene			m-Xylene			p-Xylene			
No.	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	C_{real}	$C_{meas.}$	RE%	RE%[a]
11	55.000	54.985	-0.03	35.000	34.954	-0.13	45.000	45.041	0.09	65.000	64.912	-0.14	25.000	25.087	0.35	0.15
12	6.000	6.095	1.58	8.000	7.946	-0.68	10.000	9.954	-0.46	15.000	15.139	0.93	18.000	17.985	-0.08	0.75
13	8.000	8.119	1.49	15.000	15.020	0.13	70.000	69.990	-0.01	15.000	14.951	-0.33	15.000	14.965	-0.23	0.44
14	10.000	10.191	1.91	30.000	30.057	0.19	6.000	6.068	1.13	10.000	10.074	0.74	8.000	8.142	1.77	1.15
15	15.000	14.954	-0.31	10.000	10.002	0.02	20.000	20.021	0.10	18.000	18.069	0.38	16.000	16.022	0.14	0.19
RSD%		0.592			0.212			0.139			0.363			0.469		
Mean[b]								0.355								0.54

Note: a. The mean absolute value RE%; b. The arithmetic mean for five RSD% and mean RE%.

Table 9. The mean $RMSSPE$ and RSD

Group	Mean			RSD%
	$RMSSPE_1$ ($\times 10^{-5}$)	$RMSSPE_2$ ($\times 10^{-5}$)	$RMSSPE_3$ ($\times 10^{-5}$)	
#1	4.22	–	–	0.163
#2	193.15	5.29	–	0.375
#3	136.28	79.47	5.27	0.355

4.8. The comparison of the prediction results in all the three Groups

From Tables 2, 3, 5, 6, 8, the mean $RMSSPE$ and RSD for the above three groups are obtained and listed in Table 9. The mean $RMSSPE_1$ for Group #1, $RMSSPE_2$ for Group #2 and $RMSSPE_3$ for Group #3 are 4.22×10^{-5}, 5.29×10^{-5} and 5.27×10^{-5}, respectively, which are all in the same order; No comparable difference for the mean RSD% lies in the three groups, either. At this point, it shows the residual library search accompanied with iterative loop algorithm to correct the spectrum is an effective tool to solve the influence for multi-interferent in the PLS calibration method.

V. CONCLUSION

The simultaneous determination of five component air toxic organic compounds mixture is studied when using the PLS method by FTIR spectroscopy. When the prediction sample contains 1 or 2 interferents which are not modeled in the calibration step, the identification and number of the interferents are determined, and the corrected spectrum is obtained by iterative loop algorithm to eliminate the influence of the interferents. The results show that with no need of the trivial recalibration, the method discussed in this paper can effectively correct the spectrum to eliminate the influence of multi-interferent, such as two interferents, while the measured precision is not reduced in the simultaneous determination of multicomponent mixture.

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