NEW METHOD AND CORRELATION SPECTROMETER FOR REMOTE MEASUREMENT OF THE NITROGEN DIOXIDE CONTENT IN THE ATMOSPHERE

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A new remote method, a portable correlation spectrometer, and results of measurements of the nitrogen dioxide concentration in air near the ground, performed with a sensitivity of up to 0.5 ppb *based on the scattered solar radiation at distances of up to* 10 km. *are presented.*

Optical correlation spectrometers, in which the total content of the gaseous pollutant between the source of radiation and the correlation spectrometer is determined by measuring the mutual correlation of the spectrum of the received radiation and the absorption spectrum of the gaseous impurity, modeled as the transmission function of the optical channel of the correlation spectrometer, are promising instruments for remote analysis of trace gaseous components of the atmosphere.[1]

Wide application of the technique of correlation spectrometry for fast analysis of the concentrations of gaseous impurities in air has thus far been hampered by the need to insert at a known distance a mirror reflector or an autonomous radiation source, and in addition the average concentration of the impurity on the path is obtained by dividing the value of the total impurity content, measured by the correlation spectrometer, by the distance from the radiation source to the correlation spectrometer. In this paper we present a measurement method in which there is no need to use an optical reflector, and we describe a correlation spectrometer based on a tunable Interference-polarization filter.

We shall study the solar and scattered radiation from the sky, illuminating a horizontal path near the ground, along which the line of sight of the correlation spectrometer is directed. The radiation scattered along the horizontal path into the objective of the apparatus contains the information about the nitrogen dioxide concentration along the path.

The output signal R of the correlation spectrometer, receiving the sky light scattered in the direction of the horizon, has the form

$$R = \frac{\sum_{i=1}^{n}\sum_{j=1}^{k}\left[J_{ij}^{(1)} - J_{ij}^{(2)}\right]\cdot\Delta\lambda_j}{\sum_{i=1}^{n}\sum_{j=1}^{k}J_{ij}^{(1)}\cdot\Delta\lambda_j}, \qquad (1)$$

where $J_{ij}^{(1)(2)} = J_{ij0}^{(1)(2)}\cdot\exp\left\{-\rho\sigma_j^{(1)(2)}l_1 - \alpha_1 l_1\right\}$ and $J_{ij0}^{(1)(2)}$ is the intensity of the sky light scattered along the horizon into the objective of the instrument from a distance l_1 in the spectral intervals $\Delta\lambda_j$, coinciding; respectively, which the neighboring minima and maxima of the absorption spectrum of NO_2; whose average absorption cross sections are $\sigma_j^{(1)}$ and $\sigma_j^{(2)}$; α_1 is the average aerosol and molecular attenuation coefficient on the section l_1 along the horizontal path. Setting

$$\sigma_j^{(2)}\cdot\rho\cdot l_1 \ll 1, \quad \alpha_1 = \alpha, \quad J_{ij0}^{(1)} = J_{ij0}^{(2)}, \quad \Delta\lambda_j = \Delta\lambda,$$

$$\frac{\sum_{j=1}^{k}(\sigma_j^{(2)} - \sigma_j^{(1)})}{k} = \frac{\sum_{j=1}^{k}\Delta\sigma_j}{k} = \overline{\Delta\sigma}, \qquad (2)$$

we obtain

$$R = \rho\cdot\overline{\Delta\sigma}\cdot\alpha^{-1}.$$

Thus the signal from the correlation spectrometer, receiving the sky light scattered along the horizon, is equal to the product of the concentration ρ of the gas being measured by the average differential absorption cross section $\Delta\sigma$ and by effective path length α^{-1}, which is defined as the inverse aerosol and molecular attenuation coefficient at the wavelength λ. In the practice, for the scattered sunlight the condition $J_{ij0}^{(1)} = J_{ij0}^{(2)}$ does not hold owing to the nonuniformity in the spectrum of the solar radiation and the absorption of radiation by the gas being measured up to the moment of scattering on the horizontal path, so that the signal of the correlation spectrometer has the form

$$R = \overline{\Delta\sigma}\cdot\rho\cdot\alpha^{-1} + R_0, \qquad (3)$$

where R_0 is the zero signal, which for the vertical component of the radiation illuminating the horizontal path can be obtained by sighting the instrument vertically upwards or at another, smaller angle, sufficient for the signal R to drop to R_0. For this rea-

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son, in accordance with the geometry of the experiment (Fig. 1), during the measurements based on the scattered solar radiation the horizontally polarized component is used in the correlation spectrometer to separate the component of the radiation corresponding to vertical illumination of the horizontal path.

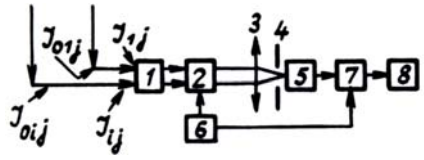

FIG. I. Block diagram of the portable, correlation spectrometer.

For this reason beams of radiation illuminating the horizontal path from the side are attenuated. They are attenuated by multiple scattering, pass over a long undetermined path in the air near the ground, and are strongly absorbed by the nitrogen dioxide. The maximum height of the horizontal path above the earth's surface is determined by the error arising in the calculation of the zero signal R_0 owing to illumination of the path from below by radiation scattered in the atmospheric air, reflected from the earth's surface, and undergoing appreciable absorption by nitrogen dioxide in the process of this downwards-upwards propagation. The error in determining R_0 can apparently be neglected for horizontal paths located at heights significantly less than the effective length of the sounding path. Otherwise, when the height of the sounding horizontal path is increased it is necessary to take into account the signal R_0, which has the form

$$R_0 = \frac{R_0^{(1)} J^{(1)}(\lambda) + R_0^{(2)} J^{(2)}(\lambda)}{J^{(1)}(\lambda) + J^{(2)}(\lambda)}, \qquad (4)$$

where $J^{(1)}(\lambda)$ and $J^{2\cdot}(\lambda)$ are the intensity of the radiation Incident on the path from above and below, respectively, and $R_0^{(1)}$ and $R_0^{(2)}$ are the corresponding zero signals, obtained in the direction of the line of sight of the correlation spectrometer upwards or downwards.

Thus for high paths $J^{(1)}$, $J^{(2)}$ and $R_0^{(2)}$ must also be measured. The accuracy of the method is limited by the spatial nonuniformity of the intensity and the spectral characteristics of the radiation illuminating different sections of the horizontal path.

The attenuation coefficient a can be calculated from an empirical formula that takes into account its relation with the experimentally obtained values of the meteorological visibility range L [km]:

$$\alpha(\lambda) = \frac{3.91}{L} \cdot \left(\frac{\lambda}{0.55}\right)^{-n}, \qquad (5)$$

where $n = 0.585\, L^{1/3}$.

Keeping in the mind the fact that the absorption band of nitrogen dioxide has a characteristic extended structure from 350 to 475 nm and the value of the spectral attenuation coefficient on the optical path is related with the wavelength by the expression (5). the method under study makes it possible to change, by regulating the position of the transmission band of the light filter 1 (Fig. 1), the effective length of the sounding path and, relating the increment to the received signal to the change in the length of the sounding path, to obtain not only the average local nitrogen dioxide concentrations along the path but also the local concentrations in a definite range of distances. Table I gives the possible ranges of the length of the sounded horizontal paths as a function of the meteorological visibility range. These ranges were obtained from the limits of the bands in the absorption spectrum of some gases. The absorption bands of the gases were chosen in the regions of the spectrum where scattered solar radiation is present in the atmosphere near the ground.

TABLE I

The effective length of the optical path of a correlation spectrometer (in kilometers) for measuring different gases as a function of the meteorological visibility range

L, km	SO_2	CS_2	HCHO	J_2 (vapors)	NO_2
	300-315	310-330	300-360	525-600	350-475
10	1.2-1.3	1.2-1.3	1.2-1.5	2.4-2.9	1.4-2.1
20	1.9-2.1	2.0-2.3	1.9-2.6	4.7-5.9	2.5-4.0
30	2.5-2.8	2.7 -3.0	2.5-3.5	7.0-9.0	3.4-5.9
50	3.5-3.9	3.7-4.3	3.5-5.1	12-15	4.8-9.3

Note. The regions of absorption of the gases studied are presented in nanometers.

If the statistical error in the measurements in about 10%, then for sulfur dioxide (SO_2) and carbon disulfide (CS_2) gases only one distance-resolved value of the local concentration can be obtained between the maximum and minimum lengths of the sounded path. For formaldehyde (HCHO), iodine vapor (I_2), and nitrogen dioxide (NO_2) from several to several tens of distance-resolve values of the local concentrations can be obtained. The new method proposed here for determining the content of gaseous pollutants in the atmosphere with a passive radiometer is in many cases a good alternative to the method of lidar horizontal sounding of the atmosphere, since it does not require the use of an optical reflector. The effective length of the sounded path α^{-1}, which for different meteorological conditions ranges from several to tens of kilometers, makes it possible with an instrument insensitivity of 5 ppm · m to measure a minimum nitrogen dioxide concentration averaged over the path from several to 0.5 ppb.

Figure 1 shows a block diagram of the portable correlation spectrometer for measuring the nitrogen dioxide content in air against the background of scattered solar radiation or from an autonomous

source of radiation. The instrument contains a light filter 1, a tunable interference-polarization filter 2, a receiving objective 3, a diaphragm 4, a photodetector 5, a generator 6, an electronic detection circuit 7, and a digital indicator 8. In a parallel beam of light, collected by the objective 3, through the diaphragm 4 at the input of the photodetector the light filter 1 separates the part of the spectrum containing the characteristic structure of the absorption band of NO_2 centered at $\lambda = 442$ nm and having a width 8 nm, while the tunable interference-polarization filter 2 periodically separates in it sections of the spectrum corresponding to the maxima and minima of absorption by NO_2. The degree of modulation of the output current of the photodetector 5, which is proportional to the total content of NO_2, is detected by the electronic detection circuit 7 and fed into the digital indicator 8.

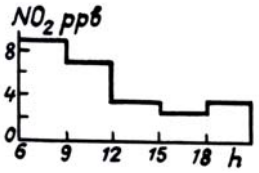

FIG. 2. The daytime behavior of the nitrogen dioxide concentration near the town of Ryl'sk

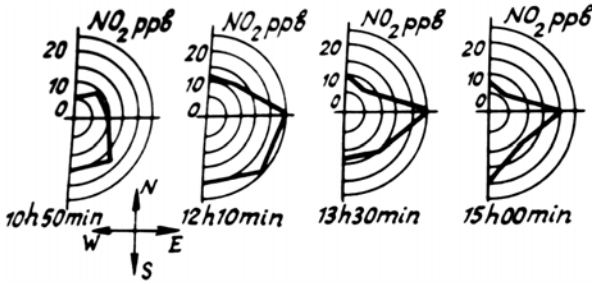

FIG. 3. The result of measurements of the nitrogen dioxide concentration as a function of the azimuthal angle in the town of Dolgoprudnyi on March 23, 1989

The generator 6 controls the tuning of the interference-polarization filter and the operation of the electronic detection circuit. The measureable range of NO_2 concentrations is 5–1000 ppm · m. The time required for a separate measurement is 3 sec, and 5 W of power at 12 V are required for operation. The mass of the instrument is 2 kg. Calibration of the instrument is performed based on an optical cell filled with nitrogen dioxide gas at a known concentration. The method described above and the spectrometer implementing it were used to measure the daytime behavior of the nitrogen dioxide content in June 1989 near the town of Ryl'sk in the Kursk Province (Fig. 2). The height of the sounded path above the ground was equal to 3 m. The results of the measurements, averaged over 7 days of observations, show a significant (by a factor of 2.5) drop in the nitrogen dioxide concentration from morning to noon. The determination of the effective length of the sounded path α^{-1} made the main contribution to the relative measurement error.

The correlation spectrometer was used to determine the NO_2 content in a vertical column of air above Moscow. On July 27, 1989 at 12 h 30 min local time the spectrometer aimed vertically was placed in an automobile moving from the center of the city to the nearest suburbs. In addition, the change in the total NO_2 content in the vertical column of air was recorded by a well-known method, described, for example, by Sandroni,[2] against the background of the scattered solar radiation. A decrease of the total NO_2 content by 40 ppm · m was clearly observed. At the start of the route in Moscow the NO_2 concentration was measured by the method described above in a horizontal plane. The effective path length was equal to about 1 km, and the NO_2 concentration in the air at a height of 80 m above the ground ranged from 60 to 80 ppb depending on the azimuth. Measurements of the nitrogen dioxide concentration as a function of the azimuthal angle were performed from a rooftop of a five story building located in Dolgoprudnyi in the northern suburb of Moscow. Figure 3 shows some results of observations in the course of the day on March 23. 1989. The effective path length, determined from the meteorological visibility range, was equal to 5 km. It can be clearly seen that the nitrogen dioxide nitrogen concentrations in the south-eastern sector of the observations, where the industrial regions of Moscow and the suburban zone are located, is 1.5 to 2 times higher than in the northern and north-eastern directions of observations.

The correlation spectrometer and the new remote method of measurement, proposed in this paper, make it possible to perform during daylight automatic continuous monitoring of the nitrogen dioxide content in air in rural and urban regions, on horizontal paths up to 10 km long. The method can be used to determine the content of other gaseous pollutants in the troposphere from vehicles moving on the ground and aircraft. The accuracy of the method is limited by the accuracy of the determination of the attenuation coefficient of radiation at the wavelength used for the measurements, the nonuniformity of the illumination of the path, and the distribution of the measured gaseous impurity along the path.

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