Laser spectroscopy techniques in measurements of methane evolution from coal samples of the Kuzbas coal beds

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The diode laser technique with the use of a high-sensitive methane detector is suggested for studying methane concentration in coal samples and kinetics of its outflow into the atmosphere. The technique is characterized by high measurement accuracy, the ease of the experiment, and a small amount of coal samples required for the analysis. Measurement results on the methane evolution from coal samples of the Kuzbas coal beds are given and the kinetics of its outflow into the atmosphere is described. The level of methane residual of a coal sample is determined as $2.06 \cdot 10^{-4}$ kg/kg.

Introduction

The coal mining is accompanied by the intensive evolving of gas from the coal. When damaging the coal bed integrity, gas is evolved from the bed and arrives into the exhausted space and mine excavations. The evolved gas mainly (~98%) consists of methane, and its accumulation can result in gas and coal-dust explosion, fire, and sudden gas outburst. Besides, methane, entering into the atmosphere due to degassing of coal beds and ventilation of mine excavations, participates in the global warming. The study of methane concentration in coal and especially kinetics of its outflow gives a physical basis for justification of coal methane production and processing profitability, allows forecasting gas outbursts and working out methods of their control.[1]

To determine gas volume in coal beds, coal samples are used, taken in coalmines in field conditions using a special technique. At present, Raven Ridge Resources equipment (USA) is used for gas evolution testing and gas-content determination at the Institute of Coal and Coal Chemistry (ICCC) SB RAS. The equipment includes a set of pressure vessels for coal samples, thermostats for maintaining the preset sample temperature, and manometers to determine the volume of the evolved gas. In estimation of gas content in coal beds, the approaches, described in Ref. 2, are used, as well as analytical software developed with accounting for recommendations of Gas Technology Institute (USA) for determining coal bed gas content.[3]

In this work, a new technique is suggested for measuring kinetics of the methane emission and its content in coal samples, using a high-sensitive laser methanometer.

Laser methanometer

The methanometer is a laser spectrometer based on a frequency-tuned Fabry—Perot diode laser (DL) and a multipass optical cell.[4] The block diagram of the detector is shown in Fig. 1.

The detector includes:

1) optical part, consisting of a diode laser; two optical cells, one of which is multipass with a tunable length of the optical path (analytical channel) and another (the reference one) is single-pass; two photodetectors (PD), and the focusing optics;

2) Pentium PC;

3) multifunctional Input/Output **AT-MIO-16E1** (or **AT-MIO-16E4**) board produced by National Instruments Inc. (NI-DAQ board), inserted in the PCI computer bus;

4) interface unit (IU) in the PC front;

5) program for the detector control.

The detector employs the GaInPAs DL as a radiation source. The operating temperature is 0 … +50°C. Laser radiation frequency is tunable by the current and temperature variation in a range 6000–6080 cm^{-1} (1.645–1.666 μm), where sufficiently strong methane absorption lines are observed. The DL radiates several (5–10) longitudinal modes; the radiation power of one of them is about 70% of the total laser power (3 mW); the width of an individual DL radiation mode is 10^{-3} cm^{-1}. The laser frequency of the mode with the highest power is tuned to the frequency of the methane absorption line center by varying the DL temperature. A temperature sensor (thermistor) located near the laser is used for DL temperature measurements in the detector. The long-term temperature stability of the DL is 10^{-2} deg.
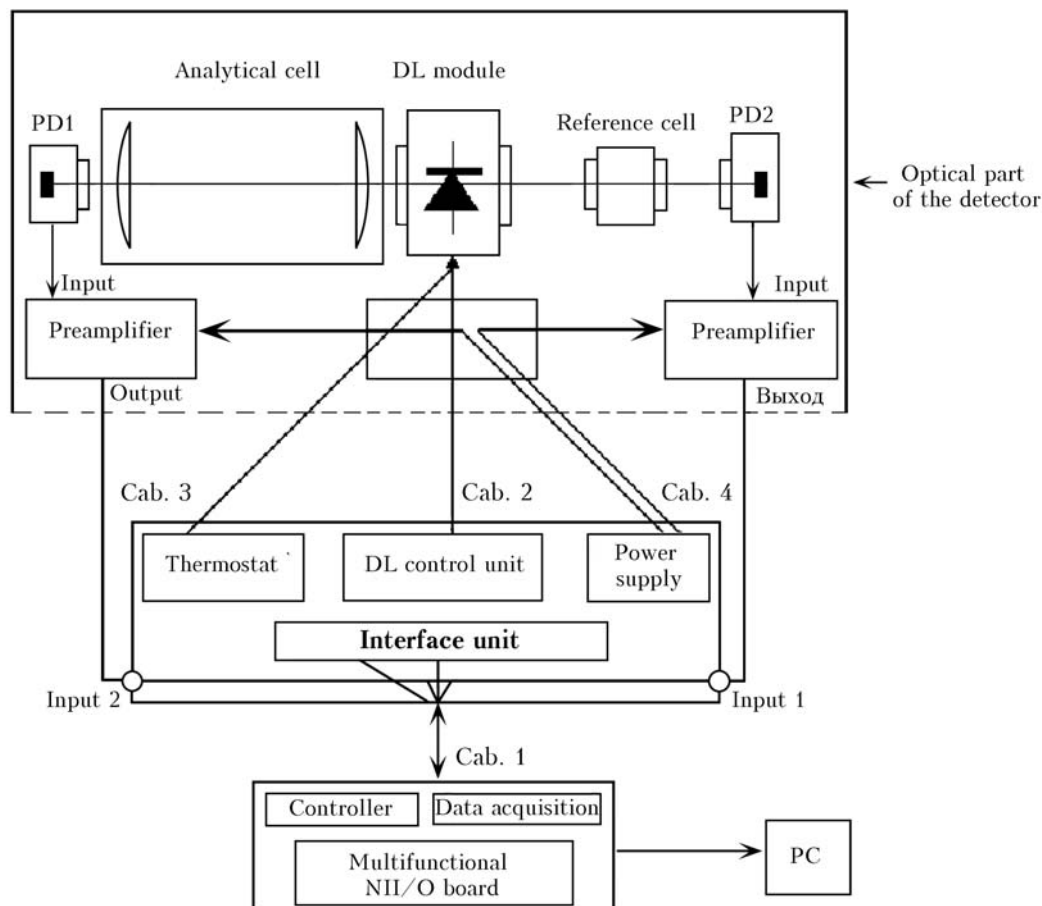
Fig. 1. Block diagram of the laser methane detector.

The diode laser operates in the pulse-periodic mode with a period of 4.5 ms and a pulse width of 4 ms. Current pulses of trapezoidal shape power the laser. This allows scanning the DL frequency in a range of about 1 cm^{-1} during a pulse and recording the transmission spectrum of an individual methane line. The DL radiates in two opposite directions. The principal laser beam comes into the multipass analytical optical cell with an output photodetector. The atmospheric air is continuously pumped through the cell.

Laser radiation in the opposite direction passes through the reference cell, filled with the methane–nitrogen mixture at a certain methane concentration, and comes to another photodetector. The technique of determination of the methane concentration is based on calculation of the correlation function of signal forms (absorption spectra of the "methane–nitrogen" mixture and atmospheric air) in both channels. This allows one to attain a high detector selectivity with respect to other gases.

The Chernin matrix system of 0.75 m basic length and 157.5 m optical path length was used in the multipass cell (at a mirror reflectivity of 0.998). The cell volume was 14 litres. Continuous pumping of atmospheric air through the cell was carried out with a membrane pump at a rate of 1.67 m^3/s.

The methanometer was controlled by the NI-DAQ board and IU (see Fig. 1); IU provides for agreement between the board and the optical part. The multifunctional NI-DAQ board (AT-MIO-16E4) includes two output channels (DAC), input channel (ADC), which can operate with 16 inputs when using multiplexer, the timer, and the buffer memory. Two DACs of the board are used for laser and Peltier element powering. Signals from photodetectors of the reference (input 1) and analytical (input 2) channels, as well as the temperature gage are sent to the ADC.

To power the DL, the control program switches on the generation of the trapezoidal current pulse train. Pulse parameters are preset to provide for the best generation mode for the DL (i.e., tuning to a methane absorption line) and a sufficient number of points (200–1000) in each pulse. Such generation mode in a train (from 20 to 170 pulses) allows the processing of signals averaged over each train during a time interval between trains.

The preset DL temperature and its stabilization are attained with the program control unit, taking into account the proportional (P), integral (I), and differential (D) components. In addition, the program unit allows frequency stabilization by the position of methane absorption line center in the reference cell.

The processing of signals from preamplifiers of photodetectors and calculation of methane concentration are carried out with the use of the control program synchronously with the laser pulse generation. First, signals in both channels (inputs 1 and 2) are averaged over a pulse train; then a region is separated in the averaged signals, including the methane absorption line. Again, a shape of this line is calculated with accounting for the width and waveform of the laser radiation line, and the three-step differentiation of signals at the separated region is carried out, accompanied with averaging high frequencies in order to distinguish a weak absorption line in the analytical channel. Then the correlation coefficient of differentiated signals is calculated proportionate to the methane concentration in the analytical channel.

The program of control for the gas-analyzer was developed in LabView (v. 5.0) environment, working under MS Windows-95 (or 98), and includes two program units **DRIVE.vi** and **METHOD.vi**. **DRIVE** is the main program used to run and control all program units including the DL one. Processing signals and calculating the methane concentration are performed by the **METHOD** unit. The calculated values are transferred back to the **DRIVE** program, where the time dependence of concentration is real-time plotted simultaneously with filing.

On the base of the preformed laboratory detector tests and field measurements,[4] principal specifications of the detector have been determined.

The threshold sensitivity is 0.03 ppm.

The range of methane concentrations is 0.03–10000 ppm (1%) (for higher concentrations, the detector can be used after changing the measurement technique).

The relative measurement error of the background methane concentration is about 50%, it is determined by the long-term instability, caused by zero drift (±0.5 ppm for 5 h). To take it into account, zero is to be determined and corrected every 3 hours.

The selectivity of methanometer is $4 \cdot 10^5$ for CO_2, more than 10^6 for CO, 10^5 for H_2O, and $2 \cdot 10^4$ for propane and butane.

The time of one measurement is 2 ms÷12 s.

The time constant of the detector as a whole is 99 s with accounting for the pumping rate $(9.4 \cdot 10^{-5}$ m^3/s) and cell volume (0.014 м^3).

The total detector mass without PC is 15 kg.

The size is $0.50 \times 0.50 \times 0.95$ m^3.

Measurement technique and results

To study kinetics of the methane emission and determine the gas content in coal beds, we used coal, sampled by a special technique under actual conditions in mines[2] in the form of cores from wells or coal slack from blustholes bored in a coal bed. When sampling, the time, spent for coal recovery from the coal bed, temperature, and barometric pressure are recorded. The recovered coal is placed into a pressure vessel, which is transported into a laboratory for measurements.

The methane mass Q (kg/kg) evolved from the coal sample mass unit and temperature dependence of the evolving rate $F(t) = \Delta Q(t)/\Delta t$ are determined from measurements of the methane concentration $C(t)$ (kg/m^3) in the analytical cell of the laser methanometer. Before the measurements, the atmospheric air is pumped through the analytical cell and the atmospheric methane concentration $C_0(t)$ is recorded. While measuring, the pressure vessel with the coal sample is connected with the analytical cell by a valve, and atmospheric air is continuously pumped through the vessel and analytical cell of the methanometer (Fig. 2).
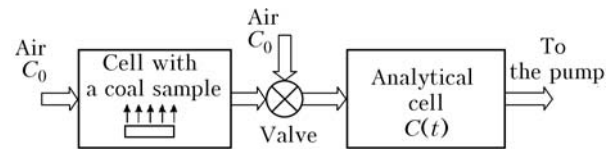

Fig. 2. Scheme of experiment.

Consider the methane mass balance at the detector input and output. During the time of sample transportation Δt_a (s) and measurement Δt_m (the time, during which atmospheric air is continuously pumped through the vessel with the coal sample and the analytical cell), the following mass of methane is evolved into the pressure vessel from the coal sample:

$$Q = \int_{\Delta t} F(t) M_{coal} dt, \qquad (1)$$

where $\Delta t = \Delta t_a + \Delta t_m$; M_{coal} is the mass of the coal sample.

While pumping atmospheric air through the vessel with the coal sample and analytical cell, the mass of methane evolved into the methanometer is

$$M_+ = Q + S_0 \int_{\Delta t_m} C_0(t) dt, \qquad (2)$$

where S_0 is the gas volume under atmospheric pressure passing through the analytical cell in unit time, m^3/s.

At the same time, the mass of methane passing through the analytical cell in the measurement time Δt_m is

$$M_- = S_0 \int_{\Delta t_m} C(t) dt. \qquad (3)$$

Equating Eqs. (2) and (3), obtain the sought methane mass

$$Q = \frac{S_0 \int_{\Delta t_m} \left(C(t) - C_0(t) \right) dt}{M_{coal}}. \qquad (4)$$

Since measurements of $C_0(t)$ in time Δt_m is impossible and the concentration variations are less that self-sensitivity of the detector, $C_0(t)$ in Eq. (4) can be changed to its preliminary measured mean value:

$$Q = \frac{S_0 \int\limits_{\Delta t_m} (C(t) - C_{0m})\mathrm{d}t}{M_{\mathrm{coal}}}, \qquad (5)$$

where

$$C_{0m} = \frac{1}{\Delta t_a} \int\limits_{\Delta t_a} C(t)\mathrm{d}t. \qquad (6)$$

The registration of the temporal dependence of methane concentration in the air passing through the volume with the coal sample, allows also studying the kinetics of methane emission from the sample:

$$F(t) = \frac{S_0 (C(t) - C_{0m})}{M_{\mathrm{coal}}}. \qquad (7)$$

The technique was tested with a sample of the coal slack (Fig. 3) of $78.7 \cdot 10^{-3}$ kg taken from a depth of 300 m on December 3, 2007. The sample was placed into the pressure vessel 1 hour before the measurements.

Fig. 3. Analyzed sample of coal slack.

Figure 4 shows the methane concentration curve recorded while pumping air through the volume with the sample.

The pumping rate S_0 was $1.65 \cdot 10^{-4}$ m^3/s. To calculate the mass of the evolved methane, above equations (4)–(6) were used. Figure 5 illustrates the kinetics of the methane emission.
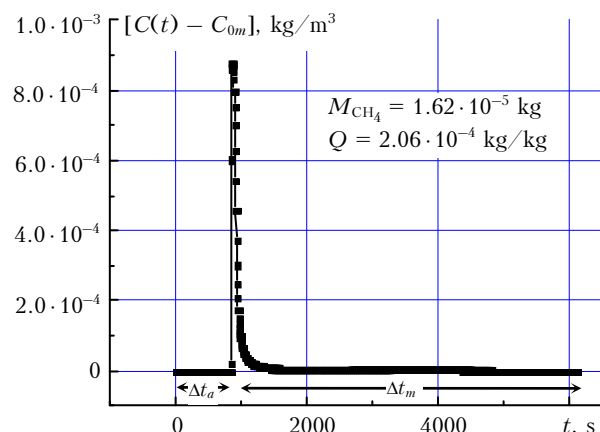

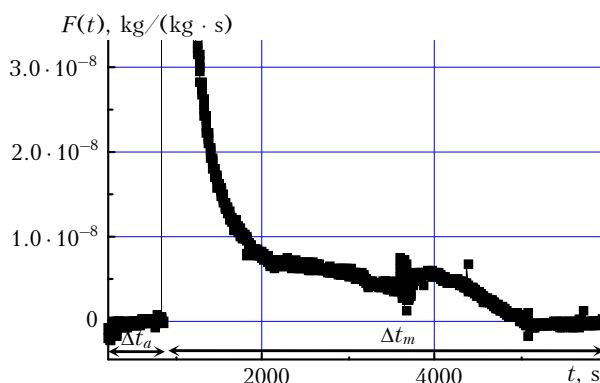**Fig. 4.** Temporal dependence of methane concentration emitted from the sample in Fig. 3.

Fig. 5. Kinetics of methane emission from the coal sample.

Conclusion

In this work, the technique with the use of a high-sensitive methane detector based on a diode laser is suggested for studying methane concentration in coal samples. In contrast to common techniques for estimation of coalbed gas content, the laser methanometer allows recording just the methane content in coals and studying the kinetics of its outflow into the atmosphere. The technique is characterized by ease of experiment and a decrease in amount of coal samples required for the analysis and analyzing time by more then a factor of 100.

References

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