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Ground-Based Measurements of Total Ozone Content by the Infrared Method

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Abstract—To interpret the ground-based measurements of the spectra of direct solar infrared radiation with the help of a Brucker Fourier-spectrometer, a technique for determining the total ozone content (TOC) was developed and implemented. The TOC was determined using six spectral intervals of an ozone-absorption band of 9.6 μm and the shortwave panel of a carbon-dioxide-absorption band of 15 μm, where the impact of other atmospheric parameters on the measured solar radiation was reduced to a minimum. The potential errors of the infrared method for determining the TOC for the chosen spectral scheme with the influence of measurement errors and vertical profiles of temperature are less than 1% for different signal-to-noise ratios and zenith angles of the sun. We analyzed 269 high-resolution (0.005–0.008 cm^{-1}) spectra of solar infrared radiation measured in Peterhof over 52 days from March to November, 2009. The resulting values of TOC were compared with the results of independent ground-based TOC measurements in Voeikovo (Main Geophysical Observatory) using a Dobson spectrophotometer and an M-124 ozonometer, as well as with the Ozone Monitoring Instrument (OMI) satellite data. The mean errors between the results of TOC measurements with the help of the three ground-based probes constitute no more than 0.4%. The rms errors between data obtained by the Brucker spectrometer and the given satellite and ground-based probes constitute 3–4%. A comparison between different series of measurements indicated that the upper estimate for the error of TOC measurements by the Brucker spectrometer was 2.5–3% (when the possible spatial and temporal errors in measurements are disregarded). An analysis of the diurnal variations in the TOC measurements for stable atmospheric conditions yields an upper estimate of ~3 DU (around 1%) for the random component of error in TOC measurements by the Brucker spectrometer.

Keywords: ozonometry, spectroscopic measurements, remote sensing, atmosphere.

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1. INTRODUCTION

In view of the importance of ozone in the formation of surface UV irradiance and radiative properties of the atmosphere, the ozone content is monitored using different remote (ground-based, satellite, aircraft, and balloon-based) and local methods. The total ozone content (TOC) is the most accessible for measurements and, at the same time, a very informative parameter of the state of the ozone layer. Due to the fact that the state of equipment can be constantly checked and, accordingly, the data quality can be controlled, the results of ground-based TOC measurements become principal also for other types of ozone measurements.

Since the first studies of the atmospheric ozone layer, many different types of equipment have been proposed for measuring the TOC [1]. The highest contribution to the progress of ozonometry was made by Dobson's works [2, 3]. As early as in the 1930s, measurements performed with the help of spectrophotometers designed by him laid the foundations of TOC observations. Until now, these probes have remained the most accurate instruments for TOC measurements. In the early 1960s, observations on the basis of M-83 filter ozonometers had been initiated [4], which were later replaced by the M-124 ozonometers [5]. Since the mid-1970s, Brucker spectrophotometers have appeared [6, 7]. The World Meteorological Organizations (WMO) united most TOC-observation stations into a worldwide ozone network and probes of the abovementioned three types have become its instrumental basis.

The strict requirements for accuracy in TOC measurements (no more than 5–10 DU) formulated by different international groups (see, for example, [8]) have stimulated improvements in measuring equipment and techniques for processing measurement data. A prospective ground-based measurement technique for TOC is based on measurements of solar infrared radiation spectra with a high spectral resolution [9, 10]. For example, the possibilities of TOC measurements with the help of the infrared method with errors of ~1 DU (i.e., with a relative error of ~0.3–0.5%) are discussed in [11]. In this case, however, there are many requirements for the characteristics of the instrument, information used a priori, and methods for interpreting measurement results. It is also significant that this method makes it possible to obtain from ground-based measurements some data on the vertical profiles of the ozone content [12–14].

To implement the ground-based infrared method for determining the vertical profiles of the ozone content in Russia, we present examples of infrared radiation spectra with a high spectral resolution, describe and investigate a simple technique for determining the TOC, demonstrate examples of its use, and analyze the accuracy of the infrared method on the basis of a comparison with data of independent measurements and an analysis of the measurement data proper. The independent measurement data include traditional ground-based measurements using M-124 and Dobson probes in the branch of the Main Geophysical Observatory (in Voeikovo) as well as Ozone Monitoring Instrument (OMI) satellite measurement data.

2. GROUND-BASED INFRARED METHOD FOR THE TOC

The infrared method was implemented and analyzed at St. Petersburg State University on the basis of high-resolution measurements of direct solar infrared radiation with the help of a Brucker Fourier spectrometer (Petrodvorets, 2009). The main specifications of this probe and some examples of its use for determining the total content of different gases can be found in [15–17].

Ground-based infrared measurements of TOC rely on the interpretation of direct solar radiation measurements in different areas and spectral ranges (most often in ozone-absorption bands close to 4.8 and 9.6 μm). For measurements with a high spectral resolution, one can use hundreds of individual spectral lines in these bands as well as additional measurements for taking into account (excluding) the influence of atmospheric temperature and "hindering" gases (first of all, water vapor). In many studies [11–14], the errors of the infrared method was estimated. Depending on the spectral ranges in use, the quality of a priori data, and the specifications of probes, the general errors in the determination of TOC by this method are estimated to be from ~0.3 to 3–4%.

2.1. Ground-Based Spectra of Direct Solar Radiation

The main specifications of the IFS-125 Brucker Fourier spectrometer were considered in detail [15–17]. The measurements under consideration use a F3 filter allocating the spectral range from 650 to 1400 cm^{-1}. Over 52 sunny days from March 9 to November 5, 2009, 267 high-quality spectra have been registered. Let us note that all measurements use an MCT radiation receiver and the angular aperture of the probe was 2.5°. The spectral resolution of measurements in the chosen spectral ensemble was 0.005–0.008 cm^{-1}. In most of the spectra, the interferograms were averaged with respect to 10 scans; however, in some spectra, their number is smaller. The number of spectra reached 10–15 in some days of measurements and 1–2 in other days. The zenith angle of the sun during the measurements changed from 36.5° to 88.9°. Some measurements involve observed semitransparent clouds or mist, which slightly influence on the quality of spectra. There were 113 measurements of spectra in March–April, 115 in June–August, and 39 in September–October, 2009. To apodize the calculated spectra, we used a tool function of the form $\varphi(x) = D\frac{\sin^2(\pi Dx)}{(\pi Dx)^2}$, where $D = 100$ cm (course difference), which makes the calculated and measured spectra well consistent. The typical signal-to-noise ratios in the analyzed spectra constituted 100–150.

2.2. Choice of Optimal Spectral "Windows" of Solar Spectra

The solar radiation passing through the atmosphere $I_{\Delta\nu}\downarrow$, measured at a height level with pressure p_0 in a finite spectral interval $\Delta\nu$ with account for the tool function $\varphi(\nu)$, of the probe, can be expressed as

$$I_{\Delta\nu}\downarrow = \int_{\Delta\nu} \varphi(\nu) S_\nu \exp\left\{-\frac{\sec\theta}{g}\int_0^{p_0}\sum_j k_{\nu,p,j}q_{p,j}\,dp\right\}d\nu. \quad (1)$$

Here, S_ν is the spectrum of solar radiation on the boundary of the atmosphere [18]; $k_{\nu,p,j}$ and $q_{p,j}$ are the coefficients of absorption at all lines and continuums and mixing ratios of different atmospheric absorbing gases, respectively (j is the gas index), at a level with pressure p; θ is the zenith angle of the sun; and g is the gravitational acceleration.

To calculate the solar-radiation spectra, the parameters of the fine structure of the absorption band were taken from the HITRAN-2004 database [19] and the vertical profiles of temperature and content of gas components for summer (AFGL-86 [20, 21]). Although the measurements of solar radiation are performed at lines of ozone absorption, the calculations also include the absorption of other gases: particularly, water vapor (continual and selective) and carbon dioxide.

The optimal spectral ranges of the solar radiation spectra for determining the TOC were chosen with the help of the following criteria:

(1) The maximal sensitivity of measurements of solar spectra to TOC variations.

(2) The minimization of the "hindering factors" (uncertainties in specifying the vertical profiles of temperature and water-vapor content).

(3) The quality of a priori spectroscopic data.

Because one cannot constantly use radiosounding data on vertical profiles of temperature and humidity,

Table 1. Spectral ranges (in cm^{-1}) and number of spectral "points" used in calculating the TOC

Range	773.1–773.4	987.4–987.6	989.8–990.0	993.6–993.8	1002.6–1002.8	1044.0–1044.2
Number of spectral "points"	159	106	107	106	106	106

when choosing spectral ranges for their use to determine the TOC, we choose spectral ranges ("windows") with a minimal impact of uncertainty in these parameters.

Using the channels recommended for the determination of the ozone content in [22] as a first approximation, we took around 20 spectral ranges of a width of 0.2 to 0.4 cm^{-1} in the longwave range and in the center of the ozone-absorption band of 9.6 μm and in the shortwave panel of the carbon-dioxide-absorption band. After this, we calculated and analyzed the variation derivatives with respect to the vertical profile of ozone content, demonstrating the sensitivity of radiation to ozone-content variations in different layers of the atmosphere, as well as the variations of radiation in dependence of variations in the TOC, temperature, and water content. We disregarded the spectral ranges where the radiation is significantly more sensitive to changes in other parameters (except TOC), as well as those ranges where the experimental data are not clearly described by the model (using HITRAN-2004 parameters).

Table 1 presents the chosen spectral ranges with an indication of the number of spectral "points" used in our technique of TOC determination by measurements of solar-radiation spectra with the help of a Brucker spectrometer. The solution to the inverse problem involved a total of 690 spectral indications in solar-radiation spectra. The use of a large number of measurements makes it possible to minimize the effect of random errors in the measurements.

2.3. Technique for Interpreting Ground-Based Measurements

The inverse problem of TOC determination can be formulated as the solution of an equation where the vector **y** of measured radiation depends on the vector **x** of atmospheric parameters to be found:

$$\mathbf{y} = \mathbf{F}(\mathbf{x}_i) + \boldsymbol{\varepsilon}. \tag{2}$$

Here, $\mathbf{F}(\mathbf{x})$ is the nonlinear (in the general case) operator of the direct problem; $\boldsymbol{\varepsilon}$ is the vector of measurement errors caused by noises of different origins and systematic errors. To simplify the solution to the inverse problem, we used a multiplier adjusting the initial profile of the ozone content for obtaining data on TOC. Let us note that these initial profiles were different for different seasons and chosen from multiyear data of observations conducted in Potsdam (Germany) [21], which is located at midlatitudes like St. Petersburg. Because there are systematic errors in the measurements and to compensate the uncertainty stemming from the use of a continual attenuation of solar radiation induced, for example, by aerosols, we use (for the inverse problem) coefficients of the correction function as the linear term

$$I_{\mathrm{corr}} = c_1 \frac{\nu_2 - \nu}{\nu_2 - \nu_1} + c_2 \frac{\nu - \nu_1}{\nu_2 - \nu_1}. \tag{3}$$

Here, c_1 and c_2 are correction coefficients that are constant in a spectral range limited by the wavenumbers ν_1 and ν_2, which are shifts of the radiation rate from its true position at the boundaries of the calculation domain. It should be noted that the coefficients c_1 and c_2 are determined separately for the two ranges: the shortwave panel of the carbon-dioxide-absorption band of 15 μm and the ozone-absorption band of 9.6 μm.

The solution to nonlinear equation (2) can be interpreted as the limit of a sequence of linear problems, each of which is solved by the method of statistical regularization; here, the a priori information about the solution and measurement errors remain unchanged, while the linear approximation to the operator $\mathbf{F}(\mathbf{x})$ is gradually adjusted in the vicinity of the solution. The iteration process for finding the most probable estimate for $\hat{\mathbf{x}}$ is expressed as

$$\begin{aligned}\mathbf{x}_{i+1} &= \mathbf{x}_i + \left(\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_\varepsilon^{-1} \mathbf{K}_i\right)^{-1} \\ &\times \left(\mathbf{K}_i^T \mathbf{S}_\varepsilon^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)] - \mathbf{S}_a^{-1} (\mathbf{x}_i - \mathbf{x}_a)\right),\end{aligned} \tag{4}$$

where $\mathbf{x}_a$ an a priori given vector. The profiles of temperature and humidity are given by their monthly averaged values on the basis of multiyear data obtained from different stations located at midlatitudes.

When the inverse problem is solved using formula (4), the spectral error in the measured and calculated radiation is minimized. This same error is a criterion for the termination of the iteration process of solving the nonlinear inverse problem when the error becomes comparable to the probe noise. As an example illustrating the quality of the solution to the inverse prob-

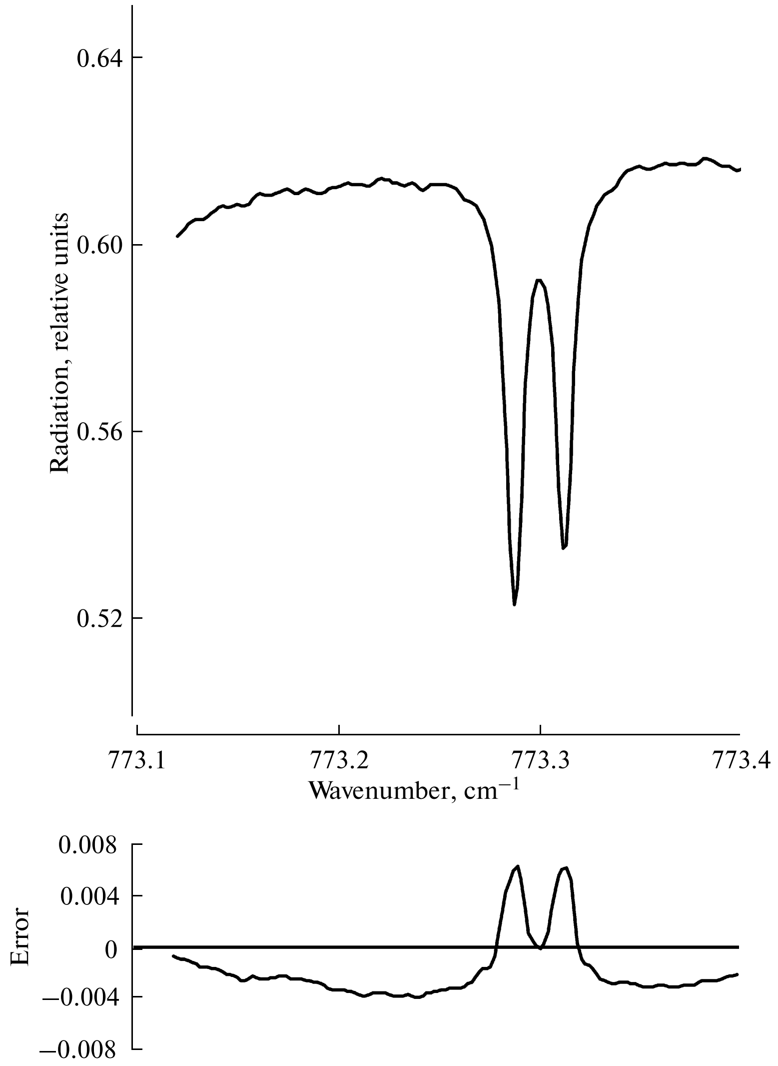

Fig. 1. Spectral range 773.1–773.4 cm^{-1} (top) measured at 12:08 on May 25, 2009, and error in radiation resulting from the solution of the inverse problem.

lem, Fig. 1 shows the measured and calculated spectra (May 22, 2009, measured at 12:08), as well as the error in radiation after solving the inverse problem. The signal-to-noise ratio for this measured spectrum is around 150. It can be seen from Fig. 1 that the error does not exceed the given noise of measurements and the error maximum falls on the line of ozone absorption. The typical form of discrepancy between measured and calculated (obtained from the solution to the inverse problem) spectra may speak about some shift with respect to the wavenumber between the measured and calculated spectra.

2.4. Estimates for Errors of Ground-Based Measurements of TOC

The errors in TOC measurements with the help of the infrared method in use depend on many factors: the specifications of the probe, the choice and number of spectral ranges, the accuracy in specifying the vertical profiles of temperature and content of "hindering gases," etc. In [14], the authors analyzed how the accuracy of calculated TOC in the atmosphere is influenced by factors such as the spectral resolution of a probe, the signal-to-noise ratio, the spectral mechanism of measurements, the availability of data on surface ozone concentrations, and the accuracy in specifying the profiles of temperature and humidity. Because the Brucker spectrometer had not been used for measurements at that time, all the estimates were obtained for an idealized probe with assumed characteristics and solar position at the zenith. At present there is a formidable database of measured spectra with parameters that are currently quite definite (such as the spectral resolution, the signal-to-noise ratio for some zenith angles of the sun, etc.). Therefore, we have continued the investigation into the potential possibilities of the infrared method for TOC under

Table 2. Potential errors in TOC measurements

Range	I Signal/Noise = 150 Solar zenith angle = 55° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 5\%$	II Signal/Noise = 100 Solar zenith angle = 55° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 5\%$	III Signal/Noise = 200 Solar zenith angle = 55° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 5\%$	IV Signal/Noise = 150 Solar zenith angle= 35° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 5\%$	V Signal/Noise = 150 Solar zenith angle = 75° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 5\%$	VI Signal/Noise = 150 Solar zenith angle = 55° $\Delta T = 5°$ $\Delta q_{H_2O} = 5\%$	VII Signal/Noise = 150 Solar zenith angle = 55° $\Delta T = 1.5°$ $\Delta q_{H_2O} = 20\%$
TOC	0.6%	0.8%	0.4%	0.8%	0.2%	0.6%	0.6%

specific characteristics of the probe operating at St. Petersburg State University and for chosen optimal ranges of the solar spectrum.

After choosing the spectral channels, we checked a series of calculations to determine how stable the chosen spectral scheme is and what factors can influence the potential accuracy of the method. The signal-to-noise ratio in measured spectra of the spectral range of interest to us constituted 100–150. This ratio can be slightly improved, for example, through averaging a few spectra measured in a row within approximate air-mass values (schemes II and III in Table 2). Because the measurements were performed throughout a whole clear day and in different seasons, we analyzed the dependences that the accuracy of the TOC calculation has on the solar zenith angle (schemes IV and V) and on errors in specifying the profiles of temperature and water content (schemes VI and VII).

For estimates of the potential error of the infrared method, we took the ozone profile to be 40%. In this case, the a priori variations in TOC constituted 20%. In numerical studies of the potential error of the infrared method, we used calculations of the matrix of errors in the remote method of measurements of **S**:

$$\mathbf{S} = \left(\mathbf{S}_\mathbf{a}^{-1} + \mathbf{K}^\mathbf{T}\mathbf{S}_\varepsilon^{-1}\mathbf{K}\right)^{-1}. \qquad (5)$$

Here, $\mathbf{S_a}$ is the a priori matrix of variations in the aggregate sought vector of the state of the atmosphere (in our case, the ozone content, temperature, water content, etc.), **K** is the matrix of variational derivatives of radiation with respect to atmospheric parameters, $\mathbf{S}_\varepsilon$ is the matrix of uncorrelated errors in measurements of solar radiation, and the subscript **T** means transposition. Let us emphasize that the analysis of the potential accuracy of the infrared method covers not only the errors of measurements, but also possible errors in specifying the profiles of atmospheric temperature and humidity.

Table 2 shows the main results of estimation for the potential errors of the infrared method used at St. Petersburg State University. The second column of Table 2 (scheme I) includes the typical values of the potential error in TOC measurements for some average and/or most probable parameters, such as a signal-to-noise ratio of 150, a solar zenith angle of 55°, an uncertainty in the temperature profile of 1.5 K, and an uncertainty in specifying the profile of the water content of 5, which can be obtained from radiosounding data. It can be seen from this table that the potential accuracy of the TOC calculation is 0.6%. In the third and fourth columns of Table 2, the value of the signal-to-noise ratio is changed to 100 (scheme II) and 200 (scheme III), respectively. Here, the error in the TOC calculation falls by 50% when the signal-to-noise ratio increases from 150 to 200 and it increases by 50% when the ratio decreases to 100.

The fifth and sixth columns of Table 2 show that the potential error in the TOC calculation increases twofold at small solar zenith angles (35°, scheme IV) and, on the contrary, decreases twofold at large zenith angles (75°, scheme V). It can be concluded that the TOC accuracy at a low solar position increases due to an increased optimal depth of the atmosphere. It should be noted that this conclusion ignores such an important source of errors at large zenith angles as the variation in the solar zenith angle during interferogram measurements.

The seventh and eighth columns indicate that the severalfold increase in uncertainty in specifying the profiles of temperature and water content has almost no effect on the estimates for the potential accuracy of TOC, which indicates that the set of channels used by us made it possible to minimize the influence of these "hindering" atmospheric parameters. Thus, there is no need for additional radiosounding data in interpreting the spectral infrared measurements.

It should be emphasized that the TOC errors shown in Table 2 are potentially possible because the numerical estimation ignores a number of key factors influencing the TOC accuracy in interpreting real-measurement data (namely, the errors in specifying the spectral tool function of the probe, the influence of the a priori profile of ozone, the errors in specifying the spectroscopic parameters of spectra lines, etc.).

3. TOC MEASUREMENTS USING OTHER PROBES

3.1. Ground-Based TOC Measurements by a Dobson Spectrophotometer and an M-124 Ozonometer

The ground-based TOC measurements were conducted in the branch of the Main Geophysical Observatory (in Voeikovo) located 50 km from Peterhof with the help of a Dobson spectrophotometer and an M-124 filter ozonometer. The TOC measurements on these probes are based on a differential method that registers UV radiation in the wavelength range from 290 to 350 nm in two or more spectral ranges with a further determination of the ozone content by the logarithm of ratio of measured flows. The Dobson spectrophotometer is a double quartz monochromator taking the following pairs from the incoming radiation spectrum: 305.5/325.4 nm, 311.45/332.4 nm, and 317.6/339.8 nm [2]. The observations are generally performed relative to the direct sun, and the error in a unit measurement of TOC is no more than 2%.

Dobson spectrophotometer no. 108 (Main Geophysical Observatory in Voeikovo) serves as a benchmark probe in the ozonometric network of the Russian Federal Service on Hydrometeorology and Environmental Monitoring and has been checked regularly (once every four years) within the framework of international comparisons with the benchmark probe. In the period from 1984 to 2009, the errors with measurement results from the benchmark probe were no more than 1%. The most recent comparisons were conducted in Spain in September, 2009, and the error constituted 0.2%.

The M-124 filter ozonometers use UV light filters providing two spectral ranges of a width of around 20 nm with maxima at wavelengths of 302 and 326 nm [23]. The multiyear measurements with the help of an M-124 ozonometer indicated that their error of unit measurement of TOC with respect to a direct sun (at zenith angles between 20 and 70°) is no more than 5% and the error in the calculation of the daily averaged TOC value constituted 3%.

The TOC observations were made with the help of M-124 ozonometer no. 403 (the results of these measurements were compared with the results of measurements with the Brucker Fourier spectrometer), which is the operational probe in the Voeikovo ozonometric station: the measurements were daily (eight sessions per day). On clear days, parallel observations with the Dobson spectrophotometer were conducted (the maximum errors for this probe were no more than 10 DU).

3.2. Satellite Measurements of TOC Using an Ozone Monitoring Experiment Probe

The Ozone Monitoring Experiment (OMI) probe continues the series of horizontally scanning satellite spectrometers for nadir measurements of outgoing (reflected and scattered) radiation in different spectral ranges (such as TOMS, GOME, and SCIAMACHY). The OMI probe [24] operates on board of the American AURA satellite, launched in 2004 into near-polar solar-synchronous orbit. The probe measures the spectra of outgoing radiation in the range from 270 to 500 nm with a resolution of ~0.4 nm. The scanning scheme of OMI makes it possible to perform a daily global mapping of the TOC field with a spatial resolution of ~13 × 24 km^2 at the nadir. To extend the series of multiyear measurements with the help of the TOMS satellite equipment (started in 1978), we interpret the OMI measurement data using the TOMS algorithm version 8. This algorithm employs measurement data on outgoing radiation in several spectral channels of the UV range (~310–360 nm) with a resolution of ~1 nm. This technique is based on the regression approach: using a radiation model, the field of outgoing radiation is calculated in advance for different values of ozone content under different observational conditions and different parameters of the atmosphere and underlying surface. Then, based on the measurement results, the TOC value corresponding to this radiation is determined [25]. In addition, to utilize the advantages of multiwave spectral measurements by the OMI, we also use an alternative algorithm for interpreting the measurement results on the basis of the differential optical absorption spectroscopy (DOAS) technique, minimizing the error between the absorption obtained by measurements and calculated using a linear combination of a certain molecular absorption spectra (O_3, NO_2, H_2O, O_4) [26]. In this study we used the OMI data from the main version of processing (OMI–TOMS) with a declared error smaller than 2% [27].

4. COMPARISON OF THE RESULTS OF DIFFERENT TOC MEASUREMENTS

In comparing the TOC values obtained with the help of different methods and probes, we used daily averaged measurement data by a Brucker probe because the TOC data available to comparisons are averaged daily. Figure 2 shows the TOC evolution in time obtained on the basis of measurements with four probes. It can be seen from this figure that the TOC evolution in time according to the data of different probes are very consistent with one another qualitatively and quantitatively. The amplitude of TOC changes by the Brucker spectrometer data are slightly less than by the OMI or N-124 data. This is seen especially well in the early spring period of measurements, when the TOC values are sufficiently large (around 400 DU). In addition, one can see that the Brucker spectrometer data for August 2009 and at small TOC

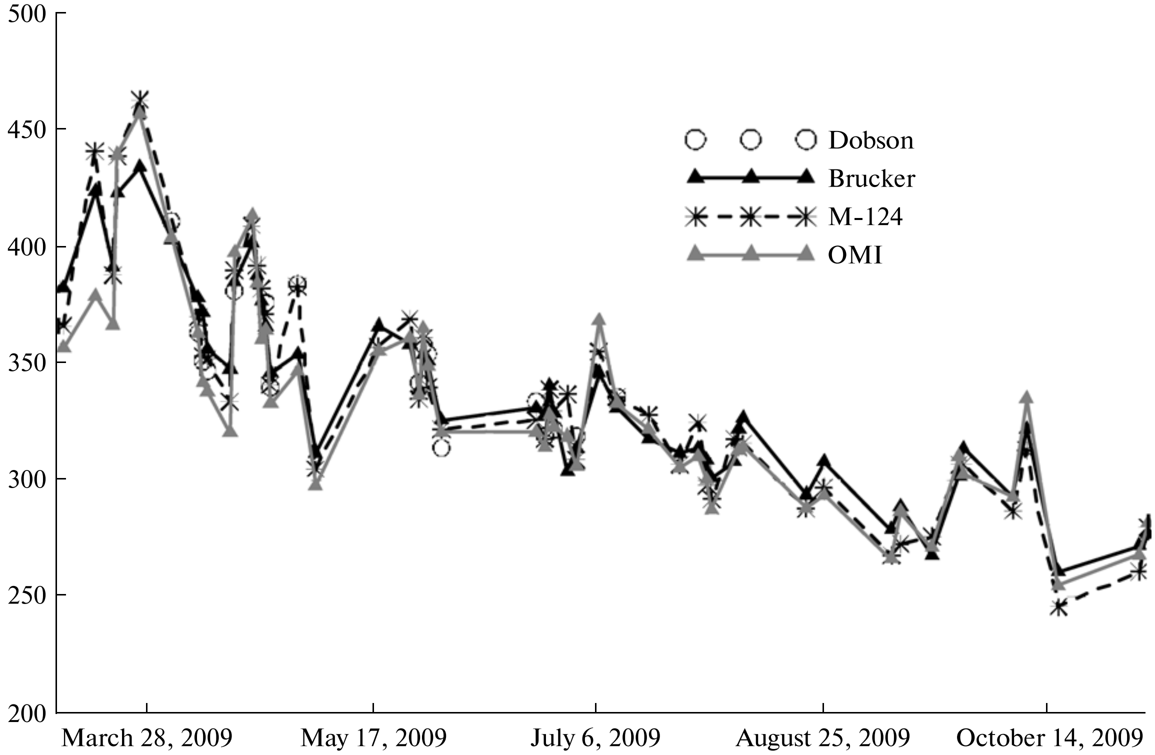

Fig. 2. TOC evolution in time in the St. Petersburg region on the basis of measurement data obtained with the help of different probes.

values (less than 300 DU) are somewhat overestimated in comparison with other probes.

For a more detailed comparison, we analyze the average and rms errors as well as the correlations between data of different probes. Because the data ensembles for OMI and M-124 probes are more representative (52 days), the main focus is placed on the analysis of these ensembles. The TOC-measurement data obtained by the Dobson spectrophotometer are available only for 17 days. The relatively small ensemble may yield statistically unreliable data on the discrepancy between compared data.

Table 3 shows the statistical characteristics of a pairwise comparison between the results of TOC measurements by Brucker, Dobson, M-124, and OMI probes. The average and rms errors, as well as the coefficients of correlation between measurements by different probes, are presented. The correlation coefficients are close to unity with a maximum value of 0.97 for the Brucker–M-124 pair. The correlation between measurement data obtained by the Dobson spectrophotometer and other probes is slightly worse, which may be caused by the small amount of measurement data provided by the Dobson spectrophotometer.

When analyzing the errors between the results of measurements conducted with the help of different probes, one may notice that the average error (the third column in Table 3) between Peterhof (Brucker) and Voeikovo (Dobson, M-124) constitutes less than a percent. At the same time, the average error of measurement data from the OMI satellite data is 1–2% and OMI yields, on the average, lower values of TOC.

Analyzing the rms error, it can be seen that its maximum (4%) is observed between the ground-based measurements by the Brucker spectrometer and the results of OMI satellite measurements. The RMS between TOC measurements with the help of OMI and M-124 probes is also close to 4%.

The rms errors between the Peterhof and Voeikovo measurements is 3–3.5%. These errors can be explained by both the errors of measurements themselves and the spatial and temporal variations of ozone. Turning to Fig. 2, which shows the time evolution of TOC in St. Petersburg, we can see that, in some periods (April–July, 2009), the results of measurements in Peterhof and Voeikovo are very consistent, while the errors are considerable in other days (March and August, 2009). In this case, for higher TOC values (March), the Brucker spectrometer yields lesser values than M-124. This testifies that our infrared method of TOC measurements may reduce the TOC variations observed in the atmosphere.

In addition to the correlations shown in Table 3, Fig. 3 demonstrates the rate of consistency between the measurement results depending on the TOC value. The average TOC value over all ensembles is around 330 DU; the rms value is around 45 DU (around 15%). It can be seen from Fig. 3 that the M-124 and

Table 3. Comparison of TOC measurement data obtained with the help of different probes

Probes compared	Number of comparisons	Mean error	RMS	Coefficient of correlation
Brucker–Dobson	17	0.7 DU (0.3%)	11.4 DU (3.2%)	0.90
Brucker–OMI	51	5.3 DU (1.7%)	14.2 DU (4.1%)	0.95
Brucker–M-124	51	0.6 DU (0.4%)	11.7 DU (3.4%)	0.97
M-124–Dobson	16	−0.2 DU (−0.06%)	6.8 DU (2.0%)	0.96
M-124 OMI	50	4.6 DU (1.3%)	13.5 DU (3.8%)	0.96
OMI–Dobson	17	−5.5 DU (−1.7%)	12.2 DU (3.5%)	0.91

Dobson spectrophotometer data are very linear (this is also because there is no shifts between these data); at the same time, the comparison between OMI and Brucker spectrometer data reveals that the TOC values for OMI are slightly higher. This is more apparent for TOC values of around 340–400 DU (i.e., above average).

5. ANALYSIS OF COMPARISON RESULTS

There are a number of studies comparing the results of TOC measurements obtained by the infrared method with those obtained by ground-based (Dobson spectrophotometer and Brucker spectrometer) and satellite measurements. This is explained by the difference in the spectral intervals, the number of spectral points, the interpretation techniques, and the characteristics of Fourier spectrometers. For example, some European stations of the Network for the Detection of Atmospheric Composition Change (NDACC) use a single spectral range (1000–1005 cm^{-1}), while other stations use additional ranges. These data are processed using the PROFFIT9 [11] and SFIT2 [12] programs.

In [28], the TOC was determined using two spectral windows near 782.5 and 789 cm^{-1}. It was shown that the average error between the results of measurements by network Brewer probes and the Brucker probe is 1.9%, which considerably exceeds the average errors between the measurements of our infrared method and M-124. In this case, the standard deviations reached ~2.2% and the rms error was ~4%. The same study also noticed that the infrared measurements reduce the TOC variations, which leads, in particular, to increased small values of TOC in summer according to the Brucker probe data. With similar comparisons, the authors of [29] derived the values of systematic errors in ~4–5% between the results of UV and IR measurements. The rms close to these values can be found in [30] for comparisons between infrared measurements with an averaged spectral resolution and OMI satellite data.

An analysis of the quality of OMI satellite measurements of TOC in comparison with measurement data obtained at five Spanish ozonometric stations indicated that the average values of errors between satellite and ground-based measurements are in the range of −1.5 to −2.5% and the standard deviations constitute 1.5–2.3% [31]. The total rms in these comparisons were 4–5%.

A massive comparison of the data of different satellite measurements with ground-based TOC measurement data by the world ozonometric network can be found in [32]. The average differences and standard deviations between the results of satellite measurement data and measurements data obtained from M-124 filter ozonometers reach 3–4% and 4.5–6%, respectively. The results of a comparison of ground-based infrared measurements of TOC at six European

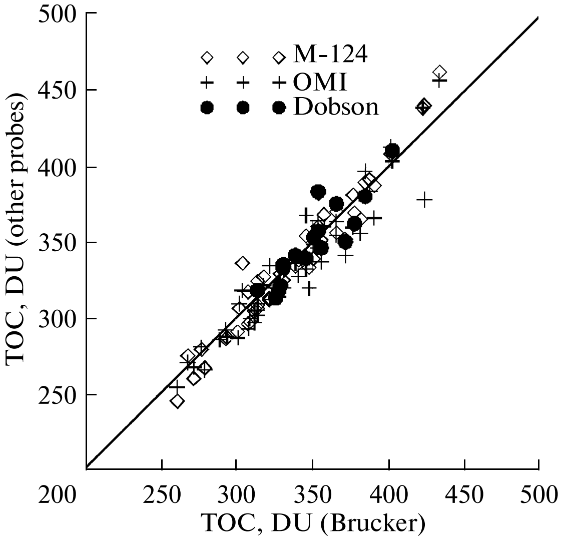

Fig. 3. Comparison between the results of TOC measurements obtained by the Brucker spectrometer and other probes.

stations with other ground-based measurement data (obtained with the help of Dobson, Brewer, and UV-visible spectral range spectrometers) can be found in [33]. An analysis of these results of the comparison between infrared measurements of TOC and measurement data obtained by the Dobson and Brewer spectrophotometers indicated that the average errors from infrared measurement data were in the range from 0.4 to 8.6% (all infrared measurements overestimate the TOC values) and the rms errors were in the range from 3.1 to 6.9%.

Assuming that the dispersions of errors between the results of a measurement series conducted by different probes is the sum of dispersions of measurement errors of different errors and dispersions of errors due to the spatial and temporal discrepancy between measurements, one can formulate a system of equations for these unknown parameters consisting of equations of the form $\sigma_{ij}^2 = \sigma_i^2 + \sigma_j^2 + \sigma_r^2$, where σ_r^2 is the dispersion due to the spatial and temporal differences in measurements, σ_{ij}^2 is the total dispersion of discrepancies between the results of measurement series by two probes, and σ_i^2 and σ_j^2 are the dispersions of measurement errors of probes. Due to the current lack of adequate data on the value of discrepancies in the TOC values conditioned by spatial and temporal variations in TOC, we assumed for the analysis of the errors in different probes that there were no spatial discrepancies (the temporal discrepancies were disregarded because in all cases we consider the daily averaged values). In this case, for the three (OMI, M-124, and Brucker) probes, we obtain a system of three equations of the form $\sigma_{ij}^2 = \sigma_i^2 + \sigma_j^2$. We restricted ourselves by these three probes, because there is a rather large uniform sample of 52 measurements. Substituting the data presented in Table 3 as the total error, we obtain upper estimates for the measurement errors of probes: 2–2.5% for M-124, 2.5–3% for the Brucker spectrometer, and 3–3.5% for the OMI satellite probe (these error ranges are associated with the absolute values of TOC).

Another estimate for random errors of single measurements of TOC on a Brucker Fourier-spectrometer can be obtained by the data of serial TOC measurements at stable atmospheric conditions. Indeed, the maximal variations in measured TOC values in June 22 and August 25, 2009 constituted 8–9 DU. Based on this, the random errors of the infrared method for calculating the TOC (implemented at St. Petersburg State University) can be estimated as ~3 DU.

6. MAIN RESULTS AND CONCLUSIONS

To interpret the ground-based measurements of the spectra of direct solar infrared radiation with the help of a Brucker Fourier spectrometer, a technique for determining the TOC was developed and implemented.

(1) Based on an analysis of numerical calculations of variations in solar radiation spectra, which are conditioned by variations in different atmospheric parameters, we selected six spectral intervals in the longwave range and in the center of the ozone-absorption band of 9.6 μm and in the shortwave panel of the carbon-dioxide-absorption band of 15 μm (a total of around 700 spectral indications), which are optimal for TOC calculations and with a minimized influence of other atmospheric parameters on registered values of solar radiation.

(2) The potential errors of the infrared method for determining the TOC for the chosen spectral scheme with the influence of measurement errors and vertical profiles of temperature are less than 1% for different signal-to-noise ratios, zenith angles of the sun, and uncertainties in specifying the "hindering" atmospheric parameters.

(3) We developed and implemented a simple technique for solving the inverse problem of TOC calculation with a scaling of the a priori (initial) profile of ozone content and derivation of two coefficients of the linear correction function accounting for the nonselective attenuation of solar radiation and unknown normalization of solar spectra. Using this technique, we analyzed 269 high-resolution (0.005–0.008 cm^{-1}) spectra of solar infrared radiation which were measured in Peterhof over a period of 52 days from March to November 2009.

(4) The TOC values obtained of the infrared method were compared with the results of independent ground-based TOC measurements in Voeikovo (Main Geophysical Observatory) using a Dobson spectrophotometer and an M-124 ozonometer, as well as with the OMI satellite data. It was revealed that the mean errors between the results of TOC measurements with the help of the three ground-based probes are very small and constitute no more than 0.4%. The rms errors between data obtained by the Brucker spectrometer and the results of measurements obtained by other probes constitute 3–4%.

(5) A comparison between different series of measurements indicated that the upper estimate for the error of TOC measurements by the Brucker spectrometer was 2.5–3% (when the possible spatial and temporal errors in measurements are disregarded). An analysis of the diurnal variations in the TOC measurements for stable atmospheric conditions yields an upper estimate of ~3 DU for the random component of the error in TOC measurements by the Brucker spectrometer. A comparison between these and earlier obtained estimates indicates that the measurements of the spectra of direct solar infrared radiation and their interpretation technique used at St. Petersburg State University are of high quality.

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