Analysis of possible application of the gas light filter correlation method to space measuring of methane content in the atmosphere

S.F. Balandin,[1] S.A. Starnovskii,[1,2] and S.A. Shishigin[1]

[1]*V.E. Zuev Institute of Atmospheric Optics,*
Siberian Branch of Russian Academy of Sciences, Tomsk
[2]*Tomsk State University of Control Systems and Radioelectronics*

Received March 10, 2008

The efficiency of the use of a passive method for correlation of gas light filters for measuring the content of methane in the atmosphere in different spectral intervals is analyzed. The effect of atmospheric gases (H_2O, N_2O) and air temperature on the measuring error is considered. The optimal concentration of methane in a correlation chamber of a space radiometer for measuring the total content of methane in the atmosphere is determined.

Introduction

Accumulation of greenhouse gases CO_2, CH_4, H_2O, N_2O in air, which have absorption bands in infrared wavelength range, leads to the change of radiative properties of the atmosphere. This process initiates melting permafrost that essentially increases emission of methane from marshes of sub-arctic zone and its accumulation in the atmosphere.[1] Therefore, the development of prompt methods for monitoring gas composition of the atmosphere, using space-borne devices, is an urgent problem for atmospheric optics, ecology, climatology.

At present, the methods are developed for determination of vertical profiles of atmospheric gases based on radiation attenuation by atmospheric gases in a range 600–2000 cm^{-1} with a spectral resolution of 0.1–0.5 cm^{-1}, which allows retrieving vertical profiles and total content of different greenhouse gases in the atmospheric column.[2,3]

The sensors of new generation IMG, AIRS, TES, SCIAMACHY, IASI, installed at satellites, were used for practical realization of these methods. The vertical profile of methane was retrieved by a calculation algorithm based on the measured brightness spectra of outgoing thermal radiation of the Earth (IMG, AIRS, TES, IASI) or spectra of solar radiation absorption by the atmosphere in IR range (SCIAMACHY). The most successful among the methane sensors operating on the orbit in 2005–2006 was AIRS (NASA), being a grid spectrometer with 2378 spectral channels in the range 3.7–15.4 μm and a resolution of ~ 0.5 cm^{-1}.

The method of correlation spectroscopy is promising for aerospace monitoring of the atmosphere.[4] A preliminary selection of optimal working wavelength ranges, in which the sensitivity of the device is maximal, is necessary for practical application of this method both to processing the radiation spectra recorded by satellite sensors of high resolution and to development of the necessary spaceborne instrumentation. In this paper we consider the principal parameters of the optical diagram of the correlation radiometer for determination from a satellite of the methane content in the atmosphere.

Method of correlation of gas light filters for vertical atmospheric paths

In the method of correlation of gas light filters, the radiation, received from the volume under study, is divided into two channels: reference and correlation. A chamber with the sought gas is situated in the correlation channel. The content of the sought gas in the volume under study is determined from the ratio of the difference of photodetector signals of each channel to their sum.

According to the model of homogeneous layers of the multi-layer atmosphere, present the total radiance $N(\nu)$ detected by an optical device of nadir type from a satellite as

$$N(\nu) = \varepsilon B_{\mathrm{e}}(\nu,\theta_{\mathrm{e}})\prod_{i=1}^{n} \mathrm{e}^{-\tau_i(\nu)} + \sum_{i=1}^{n} B_{\mathrm{a}_i}(\nu,\theta_{\mathrm{a}}) \times$$

$$\times (1 - \mathrm{e}^{-\tau_i(\nu)}) \prod_{k=i+1}^{n-1} \mathrm{e}^{-\tau_k(\nu)}, \qquad (1)$$

where ε is the relative radiative ability (the degree of blackness) of the Earth surface; $B(\nu, \theta)$ is the radiance of an absolutely black body with the temperature θ at the frequency ν; the index e is related to the Earth, the index a is related to the atmosphere; n is the number of considered successive homogeneous horizontal layers of the atmosphere; $\tau_i(\nu)$, $\tau_k(\nu)$ are the optical thicknesses of ith or kth layer of the atmosphere. The solar radiation is ignored.

0235-6880/08/10 782-05 $02.00

The difference ΔS of signals of the photodetectors in two channels of the device, based on the method of correlation of gas light filters, is[5]:

$$\Delta S = \Omega \int\limits_{\Delta\nu} \left[\eta_c N(\nu) e^{-\tau_c(\nu)} - \eta_r N(\nu) e^{-\tau_r(\nu)} \right] d\nu + J_c, \qquad (2)$$

where η_c and η_r are the transmission coefficients of the optical components in correlation and reference channels, Ω is the angular acceptance, $\tau_c(\nu)$ and $\tau_r(\nu)$ are the optical thicknesses of gases in the correlation and reference channels, respectively, J_c is the term stipulated by radiation, emitted by the gas in the correlation chamber. Let us substitute Eq. (1) into Eq. (2) and, taking into account the channel balance relationship[5] (equalizing the signals of photodetectors in the absence of the measured gas in the volume under study)

$$\eta_c \int\limits_{\Delta\nu} e^{-\tau_c(\nu)} d\nu = \eta_r \int\limits_{\Delta\nu} e^{-\tau_r(\nu)} d\nu$$

we obtain

$$\frac{\Delta S}{\eta_c \Omega} = (\varepsilon B_e - B_{a_1}) \left[\int\limits_{\Delta\nu} T_{a_1} T_c d\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_1} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] +$$

$$+ \sum_{i=1}^{n-1} (B_{a_1} - B_{a_{i+1}}) \left[\int\limits_{\Delta\nu} T_{a_{i+1}} T_c d\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_{i+1}} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] + J_c, \quad (3)$$

where $T_c = e^{-\tau_c(\nu)}$, $T_{a_i} = \prod\limits_{k=i}^{n} e^{-\tau_k}$.

Analogous calculations for the sum of signals of the photodetectors $S_1 + S_2$ allow one to write the calibration function, determined as the ratio of the difference of the detected signals in each channel of the correlation spectrometer to their sum for inhomogeneous atmosphere, in the form

$$\frac{\Delta S}{S_1 + S_2} =$$

$$= \left\{ \left[\int\limits_{\Delta\nu} T_{a_1} T_c d\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_1} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] + \frac{\sum\limits_{i=1}^{n-1} (B_{a_i} - B_{a_{i+1}})}{(\varepsilon B_e - B_{a_1})} \times \right.$$

$$\left. \times \left[\int\limits_{\Delta\nu} T_{a_{i+1}} T_c d\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_{i+1}} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] + J_c \right\} \Bigg/$$

$$\Bigg/ \left\{ \left[\int\limits_{\Delta\nu} T_{a_1} T_c d\nu + \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_1} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] + \frac{\sum\limits_{i=1}^{n-1} (B_{a_i} - B_{a_{i+1}})}{(\varepsilon B_e - B_{a_1})} \times \right.$$

$$\left. \times \left[\int\limits_{\Delta\nu} T_{a_{i+1}} T_c d\nu + \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_{i+1}} d\nu \int\limits_{\Delta\nu} T_c d\nu \right] + \frac{2 B_{a_n} \int\limits_{\Delta\nu} T_c d\nu}{(\varepsilon B_e - B_{a_1})} \right\}. \quad (4)$$

The last terms in the nominator and the denominator refer to thermal radiation of the gas chamber, Earth's surface, as well as the first and the last considered layers; they do not include the information about the sought gas. So, these terms are compensated by means of subtraction from the signal of the gas chamber of some its share, corresponding to magnitudes of these terms, which can be calculated theoretically at the known temperature distribution in the atmosphere and known parameters of the gas chamber. The technique for experimental compensation of the effect of aforementioned terms is considered in Ref. 5; and they are ignored in subsequent calculations.

Let us simplify formulae (3) and (4) for analysis of applicability of the method of correlation of gas light filters to measurement of the methane content in the atmosphere from a satellite.

The atmosphere, in which temperature linearly decreases with height, is called polytrophic. The change of temperature θ with height z in the troposphere satisfies the relationship $\theta = \theta_0 - \gamma z$, which is used for construction of the "standard atmosphere" (γ is const, θ_0 is air temperature near ground surface). The air density ρ, concentration N of well-mixed gases (methane, in particular) in the standard atmosphere change with height by the law $\rho = \rho_0[(\theta_0 - \gamma z)/\theta_0]^{(g/R\gamma)-1}$, where ρ_0 is he air density near the ground surface, g is the gravity acceleration, R is the gas constant.

At small optical thickness of the absorbing gas layer in the volume under study as compared to the optical thickness of the absorbing layer of the gas in the correlation chamber, according to the results of Ref. 6 and our calculations (see Fig. 2), the dependence of the correlation relation

$$\Delta S_{i+1}^{*} = \int\limits_{\Delta\nu} T_{a_{i+1}} T_c d\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_{i+1}} d\nu \int\limits_{\Delta\nu} T_c d\nu$$

on the total methane mass above the layer i in the atmosphere can be considered linear. The contribution of these correlation relationships in Eq. (4) is proportional to the methane mass above each layer. The difference $\Delta\mu$ between the methane content in layers i and $i + 1$, based on the vertical distribution of the gas concentration, can be presented in the form

$$\Delta\mu \approx \mu_0 \left[1 - \frac{\Delta z}{2\theta_0} \left(\frac{g}{R} - \gamma \right) \right],$$

where μ_0 is the methane content in the lower layer of the atmosphere. Relative to the total methane content in the atmosphere M_0, the methane content in the subsequent layers decreases approximately by $e^{-\mu_0/M_0}$ times. The difference of the signals (3) in two channels of the detector can be presented in the form

$$\frac{\Delta S}{\eta_c \Omega (\varepsilon B_e - B_{a_1})} \approx \Delta S_1^{*} \left(1 + \frac{\alpha_{ef}}{1 - e^{-\frac{\mu_0}{M_0}}} \right) + J_c, \qquad (5)$$

where $\alpha_{ef} \approx 0.5–0.7$ is the average value of the ratios $(B_{a_i} - B_{a_{i+1}})/(\varepsilon B_e - B_{a_1})$. The term $\alpha_{ef}/(1 - e^{-\mu_0/M_0}) \approx$ $\approx 1.9–2.7$ (at $\mu_0/M_0 = 0.3$) corresponds to the contribution of thermal radiation of homogeneous atmospheric layers into the difference of informative signals in the inhomogeneous atmosphere. The decrease in the thickness of the homogeneous layers leads to the increase of their number for description of transmission of the atmospheric column, and to increase of the accuracy of calculations. However, the main regularities of the effect of other gases and air temperature on the error in measuring the methane content in the atmosphere are described by similar correlation terms ΔS_1^*.

Taking into account the contribution of the last terms and simplifications for deriving Eq. (5), we represent the values of the instrumentation function describing the calibration curve of the device in the form

$$\frac{\Delta S}{S_1 + S_2} \approx \frac{\left[\int\limits_{\Delta\nu} T_{a_1} T_c \mathrm{d}\nu - \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_1} \mathrm{d}\nu \int\limits_{\Delta\nu} T_c \mathrm{d}\nu\right]}{\left[\int\limits_{\Delta\nu} T_{a_1} T_c \mathrm{d}\nu + \frac{1}{\Delta\nu} \int\limits_{\Delta\nu} T_{a_1} \mathrm{d}\nu \int\limits_{\Delta\nu} T_c \mathrm{d}\nu\right]}. \qquad (6)$$

Analysis of optimal conditions for measuring the methane content in the atmosphere by the correlation method

Thermal radiation of the Earth's surface in methane spectral absorption bands (1.65, 2.5, 3.5 μm) is by two orders of magnitude less than in the range 8 μm, as well it strongly varies depending on the type of the Earth's surface, therefore, methane absorption band of 8 μm is more appropriate for application of the passive method of correlation of gas light filters.

The power density of solar radiation in spectral range 8–8.25 μm beyond the atmosphere is 0.16 W/m^2. In this wavelength range, the characteristics of the Earth thermal radiation are close to that of the absolutely black body.[7] The radiance of the Earth's surface at a temperature of 300 K in the same spectral range is 1.12 W/m^2. The share of the solar radiation, reflected from the Earth's surface and scattered, in the outgoing radiation in the considered wavelength range is small, which does not allow to take it into account in around-the-clock measurements. The attenuation of this radiation by atmospheric hazes is minimal in comparison with the attenuation in other considered wavelength ranges (attenuation coefficient of the haze at a meteorological visibility range of 10 km is equal to several fractions of thousand per kilometer).[8]

Methane (CH_4), water vapor (H_2O), and nitrogen protoxide (N_2O) exert a principal effect on the transmission spectrum of atmospheric gases in wavelength range 8–8.5 μm.[9] Concentration of water vapor in the near-ground layer of the atmosphere can vary depending on the place and time from 0 to 7%. About 55% of the total content of water vapor is in the near-ground layer (0–2 km), 90% in a layer of 0–5 km, and ~10% in the upper troposphere. The content of water vapor in the stratosphere makes tenth or even hundredth fractions of a percent of the total water vapor of the atmosphere.[10]

Methane is well mixed in the troposphere. Its concentration in the Southern Hemisphere is 3% less than in Northern one. Total columnar number of methane molecules M_0 is about $3.6 \cdot 10^{19}$ mol./cm^2. Seasonal variations of the methane content in the atmospheric column above Western Siberia reach 7%.[1]

Nitrogen protoxide N_2O is present in the troposphere and even penetrates to the lower stratosphere.

Calculations of the extinction spectra of atmospheric gases were carried out using the "SPECTRA" system designed at IAO SB RAS. Spectral resolution in the calculations was 0.01 cm^{-1}.

To estimate the error in measurements of the total columnar methane content, the atmospheric model was chosen with separation to the layers: 0–5, 5–10, 10–20, 20–30, and 30–40 km.

Mean values of the temperature, pressure, concentration, and percentage of molecules in the selected atmospheric layers are presented in Table.

Spectral dependence of the molecular transmission coefficients of the vertical path of the total atmospheric column in spectral range 1200–1420 cm^{-1} is shown in Fig. 1.

Analysis of the transmission coefficients of the atmospheric gases has shown that the promising spectral ranges (the presence of strong absorption lines of methane by other gases at a minimal extinction of radiation) for measuring the total columnar methane content by the correlation method are 1220–1260 and 1298–1305 cm^{-1}.

Figure 2 shows the dependence of the correlation ratio ΔS_1^* on the relative content of methane molecules M on the path under investigation (relative to $M_0 = 3.6 \cdot 10^{19}$ methane molecules in the vertical atmospheric column per 1 cm^2) at different methane concentrations (2, 4, 9, 11, 17, 29, 50, 74, 100%) in a 10 cm long correlation chamber (a pressure of 1 atm) in the spectral ranges 1298–1305 cm^{-1} (*a*) and 1220–1260 cm^{-1} (*b*). The method sensitivity is significantly higher in spectral range 1220–1260 cm^{-1} than in the second one. Optimal methane concentrations in the

H_{atm}, km	θ, K	P, atm	$N_{\text{г}}$, 10^{19} cm^{-3}	N_2, %	O_2, %	CH_4, 10^{-3} %	O_3, 10^{-5} %	CO, 10^{-4} %	CO_2, %	N_2O, 10^{-4} %	H_2O, 10^{15} cm^{-3}
0–5	274	0.764	2.02	77.665	21	0.161	0.31	0.26	0.036	0.29	263
5–10	236	0.384	1.18	78.665	21	0.161	0.445	0.08	0.036	0.28	23.6
10–20	220	0.174	0.58	78.958	21	0.15	4.83	0.03	0.034	0.24	0.45
20–30	221	0.033	0.11	78.965	21	0.159	38.64	0.011	0.034	0.2	0.0047
30–40	238	0.0076	0.023	78.963	21	0.14	93.48	0.013	0.035	0.093	0.0013

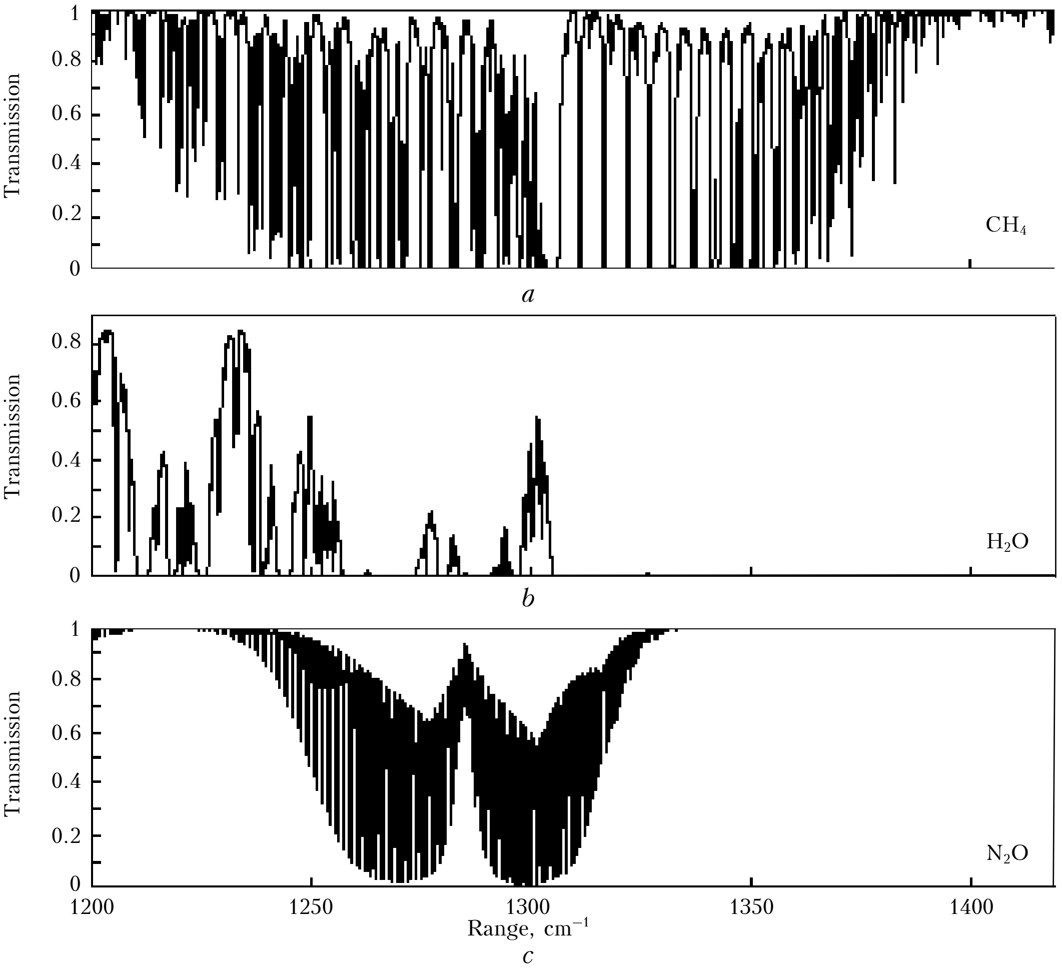

Fig. 1. Spectral dependence of the molecular transmission coefficients of the atmosphere on the vertical path by gases: CH_4 (*a*); H_2O (*b*); N_2O (*c*).

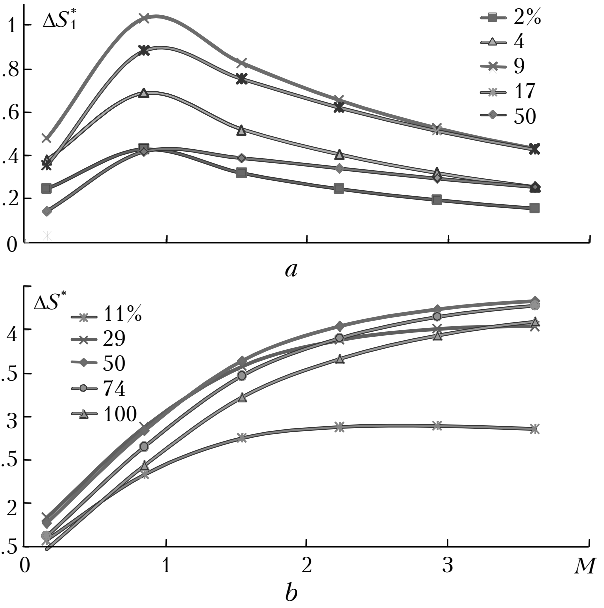

Fig. 2. Dependence of the correlation ratio ΔS_1^* on the relative mass of methane on the path under investigation at different methane concentrations in the 10 cm long correlation chamber in the spectral ranges: 1298–1305 cm^{-1} (*a*); 1220–1260 cm^{-1} (*b*).

correlation chambers in these spectral ranges are ~50% and ~10%, respectively. The correlation ratio ΔS_1^* reaches the maximum in the spectral range 1220–1260 cm^{-1} at a relative mass of the measured gas of ~3, and linear dependence of the correlation ratio on the methane quantity is observed when measuring the methane content in the atmospheric column ($M = 1$).

The correlation ratio in the spectral range 1298–1305 cm^{-1} takes maximal value at atmospheric content of methane in the correlation chamber, which makes it difficult to use the method of correlation spectroscopy in this range for measuring the methane content in the atmosphere from space.

The dependence of the instrumental function (6) in the spectral range 1220–1260 cm^{-1} at optimal methane concentration in the correlation chamber (50%) on the relative mass M of methane in the atmosphere at some variation of the air humidity and temperature is shown in Figs. 3 and 4.

The results of calculations show that the ignoring of the variation of the specific humidity in lower 5-km layer from 1.86 (winter) to 8.06 g/kg (summer) leads to a relative error in measurements of the methane content in the atmosphere of about 10%. The use of seasonal mean statistical profiles of the vertical distribution of air specific humidity[11] with root-mean-square deviations of less than 1 g/kg for cloudless weather enables one to decrease the effect of humidity on the error in methane measurement to 1%.

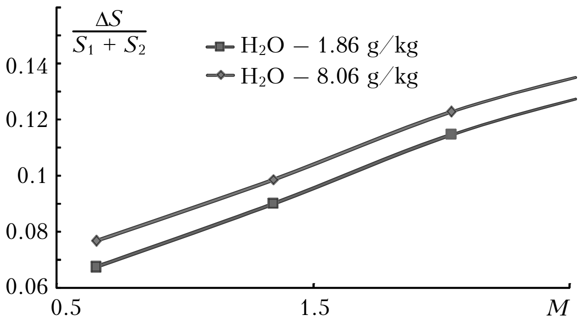

Fig. 3. Dependence of the instrumental function on the methane concentration in the atmosphere in the spectral ranges 1220–1260 cm^{-1} at specific humidity of 1.86 and 8.06 g/kg in a lower 5-km layer.

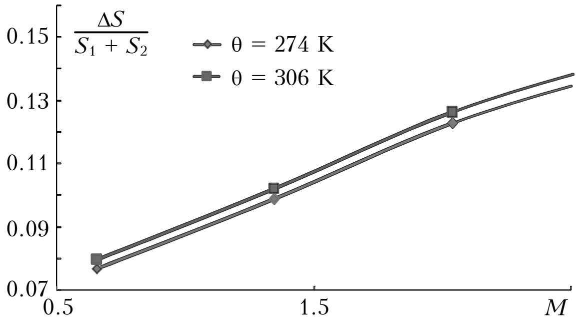

Fig. 4. Dependence of the instrumental function on the methane concentration in the atmosphere in the spectral range 1220–1260 cm^{-1} at air temperatures of 274 and 306 K in a lower 5-km layer.

The change of the mean air temperature in lower 5-km layer by 32 K introduces a 3.5% error into the measurement of methane, this error decreases proportionally to the error in setting the air temperature. The effect of the change of the N_2O concentration in air by 5% introduces less than 0.2% error in measurement of methane content.

Conclusions

As the estimates show, the relative error in measurement of methane in the atmospheric column by spaceborne correlation gas analyzer can reach 2% at the use of seasonal models of the vertical distributions of atmospheric parameters, describing distribution of temperature and specific humidity with errors of 5 K and 1 g/kg, respectively.

The passive method of the remote correlation gas analysis can be used in spectral range 1220–1260 cm^{-1} for prompt measurement of methane, when solving problems of the ecological monitoring.

References

1. K.G. Gribanov, R. Imasu, A.Yu. Toptygin, V. Bleuten, A.V. Naumov, and V.I. Zakharov, Atmos. Oceanic Opt. **20**, No. 10, 805–809 (2007).
2. F.V. Kashin, N.E. Kamenogradskii, E.I. Grechko, A.V. Dzhola, A.V. Poberovskii, and M.V. Makarova, Izv. Ros. Akad. Nauk. Fiz. Atmos. i Okeana **37**, No. 3, 339–345 (2001).
3. S.B. Petrov and A.P. Smirnov, Opticheskii Journal **67**, No. 5, 82–93 (2000).
4. A.A. Buznikov, Opticheskii Journal, No. 8, 6–11 (1992).
5. N.S. Li and N.N. Tsvik, Pribory dlya Eksper. Issled., No. 9, 132–140 (1985).
6. V.B. Dunaev, "*Analytical methods and instruments for correlation spectroscopy*," Preprint No. 614 (Institute of Physic AS BSSR, Minsk, 1990), 33 pp.
7. L.T. Matveev, *Principles of General Meteorology. Atmospheric Physics* (Gidrometeoizdat, Leningrad, 1965), 876 pp.
8. V.E. Zuev, *Propagation of Visible and Infrared Waves in the Atmosphere* (Sov. radio, Moscow, 1970), 496 pp.
9. M.S. Kiseleva, V.A. Kazbanov, I.N. Reshetnikova, G.E. Sinel'nikova, and S.N. Golovanov, Opticheskii Journal **65**, No. 11, 28–33 (1998).
10. Yu.S. Sedunov, S.I. Avdyushin, E.P. Borisenkov, O.A. Volkovitskii, N.N. Petrov, R.G. Reitenbakh, V.I. Smirnov and A.A. Chernikov, *Atmosphere. Handbook* (Gidrometeoizdat, Leningrad, 1991), 509 pp.
11. V.E. Zuev and V.S. Komarov, *Statistical Models of Temperature and Gas Components of the Atmosphere* (Gidrometeoizdat, Leningrad, 1986), 320 pp.