Observations of the ozone and nitrogen dioxide profiles in train expeditions Moscow-Khabarovsk-Moscow

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Abstract – For investigation of the vast area of Russia a mobile scientific facility based in a railway carriage was developed. It was equipped with spectrometers for remote sensing of ozone and nitrogen dioxide in the atmosphere for expeditions along a way from Moscow to Khabarovsk and back performed from February 18 to March 5, 1998 and from March 19 to April 1, 2004. A novel DOAS-type retrieval algorithm, which is applicable to UV observations with strong absorption (by ozone), was developed. It completely takes into account multiple scattering of sunlight. The linearized radiative transfer model MCC++ was used in radiance calculations. Unlike the NO2 retrieval, account of multiple scattering and albedo is significant for ozone retrieval. A modification of the twilight DOAS method used at the NDSC was applied for retrieval of nitrogen dioxide profiles basing on spectral measurements at visible wavelengths.

Keywords: Ozone, Nitrogen dioxide, Vertical distribution, DOAS technique, Air mass factors, Radiative transfer model, Retrieval algorithms.

1. INTRODUCTION

The vast area of Russia plays an important role in the global climate system and requires the intensive study. Because of insufficient overlapping of the area by observational stations, development of a mobile scientific facility is a convenient way for intensification of its systematic investigation. A mobile railway carriage has been equipped for atmosphere researches and is capable to perform continues measurements being coupled in a passenger train traveling along railroads. It has carried out eight expeditions into Russia on Transcontinental Observations Into the Chemistry of the Atmosphere (TROICA) since 1995. The expeditions have been performed in the zonal (between Moscow, 55.8N, 36.8E, and Khabarovsk, 48.5N 135.1E) and meridian (between Murmansk, 68.9N, 33.1E, and Kislovodsk, 43.7N, 42.7E) directions. Measurements of the surface properties of gases and aerosols, and other atmospheric and some supplementary characteristics were carried out continuously or episodically during the expeditions.

During the TROICA-4 expedition (February 18 -March 5 1998) the mobile carriage-laboratory was firstly equipped with a spectrometer for remote sensing of trace gases in the low and middle atmosphere. The main goals of the remote sensing instrumentation of the TROICA mobile laboratory are:

- measurements of the vertical distributions and the total contents of atmospheric compositions along the railway network in vast area of Russia, overlapping of which by stationer network of stations is insufficient;

- validation of satellite measurements by TOMS, GOME, OMI, SAGE III, SCIAMACHY et al. at extended areas;

- regular calibration of scattered over Russia network instruments using one mobile set of certified instruments.

The first TROICA expedition with remote sensing instrumentation was aimed to test different methodological approaches, nevertheless it already provides information on the O3 and NO2 distribution in the atmosphere. DOAS-like retrieval techniques (Platt 1994) employing zenith scattered sunlight spectrums were used for retrieval of gas concentrations. But the O3 retrieval has required modification of the DOAS approach, while the NO2 retrieval uses the classical DOAS retrieval technique. The point is that the NO2 retrieval uses the visible measurements with weak absorbers, what is significantly differ from UV measurements: the strongly changing O3 absorbtion causes significant changes of the layer air mass factors (Postylyakov, 2004a) within used UV spectrum. The paper describes shortly methodology used for remote sensing in the TROICA-4 expedition, presents the first results of retrieval of the O3 and NO2 contents in the atmosphere obtained during the expedition.

2. INSTRUMENT AND OBSERVED QUANTITIES

The carriage-laboratory used during the scientific expeditions TROICA-4 was equipped with a spectrometer based on the LOMO MDR-23 monochromator. The MDR-23 instrument is the grating type of the monochromator. A system of mirrors illuminated the entrance slit of the monochromator using a carriage window. It formed field of viewer about 10^{O} in the zenith direction. The slits provided a resolution of 1 nm (FWHM). We entered an additional glass filter FS-3 to form spectral sensitivity of the instrument for UV observations. The instrument hasn't absolute calibration. The rotation of the grating scanned wavelength.

The TROICA-4 spectrometer was verified during an international NO_2 comparison campaign held at Zvenigorod Scientific Station in September 1997 under the aegis of the NDSC. After the expedition it was compared again with the

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** The work was partially supported by the Russian Foundation of Basic Researches by grant 05-05-65139.

reference instrument of the Russian NO_2 network mounted stationary at Zvenigorod for regular NO2 observations (Elokhov and Gruzdev, 2000).

The photomultiplier current for scans from 302 to 335 nm and from 434 to 451 nm was recorded during the TROICA-4 expedition. Each scan in UV or visible takes about 20 s. Measurements were carried out aboard the moving and standing train. For the solar zenith angles (SZA) less than 75^O, the measurements were performed each first 15 minutes of an hour only in UV region. The UV measurements became continues for 75^O<SZA<=84^O. The UV and visible measurements were alternated for 84^O<SZA<=90^O. Only visible measurements were performed for 90^O<SZA<=96^O.

3. RETRIEVAL METHODS

3.1. Retrieval of the nitrogen dioxide profiles

The NO_2 contents were determined from spectrometric measurements of the solar radiation scattered in the zenith taken at twilight in mornings and evenings at SZA 84°-96°.

The measured spectra are analyzed using the DOAS method (Elokhov and Gruzdev, 1995, 2000, McKenzie et al., 1991). The slant column NO_2 content is determined by the nonlinear least-square method from the spectrum deformation caused by the O_3 and NO_2 absorption, single molecular and aerosol scattering, the Ring effect, the wavelength shift and stretch relative to the reference spectrum. The reference spectrum has been obtained for the used instrument from high-sun measurements at the Zvenigorod Station under stable conditions of clear-sky atmosphere at low NO_2 abundance. Precision of the NO2 slant column measurements is better than 1%.

For determination of the vertical NO_2 distribution, an atmosphere was divided into 11 layers: the surface layer 0-0.2 km, 0.2-5 km and 8 layers with 5-km thick up to 50 km. The NO_2 vertical distribution is determined as a solution of the inverse mathematical problem using the Chahine inversion algorithm (Elokhov and Gruzdev, 2000). The layer air mass factors were calculated using a spherical single-scattering radiative model and a one-dimensional photochemical model. Twilight NO_2 measurements take significant time (up to an hour or more in winter and summer), during which the NO_2 concentration undergoes photochemical changes as the sun rises or sets. The retrieved NO_2 profiles are put to the time corresponding to the solar zenith angle of 84° (It is possible to put they to other time.) The total NO_2 column is determined as an integral over all layers, the stratospheric NO_2 column as an integral above 10 km.

3.2. Retrieval of the ozone profiles

To determine the ozone contents, the differential structure of spectrum of radiation scattered in the zenith from 310 to 331 nm was used. The classical DOAS deals with weakly absorbing gases and uses properties of an approximate solution of the radiative transfer equation for the volume absorption cross section σ, satisfying the condition $\sigma << 1$. Because of the strong absorbtion at the UV wavelengths and, hence, $\sigma \geq 1$ in many cases, the classical DOAS technique doesn't work properly for retrieval of ozone using the UV spectrum.

Let separate in the volume absorption cross section $\sigma(\lambda,h)$ at altitude h and wavelength λ a dominant part $\sigma_0(\lambda,h)$ with smooth dependence on wavelength from other terms:

$$\sigma(\lambda,h) = \sigma_0(\lambda,h) + \sum_{i=1}^{n} s_i(\lambda) x_i(h) . \quad (1)$$

Here $s_i(\lambda)$ and $x_i(h)$ are the absorbtion cross sections and the number densities of i-th gas or absorbing aerosol. Let consider the reflectance of an atmosphere-surface system

$$r(\lambda) = I(\lambda) / I_0(\lambda) . \quad (2)$$

Here $I(\lambda)$ and $I_0(\lambda)$ are the measured and extraterrestrial radiance respectively. It is possible to obtain a Taylor expansion (Postylyakov, 2005)

$$r(\lambda) \approx r^{(0)}(\lambda) + \sum_{i=1}^{n} s_i(\lambda) \int dh \; x_i(h) w_\lambda(h) , \quad (3)$$

if condition

$$\sum_{i=1}^{n} s_i(\lambda) x_i(h) / \sigma_0(\lambda,h) << 1 \quad (4)$$

is satisfied.

Here

$$r^{(0)}(\lambda) = r(\lambda)\big|_{\sigma(\lambda,h)=\sigma_0(\lambda,h)} , \quad (5)$$

and

$$w_\lambda(h) \equiv \frac{\partial r(\lambda)}{\partial \sigma_h}\bigg|_{\sigma(\lambda,h)=\sigma_0(\lambda,h)} \quad (6)$$

is a partial derivative of the reflectance with respect to the volume absorbtion cross section σ_h at altitude h.

In the UV region under investigation we took:

$$\sigma_0(\lambda,h) = s_{oz}^{(0)}(\lambda,h) x_{oz}^{(0)}(h) + s_a(\lambda,h) x_a(h) , \quad (7)$$

where $s_{oz}^{(0)}(\lambda,h)$ is a smooth part of ozone cross section $s_{oz}(\lambda,h)$ and $x_{oz}^{(0)}(h)$ is some *a priori* ozone number density, $s_a(\lambda,h)$ and $x_a(h)$ are the aerosol absorbtion cross section and the number density respectively. Denoting

an operator $\mathbf{E}$ averaging an altitude-dependent cross section by

$$\mathbf{E}s(\lambda,h)=\frac{\int dh\ s(\lambda,h)w_\lambda(h)x^{(0)}(h)}{\int dh\ w_\lambda(h)x^{(0)}(h)}, \tag{8}$$

we defined

$$s_1(\lambda)=\mathbf{E}s_{oz}^{(0)}(\lambda,h), \tag{9}$$

$$x_1(h)=x_{oz}(h)-x_{oz}^{(0)}(h), \tag{10}$$

and

$$s_2(\lambda)=\mathbf{E}s_{oz}(\lambda,h)-\mathbf{E}s_{oz}^{(0)}(\lambda,h), \tag{11}$$

$$x_2(h)=x_{oz}(h), \tag{12}$$

where $x_{oz}(h)$ is the true ozone number density. Thus, the first ozone-related item $s_1(\lambda)x_1(h)$ has the smooth wavelength dependence, while the second one $s_2(\lambda)x_2(h)$ has the indented dependence . The next terms with $i>2$ may represent other minor gases and absorbing aerosols, perhaps, with indented absorbtion.

Let consider explanation (3). The functions $r^{(0)}(\lambda)$, $w_\lambda(h)$ and $s_1(\lambda)$ smoothly depend on the wavelength, while $s_i(\lambda)$, $i\ge 2$, may have a characteristic fine spectral structure. Hence it is possible to use the spectral fitting to the measured spectral reflectance $r(\lambda)$ to obtain terms $S_i=s_i(\lambda)\int dh\ x_i(h)w_\lambda(h)$, $i\ge 2$, $s_i(\lambda)$ - indented, and corresponding slant columns $\int dh\ x_i(h)w_\lambda(h)$. In particular, S_2 gives the ozone slant column density because of definitions (11) and (12).

Explanation (3) shows two main characteristics differing the UV DOAS method from the classical case. The first, it is necessary to take into consideration a linearization of radiative transfer in an atmosphere with none-zero volume absorbtion. It must be the smooth part of the volume absorbtion, which must be more larger than the indented part of the volume absorbtion. However, though some *a priori* ozone absorbtion is included in *a priori* atmosphere, the ozone slant column available for estimation relates to the full ozone profile (12) but not to the ozone increment (10). The second, the ozone absorbtion, strongly changing with wavelength, requires shortening the wavelength range used for DOAS spectral fitting because of faster changing of $w_\lambda(h)$ than in case of weak absorbtion. So we must divide the UV range into several intervals. These wavelength intervals are wide enough that it is possible to separate the typical spectral structure of the ozone absorbtion from other smooth and indented components by a fitting procedure. Such multi-interval fitting technique allows estimating the ozone vertical profile using observation at one solar zenith angle. Indeed, several intervals give differing slant columns, having information about different altitudes. If it were case with weak absorbtion and the classical DOAS were applicable, obtained slant columns would be equal.

A new retrieval algorithm based on the multi-interval DOAS approach described above was developed.

Values measured by the spectrometer are divided by the spectral sensitivity of the instrument and the extraterrestrial solar radiance convoluted with the instrument device function. Spectral fitting is performed for the obtained data divided to seven spectral intervals. It uses two smooth functions and another one obtained as the indented part of the ozone absorbtion cross section. As the result, the slant ozone columns for the seven wavelength intervals and different SZAs were obtained.

The total ozone and profile retrieval algorithms use optimal statistical estimation method with known *a priori* average and covariance matrix of ozone profile (Elansky et al., 1999).

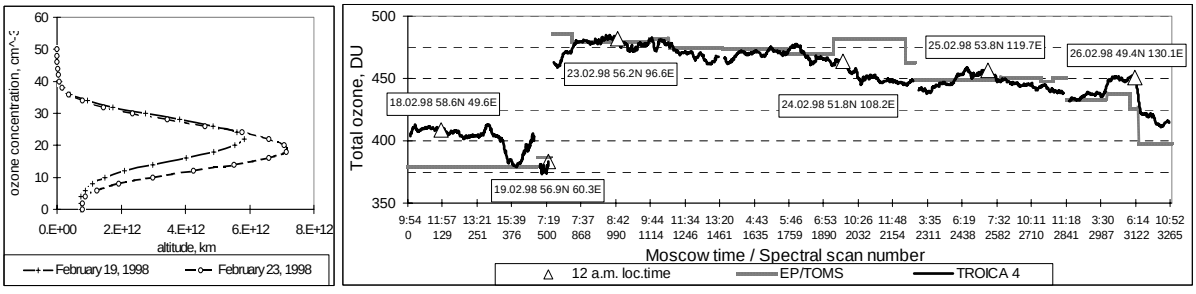

Figure 1. Ozone content measured from train during the way Moscow-Khabarovsk (a) The ozone profiles measured at evening of February 19 and 23, 1998. (b) The TOC measured from February 18 to 26, and data of TOMS. Triangles show crossing of the local midday.

The linearized radiative transfer model MCC++ (Postylyakov 2004a, 2004b) was used in radiance calculation because it allows efficiently obtaining derivatives (6) required in the ozone profile retrieval. The model takes into account all orders of scattering, the sphericity of an atmosphere, aerosol and molecular scattering, ozone and aerosol absorbtion, Lambertian surface albedo. Differ to the NO_2 retrieval, taking into account multiple scattering and albedo is significant for ozone retrieval. Numerical experiments show that use of derivatives (6) calculated in the approximation of single scattering leads to overestimation of the total ozone content by 15%. Calculation for albedo equal to 0 instead of 1 gives overestimation of the TOC by 5%.

4. OBSERVATIONAL RESULTS AND THEIR FIRST VALIDATION

Figure 1 shows the TROICA ozone measurements during the forward way from Moscow to Khabarovsk and corresponding data of the TOMS satellite instrument. The vertical resolution of the ozone profiles is 10 km. During February 18 and 19 the train moved at the periphery of an area with enhanced TOC. The TOC was equal to 380-400 DU. On February 22 the train entered into this area and began to move with this stratospheric air mass lagging behind it. Measured TOC slowly decreased from 480 to 430 DU (February 28) and had small variations. The maximum of the retrieved ozone profile shifts typically for the observed change of the TOC from February 19 to 23.

Figure 2 shows the NO2 profiles retrieved during the back way. Obtained concentrations and their variations are within expected for the season and the latitude of the observation (Elokhov and Gruzdev, 2000).

5. CONCLUSION

The modification of a spectrometer used at stationer stations for application in the moving carriage-laboratory was performed and tested in the TROICA-4 experiment. To obtain O_3 profiles, the new retrieval algorithm, employing the multi-interval approach to the DOAS technique, was developed. It shows reasonable results in interpretation of UV spectrum with the strong O_3 absorbtion. The NO_2 profiles were retrieved by the twilight DOAS technique.

The proposed approaches may be modified for retrieval of other reactive and greenhouse gases using visible and UV spectral measurements from a mobile laboratory.

6. ACKNOWLEDGEMENTS

Authors acknowledge the TOMS team for providing their data through the Internet site http://toms.gsfc.nasa.gov.

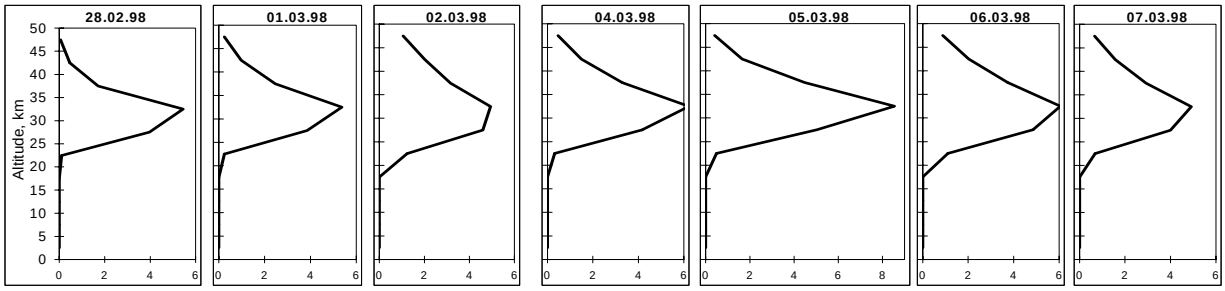

Figure 2. The vertical distribution of nitrogen dioxide at morning, SZA=84^O. Integral content in 5-km layers is shown in 10^{14} cm^2.

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