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Quantitative Analysis of Alkane Gases by Infrared Absorption Spectrometry Based on Spectral Comprehensive Pretreatment Method

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Abstract. Infrared absorption spectroscopy for quantitative analysis of alkane gases has been widely used in the fields of energy exploration, geological survey, coal-bed methane analysis, and atmospheric environment monitoring. With the rapid development of science and technology, various research fields have put forward higher requirements on the detection accuracy and detection limits of gas quantitative analysis. Spectral pretreatment is very important in the gas quantitative analysis of infrared absorption spectroscopy, which can effectively improve the detection accuracy, but there were few studies on the spectral pretreatment technology at this stage. In this paper, a comprehensive spectral pretreatment method based on spectral smoothing and noise reduction, spectral deconvolution and spectral baseline drift correction was proposed for the infrared absorption spectra of alkane gases. The optimal pretreatment parameters for alkane gases were investigated and the infrared absorption spectroscopy of typical alkane gases was pre-processed. The comprehensive pretreatment method of absorption spectroscopy can increase the probability of selecting variables with significant features in absorption spectral data, which can improve the accuracy of quantitative analysis. It also can improve the quality of some weak absorption signals and extend the lower detection limit downward in order to expand the detection range.

Keywords. Infrared absorption spectroscopy, comprehensive pretreatment, alkane gases, absorption spectroscopy characteristics

1. Introduction

Infrared absorption spectroscopy has been widely used for quantitative analysis of multi-component gases with its advantages of rapid and non-destructive analysis. In particular, infrared absorption spectroscopy of alkane gases has been a hot research topic in energy exploration, geological investigation, coal-bed methane analysis and atmospheric environment monitoring, etc. Tang's research team studied the quantitative analysis method of infrared absorption spectroscopy of alkane gases and applied it to oil and gas exploration and coal-bed methane analysis in 2011 [1]. Liu also analyzed the application

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of infrared absorption spectroscopy gas quantification methods in oil and gas exploration in 2012 [2]. Song and Liang et al. analyzed the recent research progress of infrared spectroscopy analysis in oil and gas exploration [3, 4]. Tawalbeh and Voelz designed a tunable spectrometer for geological investigation and analyzed the superiority of infrared spectral analysis in geological investigation [5]. Zhang's research team investigated the application of quantitative infrared absorption spectroscopy gases analysis methods in the field of coal bed methane analysis [6]. Some other researchers have studied the application of infrared spectral analysis in the field of atmospheric environmental monitoring [7]. With the development of science and technology, new requirements for detection accuracy have been put forward in various research fields, especially in the field of energy exploration and address survey, where the lower detection limit for alkane gas has been expanded to 1 ppm or even lower. Spectral pretreatment is very important in the quantitative analysis of infrared absorption gases, and improving the spectral pretreatment technique is one of the important ways to improve the detection accuracy and extend the lower detection limit downward. In recent years, many researchers have studied spectral pretreatment methods. Zhou et al. proposed a wavelet transform-based spectral pretreatment method, which can effectively remove spectral noise [8]. Peng et al. investigated the standard normal variate transformation and first derivative (PNV-FD) pretreatment methods and proposed the idea of segmental pretreatment [9]. Meng et al. analyzed the spectral pretreatment effect of second-order derivative, standard normal transform and multivariate scattering correction pretreatment algorithm [10]. Chen et al. studied a spectral pretreatment method based on first-order derivative and partial least squares algorithm and selected the optimal pretreatment parameters [11]. Mas et al. optimized the partial least squares algorithm pretreatment method and used the coincidence function for the optimal pretreatment parameters [12]. Hong combined the optimal pretreatment parameters with the first-order derivative and partial least squares algorithm pretreatment method [13]. Zhang et al. proposed the idea of combined pretreatment of absorption spectra [14]. Although there were more spectral pretreatment methods, none of them preprocess according to the independent characteristics of each component gas. In this paper, by analyzing the absorption spectral characteristics of each component alkane gases, a combined pretreatment method of multi-component alkane gases absorption spectra was proposed, and the superiority of this method was analyzed by the combined pretreatment results of multi-component alkane gases absorption spectra, which will improve the accuracy of the quantitative analysis model of multi-component alkane gases.

2. Methodology

The analytical flow of the comprehensive pretreatment method of absorption spectroscopy proposed in this paper is shown in Figure 1. Firstly, the characteristics such as frequency and distribution of infrared absorption spectra of typical alkane gases including methane, ethane, propane, butane and pentane were analyzed. Secondly, the optimal parameters of each component alkane gas including smoothing and noise reduction processing, deconvolution processing, and baseline drift correction processing were selected. And thirdly, the absorption spectra of multi-component alkane gases were segmented by composition and corresponding absorption spectra. Finally, the absorption spectra within each band were preprocessed with corresponding parameters to form a complete set of comprehensive pretreatment methods for infrared absorption spectra of

alkane gases.

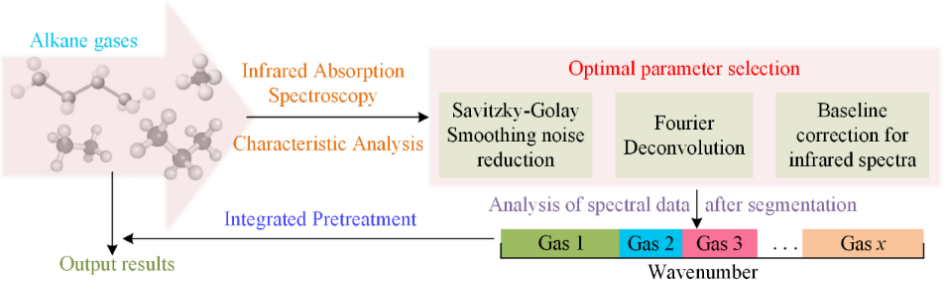


Figure 1. Integrated pretreatment method flow.

2.1. Smoothing Noise Reduction

In this paper, Savitzky-Golay smoothing was used. The idea of the algorithm is to intercept a number of points in the spectral data using a Hamming window and then fit the original absorbance curve using the least squares method. The parameters that need to be determined for spectral pretreatment using Savitzky-Golay smoothing are the width of the window (i.e., the number of smoothing points) and the number of times to fit the equation, and the number of fits must be less than the number of smoothing points.

2.2. Fourier Deconvolution

The infrared absorption spectra of some alkane gases have the phenomenon of band overlap. The Fourier deconvolution process can be used to separate the spectra with more serious overlap, so as to improve the spectral resolution and the detection accuracy of low concentration gases.

The infrared absorption spectrum is obtained by Fourier transform of the interferogram with finite long optical range difference. Fourier deconvolution is the process of deconvolution of the scanned spectrum, i.e., the actual spectrum is reconverted into an interferogram, then multiplied with the tangent function, and finally Fourier transformed to obtain the deconvolved spectrogram. The parameter to be determined in the Fourier deconvolution process is the deconvolution enhancement factor.

2.3. Spectral Baseline Drift Correction

The spectral baseline drift correction method is well established. In this paper, the adaptive smoothing parameter penalized least squares baseline correction method is used to correct the spectral baseline drift. The method is based on the original spectral signal you and a new spectral signal, so as to eliminate the spectral baseline drift, using adaptive smoothing parameter penalized least squares baseline correction method need to determine the parameters are the iteration threshold of the fitted polynomial and the penalty factor.

3. Integrated Pretreatment Results

3.1. Analysis of Alkane Absorption Spectral Characteristics

The mid-infrared absorption spectra of typical alkane gases are shown in Figure 2. The absorption spectra of each component gas overlap more seriously, and the frequencies of the absorbance signals and the degree of spectral overlap vary. Therefore, the absorption spectra of each component gas need to be segmented and preprocessed according to their characteristics and wave number positions, i.e., the spectra are reconstructed. The absorption spectra of typical alkane gases are mainly concentrated in the wave number ranges of 3200cm^{-1} to 2600cm^{-1} and 1500cm^{-1} to 700 cm^{-1}. Therefore, in this paper, the parameters of absorption spectra of alkane gases in this range are selected for pretreatment.

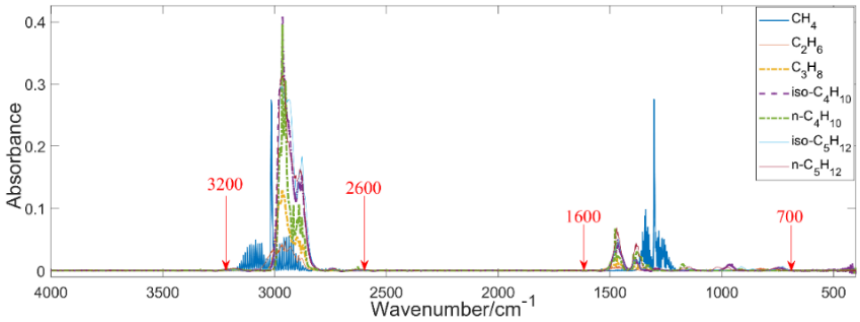


Figure 2. Mid-infrared absorption spectra of typical alkane gases.

3.2. Selection of High Frequency Alkane Gases Pretreatment Parameters

The frequencies of the mid-infrared absorption spectra of methane are relatively high compared to those of other alkane gases. The optimal pretreatment results of the absorption spectroscopy of methane are shown in Figure 3. The 7-point smoothing selected in the smoothing process can not only effectively reduce the high frequency noise, but also the distortion of the original signal is smaller. The deconvolution processing with a deconvolution enhancement factor of 1.5 can separate the absorption peaks with overlapping spectra, and the distortion of the absorption signal is small. The baseline drift correction is best when the adaptive smoothing parameter penalized least squares method is used for baseline correction, with the iteration threshold set to 10^{-4} and the penalty factor set to 10^{8}. Not only the baseline drift is successfully eliminated, but also the absorption spectral signal obtained by fitting has the smallest error with the original signal.

A part of the absorption spectroscopy signal of ethane has a relatively high frequency, and the best pretreatment parameters are selected for this part of the absorption spectroscopy. The best pretreatment results were obtained when the number of smoothing points was set to 5, the deconvolution enhancement factor was set to 1.2, and the baseline drift correction parameters were the same as those for methane. The best pretreatment results for the high-frequency part of the ethane absorbance signal are shown in Figure 4.

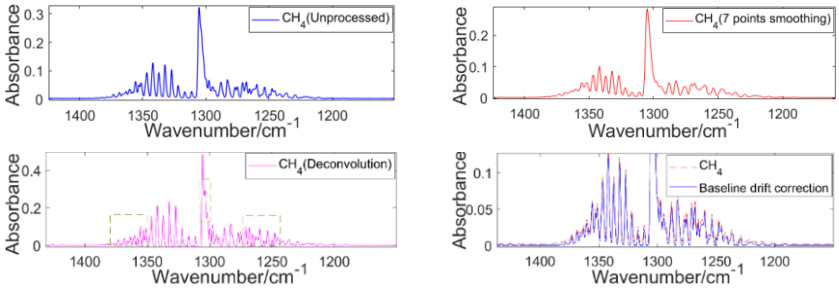


Figure 3. Pretreatment results of methane absorption spectroscopy by optimal pretreatment parameters.

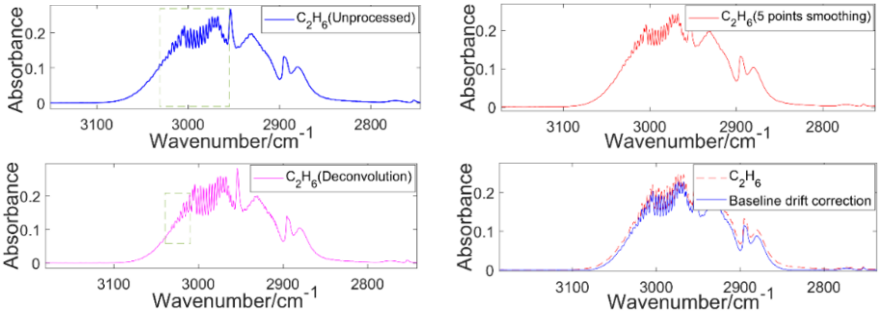


Figure 4. Pretreatment effect of ethane absorption spectra with optimal pretreatment parameters.

3.3. Selection of Low Frequency Alkane Gases Pretreatment Parameters

The frequencies of infrared absorption spectra of alkane gases other than methane and ethane are relatively low. Taking propane as an example, the optimal pretreatment parameters were selected for the alkane gases with relatively high IR absorption spectral frequencies. The best pretreatment results were obtained when the number of smoothing points was set to 3, the deconvolution factor was set to 0.8, and the baseline drift correction parameters were the same as those for methane. The integrated pretreatment results for propane are shown in Figure 5.

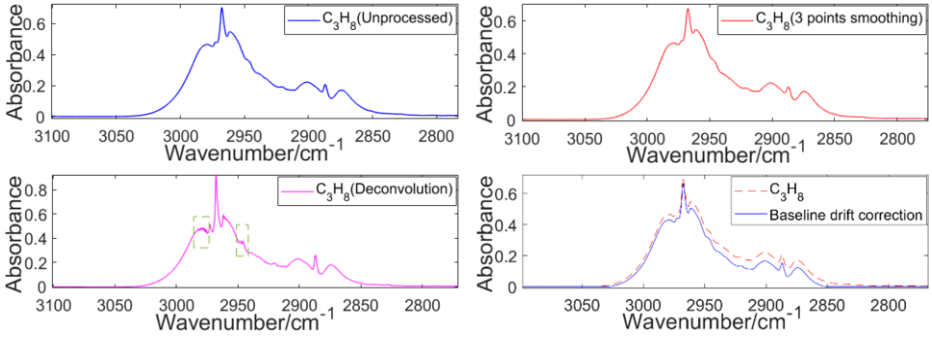


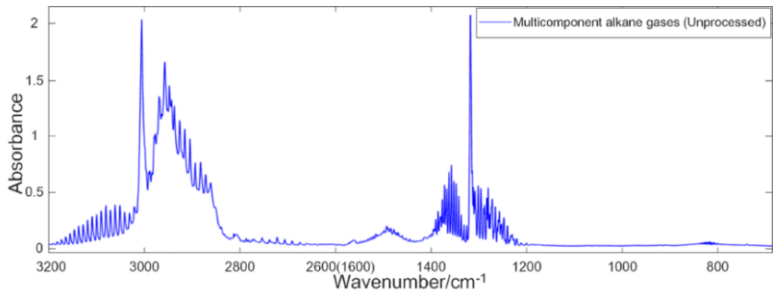
Figure 5. Pretreatment effect of propane absorption spectra with optimal pretreatment parameters.

3.4. Multi-component Alkane Gas Infrared Absorption Spectroscopy Segmentation Pretreatment

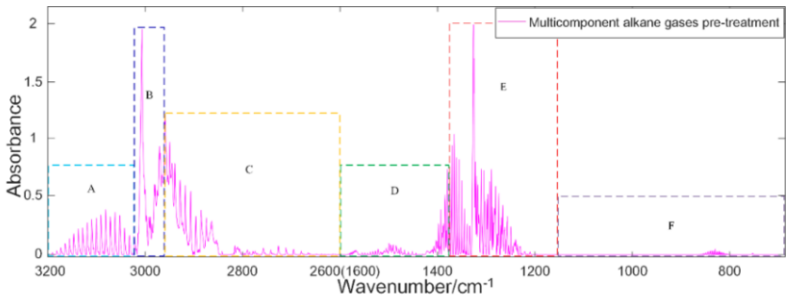
Although the infrared absorption spectra of alkane gases overlap more severely, the high-frequency components and low-frequency components are distributed in different bands. Therefore, the IR absorption spectra of multi-component alkane gases can be segmented and preprocessed according to the frequencies of the absorption spectral signals of each component gas and their absorption bands. The segmentation of the mixed-component alkane gases and the optimal pretreatment parameters within each segment are listed in Table 1.

Table 1. Selection of comprehensive pretreatment parameters for multi-component alkane gases IR absorption spectra.

	Absorption spectroscopy segmentation (cm^{-1})					
	3200-3020	3020-2960	2960-2600	1600-1380	1380-1140	1140-700
	A	B	C	D	E	F
Number of smoothing points	7	5	3	3	5	7
Deconvolution factor	1.5	1.2	0.8	1.2	1.5	1.6
Baseline drift correction iteration threshold	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}	10^{-4}
Baseline drift correction penalty factor	10^{8}	10^{8}	10^{8}	10^{8}	10^{8}	10^{8}



(a) Infrared spectrogram of the main absorption bands of multi-component alkane gases



(b) Integrated pretreatment results

Figure 6. Integrated pretreatment results for different parameters of the main absorption section of a multi-component typical alkane gases.

The absorption spectra of multi-component typical alkane gases containing methane, ethane, propane, n-butane, iso-butane, n-pentane and iso-pentane were pre-treated according to the optimal integrated pretreatment parameters, and the results are shown in Figure 6, where Figure 6a shows the infrared spectra of the main absorption bands of the multi-component alkane gases, and Figure 6b shows the graphs of the pretreatment results with different parameters according to the frequencies of the absorption spectra of each component alkane gases.

In the range A, the main component of the absorption spectroscopy is methane, which has a relatively high frequency. In the range B, the absorption spectroscopy has more alkane gases components, among which there is a high-frequency part of ethane absorption spectroscopy and it accounts for a relatively high percentage. In the range C, the components of the absorption spectroscopy include the low-frequency part of ethane and propane, butane and pentane. In the range D, the components of the absorption spectroscopy are mainly propane, butane and pentane, and the frequency is low. In the range E, the components of the absorption spectrum are mainly methane with relatively high frequencies. the components of the absorption spectrum in the F range contain propane, butane and pentane, and although the absorbance in this region is small, it has a good linear relationship with the concentration and is of significant analytical value.

The spectral overlap is also a little more serious in the higher frequency bands, so the deconvolution factor chosen is also relatively large. This enables the spectral overlap to be separated effectively. Of course, the deconvolution factor should not be too large, generally not greater than 2, to prevent distortion of the absorption spectroscopy signal affects the detection accuracy.

The infrared absorption spectroscopy is mainly obtained by scanning the spectrometer. The absorption spectroscopy noise of the spectrometer scan is gradually increasing from the center band to both sides. In the selection of smoothing noise reduction parameters is also from the center of the band gradually increase to both sides, so as to reduce the noise at the same time to minimize the distortion of the absorption spectroscopy signal.

The baseline drift of the absorption spectroscopy is mainly caused by the operating hours of the detection system and the changes in the environment, and the degree of drift or the trend of drift is the same for the whole band. Therefore, the baseline drift correction parameters are the same for the entire band.

For the absorption spectral characteristics of alkane gas, comprehensive pretreatment of the absorption spectral signal can effectively eliminate high-frequency noise, and also separate the part of the absorption spectroscopy with serious overlap, while reducing the drift of the spectral baseline. The focus of the integrated pretreatment technique is to improve the absorption spectral signal while minimizing the distortion of the absorption spectral signal. This will increase the probability of representative characteristic variables being selected in the quantitative analysis process. It facilitates the quantitative analysis of low concentration gases and improves the detection accuracy. The integrated absorption spectroscopy pretreatment method improves the quality of the weak absorption signal, which extends the lower detection limit downward, thus expanding the detection range.

4. Conclusion

In this paper, a comprehensive pretreatment method for alkane gases absorption spectra

was proposed. Firstly, the infrared absorption spectral characteristics of alkane gases are analyzed. Then, the optimal pretreatment parameters of each component gas are selected. Finally, the multicomponent alkane gas is pretreated in regions. This method can improve the accuracy of quantitative analysis of infrared absorption spectra of alkane gases and extend the lower detection limit downward, which is important for improving the quantitative analysis of alkane gases by infrared absorption spectroscopy. In addition, the integrated absorption spectroscopy pretreatment method can be applied to the quantitative analysis of other kinds of gases, and also to the quantitative analysis of ultraviolet absorption spectroscopy gases.

Acknowledgments

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References

[1] Zhu LJ, Tang XJ, et al. A method for quantitative analysis system of alkane gaseous mixture with near infrared spectroscopy. Spectroscopy and Spectral Analysis. 2011;31:69-72.
[2] Liu ZG. Study and application of spectral log technology. Oil Forum. 2012;201206004.
[3] Song LM, Wu H, et al. Application of deep learning in quantitative analysis of the infrared spectrum of logging gas. Applied Optics. 2020;59:9-16.
[4] Liang HB, Liu SQ, et al. Research on infrared spectral quantitative analysis of hydrocarbon gases based on adaptive boosting classifier and PLS. IEEE Sensors Journal. 2021;21:521-529.
[5] Tawalbeh R, Voelz D, et al. Infrared acousto-optic tunable filter point spectrometer for detection of organics on mineral surfaces. Optical Engineering. 2013;52:063604.
[6] Zhang ZR, Sun PS, et al. Novel Coalbed Methane (CBM) origin analysis and source apportionment method based on carbon isotope ratio using infrared dual-wavelength laser absorption spectroscopy. Earth and Space Science. 2018;5:721-735.
[7] Xu L, Liu JG, et al. Monitoring and analysis CO_2 and CH_4 using long path FTIR spectroscopy over Beijing. Spectroscopy and Spectral Analysis. 2007;27:889-891.
[8] Zhou FB, Zhu HQ, et al. A pretreatment method based on wavelet transform for quantitative analysis of UV-vis spectroscopy. Optik. 2019;182:786-792.
[9] Peng D, Liu YL, et al. Nondestructive detection of moisture content in walnut kernel by near-infrared diffuse reflectance spectroscopy. Journal of Spectroscopy. 2021;9986940.
[10] Meng QL, Shang J, et al. Nondestructive detection of soluble solids content in apple by visible-near infrared spectroscopy. Food and Fermentation Industries. 2020;46:205-209.
[11] Chen HZ, Liu XK, et al. Parametric-scaling optimization of pretreatment methods for the determination of trace/quasi-trace elements based on near infrared spectroscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2020;117959.
[12] Mas C, Rubio L, et al. Impact of the pretreatment of ATR-FTIR signals on the figures of merit when PLS is used. Chemometrics and Intelligent Laboratory Systems. 2020;104006.
[13] Hong SY, Wang YZ, et al. Rapid Assessment of Gasoline Quality by near-Infrared (NIR) deep learning model combined with fractional derivative pretreatment. Analytical Letters. 2022;2024219.
[14] Zhang ZSY, Gu HW, et al. Pretreatment and combined method based on near infrared spectroscopy. Laser & Optoelectronics Progress. 2022;58:1617001.