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Comparisons of Different Methods of Ground-Based Spectroscopic Measurements of the Total Methane Content in the Atmosphere

F. V. Kashin*, N. E. Kamenogradskii*, E. I. Grechko, A. V. Dzhola**, A. V. Poberovskii***, and M. V. Makarova*****

** Institute of Experimental Meteorology, pr. Lenina 82, Obninsk, Kaluga oblast, 249020 Russia*

*** Oboukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Pyzhevskii per. 3, Moscow, 109017 Russia*

**** Research Institute of Physics, St. Petersburg State University, Ul'yanovskaya ul. 1, Petrodvorets, 198904 Russia*

e-mail: pober@troll.phys.spbu.ru

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Abstract—Spectroscopic measurements of the total contents (TCs) of a number of important atmospheric gases (methane, CO, water vapor, and others) are regularly taken at the Institute of Atmospheric Physics (IFA), the Institute of Experimental Meteorology, and the Research Institute of Physics. Different systems of monitoring gaseous constituents must be intercalibrated to analyze the measurement data obtained in different regions and to use the network of ground-based measurements as a unified system of validating satellite measurements. Special programs on comparisons of the results of independent measurements of the methane TC were carried out at the IFA Zvenigorod Research Station in different seasons of 1997–1998. The basic results obtained from these programs are analyzed in this paper. It is shown that, for consistent results of total methane measurements to be obtained by different methods, their adaptation to the local conditions of measurements and the use of the unified spectroscopic information are of great importance.

INTRODUCTION

An increase in the content of greenhouse gases (CO_2, H_2O, CH_4, N_2O, and others) results in changes of the radiative properties of the atmosphere and, thus, in changes of the earth's climate. That is why, at present, there are different (first of all, ground- and space-based) systems to monitor gaseous constituents of the atmosphere. In these measurements, remote-sensing methods play a significant role. In particular, in recent years, many satellite experiments have been carried out to obtain a great body of data on variations (including long-term ones) in the total contents of ozone and water vapor and also on the vertical profiles of the content of many minor-gas constituents in the stratosphere. The remote-sensing methods are also widely used in the ground-based monitoring of the composition of the atmosphere. It is sufficient to indicate an extensive network of ground-based ozonometric stations.

In recent years, the importance of ground-based measurement systems has significantly increased because of the need to estimate and validate the results of different satellite measurements. In this case, the problems of unifying measurements and determining a true accuracy of different observation systems are very important. For example, the network of ground-based ozone observations is periodically calibrated against the Dobson gauge.

One of the most popular and widely used ground-based methods of measuring gas content is based on recording the spectra of IR solar radiation absorption. This method was first used by V.I. Dianov-Klokov and his collaborators at the Institute of Atmospheric Physics (IFA), USSR Academy of Sciences, as far back as the 1960s [1, 2]. At present, in Russia, this method is used for regular measurements of the contents of CO_2, H_2O, CH_4, N_2O, and others [3–12].

To compare the results of ground-based measurements of the contents of atmospheric gaseous constituents in different regions, as well as to validate satellite measurements, special measurements are necessary for intercalibration of different methods and instruments [2, 13, 14]. The spectroscopic methods and instruments to measure the total content (TC) of methane throughout the atmosphere were intercalibrated in such a way in September 1997 and in March–April and September–December 1998 at the IFA Zvenigorod Research Station (ZNS) [15, 16]. The Institute of Atmospheric Physics (IFA); the Institute of Experimental Meteorology (IEM); Taifun Research and Production Association; and the Research Institute of Physics (NIIF), St. Petersburg State University, took part in those measurements.

INSTRUMENTATION AND METHODS OF MEASUREMENTS

The measurement instrumentation used at the IFA, IEM, and NIIF include the following basic units: tracking solar systems, monochromators, and receiving–recording systems [11, 13, 14]. Solar spectra are measured within the same methane absorption band in the neighborhood of 3.3 μm. Figures 1a and 1b give the atmospheric transmittances (air mass m = 3) for methane and water vapor (basic absorbing components) within the spectral ranges used at the IFA, IEM (Fig. 1a), and NIIF (Fig. 1b) to determine the methane TC. The IEM range occupies the whole wave number scale in Fig. 1a and includes the IFA measurement range between 2997 and 3002 cm^{-1} (vertical lines in the figure). The NIIF spectral region (Fig. 1b) does not overlap the IFA and IEM spectral region.

The main data on the methods used for measurements are given in Table 1. It is seen that different spectral ranges, different spectroscopic data, and different data characteristics retrieved from the recorded spectra are used to determine the CH_4 TC. As a result, when different measurement methods are used, the total methane content of the atmosphere is determined with a varying accuracy.

The accuracy in determining the methane TC depends on random and systematic errors. The random error is associated with the errors of measurements and spectrogram processing; in particular, a high instrumental accuracy of IEM measurements is due to a high signal-to-noise ratio, a short spectral range recording time, and the computer processing of spectrograms. The systematic error is related to

(1) the accuracy of predetermined spectroscopic data—the intensities and halfwidths of spectral lines of absorption of all the gases in the operating spectral range, the forms of absorption lines, and the pressure and temperature dependences of these parameters (the effect of these factors was analyzed for the NIIF methods, for example, in [10]);

(2) the conformity of the model vertical profiles of methane and other gases (first of all, water vapor), temperature, and pressure to the real vertical profiles;

(3) errors in using the methods of determining the gas TC in the atmosphere.

The main task of intercalibrating the methods and instruments employed to measure the total methane content was determining and eliminating systematic errors.

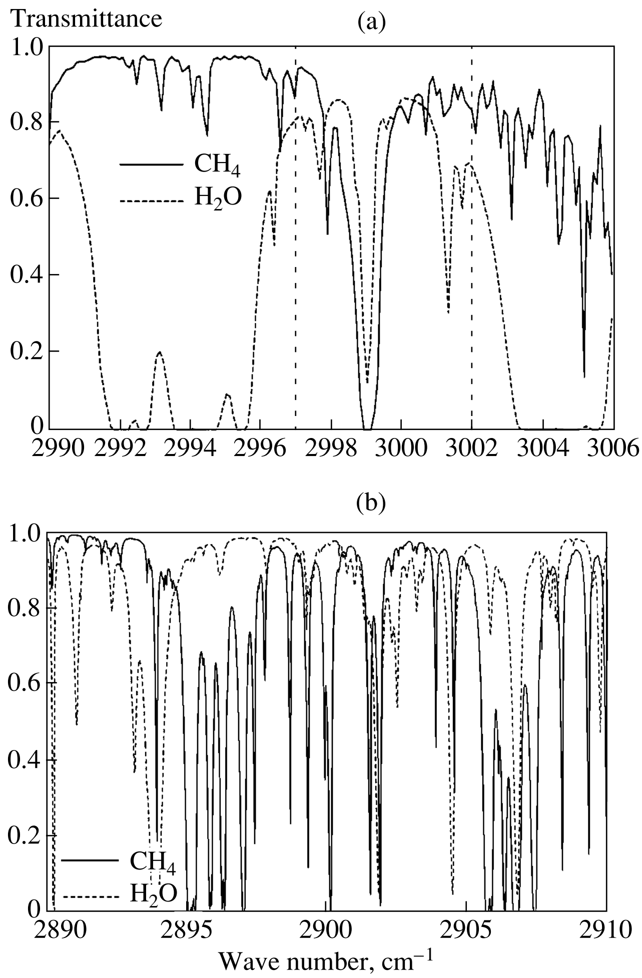

Fig. 1. Atmospheric transmittance within the (a) IFA and IEM and (b) NIIF spectral ranges.

RESULTS OF SIMULTANEOUS MEASUREMENTS

The methane TC was simultaneously measured with three (IFA, IEM, and NIIF) measurement systems at the IFA Zvenigorod Research Station (55.42° N, 36.48° E) in September 1997. Later, in March–April and September–December 1998, the measurements were taken by two (IFA and IEM) systems.

In the first stage, each group independently processed its recorded solar spectra with the use of the initial versions of measurement methods. The results of measurements taken on September 20, 1997, are given as an example in Fig. 2. The data demonstrate both random and systematic errors of different methods of spectroscopic measurements of the methane TC. It is seen that the difference between the NIIF and IFA results is about 15% and is of systematic character. At the same time, a wide scatter (up to 20%) is observed in the IFA data obtained from isolated measurements.

In the next stage of the calibration program, the initial data were refined, and the methods of interpreting the recorded spectra were improved. In the IEM method, the limits of the operating spectral range were changed, and, in accordance with comparisons between the experimental and calculated spectra, some corrections were introduced to the intensities of methane absorption lines from [18], which form the absorption

Table 1. Characteristics of the spectroscopic methods of measurements

Parameter	IFA	IEM	NIIF
Spectral range	2997–3002 cm^{-1}, line $P(2)$, band ν_3	2990–3006 cm^{-1}, line $P(2)$, band ν_3	2890–2910 cm^{-1}, band ν_3
Spectral resolution	0.35 cm^{-1}	0.33 cm^{-1}	0.6 cm^{-1}
Initial spectroscopic information	HITRAN-92 [17]	HITRAN-96 [18]	HITRAN-92 [17]
Atmospheric model	Average model corresponding to measurement conditions	Average model corresponding to measurement conditions	Average model corresponding to measurement conditions
Interpretation procedure	Analysis of integral absorption in the $P(2)$ line on the basis of preliminary calculations of model spectra	Analysis of the atmospheric transmittances in the range (involving the $P(2)$ line) between 2997 and 3000.8 cm^{-1} on the basis of preliminary calculations	Minimization of the rms difference between measured and calculated spectra
Random error in isolated measurements	Less than 10%	Less than 4%	6–8%
Random errors in daily average values	Depending on the number of measurement runs, 5–10%	Depending on the number of measurement runs, 0.2–0.4%	Depending on the number of measurement runs, 2–8%

of radiation in the short-wavelength wing of the P2 line within its basic band ν_3. In the NIIF method, the model surface temperature values used in data processing were replaced by the measured values.

Figure 3 gives the results of reprocessing the spectra obtained on September 20, 1997, with all the refinements made to the measurement methods taken into account. It is seen that the agreement has become better among the data obtained with the aid of the three (IFA, IEM, and NIIF) independent methods: the systematic differences in the values of the methane TC have disappeared. At the mean values of the methane TC between 1.22 and 1.25 atm cm, the maximum scatter of the data obtained with the aid of the three independent methods is 0.15 atm cm (approximately 10%). On this day of observations, the methane TC values were between 1.18 and 1.30 atm cm according to the IFA data, between 1.20 and 1.25 atm cm according to the IEM data, and between 1.18 and 1.27 atm cm according to the NIIF data. The spread observed in the values is due to the corresponding measurement errors (see Table 1).

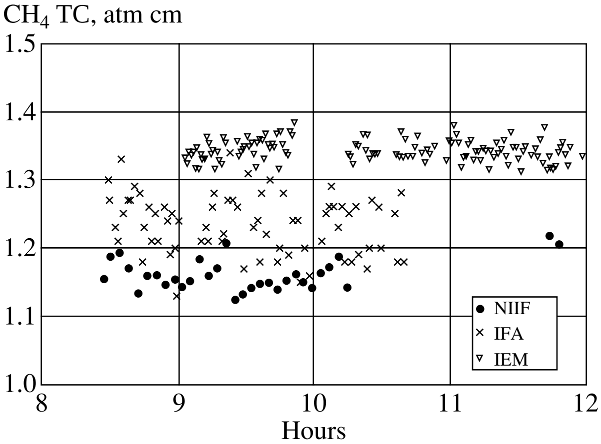

Fig. 2. CH_4 TC for September 20, 1997, before intercalibration.

The daily average methane TCs were obtained from isolated measurements. Errors in determining these values depend on the number of measurement runs during the day (under the assumption that the deviations of the results of isolated measurements from the daily average values are random). The daily average methane TCs obtained independently by the three groups at the ZNS in September 1997 and their errors are given in Table 2 and in Fig. 4. The errors in the daily average methane TCs depend on the errors of the isolated measurements and the number of measurement runs during the day. The minimum errors in the daily average methane TCs (according to the 1997 measurements at the ZNS) were ±0.02 atm cm for the IEM and ±0.01 atm cm for the IFA and NIIF.

It is seen from Table 2 and Fig. 4 that the daily average methane TCs, obtained with all the methodical improvements taken into account, are in good agreement with one another within the total errors for most of the days of joint measurements. The exceptions are September 6 and 18, for which the NIIF and IFA results are out of order, respectively.

Within a period between September 16 and 21, variations in the methane TC within 1.16–1.28 atm cm were recorded independently by the three measurement systems. The amplitude of these variations was 0.12 atm cm (10%).

In March–April and September–December 1998, simultaneous methane TC measurements were taken by the IFA and IEM groups at the ZNS. Table 3 gives the

Table 2. Daily average values of methane content in an atmospheric column (atm cm)

Date	IFA		IEM		NIIF	
	CH_4	N	CH_4	N	CH_4	N
Sept. 06	1.20 ± 0.01	34	1.201 ± 0.003	43	1.31 ± 0.03	9
Sept. 07	1.20 ± 0.02	43	1.212 ± 0.003	60	–	–
Sept. 16	1.24 ± 0.02	13	–	–	1.24 ± 0.02	10
Sept. 17	–	–	1.256 ± 0.004	53	–	–
Sept. 18	1.16 ± 0.04	7	1.242 ± 0.003	43	1.25 ± 0.04	13
Sept. 19	1.29 ± 0.02	33	–	–	1.27 ± 0.01	25
Sept. 20	1.23 ± 0.01	72	1.232 ± 0.003	134	1.22 ± 0.04	31
Sept. 21	1.20 ± 0.02	39	1.226 ± 0.002	184	1.21 ± 0.07	10

CH_4 indicates the daily average methane content of the atmospheric column and the error in the daily average value, and N is the number of spectra per day.

results of the simultaneous measurements of the methane TC for March–April 1998.

During this period, the difference between the IFA and IEM daily average methane TCs is no more than 0.047 atm cm. The differences of the daily average values are opposite in sign, and their absolute values do not exceed the sum of the IFA and IEM measurement errors. In March–April 1998, the daily average methane TCs varied in the range of 1.19 and 1.27 atm cm according to the IFA data and between 1.207 and 1.273 atm cm according to the IEM data. The mean values of the methane content of the atmosphere for this period were 1.24 ± 0.02 atm cm according to the results of both IFA and IEM measurements.

Table 4 gives the data obtained from the IFA and IEM measurements taken in September–December 1998.

According to the IFA and IEM data given in Table 4, in a number of cases, the daily average methane TCs are an agreement within the total errors. However, for some days (September 9 and 13, November 30, and December 1), the discrepancy in the results of independent measurements exceeds the total measurement errors.

The monthly average values were 1.18 (IFA) and 1.195 atm cm (IEM) in September, 1.315 (IFA) and 1.325 atm cm (IEM) in November, and 1.245 (IFA) and 1.270 atm cm (IEM) in December. Due to the small number of measurement days, monthly average methane TCs are given here only to characterize possible systematic differences in the data obtained using two independent methods. In the fall–winter period, these systematic differences between the IFA and IEM data were 3–6%.

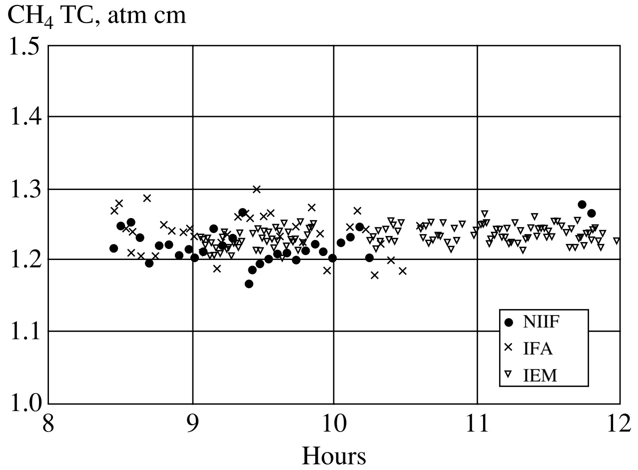

Fig. 3. CH_4 TC for September 20, 1997, after intercalibration.

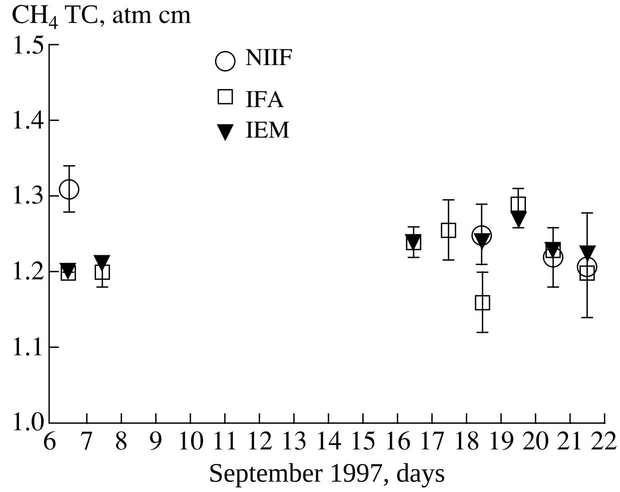

Fig. 4. Daily average methane contents obtained at the IFA Zvenigorod Research Station in September 1997.

Table 3. Daily average values of the total methane content for March–April 1998 (atm cm)

Date	IFA	IEM
March 27	1.27 ± 0.02	1.242 ± 0.004
March 28	1.24 ± 0.02	1.245 ± 0.002
March 29	1.27 ± 0.06	1.244 ± 0.003
March 30	1.24 ± 0.02	1.240 ± 0.002
Apr. 2	1.23 ± 0.04	1.264 ± 0.003
Apr. 3	1.25 ± 0.02	1.273 ± 0.002
Apr. 21	1.22 ± 0.03	1.229 ± 0.002
Apr. 22	1.27 ± 0.02	1.223 ± 0.002
Apr. 26	1.25 ± 0.02	1.230 ± 0.002
Apr. 27	1.23 ± 0.01	1.230 ± 0.002
Apr. 28	1.19 ± 0.02	1.207 ± 0.002

Table 4. Daily average values of the total methane content for September–December 1998 (atm cm)

Date	IFA	IEM
Sept. 9	1.19 ± 0.02	1.225 ± 0.006
Sept. 10	1.15 ± 0.02	1.177 ± 0.005
Sept. 11	1.21 ± 0.03	1.187 ± 0.007
Sept. 13	1.16 ± 0.01	1.212 ± 0.003
Sept. 14	1.19 ± 0.02	1.175 ± 0.004
Nov. 27	1.31 ± 0.02	1.340 ± 0.010
Nov. 30	1.23 ± 0.02	1.290 ± 0.005
Dec. 1	1.19 ± 0.02	1.345 ± 0.006
Dec. 4	1.30 ± 0.01	1.296 ± 0.005

CONCLUSIONS

Changes made in the procedures of interpreting the IR spectra of direct solar radiation allowed us to obtain a good agreement among the data obtained from the methane TC measurements taken independently with the aid of the IFA, IEM, and NIIF instrumentation. In many cases, the results of independent measurements are within the limits of errors of spectroscopic measurements of individual realizations. However, it is necessary to analyze the reasons for the differences (observed in a number of cases) in the daily average methane TCs that exceed the total errors of individual measurements.

The intercalibrated instruments used to take spectroscopic measurements of the methane TC make it possible to record variations in the methane TC from day to day with an amplitude of 10%. In a number of cases, for the daily average methane TCs (and also for the monthly averages), the differences in the results of independent measurements exceed the total errors of individual measurements.

Comparisons made for the results of the ground-based spectroscopic measurements of methane allow us to indicate possible ways of improving the measurement accuracy and data consistency:

(1) to use the results of aerological sounding in interpreting the data on the real thermal structure of the atmosphere;

(2) to use the unified data bases on the fine-structure parameters of the methane absorption band and to take special laboratory measurements of these parameters with improved accuracy;

(3) to use the optimal model vertical profiles of methane;

(4) to take measurements of surface methane concentrations simultaneously with spectroscopic measurements to monitor the presence of local disturbances.

The intercalibration of the methods and instruments employed to determine the methane TC allows one to use them for a long-term monitoring of methane in the atmosphere and also to analyze space and time variations in the gas under study on the basis of joint use of data bases of different institutions.

It should be noted that the implemented programs of joint measurements of solar radiation spectra and data interpretation are also necessary for the intercalibration of the spectroscopic methods used to measure the TCs of other atmospheric constituents. Examples of such investigations are given in [16], where the results of measurements of the water vapor TC are compared. All these measures allow one to obtain consistent results of long-term measurements of the TC of gaseous constituents for different regions of Russia and the CIS and also to develop a unified ground-based monitoring system to validate satellite measurements.

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