Laser methanometer measurements of methane emission by plants in aerobic conditions

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Received March 2, 2006

The measurements of methane emission by leaves torn off from greenhouse plants and Siberian stone pine needles, obtained with the help of a laser methane detector based on a 1.65 μm tunable diode laser, are presented. The emission was estimated via comparison of the methane concentration in the room air with its concentration in a closed incubation volume containing the torn off leaves. The accumulation time varied between 10 and 300 hours. It is shown that in spectrometric measurements of the methane emission by green mass, the ethylene emission by damaged plants should be taken into account. The ethylene has absorption lines near the methane ones. This was not taken into account in previous measurements of the methane concentration. The obtained rate of methane emission by the green mass is significantly lower $(1.6–8.7) \cdot 10^{-12}$ kg/(g · h) then the reported by other researchers.

Introduction

Methane is one of the most important organic matters in atmosphere.[1] Its concentration significantly exceeds concentrations of other organic compounds. Last years the methane content in atmosphere increases with the rate of about 1% per year; this favors the greenhouse effect due to active absorption of the Earth heat radiation by methane in the IR spectral range. The methane contribution into the greenhouse effect is about 30% of the magnitude accepted for carbon dioxide. Concentration of any gas in atmosphere is determined by a proportion between intensity of its sources and sinks. Prior to January, 2006, swamp territories (55–150 Mt/year), termitaries (20 Mt/year), forest fires (40 Mt/year), World ocean, and fresh waters (15–35 Mt/year), as well as gas-hydrates were considered as the main natural sources of methane.

In 2005, Frankenberg et al.[2] presented results of satellite monitoring of methane, which showed abnormally high methane concentration from August to November, 2003, in low latitudes over evergreen forests. The methane concentration was measured by the differential absorption method with a scanning absorption spectrometer in the range 6000–6134 cm^{-1}. The scale of the anomaly pointed out to an additional source of methane, which was not taken into account in models used by the authors. In January, 2006, F. Keppler et al.[3] published results evidencing the methane emission by green plants themselves.

The procedure for measuring methane emission and the isotopic ratio of stable isotopes $^{13}C/^{12}C$ was the following[3]: "…Green leaves (1–6 g) were placed into closed glass volumes (44 ml). Before the experiment, the volumes were cleaning by free-of-methane air during 1 hour. After keeping in the dark for 16 hours at 30 and 40°C, methane was analyzed with the mass-spectrometer at a constant flow rate (CF-IRMS). The leaf mass was dried during 24 hours at 105°C for conversion to 1 g of the dry-mass. An experiment with solar radiation was carried out when placing the glass volume in direct sun rays for 1 hour between 10 a.m. and 3 p.m. in Heidelberg…". The rate of methane emission measured by the above described procedure, varied for different species between $0.2 \cdot 10^{-9}$ and $10 \cdot 10^{-9}$ g of methane per 1 g of dry mass for 1 hour (g/g · h) at 30°C (the emission by undamaged living plants is at least 2 orders of magnitude higher). These results allowed the authors to estimate methane emission by the Earth vegetation from 60 to 240 Mt/year, which is a serious reason to revise not only a concentration–time pattern of methane in atmosphere but plant biochemistry as a whole.

This paper presents first measurements of methane emission by torn off leaves of some greenhouse plants and Siberian stone pine needles obtained by the independent diode laser spectroscopy method.

Laser methanometer and estimate of the methane emission influence on a mixture ratio in a closed volume

The methane emission by torn off leaves was studied through accumulation of methane in an incubation volume (0.005 m^3) and subsequent measuring the methane mixture volume ratio in air with a laser methanometer. The used instrument is the improved gas-analyzer that has been designed in GPI RAS on the base of a near IR diode laser (DL) and a multi-pass analytical cell.[4,5] The block-diagram of the detector is shown in Fig. 1.

0235-6880/06/05 354-05 $02.00

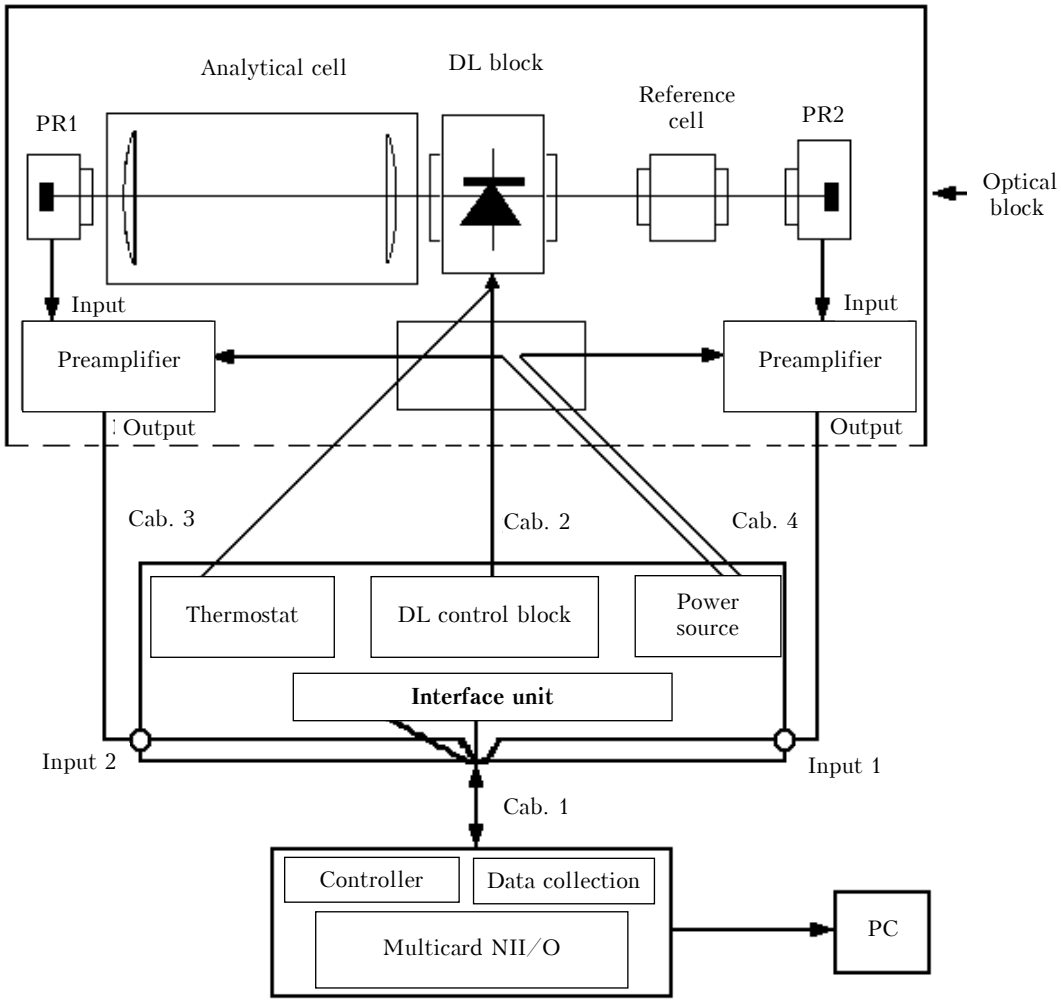

Fig. 1. Block-diagram of the laser detector of methane.

The GaInPAs DL was used as a radiation source. The working temperature was 0 – +50°C. Varying current and temperature, the laser frequency was tuned in the range 6000–6080 cm^{-1} (1.645–1.666 μm), where absorption lines of methane are present. The laser frequency was tuned by varying the temperature of DL, which was mounted on the Peltier element. To measure the temperature, a thermode (termistor), located near the laser, was used in the detector. A long-time stability of the DL temperature was 10^{-2} deg.

The diode laser operates in the pulse-periodic mode with a 4.5-ms period and a 4-ms pulse width. Power current pulses are of trapezium shape, which allows sweeping the DL frequency within approximately 1 cm^{-1} range for one pulse and recording the transmission spectrum of an individual absorption line of the gas under study. The DL radiates in two opposite directions. Its main radiation comes into the multi-pass optical cell having a photoreceiver at its output. The ambient air continuously circulates through the analytical cell.

The oppositely directed laser radiation passed through a reference cell, filled with methane of a definite concentration, to another photoreceiver. The technique for measuring methane concentration was based on calculation of correlation function of signal shapes (absorption spectra of methane–nitrogen mixture and ambient air) in both channels. This allowed a high selectivity of the device to be achieved with respect to other gases.

As a multi-pass analytical cell, the Chernin matrix system was used having a basic length of 0.75 m and an optical path length of 157.5 m. The mirror reflection coefficient was 0.998; the cell volume was 0.014 m^3. Continuous air flowing through the cell was performed with a membrane pump at a rate of 0.0002 m^3/s.

The device was calibrated using the nitrogen–methane mixture at the methane concentration of 2 ppm. Zero signal level was defined by pure nitrogen blowing. The threshold sensitivity (root-mean-square deviation for the measurement time) was 0.016 ppm, the time constant of the entire device (taking into account the pump capacity and the cell volume) was 99 s. Long-term stability specified by zero drift attained a considerable magnitude of about ± 0.5 ppm per 5 h. To exclude the drift, the zero level has been defined and corrected every 4 hours.

The total volume of the gas-analyzer analytical cell and of the incubation chamber containing the torn off leaves made about 0.02 m^3.

The rate of methane emission[3] by torn off leaves varied between $0.2 \cdot 10^{-9}$ and $10 \cdot 10^{-9}$ ($g/g \cdot h$) at a temperature of 303 K. This means that the methane emission by 100 g of green mass for 24 h in a volume of 0.02 m^3 will result in increase of the methane mixture ratio ($T = 293$ K, $P = 1.0135 \cdot 10^5$ Pa) from 0.036 to 1.8 ppm. Such increase can be easily recorded by the laser detector.

Measuring procedure and results

Measuring procedure of methane emission by green mass[3] neglects important from our point of view processes of methane desorption and adsorption by leaves' surface and volume. There exists a continuous exchange between molecules adsorbed by solids and liquids and gas molecules in a closed volume. In a steady state, the number of adsorbed molecules, proportional to the partial gas pressure in a closed volume, is to be equal to the number of surface-desorbing molecules. If the gas partial pressure (methane in our case) is equal to zero, such equilibrium breaks and the number of desorbing molecules increases together with the partial pressure up to a new equilibrium state. Note, that the number of desorbing molecules increases with the temperature rise. In view of the above mentioned, we measured methane emission by plants in the room air.

Fresh green samples (leaves or needles) were placed into a closed volume (0.005 m^3) filled with room air (at a background methane concentration of 1.9 ppm), where they were keeping during the exposure time (10–300 h). In the beginning of measurements, the analytical cell was blown by the pure nitrogen (for zero level definition) and the control air. After that, the incubation chamber was blown by the room air and then again by nitrogen. Variation of methane concentration in the incubation chamber was estimated from the amplitude of the characteristic peak in the time dependence.

First experiments, carried out with Siberian stone pine needles, torn off at a temperature of –40°C, and leaves of an indoor plant *Dieffenbachia,* showed a clearly pronounced decrease of the methane mixture ratio, especially for Siberian stone pine needles (Fig. 2).

All further measurements with different samples and longer exposures also showed the decrease rather than increase of the methane mixture ratio when the room air blowing through the incubation chamber (Fig. 3).

As it follows from the analysis of results, the decrease is caused by distortion of the analytical absorption line shape (Fig. 4).

Such a distortion can be induced by the interference with absorption lines of some gas emitted along with methane. The ethylene (C_2H_4) relates to plant hormones, which is synthesized by plants and regulates their growth, stimulates ripening and aging, participates in plant response to stress factors.[6] When damaging plants, ethylene synthesis and emission by plant leaves occur.

Figure 5 shows the comparative transmission spectra for the cell filled with the methane–air mixture and the measuring one filled with the air–ethylene mixture. Two strong absorption lines of ethylene overlapping with an analytical methane line are observed within the tuning range of the used DL.

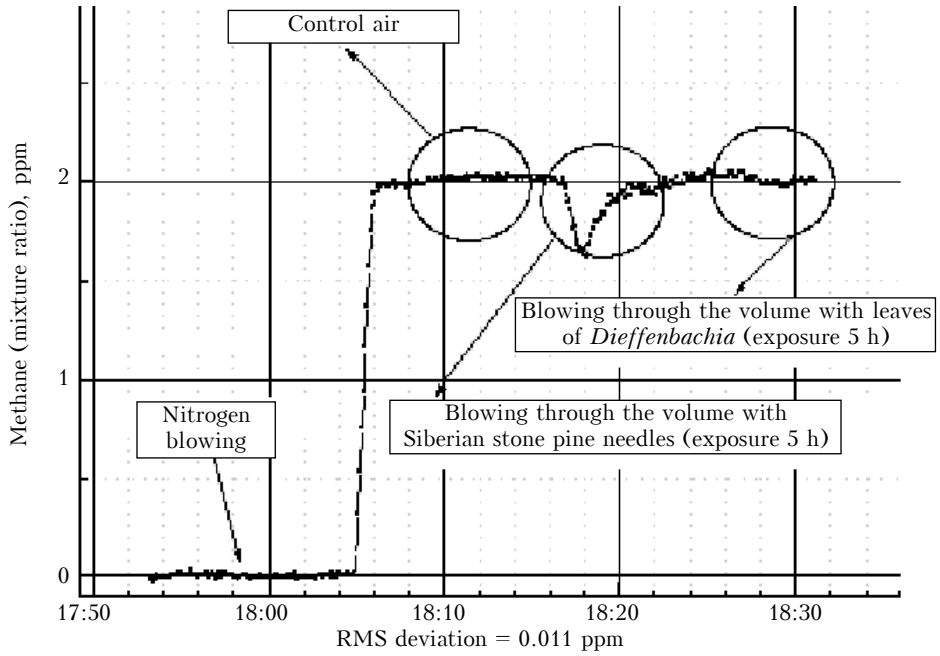

Fig. 2. Methane mixture ratio when room air blowing through a 5-liter volume with a green mass of 85 g.

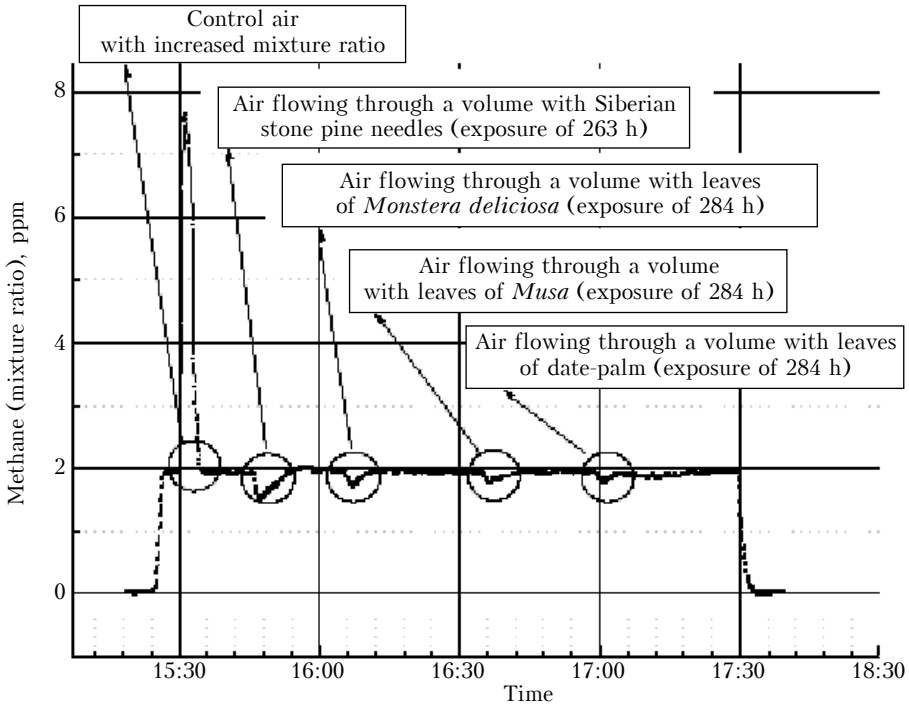

Fig. 3. Methane mixture ratio when room air blowing through a 5-liter volume with green mass of 65–100 g.

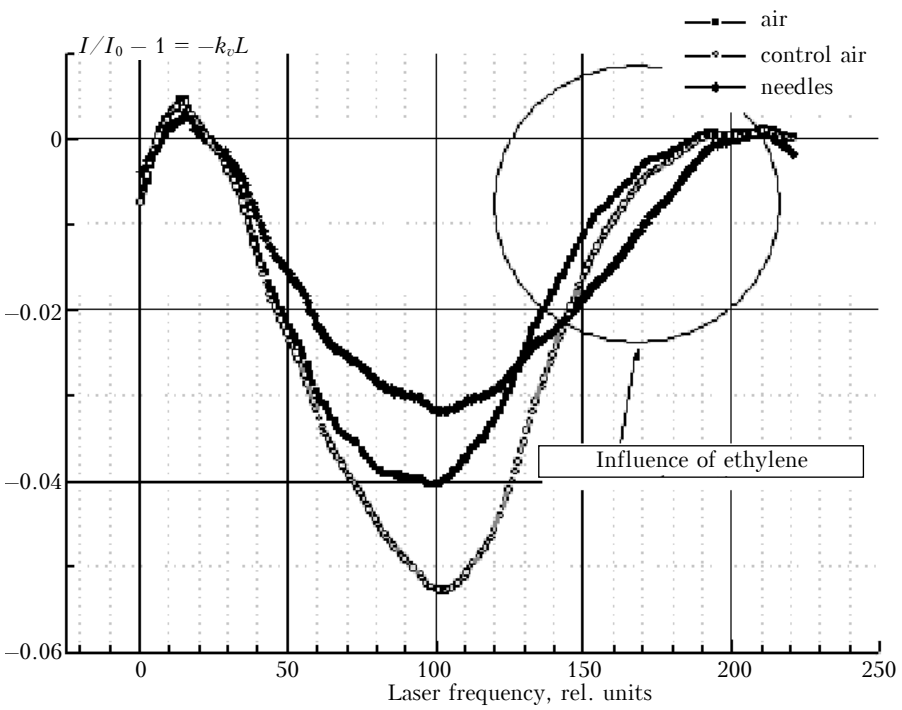

Fig. 4. Distortion of methane analytical line in the presence of ethylene in the analytical cell: I and I_0 are the intensities at the cell output and input; k_v is the index of absorption; L is the path length.

The behavior of the methane spectral line shape when blowing the incubation volume (see Fig. 4) indicates the presence of ethylene in air samples. Today there is no literature data on absorption lines of ethylene in this spectral range, therefore we cannot estimate exactly the concentration of the emitted ethylene; and our results are of a qualitative character.

Thus, we established the fact of ethylene emission by torn off leaves. Hence, to reliably detect the methane emission, it is necessary to account for the

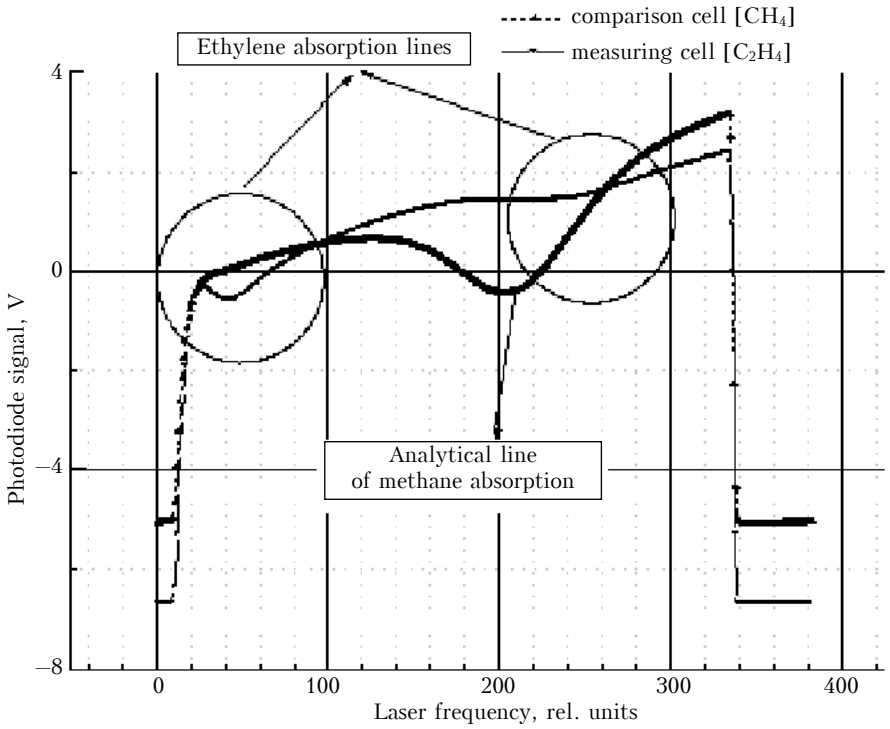

Fig. 5. Ethylene absorption lines within the range of DL tuning.

interference of methane and ethylene spectral lines within the range of DL wavelength tuning (1.65 μm). Nevertheless, we can state that methane emission by torn off leaves and Siberian stone pine needles is insignificant as compared to the data from Ref. 3.

Acknowledgements

The authors are grateful to A.I. Nadezhdinskii, I.S. Tyryshkin, B.G. Ageev, and V.A. Sapozhnikova for their help in the gas analyzer designing and the measurements.

This work is supported by the Russian Foundation for Basic Research (grant No. 373.2003.5).

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