# Study on synchronous detection method of methane and ethane with laser absorption spectroscopy technology

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## ABSTRACT

The main ingredient of mash gas is alkenes, and methane is the most parts of mash gas and ethane is a small portion of it. Fast, accurate, real-time measurement of methane and ethane concentration is an important task for preventing coal mining disaster. In this research, a monitoring system with tunable diode laser absorption spectroscopy (TDLAS) technology has been set up for simultaneous measurement of methane and ethane, and a DFB laser at wavelength of 1.653μm was used as the laser source. The absorption spectroscopy information of methane and ethane, especially the characteristic of the spectrum peak positions and relative intensity were determined by available spectral structures from previous study and available database. Then, the concentration inversion algorithm method based on the spectral resolution and feature extraction was designed for methane and ethane synchronous detection. At last, the continuously experimental results obtained by different concentration of methane and ethane sample gases with the multiple reflection cell and the standard distribution system. In this experiment, the standard distribution system made with the standard gas and two high precision mass flow meters of D07 Sevenstar series whose flow velocity is 1l/min and 5l/min respectively. When the multiple reflection cell work stably, the biggest detection error of methane concentration inversion was 3.7%, and the biggest detection error of ethane was 4.8%. So it is verified that this concentration inversion algorithm works stably and reliably. Thus, this technology could realize the real-time, fast and continuous measurement requirement of mash gas and it will provide the effective technical support to coal mining production in safety for our country.

**Keywords:** laser absorption spectroscopy; methane; ethane; spectral resolution; concentration inversion

## 1. Introduction

Gas explosion accident is the main menace in coal mining industry in China. The primary gas ingredient existing in coal mine constitutes of alkenes, and methane is the most parts of mash gas and ethane is a small portion of it, all of them are flammable and explosive. For safety, the gas concentration is needed monitoring at the mining sites. Therefore, the fast, accurate, real-time measurement of methane and ethane concentration is an urgent task for preventing coal mining disaster[1-2].

The conventional sensor for gas detection employs a catalyst head which cannot work steadily for a long time, and it's also a potential igniting source for the explosive. Tunable diode laser absorption spectroscopy (TDLAS) is a new method to detect trace-gas quantificationally based on the characteristic of the distributed feed back (DFB) diode laser with narrow linewidth and tunability. It has been broadly applied in the field of environmental monitoring, medical and industrial process[3-4] due to its high sensitivity, high selectivity, and fast time response. A further advantage of TDLAS is easily compatible with optical fibers, which makes it easy to realize in-situ remote sensing in severe conditions.

In this research, a monitoring system with tunable diode laser absorption spectroscopy (TDLAS) technology has been set up for simultaneous measurement of methane and ethane at the wavelength of 1.653μm. The absorption spectroscopy information, especially the characteristic of the spectrum peak positions and relative intensity of methane and ethane were determined. The concentration inversion algorithm method based on the spectral resolution and feature extraction was designed for methane and ethane detection. Finally, this method was evaluated under the condition of different ratio of mixed methane and ethane gases.

## 2. Measurement Principle

As TDLAS technology obeys the Beer-Lambert law, the original laser intensity is $I_0$, and the laser frequency is $\nu$, so the intensity received by detector through the absorbing medium whose length is $L$ can be expressed as Eq.(1):

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$$I = I_0 \exp(-S(T)\phi(\nu - \nu_0, T)PcL) \quad (1)$$

$$\ln(\frac{I_0}{I}) = S(T)\phi(\nu - \nu_0, T)PcL = \alpha(\nu)cL \quad (2)$$

$$A = \int_{-\infty}^{+\infty} \ln(\frac{I_0}{I})_\upsilon d\nu \quad (3)$$

Where $\nu_0$ is the center frequency of gas absorption line, $\alpha(\nu)$ is the absorption coefficient, $S(T)$ is the absorption line strength, $\phi$ is the normalized absorption line-shape function, $P$ is the partial pressure of the gas, $A$ is the integrated absorbance, as the integral area of the chosen absorption line[7]. So the gas concentration $c$ can be expressed as Eq.(4):

$$c = \frac{A}{\alpha(\nu)L} \quad (4)$$

According to Hitran database, the methane and ethane are interference free from other molecules that are naturally exist in the atmosphere (such as $H_2O$ and $CO_2$) in the spectral range near 1.653μm. In order to monitoring these gases concentration, we pick out 5 characteristic absorption spectra of methane and ethane near 1.653μm which are listed in Table 1. The absorption intensity of methane is about two order magnitude stronger than that of ethane. The absorption line spacing between methane and ethane is about 0.1 nm, so one single DFB laser whose wavelength is 1653nm is used for the gases synchronous measurement[5].

Table 1 Characteristic peak positions and the intensity

| gas | Peak position/nm | Peak intensity/ $cm^{-1}/(molecule \bullet cm^{-2})$ |
|---|---|---|
| ethane | 1653.5674 | $9.99 \times 10^{-24}$ |
| | 1653.6173 | $2.42 \times 10^{-23}$ |
| methane | 1653.7222 | $1.32 \times 10^{-21}$ |
| | 1653.7255 | $1.00 \times 10^{-21}$ |
| | 1653.7284 | $8.17 \times 10^{-22}$ |

## 3. Experiment System

The experiment system with TDLAS and multiple reflection cell was set up for simultaneous measurement of methane and ethane, as shown in figure 1. The DFB laser of 1653nm was used as the laser source which was controlled by LDC-3724 to output and then went through the optical splitter, 2% of the laser was sent through reference cell with methane of 5% concentration and detected for wavelength locking; 98% of the laser was sent through multiple reflection cell for gas monitoring. The two signals were detected, and then data acquisition and concentration inversion were carried out by computer after signal amplification and filter.

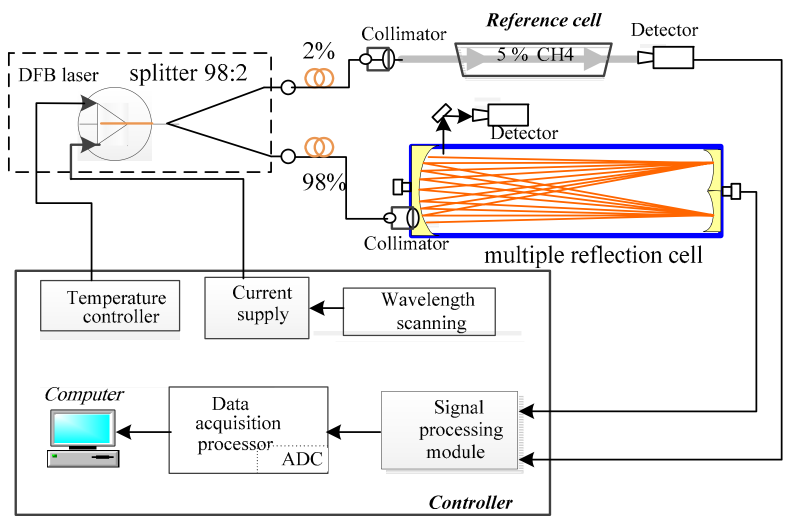


Fig.1 Experiment system setup

The absorption line is scanned by modulating the emitted wavelength of the laser around the centre of the absorption line. In first experiment, we scan the methane and ethane absorption in one current ramp period with a single sawtooth signal whose length is about 0.42nm, but the laser will not work at the starting position of the sawtooth signal. So we set up a new current ramp period, as shown in Fig.2. In this case, the laser current has two different basic levels with superimposed linear increasing current ramps whose length are about 0.21nm respectively. The two different basic levels of the current correspond to wavelengths according to the centers of the absorption lines of methane and ethane respectively, whereas the current ramps cause the modulation of the laser wavelength around the centers of the absorption lines[6].

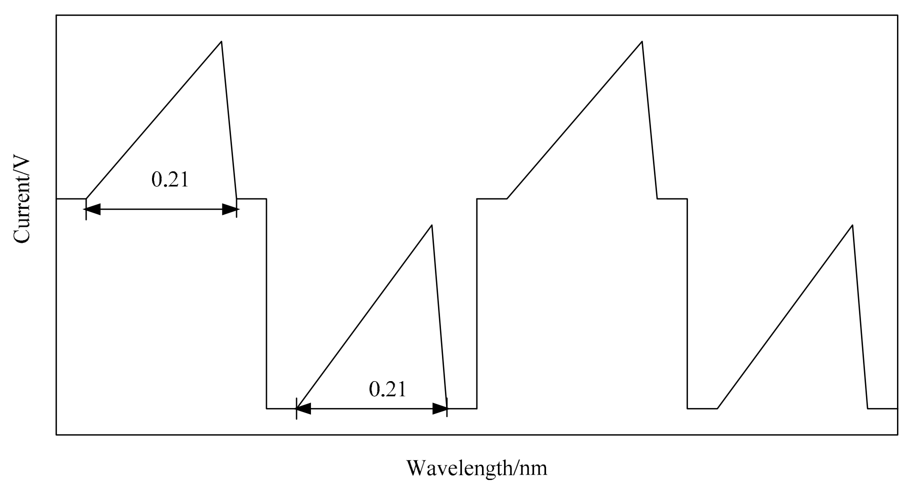


Fig.2 current ramp period for the 1653nm laser

## 4. Concentration inversion algorithm

The effective spectral resolution and feature extraction is the focus for concentration inversion. Thus, the incident intensity baseline is fitted by nonlinear polynomial fitting firstly [7]. In this step, the absorption part and no absorption part should be chose seriously based on the spectral feature extraction of methane and ethane. Then, according to the Eq.(2), we extract the absorbance curve and carry out optical intensity normalization. Thirdly, we do the correlation analysis between the extraction absorbance and the reference spectral absorbance signal, if the correlation coefficient is less than 70%, we remove the invalid data. Then the non-linear line shape fitting of Voigt profile is needed for signal processing as the absorbance curve may distort in open path monitoring and environment change. In our laboratory, we use generalized Lorentz function to simplify the calculation of Voigt function, and the L-M algorithm is used to carry out the nonlinear fitting rapidly. After that, we obtain the gas absorption peak and the integral area, and we can calculate the integrated absorbance $A$ accurately. At last, the gas concentration can be calculated. The flow diagram of concentration inversion algorithm is show in Fig.3.

When measuring concentration of multi-component gases, Eq.(2) should be expressed as

$$\ln(\frac{I_0}{I}) = [\alpha_1(\nu)c_1 + \alpha_2(\nu)c_2 + ....... + \alpha_n(\nu)c_n]L \tag{5}$$

where $n$ is the number of different gas, the optical length $L$ is equal. We pick out five characteristic absorption peaks of methane and ethane as shown in Table 1, Eq.(5) can be transformed into matrix form[8]:

$$\ln(\frac{I_0}{I}) = AcL \tag{6}$$

$$A = [\alpha_1, \alpha_2 ......\alpha_n] \tag{7}$$

$$\alpha = [\alpha(\nu_1), \alpha(\nu_2)......\alpha(\nu_i)]^T \tag{8}$$

$$c = [c_1, c_2 ......c_n]^T \tag{9}$$

In this experiment n=2, and i=3 for methane and i=2 for ethane.

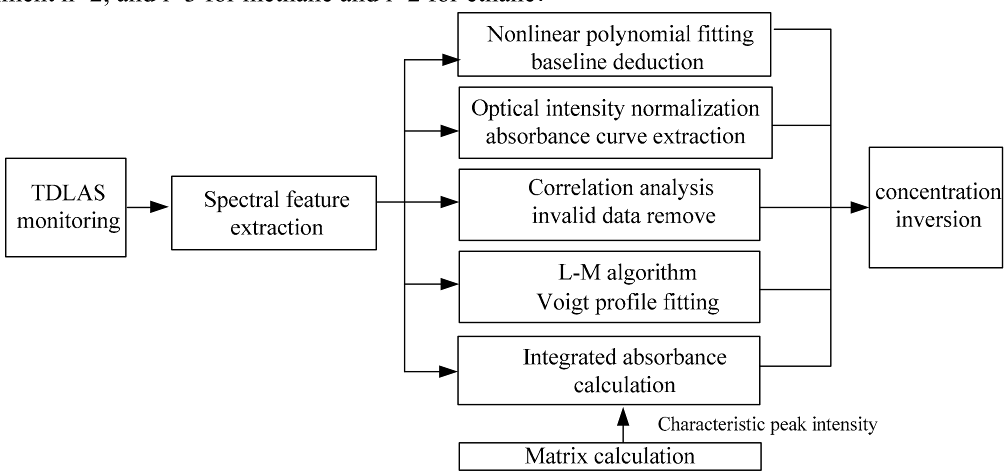


Fig.3 flow diagram of concentration inversion algorithm

## 5. Experiment results and analysis

The simultaneous measurement of methane and ethane was carried out at 1atm pressure and room temperature of 296K. The multiple reflection cell was used with absorption length of 20m. Before pumping the distributed gas for measurement, we swept the cell with high purity nitrogen gas (99%) for about 5 minutes.

In the experiment, the standard distribution system was made by our laboratory, and methane and ethane standard gas were used to make a set of different concentration distributed gases, and the relative expanded uncertainty of standard gas is about 2.0%. The standard distribution system was made with two high precision mass flow meters of D07 Sevenstar series whose flow velocity is 1l/min and 5l/min respectively. According to the mass flow mixing method, the flow velocity of standard mixed gas and $N_2$ was controlled to realize the distribution effect.

The concentration of distributed gas without considering the change of the pressure (by the ideal gas state equation: PV/T = constant) can be calculated and expressed as Eq.(10):

$$c_d = \frac{F_s}{F_s + F_{N2}} c_s \tag{10}$$

$c_d$ is the distributed gas concentration, $c_s$ is the sample gas concentration, $F_s$ is the actual flow of sample gas, $F_{N2}$ is the actual flow of $N_2$.

The standard methane gas of 0.25mmol/mol and standard ethane gas of 1.25mmol/mol was inflated into the cell recorded as the standard spectral absorption signal at first, and the gas absorption characteristic spectrum was obtained, as shown in Fig.4. Then the distributed gas was inflated slowly into the cell to observe the concentration inversion results. The average inversion concentration at steady-state was calculated as the result, as shown in Fig.5. Then the inversion concentration results were compared with the distributed concentration results to analyze the relative error, as shown in Table1.

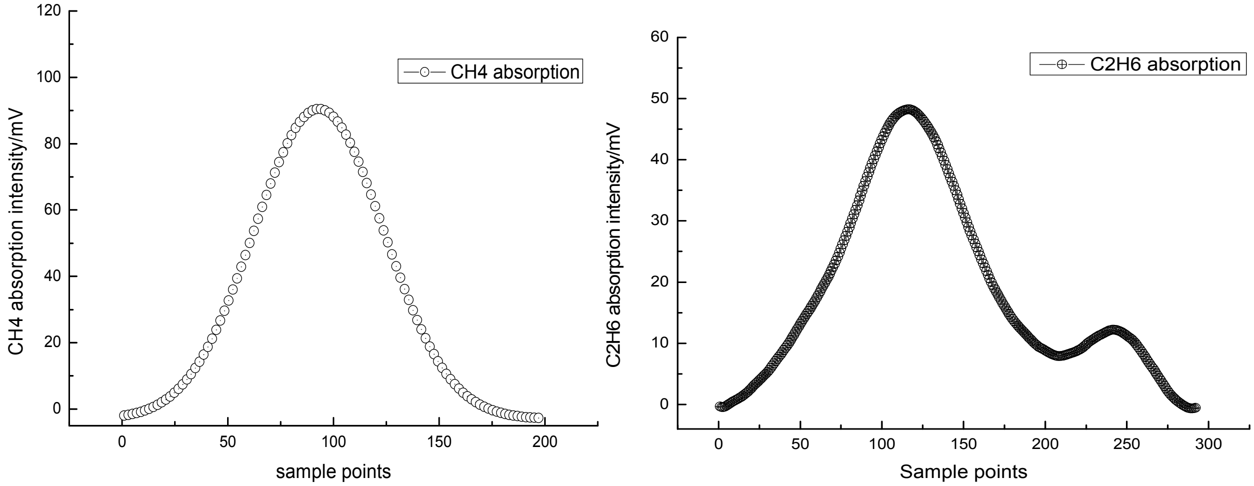


Fig.4 Spectral absorption signals under different temperature

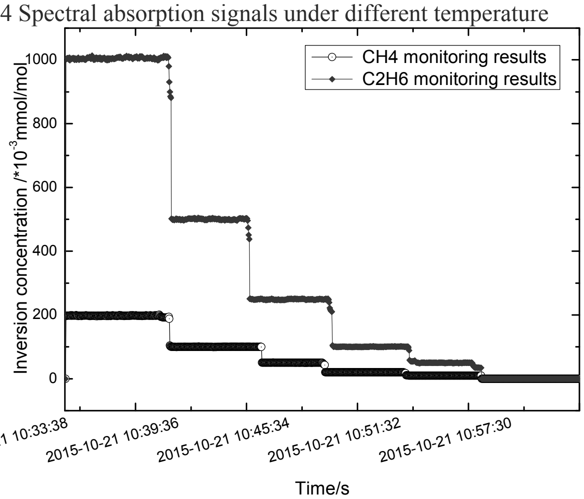


Fig.5 inversion concentration results

Table1 comparison between inversion concentration and distributed concentration

| distributed concentration /×$10^{-3}$mmol/mol | | inversion concentration /×$10^{-3}$mmol/mol | | relative error /% | |
|---|---|---|---|---|---|
| $CH_4$ | $C_2H_6$ | $CH_4$ | $C_2H_6$ | $CH_4$ | $C_2H_6$ |
| 200 | 1000 | 197.64 | 1009.39 | 1.2 | 0.94 |
| 100 | 500 | 98.28 | 510.5 | 1.7 | 2.1 |
| 50 | 250 | 51.25 | 257.25 | 2.5 | 2.9 |
| 20 | 100 | 20.62 | 104.3 | 3.1 | 4.3 |
| 10 | 50 | 10.37 | 52.4 | 3.7 | 4.8 |

$$\left(\text{relative error} = \frac{|\text{inversion concentration - distributed concentration}|}{\text{distributed concentration}} \times 100\%\right)$$

The results above show that the biggest detection error of methane concentration inversion was 3.7%, and the biggest detection error of ethane was 4.8%. So it is verified that this concentration inversion algorithm works stably and reliably.

## 6. Conclusion

In this research above, the detection technology based on TDLAS combined with multiple reflection cell was studied, and the monitoring system was set up to analyze the laser absorption spectral characteristics of methane and ethane. Then the concentration accurate inversion algorithm based on the spectral resolution and feature extraction was designed for methane and ethane synchronous detection. The multiple reflection cell was inflated the distributed mixed gases from the standard distribution system made with two high precision mass flow meters to get the measurement results. The biggest detection error was 3.7% of methane concentration inversion, and it was 4.8% of ethane concentration inversion. So it is verified that this concentration inversion algorithm works stably and efficiently. Thus, this technology could realize the real-time, fast and continuous measurement requirement of the main part of mash gas and it will provide the effective technical support to coal mining production in safety.

## Acknowledgments

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