Determining Both Tropospheric and Stratospheric CO₂ Contents Using a Ground-Based IR Spectroscopic Method

Yu. M. Timofeyev^{a, *}, G. M. Nerobelov^a, A. V. Poberovskii^a, and N. N. Filippov^a

^a St. Petersburg State University, St. Petersburg, 199034 Russia *e-mail: y.timofeev@spbu.ru

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Abstract—Results obtained from ground-based high spectral resolution measurements of solar IR radiation absorption spectra are analyzed. These measurements have been carried out in Peterhof for different ranges of electromagnetic waves to determine the atmospheric total content of CO_2 and its contents in the two atmospheric layers—the troposphere and stratosphere. Two spectral schemes to measure solar spectra within ranges of 2600 and 3100-3300 cm⁻¹ are chosen based on an analysis of errors in measurements using different spectral schemes and comparisons with independent measurements and simulation data. Time variations in the tropospheric and stratosphere mostly exceed those in the stratosphere, and such an excess reached 5–10 ppm. The reverse situation is observed in summer and early fall, when the XCO₂ values in the stratosphere exceed those in the troposphere, which is associated with photosynthesis processes (absorption of CO_2 by vegetation in the troposphere). Comparisons of ground-based measurement results with CAMS simulation data and satellite OCO-2 and ACE data show a good agreement for the total content of CO_2 and its tropospheric and stratospheric contents. The errors are within 1% if systematic discrepancies are excluded.

Keywords: climate, greenhouse gases, carbon dioxide, ground-based IR spectroscopic method, satellite observations, validation

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1. INTRODUCTION

The Earth's climate changes—caused, to a great extent, by increased contents of greenhouse gases (first and foremost, carbon dioxide)—have given impetus to the development of a global CO₂ monitoring system [1]. This system includes ground-based local and remote measurements of different types; aircraft and satellite observations; and measurements from masts, boards ships, etc. The TCCON and NDACC international ground-based spectroscopic monitoring systems are of considerable importance in obtaining such information [2, 3].

Most data obtained with these systems are in the form of total contents of gases, often in the form of average mixture ratios for the dry atmosphere (for example, XCO_2). On the other hand, measurements of solar IR radiation spectra with a high spectral resolution involve information on the vertical structure of gas contents. The possibilities to obtain data on the profiles of the O₃, H₂O, CO₂, CH₄, CO, C₂H₄, HCl, HF, and N₂O contents were considered in [4–15]. Estimates of informativeness are, as a rule, obtained from determining the number of independent parameters of vertical profiles (degree of freedom for signal (DOFS)) in measured

solar radiation spectra (2-4 parameters for the above-mentioned gases) [16].

Positive experience in using this information was repeatedly demonstrated for ozone (see, for example, [5, 6]). Such investigations were also repeatedly carried out for CO₂. Thus, some possibilities of solving the inverse problem of CO₂ profile retrieval on the basis of measurements in lines of an absorption band of 1.62 μ m (6220 cm⁻¹) were considered in [12]. A numerical analysis of informativeness showed that ground-based measurements make it possible to obtain \sim 3 independent parameters of the CO₂ profile. Experiments using a closed-loop scheme showed that the proposed measurement range is perspective; however, an analysis of real spectra revealed significant errors in solving the inverse problem and the necessity of improving both direct and inverse problems. Possibilities of using TCCON measurements to obtain data on the vertical CO₂ content profile were also analyzed in [10]. The capabilities of a mobile CHRIS spectrometer with a relatively low spectral resolution (0.135 cm^{-1}) for obtaining data on the vertical CO₂ content structure were considered in [13]. In this case, measurements of solar radiation spectra within a wide spectral range in different CO_2 absorption bands were used. Assuming

Ν	Channels, cm^{-1}	Filter	TGCs considered	TGCs determined
1	950.5–953.8	F1	H ₂ O, O ₃ , N ₂ O	H ₂ O
2	2620.55–2621.1, 2626.4–2626.85 2627.1–2627.6, 2629.275–2629.95	F3	H ₂ O, N ₂ O, CH ₄	H ₂ O, CH ₄
3	3160.14–3160.3, 3161.6–3161.8 3315.5–3316.05, 3316.87–3318.0 3344.68–3344.94	F5	H ₂ O, O ₃ , N ₂ O, CH ₄ , C ₂ H ₂	H ₂ O, O ₃ , C ₂ H ₂
4	4864.55–4865.15, 4882.84–4883.44 4885.14–4885.74	F5	H ₂ O, N ₂ O, CH ₄	H ₂ O
5	3315.50–3316.10, 3344.64–3344.94 4864.55–4865.15, 4882.84–4883.44 4885.14–4885.74	F5	H ₂ O, O ₃ , N ₂ O, CH ₄ , C ₂ H ₂	H ₂ O, O ₃ , C ₂ H ₂
6	4780-4800	F5	H ₂ O, N ₂ O, CH ₄	H ₂ O, CH ₄

Table 1. Spectral windows and filters and the gases considered and determined

that the a priori variability of the CO₂ content at different tropospheric heights amounts to 1.3-8% (~5-32 ppm), the authors of [13] obtained the number of independent parameters for the CO₂ profile within ranges of 2.6-3.5 at a solar zenith angle of 10° and 2.6-3.8 at an angle of 80° for different IR radiation ranges. Moreover, numerical closed-loop experiments made it possible to determine errors in measuring CO₂ profiles: $\sim 2.6\%$ (~ 11 ppm). The informativeness of groundbased measurements of solar radiation spectra in different spectral ranges and the behavior of averaging kernels in the inverse problem of retrieving vertical CO_2 content profiles are analyzed in [15]. It is shown in [15] that the potential informativeness may reach 3–4 independent parameters of the profile, and the potential vertical resolution varies from ~ 5 km in the lower troposphere to 20–25 km in the stratosphere.

The problems of choosing optimal spectral ranges to determine the total content of CO_2 and its profiles were also discussed in reports presented at international conferences [17, 18].

In this work, data obtained from ground-based measurements of solar IR radiation absorption spectra in different spectral ranges, which were performed in Peterhof [19], are analyzed to determine the total contents of CO₂ in the two atmospheric layers—the troposphere and stratosphere. In order to choose the most qualitative measurement data and optimal spectral ranges, at the first stage, total CO₂ contents throughout the whole atmospheric thickness are determined and analyzed. Some examples of retrieving real tropospheric and stratospheric CO₂ contents over the suburbs of St. Petersburg on the basis of spectra measured in 2018–2019 are given in this work. To analyze the accuracy of the new IR method, results obtained with this method are compared with independent satellite (ACE and OCO-2) data and simulation results.

2. RETRIEVING THE TOTAL CONTENT OF CO_2

Errors in determining the total content of carbon dioxide were estimated using the PROFIT software to process real spectral measurements. The measurement period of September 2018 to September 2019 was chosen. Six spectral schemes (see Table 1) were selected for mass data processing based on an analysis of preliminary results [15, 20]. In addition to the first five schemes considered earlier, one more scheme used in the TCCON monitoring system to process and synchronize CO₂ measurement data with those obtained with the NDACC system was added [19]. This scheme includes a wide spectral interval of 4780–4800 cm⁻¹. Note that the width of all the other microwindows in the other schemes is close to ~ 0.6 cm⁻¹. Table 1 gives the trace gas components (TGCs) taken into account in solving the inverse problem and the TGCs specified in analyzing measured spectra during the solution of the inverse problem. The WACCM v.6 model and profiles averaged over the 1980–2020 period were used as a priori information for all considered gases. Daily means of the profiles obtained in analyzing the absorption spectra of water vapor, carbon dioxide, and ozone were used as initial approximations for the corresponding gases. To solve the inverse problem, the Tikhonov–Phillips regularization with a preliminarily determined optimal regularization parameter was used and profile scaling was applied for water vapor and the other gases.

Both systematic and random errors in determining XCO_2 were calculated using the error matrices of the remote method. In this case, errors in specifying zero lines of spectra (0.1% for a shift and 0.02% for a sinusoidal interference), temperature profiles (2–5 K), and spectroscopy (2% for intensities and half-widths of absorption lines of all the considered gases) and



Fig. 1. Annual variations in the XCO_2 daily means (three-point moving average) obtained from ground-based (different schemes of solving the inverse problem) and satellite (OCO-2 in a radius of 300 km from the station) measurement data.

measurement noise from spectral residual were considered as basic sources of errors (for more details, see [20]). Random errors in measuring XCO₂ are equally determined by errors in specifying zero lines of spectra and temperature profiles and by measurement noise. The most significant contribution into a systematic error, which mainly affects the total error, is made by errors in specifying spectroscopic data. Numerical estimates show that random measurement errors amount to 0.5-1% and systematic errors (~3-4%) result from errors in specifying intensities and halfwidths of spectral lines. The above-given figures are typical of all spectral windows used.

Figure 1 shows the retrieved values of the total CO_2 content when the above-indicated spectral windows are used. It follows from Fig. 1 that there is significant (~20 ppm) systematics in the results of retrievals based on different spectral schemes. Thus, for example, schemes 4 and 6, based on measurements within a band of 4800 cm⁻¹, yield the highest XCO₂ values, and schemes 1 and 3, based on measurements within bands of 950 and 3300 cm⁻¹, respectively, yield the lowest XCO_2 values. Schemes 2 (2600 cm⁻¹) and 5 (3300 + 4800 cm⁻¹) yield mean values of XCO₂ when compared to the rest of its values. Such systematic differences may be caused by systematic differences in the parameters of the fine structure of absorption bands in different spectral ranges, by different (weak, medium, and strong) atmospheric CO₂ absorptions (for more details, see [15]), and, as a result, by differences in averaging kernels in different spectral intervals. Noticeable systematic differences in CO_2 contents, when different spectral intervals are used, have been discussed earlier in [17–20].

Note that all the spectral schemes clearly demonstrate seasonal variations in the total CO_2 content. For different schemes, the amplitudes of these variations amount to ~10–15 ppm. Note also that the highest seasonal variability is characteristic of scheme 2 and the lowest seasonal variability is associated with scheme 5.

Figure 1 also gives the XCO_2 values obtained from satellite OCO-2 measurements at distances of no more than 300 km from the St. Petersburg station. Within the indicated period, the OCO-2 measurements were performed in this radius only for 35 days under clearsky conditions, and the number of days with simultaneous satellite and ground-based observations is even smaller. It should only be noted that seasonal variations in satellite measurement data coincide with those in ground-based measurement data. In absolute values, the best agreement is between satellite data and ground-based measurement data obtained using schemes 2 and 3.

Table 2 gives the statistical characteristics of the XCO_2 ensembles: means and their variability and mean random and systematic errors. Schemes 4–6, which use microwindows in a shortwave spectral range of about 4800 cm⁻¹(see Table 1), yield the highest

means of XCO₂, and schemes 1 and 3 yield its lowest means. The variability of XCO₂ is significant for schemes 2 and 3 (7%); its variability for scheme 5 is lower (4.4%). The random errors in measuring XCO₂ are below 1% for all windows except scheme 1. Systematic errors are close to 2%, except those for scheme 1.

Ground-based measurement data on the total content of XCO₂ were compared with Copernicus Atmospheric Monitoring Service (CAMS) data on atmospheric CO₂ concentrations. The GAMS data, versions 18r3 for 2018 and FT19r1 for 2019, were taken from the cell corresponding, to a great extent, to the ground-based measurement area (59.68° N, 30.0° E, St. Petersburg and its surroundings). Data presented in the form of CO₂ concentrations at 39 vertical levels were converted to XCO₂ data for the whole atmospheric column.

Figure 2 shows the comparisons between averagedaily data obtained from the ground-based measurements using schemes 2 and 3 and CAMS data. It is shown that measurement data on the total XCO_2 content and simulation data are, on average, in good agreement; however, the CAMS data are smoother when compared with observational data, which is explained by different spatial resolutions and effects of local sources on the ground-based measurements. The results of an analysis of statistical characteristics of deviations show that the mean values of XCO₂ for the CAMS exceed those measured using schemes 2 and 3 by no more than 1%, and the standard deviations (natural variability of the XCO₂ ensembles) for the groundbased measurement data are twice those for the CAMS data. This is also explained by differences in the horizontal data resolution and by effects of local CO_2 sources on ground-based measurements.

3. DETERMINING THE TROPOSPHERIC AND STRATOSPHERIC CONTENTS OF CO₂

At the next stage, XCO_2 concentrations were retrieved for the two layers—the troposphere (0-12 km)and stratosphere (above 12 km). Methodical considerations of the solution to the inverse problem in analyzing the averaging kernel method showed that it is possible to determine CO₂ concentrations for 3-4 layers 5-10 km thick (troposphere) up to 25-30 km (stratosphere) practically for any spectral scheme. However, the mass interpretation of spectra revealed that the results are complex and there are significant differences in data obtained using different schemes. This is due to the fact that the methodical studies did not take into account some factors and sources of different errors that occur in the concrete real measurements of solar radiation spectra. Such factors and sources are often known not to the fullest extent for real measurements.

Moreover, some parameters of the instruments and measured spectra are determined (specified) in inter-

Table 2. Statistical characteristics of the XCO₂ total content ensembles measured throughout the whole atmospheric thickness: (*x*) mean, (σ) variability, (ε_{random}) mean random error, and (ε_{svst}) mean systematic error

Scheme	$x \pm \sigma$, ppm	$\epsilon_{random}, \%$	$\epsilon_{\rm syst},\%$
1	405.9 ± 5.6	2.16 ± 0.09	3.24 ± 0.17
2	411.3 ± 7.0	0.65 ± 0.09	2.11 ± 0.04
3	407.5 ± 7.0	0.71 ± 0.17	2.12 ± 0.04
4	415.7 ± 5.2	0.74 ± 0.07	2.15 ± 0.03
5	412.9 ± 4.4	0.66 ± 0.05	2.13 ± 0.03
6	414.9 ± 6.4	0.83 ± 0.08	2.23 ± 0.05

preting ground-based measurement data on solar radiation spectra with the aid of the PROFFIT software. This requires a certain volume of information contained in the measured spectra.

Therefore, we restricted our attention to the problems of determining the CO₂ content only in the two layers (the troposphere (0-12 km) and stratosphere) and selecting the most qualitative data with the aid of different criteria. To this end, we used information on the number of DOFS and on the stability of data on the XCO₂ mixing ratio during a day, which were obtained in determining total contents. Low values of DOFS indirectly point to the quality of measured spectra, in particular, the level of measurement noise. One more criterion was the selection of only those days of measurements when the XCO₂ variability did not exceed 1%.

Table 3 shows the statistical characteristics of the XCO₂ ensembles determined for the two atmospheric layers: means, variability, and both random and systematic errors. The errors in determining XCO₂ (as well as the total CO_2 content) in the two layers are maximum for scheme 1, which is caused by a low signal/noise ratio for the receiver used. The systematic error in determining the stratospheric XCO₂ content for this scheme is about 5%, which does not allow one to use this scheme for obtaining high-quality estimates. For scheme 6, the random error in determining the stratospheric XCO_2 content is slightly over 2%. However, in this case, the variability of the XCO₂ values obtained is maximum (about 25%), which makes it necessary to exclude this scheme for determining the stratospheric content of CO₂, because its natural variations are noticeably lower. For schemes 4 and 5, the mean random error in determining the stratospheric content of XCO_2 is below 2%; however, its variability (12-13%) and significant difference from its total and tropospheric contents (by 20-40 ppm) suggest that the errors are underestimated for these schemes. Note also that, in scheme 3, the only one of all the schemes, the mean stratospheric content of CO_2 is lower (by 6 ppm) than its tropospheric content. In scheme 2, the



Fig. 2. Time XCO_2 distribution for the whole atmospheric column according to CAMS data and observational Bruker (a) (scheme 2) and (b) (scheme 3) data for St. Petersburg.

mean XCO_2 value for the stratosphere is higher (by 10 ppm) than that for the troposphere; however, this difference is within the estimated systematic error of the method.

An analysis of total errors in determining XCO_2 in the two atmospheric layers for the period under consid-

eration showed that the errors for both the troposphere and stratosphere are minimum and approximately the same only for scheme 3. Schemes 4, 5, and 6 are characterized by the smallest errors in determining the XCO_2 content for the troposphere and significant errors for the stratosphere in certain periods of the year under

Scheme	Layer	$x \pm \sigma$, ppm	ε _{random} , %	ε _{syst} , %
1	<12 km	404.5 ± 6.6	2.06 ± 0.12	3.35 ± 0.17
1	>12 km	411.9 ± 7.8	4.98 ± 0.28	3.39 ± 0.22
2	<12 km	409.2 ± 9.7	0.85 ± 0.17	2.13 ± 0.68
Z	>12 km	419.0 ± 4.7	0.55 ± 0.06	2.84 ± 0.06
3	<12 km	408.7 ± 9.4	0.94 ± 0.29	2.08 ± 0.04
5	>12 km	402.7 ± 5.7	0.90 ± 0.14	2.89 ± 0.05
1	<12 km	407.7 ± 6.1	0.62 ± 0.20	2.08 ± 0.05
4	>12 km	447.8 ± 12.2	1.85 ± 0.48	3.04 ± 0.62
5	<12 km	409.0 ± 6.2	0.64 ± 0.18	2.08 ± 0.04
5	>12 km	428.2 ± 13.1	1.40 ± 0.49	2.82 ± 0.59
6	<12 km	413.1 ± 9.0	0.82 ± 0.11	2.19 ± 0.07
0	>12 km	421.3 ± 24.7	2.15 ± 0.88	2.87 ± 0.65

Table 3. Statistical characteristics of the XCO₂ ensembles measured in the two atmospheric layers: (*x*) mean, (σ) variability, (ε_{random}) mean random error, and (ε_{syst}) mean systematic error

consideration. Scheme 2 (as well as scheme 3) yields the smallest errors in determining XCO_2 concentrations for the stratosphere and significant errors in determining those for the troposphere.

Thus, schemes 2 and 3 are most appropriate for a detailed analysis of XCO_2 values for the two layers. For these schemes, the random errors in determining XCO_2 are less than one and the systematic errors caused by uncertainties in specifying the parameters of the fine structure of the absorption bands of atmospheric gases are less than 3%. Note that the systematic errors may significantly be minimized if it is possible to perform additional measurements using calibrated instruments.

It should be noted that errors in spectroscopic measurements of the atmospheric gas composition, when direct solar radiation spectra are measured with a high spectral resolution (for example, using Bruker Fourier spectrometers), depend on many factors.

The basic factors that determine the accuracy of the IR ground-based spectroscopic method of determining characteristics of the atmospheric gas content are as follows:

(1) Instrumental characteristics: signal-to-noise ratio and accuracy in specifying the instrument function and spectral referencing, in fitting spectral baseline, in excluding instrumental distortions, in considering the angular aperture of instruments, and in pointing the device at the Sun's disk.

(2) Accuracy in specifying the parameters of the fine structure of molecular absorption (intensity, half-width, and spectral line profile) and their dependence on atmospheric state parameters, in considering the atmospheric continual absorption, aerosol effects, invisible clouds, etc.

(3) Spectral windows used in interpreting measurement data.

(4) The quality of a priori information on the sought solution (initial approximation, solution variability, and atmospheric state parameters).

(5) The regularization method for inverse operators and the choice of regularization parameters.

(6) Accuracy in specifying, excluding, or considering interfering gases (above all, water vapor).

The last factor is, to a great extent, determined by the effects of water-vapor absorption in both individual lines and continual absorption. A comparative analysis of the optical CO_2 and H_2O densities and the optimization of the windows used showed the importance of independent estimates of the atmospheric moisture content during ground-based measurements, which were used in choosing measurement schemes 2 and 3.

4. ANALYSIS OF RESULTS

Figure 3 shows the time variations in the CO_2 content for the two atmospheric layers according to measurements using spectral schemes 2 and 3 with minimum random errors for the stratosphere (below 1%). It is shown that the tropospheric and stratospheric mean XCO_2 mixture ratios are, on average, sufficiently close to each other for the schemes under consideration; however, scheme 2 yields, on average, slightly higher CO_2 values for both the troposphere and stratosphere. These systematic differences are close to 5–10 ppm. The tropospheric values are higher than the stratospheric ones from November to May for scheme 2 and from November to July for scheme 3. This difference is larger for scheme 3 (5–10 ppm) and

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Fig. 3. Time variations in the XCO_2 daily means for the troposphere and stratosphere for two spectral schemes and three-point moving average.

noticeably smaller for scheme 2 (on the order of 5 ppm). Such an excess is caused by anthropogenic emissions from the megacity and reaches ~15 ppm and more in winter. The reverse situation is observed in summer and early fall, when the values of XCO_2 for the stratosphere exceed its values for the troposphere, which is due to photosynthesis processes (absorption of CO_2 by vegeta-

tion). In this case, the excess reaches $\sim 10-20$ ppm. Such an inverse vertical variation in the mean mixture ratio was repeatedly recorded during both aircraft and satellite measurements performed in summer (see, for example, [23-26]). Both schemes clearly demonstrate seasonal variations in the tropospheric content of CO₂—its minimum is observed in summer. Note also



Fig. 4. Time XCO₂ distribution for the whole atmospheric column, troposphere, and stratosphere according to CAMS data and observational Bruker data based on retrieving schemes 2 and 3 for St. Petersburg and its suburbs.

that the stratospheric values of CO_2 for scheme 2 demonstrate seasonal variations, with its maximum in fall. This is also characteristic of satellite measurement results [25, 26].

The retrieved tropospheric and stratospheric contents of CO_2 were compared with its simulation data obtained using the CAMS program (Fig. 4). This comparison shows that the CAMS data on the XCO_2 concentration throughout the whole atmospheric column and in the layer below 12 km are in good agreement with ground-based measurement data. Despite the fact that the time variations in the CAMS data are smoothed, the main trends in the XCO_2 variability recur. The results obtained for a layer of above 12 km using scheme 2 showed the worst agreement. Moreover, sufficiently significant systematic differences are observed in this case. An analysis of the statistical characteristics (Table 4) confirms that the most similar trend in the time variability of XCO₂ is observed for the troposphere and the whole atmospheric column, when the correlation coefficients R are about 0.9 (scheme 2) expected) is observed for the stratosphere (R within a range of 0.1-0.7). The smallest mean deviation (*M*) is observed for the whole atmospheric column (1-3 ppm), while the largest mean deviation reaches 15 ppm for the stratosphere. In most cases, the XCO₂ concentration according to CAMS data is higher than according to ground-based measurement data. On average, the values of S and σ are maximum for the troposphere (about 6-7 ppm for scheme 2 and about 7 ppm for scheme 3). Maximum rms deviation S (16 ppm) is observed in the stratosphere for scheme 3. In the stratosphere, the time XCO₂ variations have a less pronounced seasonal variability, but, for scheme 3, maximum CO₂ concentrations are observed in fall, which corresponds to satellite data. Stratospheric XCO₂ variations are determined by the vertical CO₂ transport from the lower layer. Therefore, the quality of parameterization of the vertical transport in the model used for the CAMS database is important in comparing CAMS results and observational data.

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and 0.7-0.8 (scheme 3). The worst agreement (as was



Fig. 5. Time XCO₂ variations for the stratosphere according to ground-based (scheme 3) and satellite (ACE-FTS in a radius of 400 km from the observation station) measurements.

The vertical profiles of CO_2 have regularly been measured using ACE instruments with the aid of the solar occultation method for over 15 years [25, 26]. These measurements yield information mainly on both stratospheric and mesospheric CO_2 concentrations. Figure 5 gives a comparison between groundbased (scheme 3) and satellite measurements of the stratospheric content of CO_2 , which shows their sufficiently good agreement if errors in both types of measurements are taken into account, as well as their low spatial coherence.

5. BASIC RESULTS AND CONCLUSIONS

Evaluating the vertical structure of the atmospheric content of CO_2 is very important in terms of the exchange of greenhouse gases between the tropo-

sphere, in which the anthropogenic factor determines an increase in its concentration, and the stratosphere. In connection with this, the development of a groundbased IR spectroscopic method of measurements, for example, of both tropospheric and stratospheric CO_2 concentrations, is of both scientific and practical interest, the more so as solar radiation spectra have regularly been measured with a high spectral resolution for a long time at the two NDACC and TCCON international networks with over 50 ground-based observation stations all over the world. In this work, the results obtained from methodical numerical studies and the processing the real ground-based measurement data on solar radiation spectra over the annual period are as follows:

(1) Numerical estimates of errors in determining the total content of CO_2 and its tropospheric and

Table 4. Statistical characteristics of a comparison between the Bruker and CAMS measurement data for three atmospheric layers (in ppm)

Vertical layer	Scheme	М	S	σ	R
The whole atmospheric column	2	0.7	4.1	4.1	0.91 ± 0.12
	3	-2.8	5.8	5.1	0.75 ± 0.24
0 12 km	2	-2.8	6.7	6.1	0.89 ± 0.13
0–12 KIII	3	-3.0	7.4	6.9	0.72 ± 0.25
>12 km	2	15.4	16.0	4.4	0.68 ± 0.21
> 12 KIII	3	-1.4	4.9	4.8	0.13

stratospheric contents have been obtained for different spectral schemes used in ground-based measurements of solar radiation spectra with a Bruker 125HR Fourier spectrometer in the vicinity of St. Petersburg. The random errors in measuring the total content of CO_2 amount to 0.5-1%, and the systematic errors caused mainly by errors in specifying spectroscopic parameters of spectral lines amount to 3-4% for different spectral windows and different measurement periods.

(2) An analysis of errors in determining both the tropospheric and stratospheric CO_2 contents for different spectral measurement schemes and different time periods shows that they vary within a wide range (1–8%). Analyzing calculations of errors in different spectral measurement schemes and comparisons with independent measurements and simulations, we have chosen two spectral schemes for measuring solar spectra in ranges of 2600 cm⁻¹ and 3100–3300 cm⁻¹ to determine the tropospheric and stratospheric contents of CO_2 .

(3) An analysis of measured solar IR radiation spectra using the PROFFIT software with the Tikhonov-Phillips regularization for the chosen optimal spectral schemes has made it possible to study time variations in both tropospheric and stratospheric CO_2 contents over the year under consideration. It is shown that the tropospheric and stratospheric mean XCO_2 mixture ratios for the dry atmosphere are, on average, sufficiently close to each other. During most of the period under consideration, the tropospheric values of XCO₂ exceed its stratospheric values. This excess amounts to 5-10 ppm, which is caused by anthropogenic emissions from the St. Petersburg megacity. The reversed situation is observed in summer and early fall: stratospheric values of XCO₂ exceed its tropospheric values, which is associated with photosynthesis processes (CO₂ absorption by vegetation in the troposphere). In this case, this excess reaches $\sim 10-20$ ppm. The seasonal cycle of the stratospheric content of CO_2 demonstrates its maximum during fall, which is in agreement with satellite measurement data.

(4) Comparisons between ground-based measurement data and CAMS simulation data showed good agreement for the total content of CO_2 and its tropospheric and stratospheric contents (as a rule, within 1%, if systematic discrepancies are excluded). The comparisons with OCO-2 and ACE satellite data also show that there is good agreement between the data obtained with the two types of measurements and that the ground-based IR spectroscopic method holds promise.

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