Estimation of systematic errors in determination of the methane concentration using diode laser detector

V.A. Kapitanov, O.Yu. Nikiforova, and Yu.N. Ponomarev

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk

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The errors in determination of the methane concentration in ambient air, connected with the difference in temperature and pressure inside the measurement cells, addition of water vapor, carbon dioxide, and ethylene in the gas probe, and the random noise, are estimated numerically. It is shown that the presence of the foreign gas spectral line in the spectrum under recording together with the analytical methane line can result in overestimated or underestimated values of the methane concentration relative to the true one. The total error in determination of the methane concentration under atmospheric conditions, caused by the presence of water vapor or carbon dioxide in the air probe, as well as by the random noise is less than 1%. Inside the measurement cells, variations of the temperature and pressure, limited by 1° and 1 Torr, respectively, yield an error not higher than 1.5%. At equal concentrations of methane and ethylene in the air probe, the error of determination of the methane concentration can reach 15%.

Introduction

Methane is one of a large group of the most important hydrocarbons in the atmosphere.[1] Its background concentration significantly exceeds concentration of other volatile organic compounds. The contribution of methane to the process of global warming makes up 30% of the carbon dioxide contribution. A change of methane content can be of interest for different atmospheric, climatic, and biological researches. This makes it necessary to develop high-sensitive instrumentation for methane diagnostics in the atmosphere.

Currently, methods of diode laser spectroscopy are successfully used for detection of methane and other greenhouse gases. A series of laser sensors for methane detection have been proposed for atmospheric studies, which are based on diode lasers emitting at room temperature in the region 1.6–1.7 μm. Multipass absorption cells,[2–5] photoacoustic detectors,[6–9] and CRD spectroscopy, i.e., radiation damping in high Q-factor resonators[10–12] are used in the sensors. They are characterized by a threshold sensitivity of ~ 0.1 ppm for CH_4, which is 20 times lower than the background concentration (1.8–2.0 ppm).

It is well known that water vapor, carbon dioxide and ethylene lines are present alongside with methane absorption lines in a region of 1.65 μm.[6] Distortions in the recorded spectrum of methane analytical line caused by these lines can result in errors at determining methane concentrations. Errors can be also caused by the difference in gas pressure and temperature in cells of the diode laser methane detector.

The goal of this work is estimating errors in determination of the methane concentration with the diode laser methane detector operating in a 1.65 μm region by means of the numerical modeling. The error can be caused by the random noise, different temperatures and pressures in cells, as well as the presence of foreign gases of various concentrations in the sample.

Method of determination of methane concentration with diode laser detector

The structure and the principle of operation of the diode laser methane detector (DLD) were described earlier in detail.[2,3,13–15] The methane triplet $R3$ of $2\nu_3$ band centered at 6046.95 cm^{-1} is used as the analytical line. The detector allows estimation of the methane concentration in different gas mixtures at pressures between 0.1 and 760 Torr. The noise level in transmission spectrum is equal to $2 \cdot 10^{-4}$ and the threshold sensitivity of DLD is 0.04 ppm at averaging over 2720 pulses. The distribution function of noise signal is normal, therefore the methane concentration estimate is free of systematic error. Relative measurement accuracy of the methane concentration is 1% until its magnitude exceeds 0.04 ppm [Ref. 2].

The DLD optical layout is shown schematically in Fig. 1.

The main components of DLD are the following: frequency-tunable diode laser, emitting in two opposite directions, and two cells, one is the reference cell, filled with the mixture of methane and nitrogen of a definite concentration and the other is the sample cell, filled with the analyzed gas mixture. The temperature in the cells is identical. The gas in the sample cell is under atmospheric pressure, while the pressure of the gas in the reference cell is selected in such a way that the absorption line widths and contour shapes in both cells are identical.

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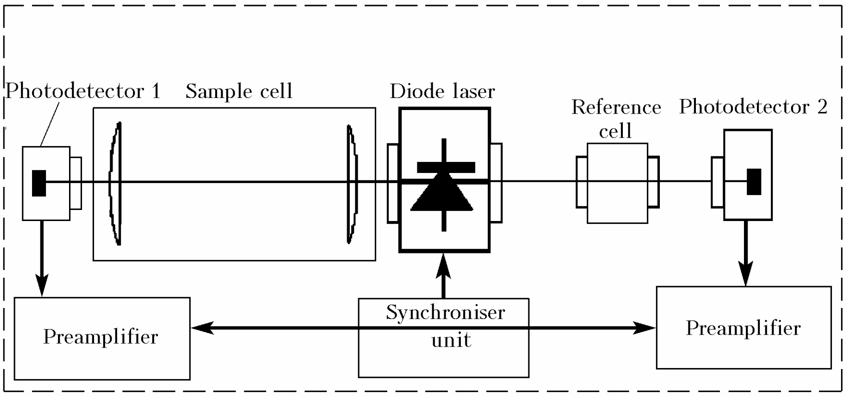


Fig. 1. Optical layout of diode laser methane detector.[2,3]

In the process of measurements, the laser radiation frequency is tuned and the intensity of the radiation, passed through the cells, is recorded with a photodetectors. This process results in spectral fragments of signals $S(\nu)$ in both cells. Then an interval of 1 cm^{-1} width is chosen and the analytical line of methane is seen as a trough in its center part. To define the transmission spectrum of each cell, the signal outside the analytical line is described by a polynomial of 3rd power (polynomial coefficients are determined from the fitting at the interval edges). The obtained $F(\nu)$ dependence characterizes the incident laser signal and is used for calculation of the transmission spectrum $T(\nu) = S(\nu)/F(\nu)$. Then $k_r(\nu)$ and $k_a(\nu)$ absorption spectra are determined in the reference and sample cells in accordance with the Bouguer law. Then, a threefold frequency differentiation of $k(\nu)$ is carried out and the correlation coefficients $K^{(i)}$ of absorption spectra or their derivatives $k^{(i)}(\nu)$ ($i = 0, 1, 2, 3$) are calculated for reference and sample channels by the formula

$$K^{(i)} = \sum_{\nu} k_r^{(i)}(\nu) k_a^{(i)}(\nu). \qquad (1)$$

The methane volume concentration $C_a^{(i)}$ in the sample (atmospheric) channel is calculated by the formula

$$C_a^{(i)} = K^{(i)}(C_r L_r / L_a) R, \qquad (2)$$

where C_r is the methane volume concentration in the reference channel, ppm; L_r and L_a are the optical path lengths in reference and sample channels, respectively, R is the calibration factor close to 1.

The results of numerical modeling

Numerical experiments were carried out for determining the CH_4 concentration by the above method in the air sample with the use of reference and sample absorption cells.

The calculations were conducted in two stages. At the first stage, the model spectra were used. Since the gas pressure in DLD cells is close to the atmospheric one, the Lorentz contour of the spectral line was used in calculations. The transmission in the cells was calculated in a window of 1 cm^{-1} width, in the center of which the analytical line was located. Its halfwidth $\gamma = 0.07$ cm^{-1} roughly corresponded to the halfwidth of methane line in a 1.65 μm region.

The simulation scheme corresponded to signal processing for determining methane concentration with the help of DLD. First, the transmission, imitating DLD signal $S(\nu)$, was calculated from the absorption spectrum. Then the transmission on spectral interval edges was described by a polynomial of degree 3 ($F(\nu)$) and the ratio $T(\nu) = S(\nu)/F(\nu)$ was calculated. After that the absorption spectrum was calculated in each channel and the concentration of the gas to be measured (target gas) was calculated from the value of the correlation coefficient of the obtained absorption spectra or their derivatives.

1. The influence of the random noise

Since random noise is an integral part of any measurement, we performed calculations illustrating its influence on the retrieved value of the methane concentration. The distribution function of noise signal is normal and, consequently, it does not introduce a systematic error in determination of the methane concentration.

When modeling signals in DLD channels, it was assumed that the absorption in them is stipulated by the methane analytical line only. The random noise was added to the calculated values of transmission spectra $S(\nu)$ in the cells. The smoothing over 25 points was carried out before each differentiation. The noise level was given in percents of the maximal signal difference in the center and off the analytical line. Since the signal amplitude in reference channel is significantly higher than in the sample one, it was assumed that the noise level in the reference cell is ten times lower. The signals at a maximal noise level of 10% in the sample cell are illustrated in Fig. 2. The signal in the reference cell is almost smooth (1% noise).

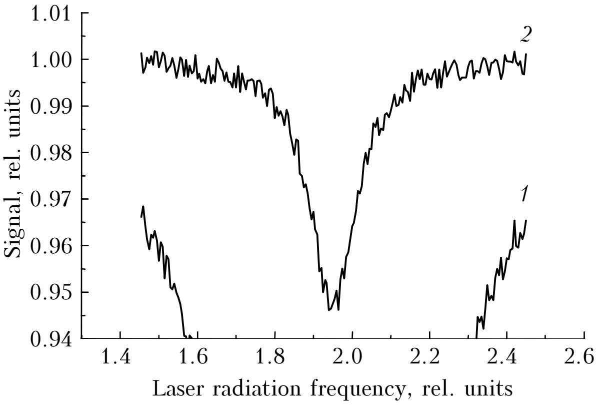


Fig. 2. Signals in the reference (*1*) and sample (*2*) channels of DLD.

Figure 3 illustrates the influence of random noise on methane concentration retrieved from the correlation coefficients of direct absorption spectra, as well as their first, second, and third derivatives. The vertical axis denotes the ratio of the retrieved methane concentration C_{measured} to its true value used in modeling C_{true} (it was assumed that C_{true}=2 ppm). Only one realization of signals in the cells was calculated for each value of noise, which then was used for retrieving methane concentration from correlation coefficients of direct absorption spectra and their derivatives.

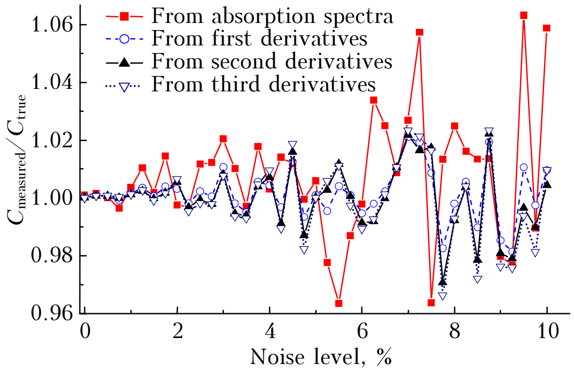
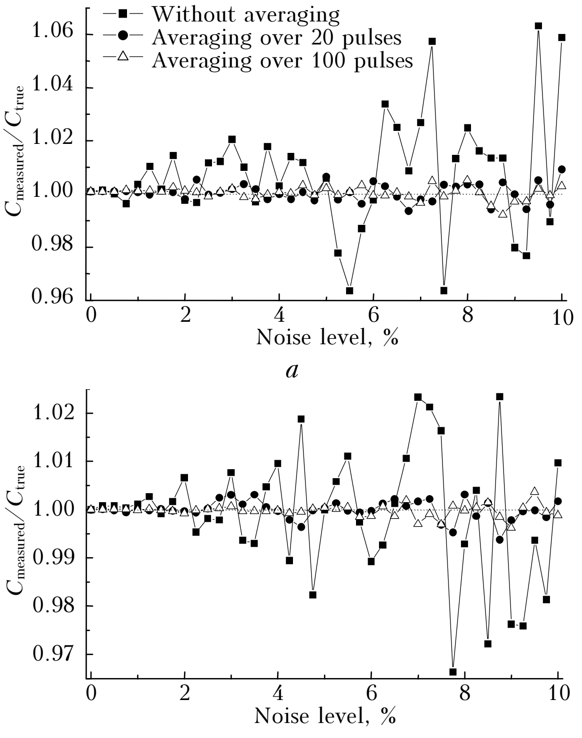


Fig. 3. Dependence of error in retrieval of the methane concentration from correlation coefficients of the direct absorption spectra and their first, second, and third derivatives on the random noise level.

As is seen in Fig. 3, when processing direct signals, the error is greater than when processing signal derivatives; the error can reach 6% at the noise level of ~10%. However, the influence of random noise can be diminished by averaging over several realizations (a possibility of averaging over 200 pulses is introduced in the processing program). The decrease of error, caused by the random noise at averaging over a series of pulses, is illustrated in Fig. 4.

It is seen that at averaging over 20 realizations the error does not exceed 1% and is twice lower when using the signal derivatives.



a

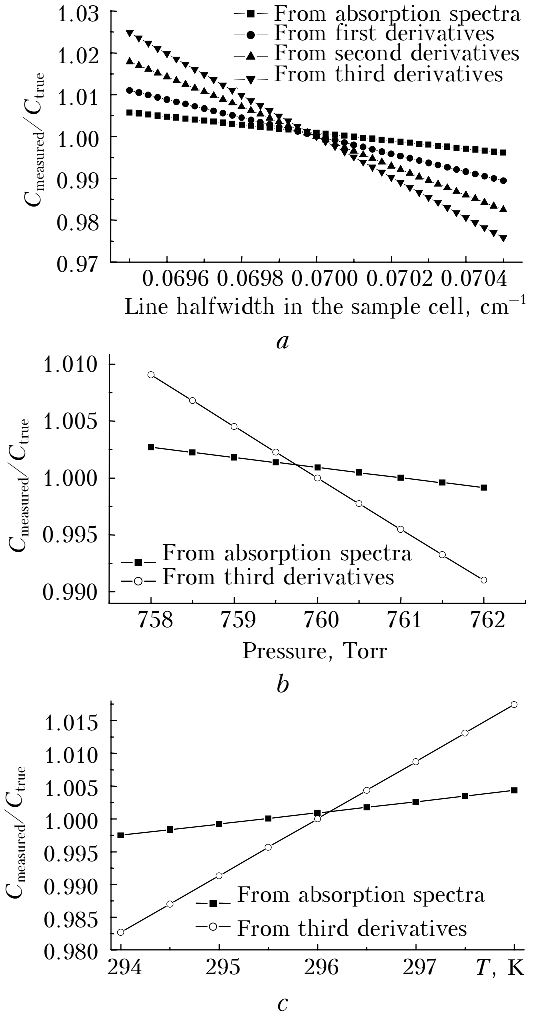
b

Fig. 4. Error in the methane concentration retrieved from the correlation coefficients of direct absorption spectra (*a*) and their third derivatives (*b*) at different levels of signal accumulation.

2. The influence of pressure and temperature differences in cells

When varying the temperature and pressure in the cell, the recorded contour shape and the width of the analytical line can change as well. Both DLD cells are situated close to each other, therefore, as a rule, the gas temperature in them is equal. The pressure of gas mixture in the DLD reference cell is selected in such a way that at atmospheric measurements of methane concentration, the contour shapes of analytical line in both cells are identical. For additional correction of the discrepancy between line shapes in the DLD channels, a calibration factor *R* is used in formula (2). However, we estimated errors on the determination of the methane concentration, caused by the difference of analytical line widths in the channels (for example, at a temperature difference of 1° or pressure deviation of 1 Torr).

The following parameters were taken in calculations for the reference cell: the temperature was equal to 296 K and the pressure to 760 Torr; the analytical line halfwidth was equal to 0.07 cm^{-1}. Provided the temperature and pressure in the sample cell were 295 K and 761 Torr, the line halfwidth was equal to 0.0704 cm^{-1}; in the case that the temperature and pressure in the sample cell were 297 K and 759 Torr, respectively, then the line halfwidth was 0.0696 cm^{-1}. In both cases the methane concentration was determined with an error caused by the difference of analytical line halfwidths in the reference and sample channels of DLD (Fig. 5).



a

b

c

Fig. 5. Dependence of the error in determination of the methane concentration on the difference in analytical line widths (*a*), pressures (*b*), and temperatures (*c*) in DLD cells.

As is seen, the technique of determination of methane concentration from the correlation coefficients of direct absorption spectra in cells is more stable to the change of line width than the technique based on the use of derivatives. The pressure change by 2 Torr in the sample cell can lead to an error of 1% in determination of the methane concentration, when analyzing third derivatives of spectra. When analyzing the direct absorption spectra this value is four times lower.

3. The influence of spectral lines of other gases

When choosing the analytical line, one of the criteria is the absence of perturbing absorption lines of other gases, though it is practically impossible to avoid the influence of neighboring lines because of high their density in spectra, for example, of H_2O, C_2H_4, CH_4. Therefore, we carried out calculations, which allowed estimation of errors in determination of the methane concentration, caused by the presence in the recorded spectra of spectral lines of foreign gases in the range of frequency tuning of the DLD radiation. It is known that some molecules with the C–H bond have strong combination vibration bands or overtones in a 1.6–1.7 μm range.[16] Moreover, when analyzing the methane concentration in atmospheric air, the influence of carbon dioxide and water vapor is possible.

a. The analysis of the influence of perturbing spectral line

When modeling signal in the reference cell, it was assumed that the absorption in the cell would be caused only by the analytical line and in the sample cell – by the analytical line and the interfering line of the foreign gas. The transmission in the cells was estimated in a spectral interval of 1 cm^{-1} width with the analytical line in the center. During calculations the center of spectral line of the foreign gas moved aside from the analytical line on the distance $\Delta\nu$. The halfwidths γ of both lines were chosen equal to 0.07 cm^{-1}. In calculations we used a 5:1 ratio of line intensities.

The effect of the perturbing gas is double. On the one hand, the additional absorption in the atmospheric sample cell increases the signal and can result in an overestimated value of the concentration of the target gas, particularly, if the line centers are close to each other. It is evident that when centers of both lines coincide, the absorption caused by the perturbing gas can not be distinguished from the absorption caused by the target gas. This inevitably leads to concentration overestimation. On the other hand, the presence of absorption line close to the edge of the fitted window influences the spectral dependence of the derived function $F(\nu)$ and can both increase and decrease the retrieved value of the target gas concentration as compared to the true one.

Figure 6 illustrates the influence of the perturbing gas on the error in retrieval the concentration of the target gas using the correlation coefficient of third derivatives of the absorption spectra in reference and sample channels depending on distance $\Delta\nu$ between lines.

The calculations were made for equal concentrations of the foreign and the target gases. In the top-center of Fig. 6 model signals in both DLD cells for the distance $\Delta\nu = 5\gamma$ between lines with a 5% noise are shown. Spectra of signals $S(\nu)$ are illustrated to the right and to the left, as well as the absorption spectra and their third derivatives corresponding to the distance between lines $\Delta\nu = 2\gamma$ and 0.85γ. It is seen that depending on the position of foreign gas absorption line relative to the analytical line center at the chosen calculation parameters, the concentration can be determined with

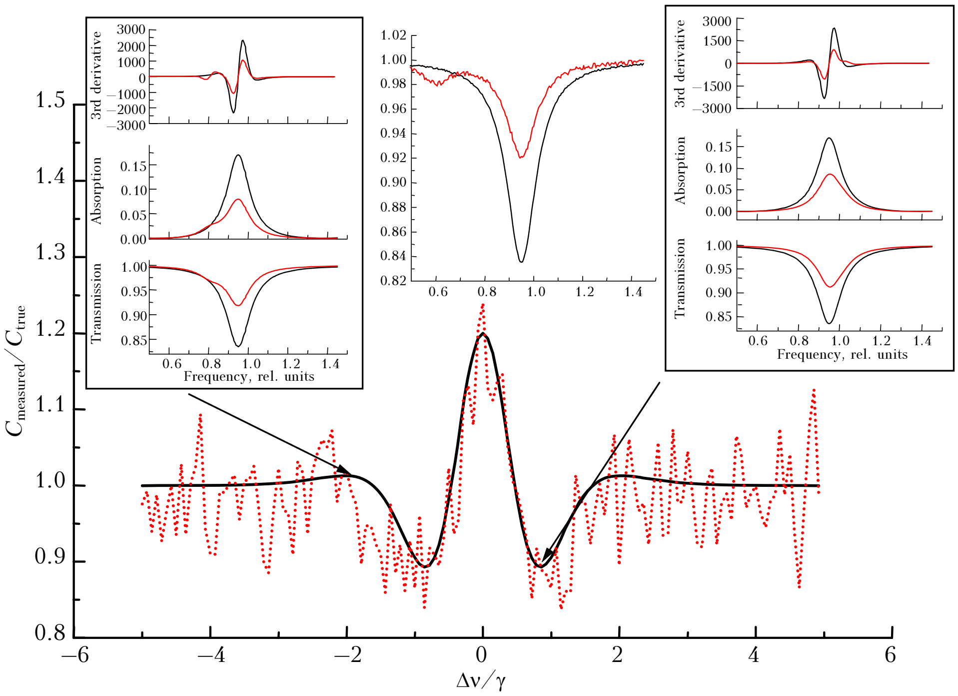


Fig. 6. Influence of the position of perturbing line on the ratio of the retrieved methane concentration to the true one when the correlation technique is used for third derivatives of signals in the absence of noise (solid line) and at a 5% noise (dotted line).

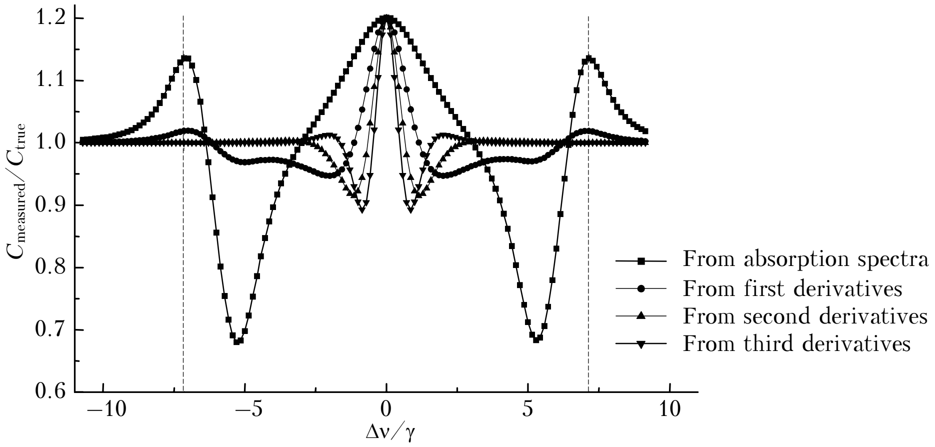


Fig. 7. Ratio of retrieved and true methane concentrations depending on the distance Δν between the centers of perturbing and analytical lines.

an error between −10 and +20% even in the absence of random noise. Note also that the width of the spectral interval, in which the center of foreign gas line has to be located in order to significantly distort the retrieved concentration value of the target gas, does not exceed 4γ. Beyond this range the presence of 5% random noise completely masks the influence of perturbing spectral lines.

Figure 7 illustrates the error in determination of the target gas concentration from the correlation coefficient of direct absorption spectra and their first, second, and third derivatives, depending on the position of perturbing line center. Vertical dotted lines denote borders of the fitted window.

As is seen in Fig. 7, the influence of perturbing spectral line is the most significant in the analysis of direct absorption spectra: with the chosen calculation parameters, the concentration can be determined with an error ranging from −30 to +20%. When using the derivatives, the absolute value of the error decreases and the spectral interval, at which the influence of foreign gas lines is seen, becomes narrower. This fact increases the selectivity of the method relative to other spectral lines.

In contrast to the case of computing the target gas concentration from the correlation coefficient of the direct absorption spectra, at the use of the second and third derivatives, the perturbing line does not change the derived value of the target gas concentration by more than 2%, provided the two lines are separated by more than 1.5γ, i.e., if the perturbing line does not fall within the core of the target line. However, the use of each following derivative leads to a more significant underestimation of the target gas concentration, if there is a line at a distance $\Delta\nu$ in the spectrum of the analyzed sample, corresponding to the curve minimum in Fig. 7.

b. The estimation of influence of H_2O *and* CO_2 *spectral lines*

According to the data of HITRAN-2004, there is a weak H_2O line at 6046.78 cm^{-1} with intensity of $3.67 \cdot 10^{-26}$ cm^{-1} /(molec $\cdot$ cm^{-2}), as well as a stronger line at 6047.79 cm^{-1} with intensity of $8.31 \cdot 10^{-25}$ cm^{-1}/(molec $\cdot$ cm^{-2}) near the methane analytical line centered at 6046.95 cm^{-1}.

The modeling was carried out for a spectral interval of 1 cm^{-1} around methane analytical line. The pattern of absorption spectrum of 1 cm^{-1} width with the analytical line in the interval center at different concentrations of water vapor in the analyzed sample is illustrated in Fig. 8.

The error in determination of the methane concentration was estimated taking into account only one closest H_2O line, as well as with accounting for the influence of both lines (Fig. 9). The vertical lines denote the H_2O concentrations: 3353, 10060, 37160, and 55270 ppm, which correspond to temperature of 15°C, humidity of 20 and 60%, as well as temperature of 28 and 35°C and humidity of 100%.

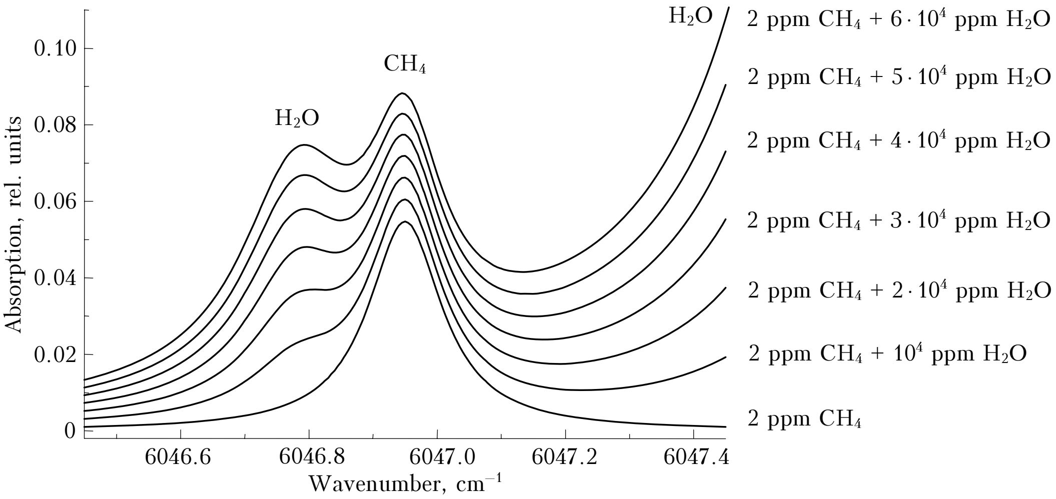


Fig. 8. Fragment of absorption spectrum of 1 cm^{-1} width around the methane analytical line at different concentrations of water vapor in the analyzed sample.

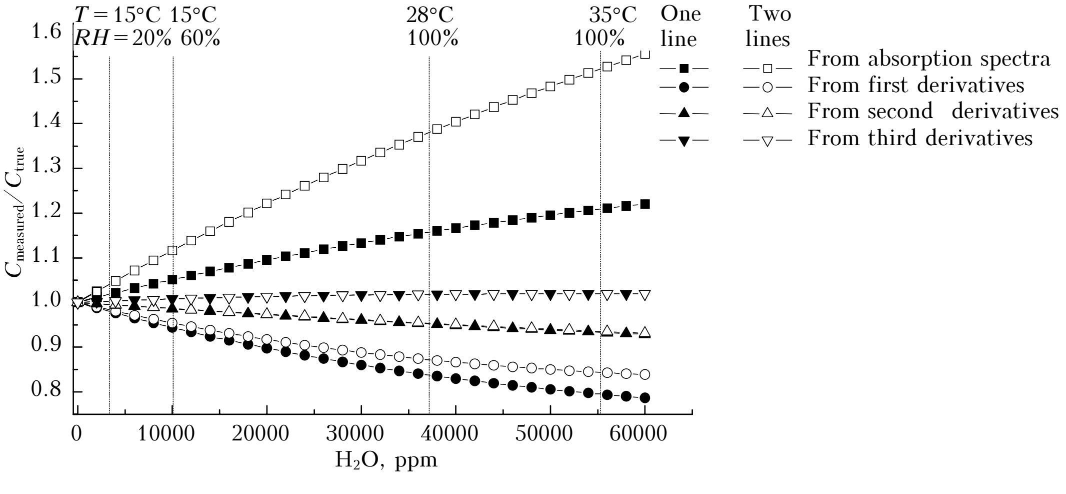


Fig. 9. Dependence of error in the retrieved methane concentration on the water vapor concentration in the analyzed sample with accounting for one H_2O line, the closest to the analytical one, and the both lines.

It is seen in Fig. 9 that the accounting for the air humidity is very important for processing of absorption spectra and to a lesser extent for the processing of their first derivatives. When retrieving the methane concentration from the second derivatives, the retrieval error does not exceed 7%, for the third derivatives it is less than 2% even at the maximal humidity.

When using the third derivatives of absorption spectra, two circumstances should be taken into account: 1) the error induced by the humidity leads to overestimated but not underestimated value of methane concentration; 2) this error is caused just by the distortion of the analytical line contour shape by the closest H_2O line, and not by the effect of a strong line wing when determining $F(\nu)$, because the calculation results with accounting for one or two lines coincide.

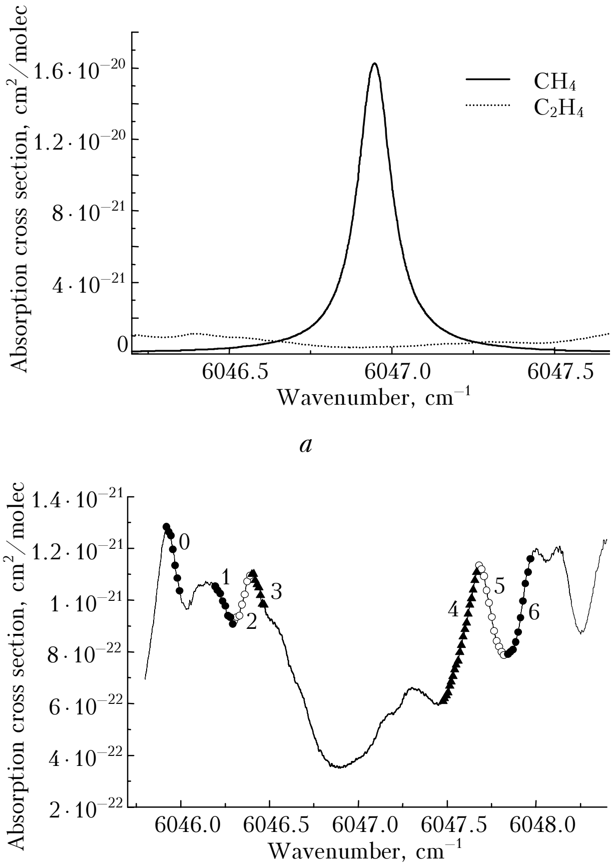
According to the HITRAN-2004 data, there are two weak CO_2 lines centered at 6046.81 and 6047.26 cm^{-1} with intensities of $4.84 \cdot 10^{-26}$ and $3.54 \cdot 10^{-26}$ $cm^{-1}/(molec \cdot cm^{-2})$ close to the methane analytical line. In calculations, two stronger spectral lines, centers of which are beyond the modeled spectral interval of 1 cm^{-1} width (6046.25 cm^{-1}, $5.31 \cdot 10^{-25}$ $cm^{-1}/(molec \cdot cm^{-2})$ and 6047.89 cm^{-1}, $6.56 \cdot 10^{-25}$ $cm^{-1}/(molec \cdot cm^{-2})$) were also taken into account. It has been shown that for atmospheric air, when carbon dioxide content does not exceed the tenth share of a percent, the presence of CO_2 in the sample under analysis hardly influences the retrieved value of methane concentration. However, when studying the gas exchange in plants, the carbon dioxide concentration can reach $2–2.5 \cdot 10^4$ ppm [Ref. 17], and the systematical error in methane concentration determination can reach 15% at the use of the absorption spectra and 7% at the use of their third derivatives.

c. Estimation of the influence of ethylene spectral lines

Data on ethylene lines in 1.6 μm region are absent in HITRAN database, though ethylene spectra in this region have been studied experimentally. In particular, methane and ethylene spectra in 5900–6250 cm^{-1} region with 0.1 cm^{-1} resolution were obtained[6] using the photoacoustic spectrometer with a pulse laser. The measurements of ethylene absorption cross sections in a narrow region close to 1.625 μm were conducted by CRD spectroscopy with the DFB diode laser.[18] Methane spectra in the region of 1.65 μm were registered by two-channel photoacoustic spectrometer with 10 MHz resolution.[19]

Along with methane, ethylene can be contained in the analyzed samples, distorting the recorded spectrum of the methane analytical line and causing errors in determination of the methane concentration.

When modeling numerically the influence of ethylene spectral lines, the same procedure of signal processing was considered, where experimental spectra of the methane and ethylene in the range of 6040–6050 cm^{-1} were used,[20] recorded with the near-IR diode laser spectrometer with two resonance photoacoustic detectors.[21] The spectral resolution was $2 \cdot 10^{-4}$ cm^{-1} and the threshold sensitivity was $4 \cdot 10^{-23}$ cm^2/molec. Methane and ethylene spectra in a 3 cm^{-1} interval are illustrated in Fig. 10.

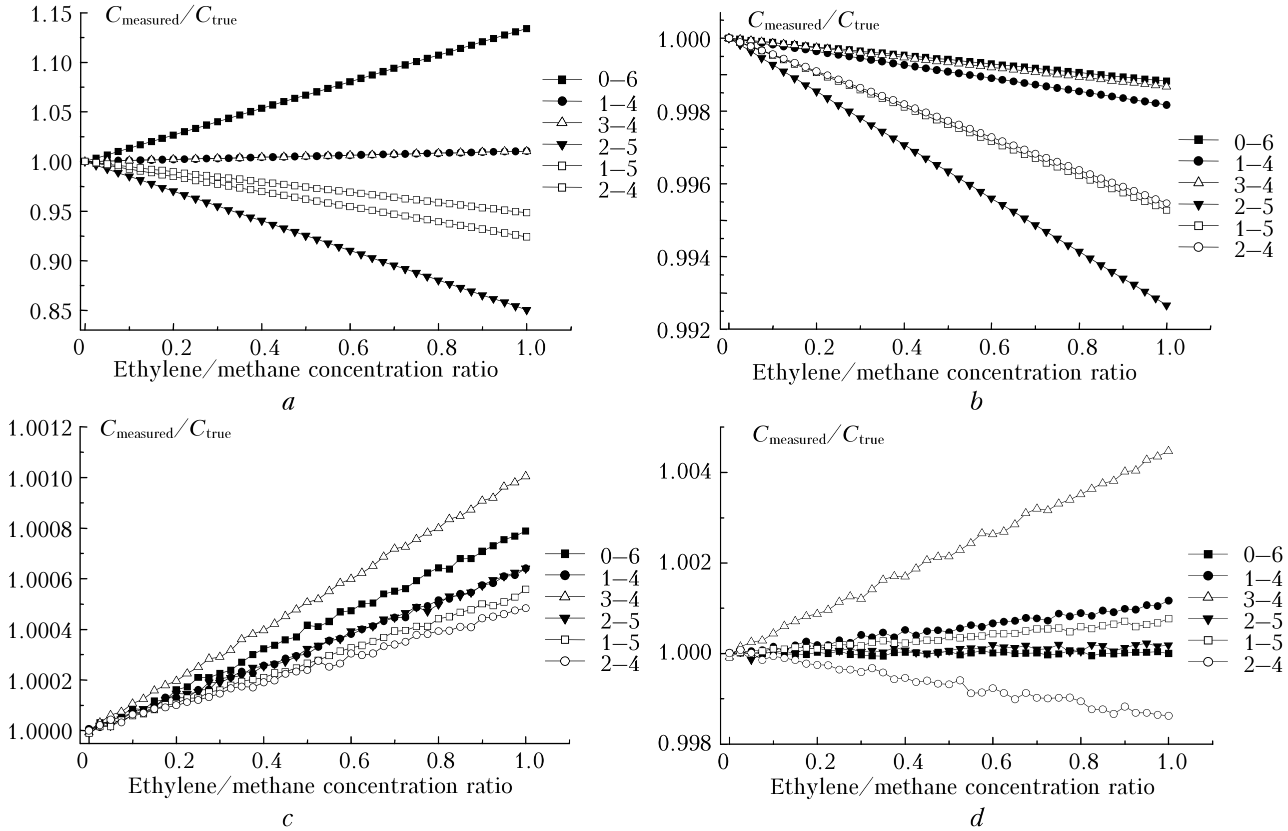


a

b

Fig. 10. Methane and ethylene experimental spectra (*a*), ethylene spectrum with identification of different intervals defining the left and right edges of the fitted window (*b*).

Since the ethylene absorption cross section is approximately 20 times less than the methane absorption cross section in the center of analytical line, the presence of ethylene in the sample can lead to errors in determination of the methane concentration, mainly, due to $F(\nu)$ function distortion at the edges of the fitted window. Figure 10*b* illustrates the portion of the ethylene experimental spectrum, in which the intervals with different inclination are shown. In further calculations the fitted window was chosen in such a way that the marked intervals were at the window edges and were used in calculation of $F(\nu)$. The error in determination of the methane concentration, caused by the presence of ethylene in the analyzed sample at different choices of the edge intervals is illustrated in Fig. 11.



a *b* *c* *d*

Fig. 11. Error in determination of methane concentration due to the presence of ethylene in the analyzed sample for several choices of the edge intervals of the fitted window, when using direct absorption spectra (*a*), their first (*b*), second (*c*), and third (*d*) derivatives at correlation coefficient calculation.

It is seen that at least with the chosen variants of fitted window edges, the error in the retrieval of the methane concentration from correlation coefficient of third derivatives of the absorption spectra, caused by the presence of ethylene in the analyzed sample, is less than 0.5% (at ethylene concentration less than 2 ppm).

Conclusion

The presence of measurement noise at the averaging cannot yield error higher than 1% in determination of the methane concentration by DLD, even when calculating correlation coefficient of direct absorption spectra. For third derivatives of the spectra this error is about tenth shares of a percent.

A difference of temperatures and pressures in cells equal to 1° and 1 Torr, respectively, can yield 1–1.5% error, when using third derivatives, this error is significantly lower for direct absorption spectra.

When studying atmospheric air, the presence of water vapor and carbon dioxide also does not lead to methane concentration error higher than 1%. However, the error, caused by absorption lines of these gases, can become significant when studying gas exchange of biosystems with the atmosphere, because in this case CO_2 and H_2O concentrations in the analyzed sample can exceed the values typical for atmospheric air by an order of magnitude and even more. In any case, the presence of water vapor or CO_2 in the sample under study, when calculating the correlation coefficient of third derivatives of absorption spectra in DLD cells, can lead to overestimated but not underestimated values of the methane concentration.

At equal concentrations of ethylene and methane in the analyzed sample, the error in determination of methane concentration can reach 15% when calculating the concentration from absorption spectra correlation in both cells, notwithstanding the fact that in 6045–6048 cm^{-1} region the cross section of ethylene absorption is significantly (more than tenfold) less than methane absorption cross section close to the analytical line center.

When using the second or third derivatives, the absorption line of the foreign gas in the sample can distort the measured value of the analyzed gas concentration by more than 2% only in the case when the distance between the lines is ≤ 1.5–2 halfwidth of the analytical line. Therefore, it is more important to take into account the influence of ethylene when measuring not in 1.65 μm, but in 1.63 μm region, where strong ethylene lines are close to methane lines.[6]

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