



On-line multi-component alkane mixture quantitative analysis using Fourier transform infrared spectrometer



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ABSTRACT

Fourier transform infrared spectrometer (FTIR) has been widely used to analyze multi-component gas mixture for more than ten years because of its potential benefits. However, it is a challenge to analyze multi-component alkane mixture on-line with FTIR because their absorption spectra overlap with each other extensively. In this paper, the methods of feature extraction and selection based on Tikhonov regularization (TR), and the modeling methods based on neural network (NN) are discussed in the practical conditions of alkane mixture analysis with FTIR. Then, the proposed methods compared with gas chromatograph (GC), normally regarded as the standard way for quantitative gas analysis, are used for gas well logging to analyze the mixture of methane, ethane, propane, iso-butane and n-butane on-line. By comparing the well logging curves obtained from FTIR with the ones from GC, it is shown that the logging curves analyzed with proposed method are good matches with the ones obtained from GC, which means that our analysis results are accurate. At the end of this paper, a calibration transfer is used to calibrate additional 18 instruments with a few sets of samples. And the work introduced in this paper demonstrates that FTIR can also be used in analyzing multi-component gas with close molecular structure accurately and the analyzer can be produced in mass.

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1. Introduction

Quantitative analysis of gas composition and concentration, especially organic gases, is applied in many fields [1–4]. In precise quantitative analysis of gases, mass spectroscopy (MS), gas chromatography (GC) and infrared spectroscopy are often used. Sometimes two of which are combined to ensure the accuracy of analyzing mixed gases. In the past decades, the concentrations of the relevant species are often determined with MS or GC. For example, in both decomposition gas of organic substance and coal-fire gas [5,6], there exist many such components as ethane, propane, butane, and so on. Nowadays, these gases are always analyzed with GC. Both MS and GC can provide high-accurate analysis results, but they can only provide *ex situ* information; thus early warning signal can't be obtained on time.

Infrared spectroscopy is commonly used for *in situ* studies. Additionally, it has many potential benefits such as fast analysis and update rate, no carrier gas requirement, less susceptible to clogging, etc., and is called the best way toward green analytical chemistry [7]. But on the other contrary, although a spectrum is relatively easy to measure, converting spectrum to absolute concentration values is difficult because the measured spectrum is the convolution of the transmission spectrum and the

FTIR apparatus function [8], which make some absorbances nonlinear to gas concentration. When there are several analytes whose absorption spectra overlap extensively, the difficulty may arise greatly. If these gases can be analyzed with FTIR at scene, many disasters such as coal-fire may be monitored and even be prevented. And it may be a great progress for the application of infrared spectroscopy.

In order to overcome above difficulties and obtain accurate analysis result, many analysis technologies have been presented and practiced [9–15]. But it is regretful that it is still a challenge to analyze multi-component of alkane gases because of above difficulties. When interferences exist in the analyzed gas mixture at scene, it may be more difficult. The more such components, the more difficult it is. For alkane gas analysis, Maris [14] has analyzed ethane and propane mixture. We have also tried to analyze alkane gas [15]. For Maris' work, the component number of analytes is less than 5, and it was relatively easy to be analyzed. For our previous work, on one hand, all the testing sample spectra were also prepared in laboratory; there were neither interferences nor spectral baseline drift because of little change in working circumstance and parameters of spectrometer. On the other hand, the concentration range is relatively little, one analysis model is enough to fit the concentration range requirement.

In this paper, five components of light alkane mixture, including methane, ethane, propane, iso-butane and n-butane, are chosen as target analytes while both iso-pentane and n-pentane are chosen as

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interferents. Samples for system calibration are prepared at first. Then, analysis method is introduced in detail. The concentration of gas mixture ranges from 0 to 100%, continuous working time of spectrometer is longer than several months. Finally, the performance of the multi-component gas analysis method is tested with wellhead gases. In order to verify the method, the analyzed gas mixture is also analyzed by GC instrument on-line but *ex situ* at the same time. By comparing the analysis records, it is found that well logs obtained with FTIR almost overlap with that obtained with GC except some fast changing details. So the method presented in this paper fits for requirements of analyzing multi-component alkane gases on-line.

In the end of this paper, calibration transfer is used to calibrate additional 18 instruments. The small mapping errors between primary and secondary spectra show that the calibration model can be transferred to other instruments with a small set of samples. And the work introduced in this paper is very useful in practice, especially in the field of gas well logging.

2. Materials and methods

For multi-component gas analysis, the analysis model of every component of gas must be built with calibration sample prepared with the analysis instrument. In this section, the gas analysis instrument and its parameters are introduced at first, and then the approach to these models is introduced in details. All the algorithms are programmed and performed using Matlab 6.5.

2.1. Instrument parameters and sample preparation

The type of the FTIR used to analyze multi-component mixed gas is Tensor 27 made by Bruker. Its mid-infrared source is global light source. And the full radiant power is measured with a standard deuterated triglycine sulfate (DTGS) detector. The optical path is 10 cm. The spectral resolution is set as 4 cm^{-1} , and the spectral range is set as $400\text{--}4000\text{ cm}^{-1}$. The reason for setting such spectral resolution is a tradeoff between scanning time and precision. The apodization function is chosen as Norton–Beer medium since it can provide good linearity [16].

Because the measure FTIR spectrum suffers from both pressure and temperature of the measured gas, in order to obtain high measurement accuracy, the pressure of the mixed gases is always measured with a manometer mounted in the gas cell of spectrometer and is kept typically in the range 720–760 Torr, and the temperature is measured with platinum resistance temperature detectors (RTDs) and kept at 300 K. The precision of the RTDs is better than 0.03 K, or 0.01% in 300 K.

In order to build and verify the analysis model, about 6000 sets of gas samples¹ are prepared for building, and about 1000 sets for testing the analysis model of the analyte. The reason for preparing so many samples is that gas concentration range from 0 to 100% and some absorbances are non-linear to gas concentration. Among these samples, only a small portion of them is standard gases bought from standard gas companies directly while a large part of them is prepared with a multi-component mixed gas blending system constructed with flow controllers.

2.2. Feature extraction and selection

Feature extraction and selection are often used to improve signal-to-noise-ratio (SNR) and selectivity of input of analysis models. And the difficulty in building analysis model of every component of the analytes may be decreased.

Common methods for accomplishing feature selection are forward selection, stepwise regression (SWR), genetic algorithms (GA), and simulated annealing, Tikhonov regularization (TR), etc. [10]. Here, all the features of the analytes are selected through forward selection, the simplest one to be performed, or TR. The principle of feature selection is that sensitivity is as high as possible and cross-sensitivity is as low as possible.

2.2.1. Forward selection

The spectra of all the analytes with 1% volume specific concentration are shown in Fig. 1 (Page 24). From this figure, it is easy to find that there is no strong overlap among the spectra of the analytes when the wavenumber is less than 1300 cm^{-1} . So we can determine the features of all the analytes by comparing the shape of absorption spectra of every component of the analytes. For instance, for n-butane, such a combination of absorbances can be used as its feature variable:

$$t_5 = A_{1007.1} - A_{968.44} \quad (1)$$

where t_5 denotes the feature variable of fifth analytes, i.e. n-butane; A_x denotes the absorbance at wavenumber of x . These two spectral lines are denoted with dash-dot lines in Fig. 1.

2.2.2. Tikhonov regularization (TR) [10]

From Fig. 1, one can also find that, the sensitivity of the absorbance between 2800 cm^{-1} and 3100 cm^{-1} is higher than that whose wavenumber is less than 1300 cm^{-1} . When gas concentration is low, this region can be used for gas analysis because of its high sensitivity. But for this region, all the spectra of the analytes overlap with each other extensively. And it seems difficult to perform feature extraction and selection by comparing absorption spectra. Here, TR is used to do this work.

Although TR aims to linear system, it can also be used for feature extraction of nonlinear spectrum system. In fact, in many research fields, nonlinear system is treated as linear system for the view of convenience. Certainly, relatively great errors will be produced if the analysis model built with TR is applied in multi-component gas mixture analysis when the spectrum system is nonlinear. This is the reason that nonlinear analysis model built in following section is needed to get high analysis accuracy.

The model of TR is

$$\mathbf{y} = \mathbf{X}\mathbf{h} + \mathbf{e} \quad (2)$$

where \mathbf{X} contains calibration spectra for m samples measured at w wavelengths, \mathbf{h} is the $w \times 1$ regression vector, the $m \times 1$ vector holds the quantitative information for the analytes, i.e. concentration of gases, and \mathbf{e} is an $m \times 1$ vector representing random error. As shown in Eq. (2), \mathbf{h} contains coefficients determining how each respective wavelength is used to predict \mathbf{y} ($\hat{\mathbf{y}} = \mathbf{X}\hat{\mathbf{h}}$). And it can be estimated through generalization of the TR, expressed as:

$$\min(\|\mathbf{X}\mathbf{h} - \mathbf{y}\|_a^a + \lambda \|\mathbf{L}\mathbf{h}\|_b^b) \quad (3)$$

where $\|\cdot\|_p$ signifies the regression vector p -norm, a and b represent the same or different norms, $1 \leq a, b < \infty$; Symbol λ in the right term symbolizes the regularization meta-parameter controlling the weight given to right term relative to the left term; And matrix \mathbf{L} denotes a regulation operator that enforces the estimate of \mathbf{h} to belong to corresponding subspaces of well-behaved functions.

In this paper, both a and b are set as 1 to minimize the effect of outliers in calibration samples, the corresponding element in \mathbf{L} to A_i as transmittance T_i , λ is determined as 0.5. Finally, gradient descent

¹ Anyone can download the calibration samples from my network disk: <http://pan.baidu.com/s/1hqrKdJe>.

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