Long path DOAS measurements of atmospheric pollutants concentration

Pavel P. Geiko[*a,b], Sergey S. Smirnov [a,b], Ignatii V. Samokhvalov[a]

[a]Tomsk State University, Tomsk, Russia

[b]Institute of Monitoring of Climatic and Ecological Systems SB RAS, Tomsk, Russia

ABSTRACT

A differential optical absorption spectroscopy gas-analyzer consisted of a coaxial telescope, a spectrometer, an analyzer and retroreflector was successfully tested. A high pressure 150-W Xe arc lamp was employed as a light source. In order to record the spectra, a monochromter with a grating and photodiode array was used. Gas analyzer spectral data bank includes more than 35 moleculas absorbed in UV spectral region. The measured absorption spectra were evaluated by using a least-squares fit to determine the average mixing ratio of each species in the atmosphere. As a result of experiments time series of concentrations of gases polluting the atmosphere were trace measured. Minimally detected concentration on pathlength 480 m is the unit of ppb at the time of accumulation of 2 min. The results of the field test measurements of pollutants in Tomsk city are presented.

Keywords: differential optical absorption spectroscopy, UV spectra, gas-analyzer,

1. INTRODUCTION

In connection with the global environmental problem of air pollution, there have been growing interests in advanced techniques to monitor air pollution in the open atmosphere. Differential optical absorption spectroscopy (DOAS) is a widely used method to determine concentrations of atmospheric species in the troposphere simultaneously. Since the 1980's, DOAS has been considered a powerful technique for detecting pollutants since 1980's [1,2], it has been used for ground based applications as well as satellite measurements, for both active and passive instruments. DOAS system allows quantitative measurement of atmospheric trace gas concentrations by recording and evaluating the characteristic differential absorption of a UV/Visible radiation over a long path in the open atmosphere. Different atmospheric species will leave their absorption fingerprints in the spectra from which concentrations could be retrieved.

The DOAS system is able to scan the UV/Visible spectrum from 250 nm to 700 nm. This makes it possible to study the atmospheric chemistry of the measurement area and the boundary layer. DOAS is a very unique technique that can measure the NO_3 concentration intact [3]. The DOAS measures the average concentrations of atmospheric trace gas species in a column several kilometers long and offers a three-dimensional map of the extent of pollution in an observation area. DOAS allows one to search for unknown species from the residual structure. The DOAS instrument shares the advantages of most other spectroscopic techniques, such as differential absorption lidar (DIAL) [4], including inherent calibration, high sensitivity up to several ppb or ppt [5,6], and the capability of monitoring the large areas. It should be noted and some disadvantages with DOAS: 1) Atmospheric turbulence induce intensity variations in the spectra. 2) Only a limited number of molecules have suitable absorptions in UV and visible region. 3) Rain, snow, fog and clouds make measurements impossible due to the strong attenuation in the UV/Visible spectral region.

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[*] ppg@imces.ru; phone +7-382-249-1950; fax +7-382-249-1950; www.imces.ru

DOAS instruments are potential alternatives to conventional instruments to monitor air pollution, but they are still regarded as instruments of the future. Several groups have detected troposphere pollution by using commercial and lab DOAS systems [3,5,6]. We modernized and tested DOAS system [7,8] and show some tested results. In order to reduce the magnitude of the residual spectrum, we improve the algorithm by considering the lamp emission structure as a reference spectrum. Gas analyzer can detect standard pollutants NO_2, SO_2, and O_3, formaldehyde, aromatic species, monocyclic hydrocarbons.

2. PRINCIPLES OF DOAS METHOD AND EXPERIMENTAL SETUP

The basic equation of absorption spectroscopy, describing pure absorption of a single species in a homogeneous media, is Beer-Lamberts Law, equation 1.

$$I(\lambda) = I_0(\lambda) \cdot \exp\{-L(\sum_{j=1}^{J} \sigma_j(\lambda)C_j + \sigma_M(\lambda)C_M + \sigma_R(\lambda)C_R)\} \tag{1}$$

where $I_0(\lambda)$ denotes the unattended reference intensities emitted from some suitable source of radiation. $I(\lambda)$ is the the measured intensity of the radiation after it has passed through a layer of thickness L, C_j is the average concentration of species j at wavelength λ. $\sigma_j(\lambda)$ - the absorption cross-section of molecule j, which can be taken from the literature or can be measured in advance in the laboratory, $\sigma_M(\lambda), \sigma_R(\lambda)$ - the cross-section of Mie and Rayleigh scattering.

If $\sigma_j(\lambda)$ is known, the trace gas concentration C_j can be calculated by introducing a column optical depth $\tau(\lambda)$ for a given wavelength:

$$\tau(\lambda) = \ln(\frac{I_0(\lambda)}{I(\lambda)}) = \{L(\sum_{j=1}^{J} \sigma_j(\lambda)C_j + \sigma_M(\lambda)C_M + \sigma_R(\lambda)C_R)\} \tag{2}$$

It is generally assumed that the attenuation due to Rayleigh scattering and Mie scattering, along with any optical transmission function of the system, is slowly varying with wavelength. The absorption cross-section of a given molecule can be split into two parts: one slowly varying with wavelength, and other rapidly varying:

$$\sigma_j(\lambda) = \sigma_{j0}(\lambda) + \sigma'_j(\lambda), \tag{3}$$

where $\sigma_{j0}(\lambda)$ varies monotonically with the wavelength λ, for instance, describing Mie Scattering, and Rayleigh Scattering. This rapidly varying cross section , $\sigma'_j(\lambda)$ is also called differential absorption cross section , $\sigma'_j(\lambda)$ shows a rapid variations with λ, mostly due to an absorption line. The definition of the threshold between the slow and the rapid variations of the absorption cross-section with wavelength depends on the observed wavelength interval, the width of the absorption bands to be detected, and the appearance of other absorption and emission structures, which should be removed from a spectrum.

The measured spectrum is fitted by the absorption spectra of the trace gases absorbing in the respective spectral range and a polynomial of a specified degree by means of a non linear least squares fitting algorithm. Let's substitute the expression (3) into the formula (1), while the slow variety part included the polynomial:

$$I(\lambda) = I_0(\lambda) \cdot \exp\{-L\sum_{j=1}^{J} \sigma'_j(\lambda)C_j + \sum_p b_p\lambda^p\}, \tag{4}$$

where $\sum_p b_p\lambda^p$ is the polynomial p - th order.

We obtain the expression (5), depending on the optical depth, of the polynomial order p, concentration and length of atmospheric trace.

$$\ln(I(\lambda)/I_0(\lambda)) = -L \cdot \sum_{j=1}^{J} \sigma'_j(\lambda)C_j + \sum_p b_p \lambda^p , \qquad (5)$$

Equation (5) can be represented as a discrete form:

$$D_k = \ln(I(\lambda_k)/I_0(\lambda_k)) = -L \cdot \sum_{j=1}^{J} \sigma'_j(\lambda_k)C_j + \sum_p b_p \lambda_k{}^p , \ k=1, n \qquad (6)$$

Here n is the number of discrete signal samples.

In fact equation (6) represents a system of linear equations that can be written in matrix form and use to solve of a particular numerical method that provides the best stability, such as the singular value decomposition of a matrix [6].
In order to correctly determine gas concentration, cross sections of the atmospheric species have to be convolved to the wavelength resolution of the instrument. Another way of dealing with this problem would be to measure cross sections with the instrument in a controlled environment with known concentrations.
A typical DOAS instrument consists of a continuous light source, i.e. a Xe-lamp, and an optical setup to send and receive the light through the atmosphere. In our research we used a modernized version of the gas analyzer DOAS-M1 [6,7,8]. Figure 1 shows a schematic view of our DOAS system.
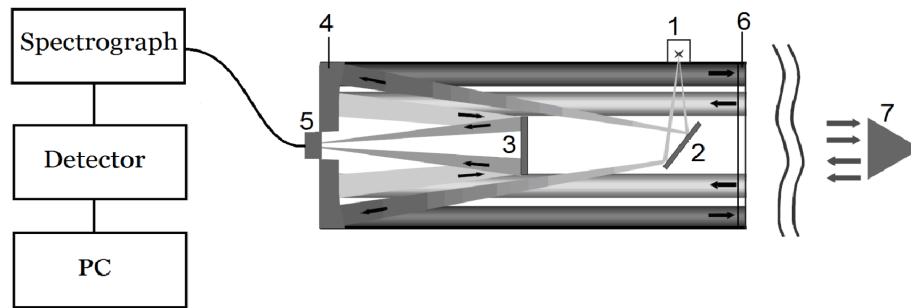

Fig. 1. Schematic diagram of the DOAS system: (1) Xe lamp, (2) turning flat mirror, (3) flat secondary mirror reflector, (4) the main spherical mirror, (5) fiber optic guide, (6) protective glass, (7) retro-reflector

Our system consisted of a spectrometer with a photodiode array, a coaxial telescope, and an analyzer. A 150-W Xe arc lamp with a 2-mm arc length was employed as the light source. The Xe beam mounted at the focal point of the main mirror is collimated, with a divergence about 1 mrad, through the telescope. The coaxial telescope with a 200-mm main spherical mirror, and the light source is put through the hole of the main mirror on the back of telescope. The telescope of the DOAS system is a single unit of the transmitter and the receiver and is faced toward a set of retro-reflectors. For recording the spectra, a monochrometer with grating and a photodiode array was adopted, the signal from which is digitized by an analog-digital converter and comes to a computer for further processing. Optical fiber guide has a 200-μm core diameter used for transmitting the light into the spectrometer is a Czerny-Turner type. A spectral resolution (FWHM) was 0.25 nm around 280 nm. The instrument is completely automated and after adjustment works in an independent mode without intervention of the operator.

3.   MEASUREMENT RESULTS

To prepare the corresponding reference absorption cross-sections, we convoluted the absorption spectra by using mercury line spectra and interpolated according to the dispersion of the pixels of the photodiode array. We convoluted the reference spectra according to the instrumental function and dispersed them by using the number of pixels. We chose Hg line for the convolution. The evaluation to find the concentration of each gas species in the appropriate wavelength

range was done sequentially by taking the logarithm, filtering, and performing the non-linear fit. Using a nonlinear least squares fitting algorithm, we fitted the measured spectrum by using a linear combination of the absorption spectra of the trace gases absorbing in the respective spectral range and a polynomial of the fifth degree as an additional high-pass filter. The fitting algorithm used the Levenberg-Marquard method [9]. This algorithm has a linear part for retrieval of the trace-gas absorptions and a nonlinear part to account for possible spectral shifts between the measured and the reference spectra.

The aim of the linear fitting process was to minimize the sum over the differences between the measured optical depths of the individual diode elements in the selected wavelength range and the respective values of polynomial coefficients and gas concentrations in the fitted reference spectra. To minimize measurement errors it is necessary to eliminate sources of these errors or to introduce a correction coefficient. The main sources of error in the measurement include: 1) the fact that a lamp emission spectrum is not perfect (contains subtle structures in the spectrum); 2) a sensitivity of individual pixels of a photodiode array (different sensitivity); 3) parasitic structures formed during recording of spectra (a reference signal and a trace signal); 4) the fact that the influence of oxygen absorption is neglected; 5) inaccuracy of determination of the absorption cross-section of gases; 6) inaccurate determination of the optical path length.

Measurements were conducted in Tomsk city ($56^0 30'$ north latitude and 85^0 longitude), square South in the period from January to May 2015. The path length varied from 240 to 500 meters. There was an opportunity to use continuous measurements of meteorological parameters, because ultrasonic meteorological station was taken near measurement place. Measurements were performed in the spectral region 202 - 355 nm.
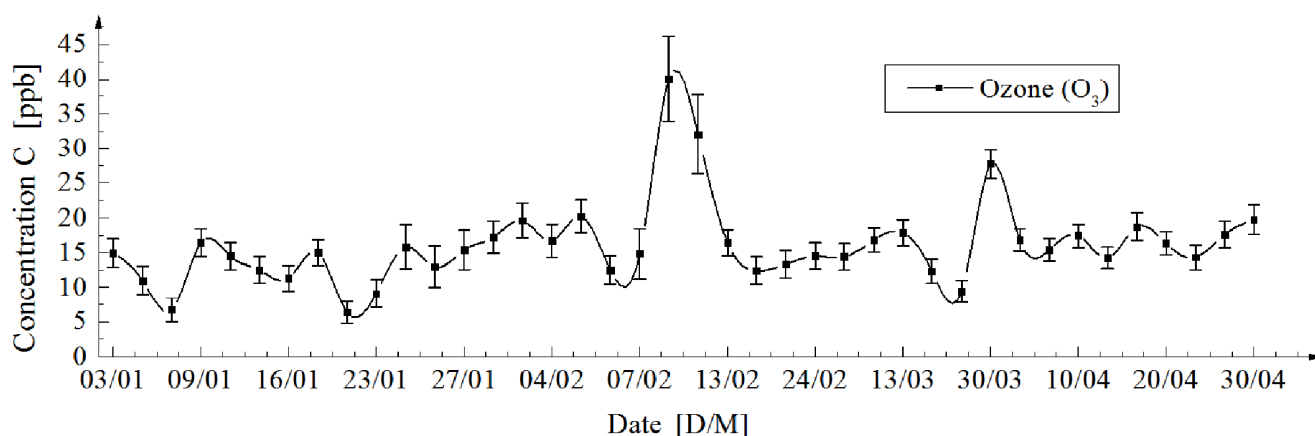

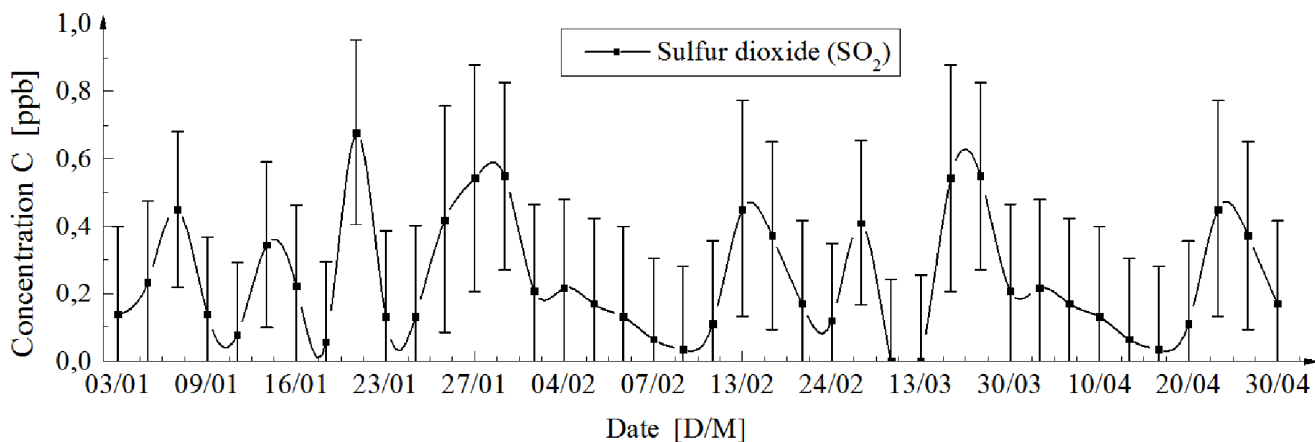Fig. 2. Long-term variations of O_3 concentration

Fig. 3. Long-term variations of SO_2 concentration

Figure 2,3 shows dependence of the concentration of ozone and sulfur dioxide for the period from first decade of January to April. Between 3:00 a.m. till 17:00 of the day for the all period of measurements, observed excess of the average daily maximum permissible concentration (MPC). From 14:00 to 16:00 in 90% of cases, the excess of MPC was in 2 times.

It is noticed that 60% of all measurements the value of concentrations of sulphur dioxide exceeds the average daily maximum permissible concentration by a factor of 1.2. From the analysis of the measurement results were revealed some peculiarities. Thus 60% of all measurements, the value of concentrations of sulphur dioxide exceeds the average daily maximum permissible concentration 1.2 times; for ozone from 14:00 to 16:00 of the day in 90% of all daily measurements seen the exceeding of the average daily MPC by 2 times. Comparing the wind direction and the results sensing, were you-revealed some regularities: So, for ozone concentration is increasing in the West and North-West wind directions. Figure 4 shows the measured variation of NO_2 concentration.
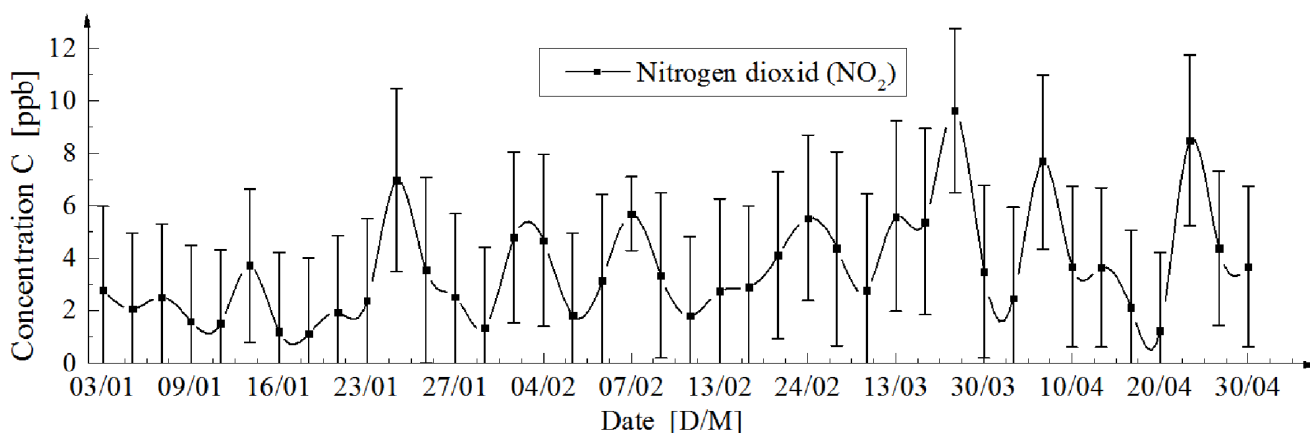

Fig. 4. Long-term variations of NO_2 concentration

Correlation coefficients of O_3 and NO_2 is about -0.4 during days of rainy weather and dense smog and reached −0.8 in various cloudless periods and. At sunrise, the concentration of ozone increased and reached a maximum after noon; then, it started to decrease and reached a minimum near midnight. However, the concentration of NO_2 was anti-correlated with O_3. When NO_2 is exposed to tropospheric radiation, it photodissociates at $\lambda < 420$ nm to give nitric oxide. After dissociation, an oxygen atom and a NO_2 molecule play roles as the only significant anthropogenic sources of O_3 in the troposphere.

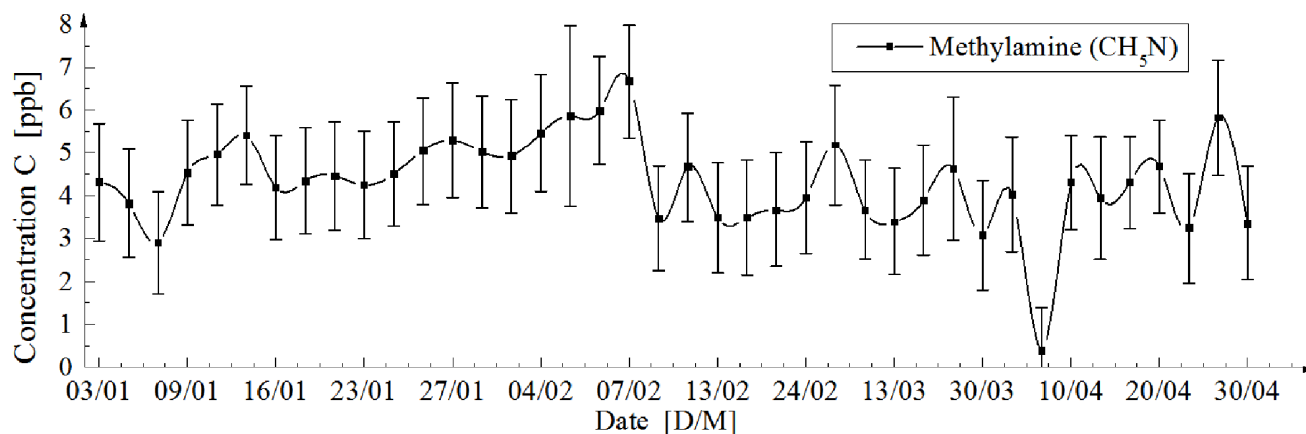The examples of long-term variations of some gas concentration are given below in figures 5-8.

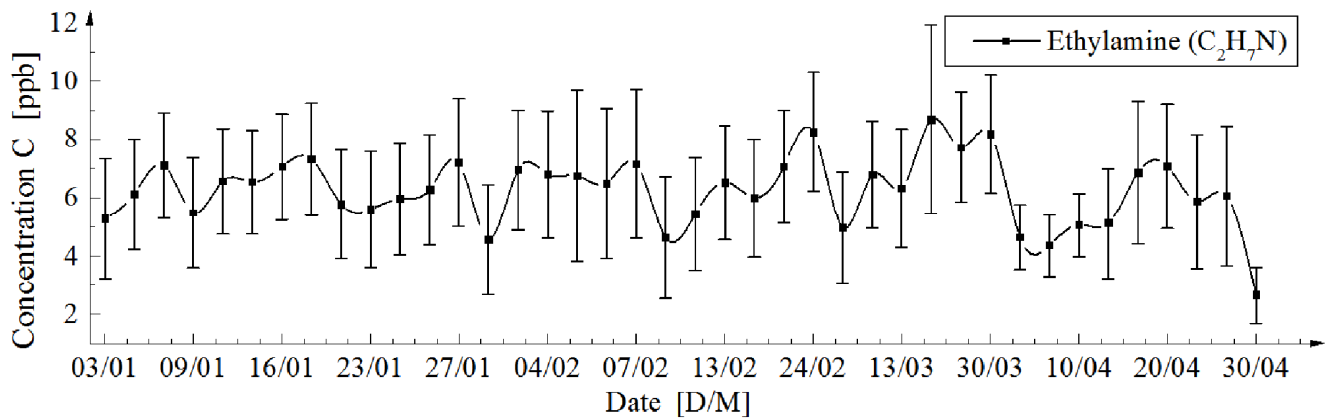Fig. 5. Long-term variations of Methylamine CH_5N concentration

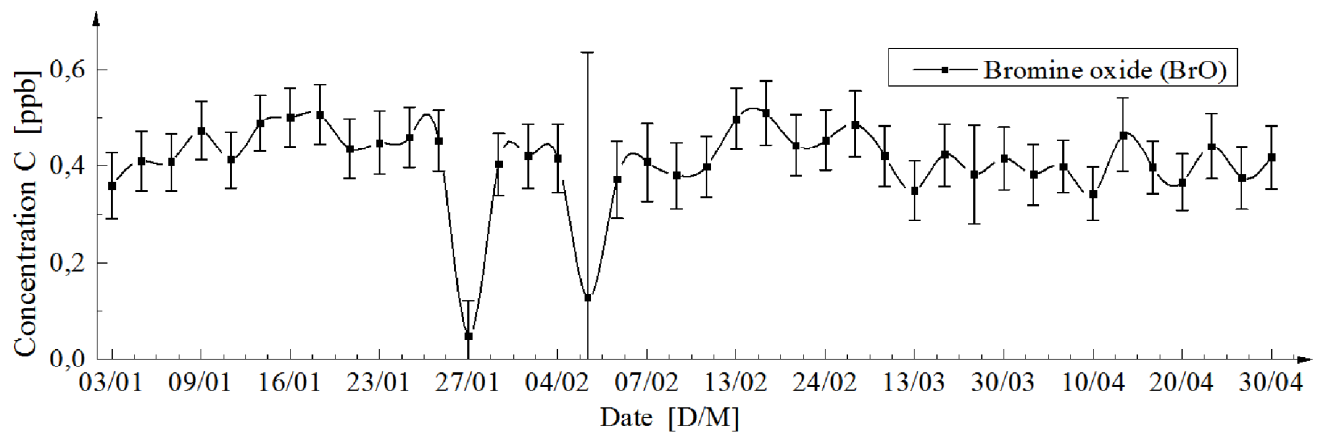Fig. 6. Long-term variations of Ethylamine CH$_5$N concentration

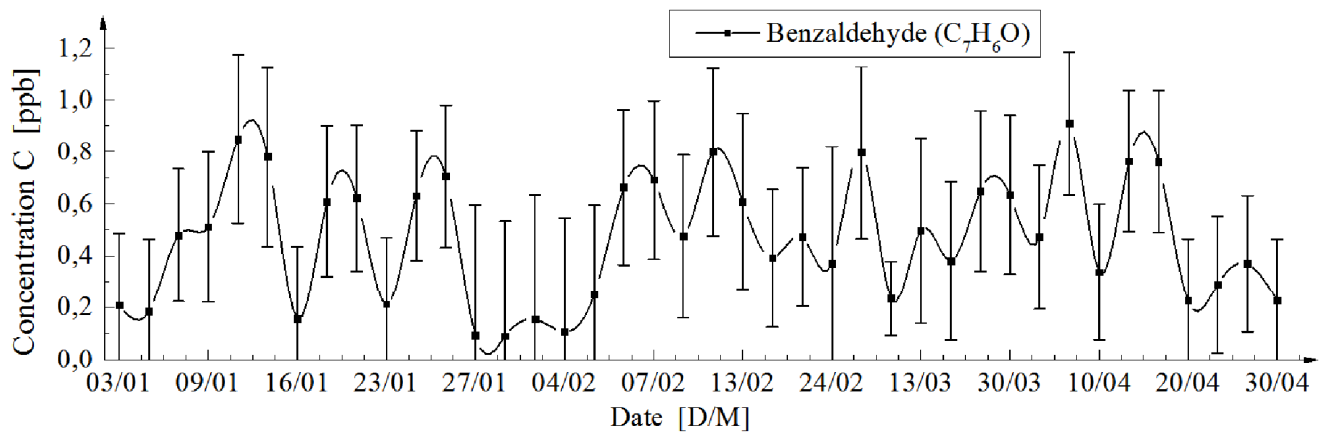Fig. 7. Long-term variations of BrO concentration

Fig. 8. Long-term variations of Benzaldehyde C$_7$H$_6$O concentration

The concentration of air pollutants greatly depends on time and location, and fluctuations those associated with the feature income sources of air polluting, and the influence of meteorological and topographical factors. For example, the

humidity significantly change the number and qualitative composition of pollution, especially in the presence of air hygroscopic particles and gases and reaction able vapors and chemicals (halogen and their compounds, nitrogen oxides, substance groups PAN and others).

4. SUMMARY

Differential optical absorption spectroscopy is a powerful measuring tools which has been used successfully for atmospheric species retrieval, with high sensitivity for both local and global conditions. The DOAS system was successfully tested. The main sources of error in the measurement are considered. The system consisted of a coaxial telescope, a spectrometer, an analyzer and retroreflector, a high pressure Xe arc lamp was employed as a light source. Identification of desired gas and determination of value of the concentration occurs by evaluating the measured spectra. The measured spectra were evaluated by using a least-squares method. The results of synchronous continuous measurements of concentration some atmospheric polluting gases by the DOAS method in Tomsk are presented. The minimal detected concentration is some units of ppb on pathlength 500 m with 2 min accumulation time.

ACKNOWLEDGMENTS

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