

# Measurements of NO<sub>2</sub> and Analysis of Submicron Aerosol Composition in the ARM-Related Experiment at Zvenigorod in March-April 2002 and During Forest and Peatbog Fires in July-September 2002

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## Introduction

One insufficiently explored problem is the effect of pollution of the lower troposphere by nitrogen oxides on the chemical composition and microphysical properties of atmospheric aerosol. Earlier experimental studies showed that submicron aerosol collected during anthropogenic pollution episodes in winter could contain the nitric acid component (Shukurova et al. 2001). In this study, we present results which show that similar effect can take place in warmer period, during episodes of anthropogenic pollution as well as during smoke episodes related to forest and peatbog fires.

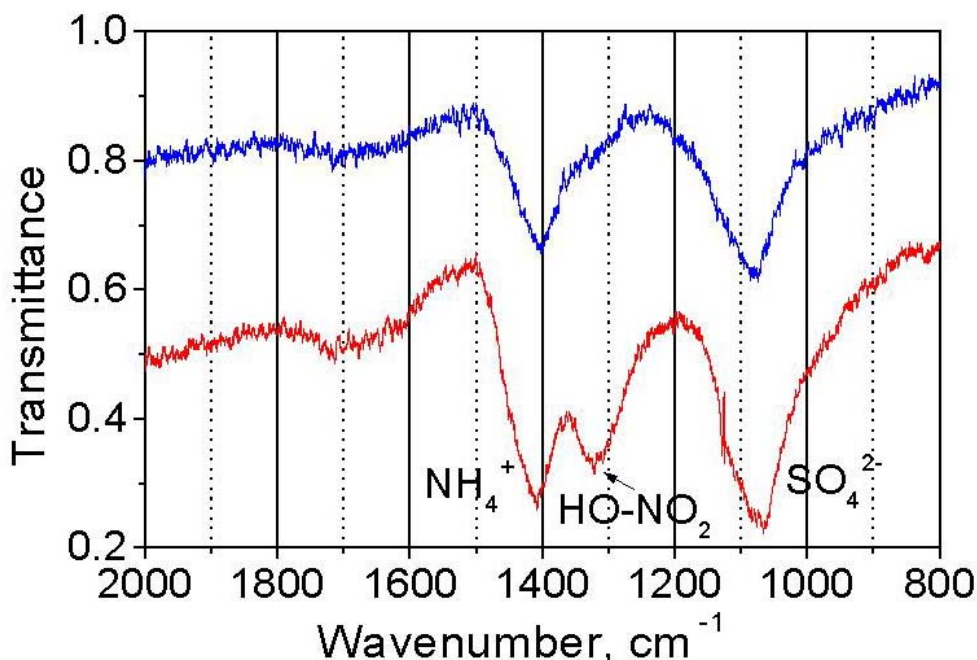
During the complex aerosol-radiation-cloudiness experiment at Zvenigorod Research Station (50 km to the west of Moscow) in the spring of 2002 we have carried out regular spectrometric measurements of the NO<sub>2</sub> abundance. At the same time, submicron aerosol was deposited on germanium plates transparent in IR spectral range using cascade impactor. The same measurements were done during the period of the forest and peatbog fires near Moscow in July-September 2002.

Characteristic diameter of aerosol particles deposited in the submicron cascade is within 0.7–1.3 μm. The aerosol samples were collected in daytime during two-to-three days, with interruptions; the duration of sample collecting was about 24 hours. Identification of chemical compounds in the aerosol samples was done with the use of transmittance spectra of the samples measured with resolution 8–10 cm<sup>-1</sup> by two-beam spectrophotometer UR-20 in the wave number range 500–5000 cm<sup>-1</sup>.

The NO<sub>2</sub> abundance was measured with the help of spectrophotometer detecting zenith-scattered solar radiation in the spectral range 435 – 450 nm during morning and evening twilight (at solar zenith angles 84°–96°) (Elokhov and Gruzdev 2000). The method used allows retrieving the NO<sub>2</sub> vertical distribution and, in particular, estimating the integral (column) abundances of NO<sub>2</sub> in the lower troposphere (0-5 km) and, separately, in the surface layer (the thickness of the surface layer varies and depends on meteorological conditions). The derived abundance of NO<sub>2</sub> in the surface layer occurs to be more appropriate of the surface layer pollution than the local concentration of NO<sub>2</sub> (Shukurova et al. 2001).

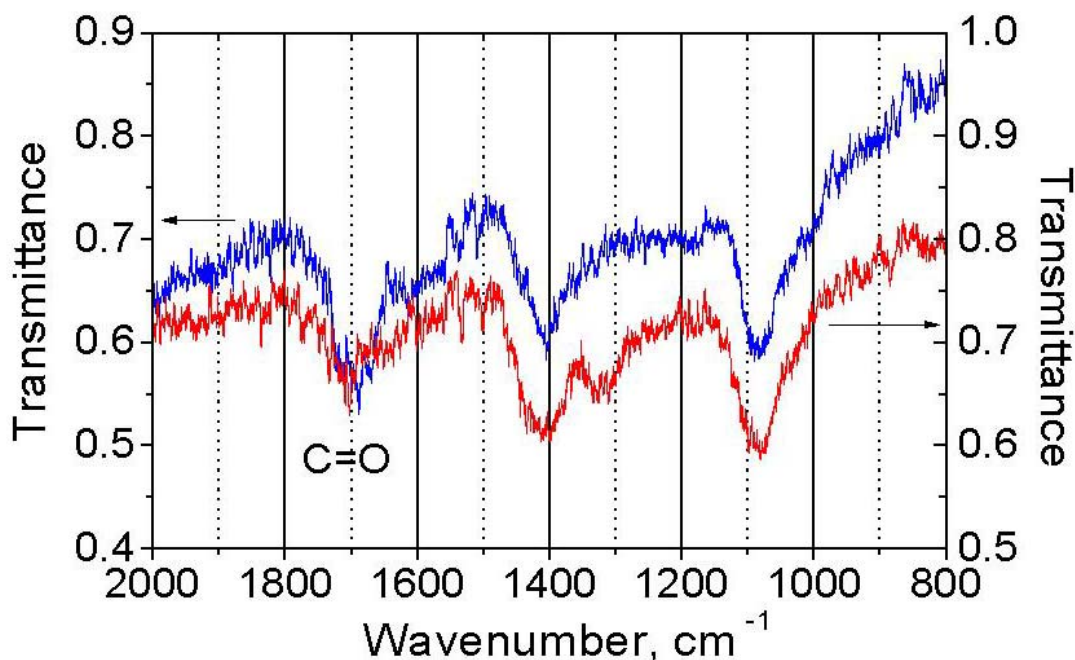
Results of the measurements show that episodes of large  $\text{NO}_2$  abundance in the surface layer had occurred during the two experiments. During the spring experiment, the observed high  $\text{NO}_2$  abundances were related to anthropogenic pollution episodes. For the period of the fires, the high values of the surface layer  $\text{NO}_2$  abundance were only observed during episodes of large concentration of smoke aerosol transported from the fire area.

Analysis of transmittance spectra of aerosol samples has revealed the presence of the nitric acid component in the submicron aerosol samples collected during episodes of high values of surface layer  $\text{NO}_2$  abundance for the spring experiment and in summer during the smoke episodes. Transmittance spectra of two aerosol samples collected in March 20–22 (red) and March 23–25 (blue) are shown at Figure 1, for periods of high and low abundance of surface layer  $\text{NO}_2$ , respectively. The both spectra in Figure 1 contain the ammonium sulfate absorption bands around  $1080\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  peculiar to anion  $\text{SO}_4^{2-}$  and cation  $\text{NH}_4^+$ , respectively. In the context of this work, the most remarkable feature of the red curve in Figure 1 (the spectrum corresponding to the period of the high surface  $\text{NO}_2$  abundance) is the absorption band around  $1320\text{ cm}^{-1}$  that can be attributed to vibration frequency of the chemical bond  $\text{HO}-\text{NO}_2$  or, less likely, can be related to nitro-complexes (Nakamoto 1986). Therefore, nitric acid seems to be present in this aerosol sample, together with sulfates. Similar feature was found in spectra of aerosol samples collected in wintertime under conditions of high surface  $\text{NO}_2$  abundance (Shukurova et al. 2001).



**Figure 1.** Transmittance spectra of submicron aerosol samples collected in March 20–22 (red) and March 23–25 (blue), corresponding to periods of high and low abundance of surface layer  $\text{NO}_2$ , respectively.

Transmittance spectra of two submicron aerosol samples collected during periods of September 5–7 (red) and August 30–September 1 (blue) are shown in Figure 2. The both periods are characterized by strong smoke and very large concentration of aerosol transported from the fire area. However, the former period includes the day (September 7), when the high  $\text{NO}_2$  abundance was observed in the surface layer, while the latter period is characterized by near-zero surface layer  $\text{NO}_2$  abundance. As in Figure 1, the spectrum corresponding to high surface  $\text{NO}_2$  abundance in Figure 2 contains the absorption band  $1320\text{ cm}^{-1}$ , while this band has not been revealed in the spectrum corresponding to zero surface  $\text{NO}_2$  abundance.



**Figure 2.** Transmittance spectra of submicron samples collected during periods of strong smoke and very large concentration of aerosol, September 5–7 (red) and August 30–September 1 (blue). The former period includes the day (September 7), when the high  $\text{NO}_2$  abundance was observed in the surface layer, while the latter period is characterized by near-zero surface layer  $\text{NO}_2$  abundance.

This experimental study shows that boreal forest and peatbog fires, together with direct anthropogenic emission to the atmosphere, are major sources of nitric oxides in the lower troposphere. Heterogeneous chemical reactions on the surface of aerosol particles are believed to be responsible for transformation of nitrogen oxides to the nitric acid component in aerosol particles under conditions of large abundance of nitric oxides in the lower troposphere.

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