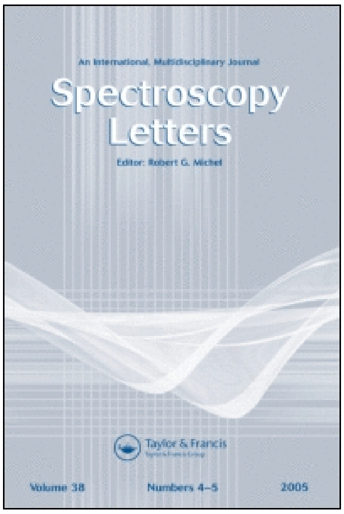

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Junde Wang[a]; Malcolm R. Clench[b]; Tianshu Wang[a]; Zuoru Chen[a]; Yunhua Luo[a]; David J. Mowthorpe[b]; Michael Cooke[b]
[a] Laboratory of Advanced Spectroscopy, Nanjing University of Science & Technology, Nanjing, China
[b] School of Science, Sheffield Hallam University, Sheffield, UK

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THE QUANTITATIVE ANALYSIS OF MULTICOMPONENT GASEOUS MIXTURES OF ORGANIC COMPOUNDS BY FT-IR

Keywords: Fourier transform infrared spectroscopy; organic compound analysis

Junde Wang [a,*], Malcolm R. Clench [b], Tianshu Wang [a], Zuoru Chen [a], Yunhua Luo [a], David J. Mowthorpe [b], Michael Cooke [b]

[a] *Laboratory of Advanced Spectroscopy, Nanjing University of Science & Technology, Nanjing 210014, China*

[b] *School of Science, Sheffield Hallam University, Pond Street, Sheffield S1 1WB, UK*

Abstract

Fourier transform infrared classical computation method applied to the direct quantitative analysis of multicomponent gaseous mixtures of the organic compounds was described in the paper. For the analysis of multicomponent mixtures a number of important problems, such as select of quantitative optimal peak windows and calibration of the spectral band overlapping between the compounds, had been discussed. The FT-IR software for multicomponent simultaneous determination of up to 10 compounds in a gaseous mixture had been completed. The software can provide two kinds of the linear and non-linear fits for the calibrating concentrations of the interference components. The accuracy, precision and time of the analysis were satisfactory. The results indicate that the method can be used for the simultaneous quantitative analysis of the multicompounent gaseous mixtures of the organic compounds even if there are serious overlaps of the infrared spectral absorption bands of the compounds.

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* Corresponding author.

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1. Introduction

FT-IR gaseous multicompounent determination has been applied in many areas, such as air pollution analysis, industrial process control, combustion product analysis [1-5]. Junde Wang et al. [6] recently summarized the analysis for multicompenent gaseous mixtures by FT-IR.

Monitoring and controlling the organic gases become an urgent problem. A clear need for sensitive, accurate and versatile monitors for the organic gases has motivated the development of new approaches to chemical analysis[1,2,7,8]. Though these approaches are accurate for monitoring individual compounds or identifications of the compounds, most of them can not be used to monitor multicomponent analysis or identification of the organic gaseous compounds simultaneously. Because Fourier transform infrared spectroscopy has many advantages, such as multiplex advantage, high optical throughput, high spectral resolution, accurate frequency measurement and data processing advantage, it can overcome the difficulty mentioned above. But the simultaneously multicomponent analysis of the organic gaseous compounds is not easily completed by the common FT-IR analytical methods owing to the serious overlapping of the spectral bands of the organic compounds. Therefore it is very important to investigate a direct FT-IR method for simultaneously multicomponent qualitative and quantitative analysis [9-13].

At the some time, a number of computation programs of the analysis have also been developed to assist the chemists in the quantitative analysis with FT-IR, such as Inverse Least - Squares(ILS) [14], Classical Least - Squares(CLS) [15], Partial Least - Squares(PLS) [16], Principal Component Regression(PCR) [17], Artificial Neural Network [2] methods and so on. More recently, Hakli et al.[18] used classical fit for simultaneous determination of the hydrocarbons in a gaseous mixture. All the spectra were recorded at lower resolution of 8 cm^{-1} in the wavenumber range from 4000 to 1000cm^{-1}. A gas cell path length of 4 cm was used. The analytical concentration range is about 0.49 - 1.27 % (v/v). All these methods are based on Beer's law and are successful in the quantitative analysis of multicomponent mixtures, i.e., there are the linear relationships between the concentrations and absorbances, even there are serious overlaps of the spectral bands. The quantitative prediction abilities of these multivariate calibration methods for infrared spectral quantitative analysis had been evaluated by Thomas[19].

The intent of this study is to try to presents a software for an effective method for the quantitative FT-IR spectral analysis of multicomponent organic gaseous compounds. The method must have these abilities, such as the calibration of the overlaps of the infrared spectral bands located the analytical peak, the baseline calibration, optimal quantification peak window selection, etc. In addition, the solfware is also suitable when there is non-linear relationship between the component concentration and their absorbance for the calibration of spectral band overlaps. The results demonstrated that the computation method is a simple, rapid and precision method for direct quantification of multicomponent organic gas mixtures even in these cases where there are serious overlaps of the spectral bands.

2. Experimental

A Nicolet 170SX FT-IR spectrometer equipped with a globar light source, TGS detector with KBr window and a KBr beamsplitter was used. The data were collected by using 32 co-added interferograms in the spectral region from 4000 to 400 cm^{-1} at 2 cm^{-1} spectral resolution, which is optimal for the analysis of organic gas mixtures because 2 cm^{-1} spectral resolution can both provide the required information and not require the use of excessive computative time[7]. The data system was a Nicolet 1280 data station equipped with 4096 byte of RAM and a 24 Mbyte winchester disk drive.

A 10 cm long, KBr window gas cell was used to collect samples through a vacuum system. The pressure of the samples was read out on the pressure meter.

Each sample analyzed in this work was contained two to five different organic compounds.

3. Theory

Generally, the relationship between the concentration and absorbance is shown below:

$$A_i = a_i b C_i^n + A_{0i}$$

where A_i = absorbance value measured at the frequency, ν_i (cm^{-1}).

a_i = absorptivity at the frequency, ν_i (cm^{-1}), for the component i.

b = path length of the radiation through the sample (i.e. cell thickness).

n = the power for the concentration. $n = 1$ and $A_{0i} = 0$ for Beer's law.

A_{0i} = blank

If there are m components in an unknown sample, at least m reference samples and m characteristic frequencies are required for the analysis. The m equations in the simultaneous equation will be listed at the m characteristic frequencies. The simultaneous equation can be expressed with a single equation as follows :

$$A_i = \sum_{i=1}^{m} a_i b C_i^n + A_{0i} \qquad \text{for } m \text{ components in an unknown sample}$$

where i is the number of the reference samples, $i = 1, 2, \cdots m$.

The quantitative analysis of the sample is accomplished through two steps : the calibration and analysis computation of the concentration of the unknown sample. In the first step, a set of reference samples of known concentrations for all components are entered into the spectrometer to collect their spectra, then the names and the numbers for all the components, the frequencies used for quantitative analysis, and start and end frequency values of the optimal peak windows corresponded to these frequencies of the quantitative analysis and the numbers of the optimal peak windows are stored. Through the calibration menu of the quantitative analysis software, we can obtain all the reference coefficients, such as the absorbance values A_i , the absorptivities a_i and A_{0i} in the simultaneous equation. So the calibration is necessary, and the key of the analytical accuracy. The second step is the analysis : firstly, the desired sample is entered into the spectrometer to collect their spectrum. After the names and the numbers for the components are entered into computer, the spectrum is automatically analyzed for the concentrations of these components in desired sample by using the parameters established in the calibration program.

4. Results and Discussion

4.1. the fit models in the quantitative analysis software

Because there are overlaps between the infrared spectral bands of both the interference and desired components, it is necessary for the calibration of the spectral bands. There are 6 fit models of the relationships between their absorbencies and component concentrations in the calibration program of our quantitative analysis software. 6 fit models can be selected as follows :

1) No fitting (comonent does not contribute to the band the desired sample).
2) Linear fit going through (0,0) point (Beer's law).
3) Linear fit with an intercept (blank effect).
4) Non-linear to the power of 2 for the concentrations of the interference components.
5) Non-linear to the power of 3 for the concentrations of the interference concentrations.
6) Non-linear to the power of 4 for the concentrations of the interference concentrations.

4.2. The peak window and measurement frequency

To obtain good accuracy of the quantitative analysis of organic gas multicomponent mixtures, it is very important to select the optimal peak windows. The corrected selection of the peak windows can decrease the number of the overlaps of the infrared spectral bands of the organic gas compounds and the limit of the detection, and increase the precision of the analytical detection. For corrected measuring absorbances, the selection of the start and end frequencies of the optimal peak window is also very important because the baseline of the peak window is drawn between the start and the end frequencies of the peak window. In this paper the optimal peak windows are listed in Table 1.

4.3. The selection of the fit models

We must choose the suitable fit model before the reference sample calibration and desired sample analysis. Now we only give methanol spectral

Table1. The optimal peak window and frequency used for quantitative analysis of organic compounds

Compound	Window, cm^{-1} Start	End	Measured frequency, cm^{-1}
Acetal dehyde	1025	1180	1130
Acetone	1211	1224	1218
Acetonitril	960	1140	1045
Acrylonitrile	830	1060	955
Benzene	669	680	673
Butyl acetate	1150	1330	1240
Carbon tetrachloride	788	807	795
Chloroform	1180	1260	1220
Ethyl oxide	770	870	875
Freon 11	810	890	1130
Freon 114	810	990	1218
Hexane	2770	3020	2970
Methanol	1024	1045	1037
Methe ethy ketone	1630	1830	1745
Methyl isobutyl ketone	1320	1400	1370
Methyl propyl ketone	1130	1225	1175
1-Propanol	940	1180	1065
2-Propanol	1150	1270	1215
Propylene oxide	2730	3125	3010
Pyriding	1550	1630	1588
Styrene	650	745	695
Tetrachloroethylene	886	928	914
Tetrahydrofuran	980	1140	1085
Toluene	765	840	815
Vinyl chlorid	675	780	730
Vinyl fluoride	1060	1230	1170
o-Xylene	710	770	739
p-Xylene	760	860	795

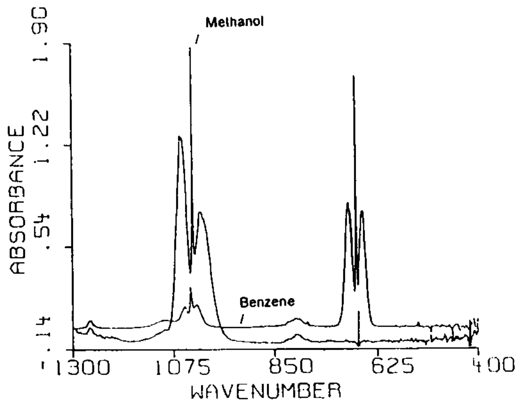

Fig.1. The overlap between the spectral bands of methanol and benzene in the spectral range from 1024 to 1037 cm^{-1}.

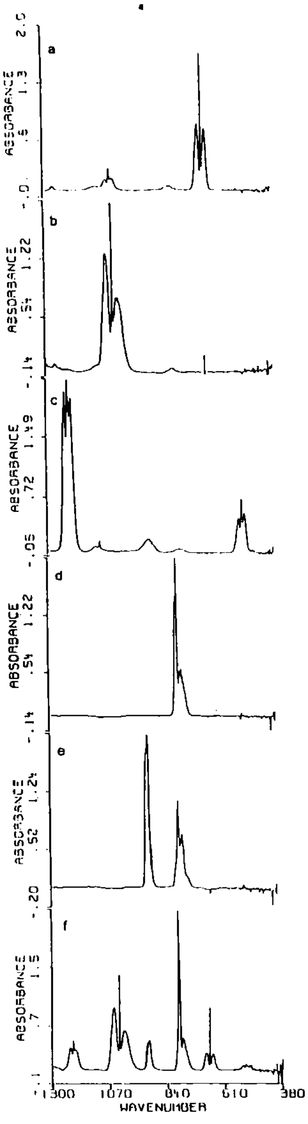

Fig. 2. Five organic gas compounds and their mixture FT-IR absorption spectra. a.Benzene, b.Methanol, c.Acetone, d.Carbon tetrachloride, e. Tetrachloethylene, f. Five-component mixture.

Table 2. Comparison of results obtained for the analysis of sample by using FT-IR and GC methods

	Concentration, (x100ppm)			
	Actual	FT-IR		GC
Compound		measured	RSD%	
Benzene	0.30	0.37	4.6	0.28
Methanol	3.65	3.55	3.5	3.68
Acetone	2.45	2.49	3.2	2.47
Carbon tetrachloride	5.24	5.21	3.7	5.31
Tetrachloroethylene	1.53	1.60	4.5	1.57

band from 1024 to 1037 cm^{-1} interfered by benzene spectral band from 1028 to 1030 cm^{-1} as an example shown in Fig.1.

There are the linear relationships for the interferes between various compounds in our experiment. So we select linear fit with an intercept for the calibration and analysis.

4.4. The quantitative analysis of organic gas mixture

This work make the quantitative analysis of the mixture of five-component organic gas mixture, such as acetone, benzene, carbon tetrachloride, methanol and tetrachloroethylen. These componenets and their mixture spectra in the spectral region of 1300 - 380 cm^{-1} and optimal peak windows for the quantitative analysis are shown in Fig.2. Because there is not the interference of H_2O and CO_2 in the atmosphere in the spectral region from 1400 to 650 cm^{-1}, this spectral region used for thier quantitative analysis is successful. The comparison of analytical results by using FT-IR and GC for five-component organic gas mixtures is listed in Table 2. The comparison of actual and results obtained by FT-IR and GC is good agreement. The precision of this method is indicated by relative standard deviation(RSD%). The RSD% is 2 - 5% for the determinations of 11 times. The good agreement indicated that accurate results can be obtained by the FT-IR method.

5. Conclusion

The efforts in this work are centered on fully automating the classical computation procedure for the quantitative analysis of mixture, on the studies of calibration fit models and overcoming interference of the overlaps of the spectral bands of the organic gas components in the mixture, and on the selections of both the optimal peak windows and measurement frequencies.

The FT-IR classical computation method applied to the direct quantitative analysis for multicomponent gaseous mixtures of organic compounds can obtain the accurate quantification results in fast measurement time. It is the main advantage of this method.

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