Results of Full-Scale Experiment on Registration of Nitrogen Dioxide Using Videospectroradiometer Gas-Viewer

A.V. Afonin[a], V.S. Davydov[a], I.N. Sivyakov[a] and A.I Rechetnicov[b]

[a] Russian Scientific Centre “Vavilov State Optical Institute”, St.-Petersburg – (Afoninav, Davidov1)@lycos.com
[b]Voyeikovo Centre for Atmosphere Remote Probing - AlexR@AR8374.spb.edu

Abstract – Here are presented the results of a full-scale experiment on the evaluation of nitrogen dioxide contents in the exhaust plumage from a heat power plant chimney based on registered data on the radiation in the NO_2 absorption spectral band at 434-448 nm using a digital videospectroradiometer gas-viewer. The information treatment technique allows the extraction of the contents of nitrogen dioxide that is not visually observable against radiation diffused by the atmosphere in the instrument viewing field of 17.8×23.2°. The results of the full-scale experiment agree with the estimations of NO_2 concentrations accepted for a heat power plant chimney exhausts, which corroborates the possibility of operative remote monitoring of the nitrogen dioxide exhausted by industrial enterprises.

Keywords: remote monitoring, nitrogen dioxide, digital videospectroradiometer.

1. INTRODUCTION

A wide-angle videospectroradiometer gas-viewer (VSR-GV) has been created for the remote control over the sources of nitrogen and sulphur dioxides exhausts in order to make it possible to visualize the picture of the spatial distribution of these gases in the surface layer of the atmosphere. Since gas clouds containing nitrogen and sulphur dioxides are normally invisible for a naked eye, their distant monitoring by means of one-channel spectrometers is difficult and does not provide a picture presenting the gas cloud movement. The VSR-GV apparatus represents a correlation two-channel instrument in which the optical isolation of the absorption spectra of NO_2 and SO_2 pollutant gases is implemented by using an interference polarizing filter (IPF) in combination with a narrow-banded interference filter (NIF) that passes the operational range of spectrum and suppresses the background radiation.

The spectral scheme of the VSR-GV and the suppression of the background radiation were dwelt on elsewhere (Afonin, 2001a,b). One channel of the instrument is tuned at the regions of strong absorption of the gas under analysis while the other is at the regions of that gas’ weak absorption. The result of applying such a registration method is that, the effects from the aerosol selectiveness are eliminated and those from other gases present are substantially reduced, especially in the region of SO_2 absorption (that is the spectral range near 300 nm), where other gases can also display absorption. Eventually, at the photodetectors’ outputs, which employ cooled CCD-matrices, two images of the detected object are generated that correspond to the regions of the maximum and the minimum transmission in the absorption bands of NO_2 and SO_2 isolated by the IPF in the specified spectral range. The present paper reports the results of a full-scale experiment on the registration of the spatial image of the exhaust plumage from a gas-working power plant chimney, therefore, only those VSR-GV parameters that relate to nitrogen dioxide will be considered further in the article.

2. PRINCIPAL

Fig. 1 presents the optical scheme of the one measuring channel of the instrument with a wide-angle IPF with a tunable spectral range of its passing band.

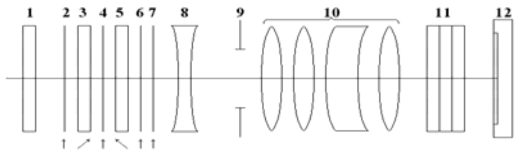

Fig. 1. Scheme of the spectral filtration channel.
1 – protective window, 2 – input polarizer, 3 – *l*/2 crystalline quartz plate, 4 – half-wave crystalline plate, 5 – *l*/2 crystalline quartz plate, 6 – quarter-wave crystalline plate, 7 – output polarizer, 8 – input telecentric objective lens, 9 – aperture diaphragm, 10 – telecentric objective lenses, 11 – NIF and colour glass filters, 12 – CCD-matrix.

The description and characteristics of the wide-angle IPF are reported (Afonin, 2004c). Each stage comprises an input and an output polarizers, (2 and 7 in Fig. 1), two crystalline quartz plates, 3 and 5 of equal 1.6 mm thickness, and crystalline phase plates, $\lambda/2$ (4) and $\lambda/4$ (6), respectively. The phase plates are made from mica slices glued between crown glass plates. The orientation of the polarizers’ passing direction with respect to that of crystallographic axes of the birefringent components is indicated in Fig. 1 by arrows. The passing directions of the input polarizer of the both channels are positioned in the vertical plane, which excludes the influence of the incident radiation polarization on the measurement results. The spectral dependence of a stage transmission is expressed by the relation

$$\tau(\lambda) \simeq Cos^2\left(\frac{2\cdot\pi\cdot l\cdot\mu}{\lambda}\right) \qquad (1)$$

Where l = the thickness of the crystalline plate
μ = the birefringence coefficient

Coefficient μ is a function of wavelength λ and temperature. A spectrum described by expression (1) shifts in the wavelength range when polarizer 7 is turning. The principal directions of the polarizers and the birefringent plates are mutually oriented in such a way that in the both channels, a clockwise turn of polarizer 7 as viewed from the side of the detector displaces the spectrum toward shorter waves. A 90° turn of polarizer 7 shifts the transmittance curve by a half-period.

In the first IPF channel one of the transmission maxima is tuned at 439.5 nm, whereas in the other one the transmission minimum is. The tuning is done at an operational temperature of the IPF unit, which is equal to ~37°C, for convenient implementation of the thermostat in order to use the instrument in the field conditions. The resultant filter mainly meets the requirements put to the formation of the VSR-GV spectral sensitivity function in a wide viewing angle 17.8×23.2°, which allows one to obtain the images of large-scale clouds of nitrogen dioxide.

In Fig. 2 are shown experimental transmittance spectra of VSR-GV channels containing IPF and NIF, which were obtained under a normal incidence of the light beam.

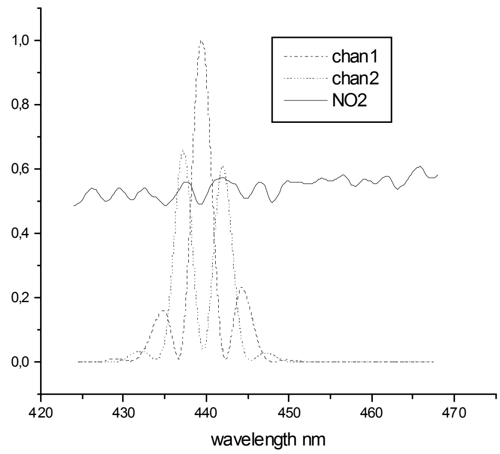

Fig. 2. Experimental transmittance spectra of the two IPF channels and of a cuvette containing NO_2.

These transmittance spectra are in good agreement with that of cuvettes containing nitrogen dioxide, which are also presented in the figure, and also with the transmittance spectra calculated for optimal filters that are reported in paper (Afonin, 2001a). The transmittance spectra of the instrument channels are normalized to channel 1 maximum transmittance.

It should be noted that the determination of gas concentration in the calibration cuvettes were carried out by an optical method that definitely took into account the transmission of the cuvettes themselves. When certifying the cuvettes with gas only the total spectral transmittances $\tau_c(\lambda)$, were measured, therefore, for the determination of NO_2 concentration a simultaneous solution of equations (2) for two wavelengths was used,

$$\tau_c(\lambda) = \tau(\lambda) \cdot \tau_g(\lambda) \qquad (2)$$

Where $\tau(\lambda)$ = nitrogen dioxide transmittance
$\tau_g(\lambda)$= transmittance of the cuvettes

The cross-sections of NO_2 absorption under standard conditions (at 298ºK) were taken from (Schneider, 1987) for wavelengths λ_1=439nm and λ_2=438nm and were, respectively, $\sigma(\lambda_1)=6.33\cdot10^{-19}cm^2mol^{-1}$ and $\sigma(\lambda_2)=4.05\cdot10^{-19}cm^2mol^{-1}$. Considering that, $\tau_g(\lambda_1)=\tau_g(\lambda_2)=\tau_g$, we obtain equations for the evaluation of gas contents in the cuvette.

$$C_{PPM} = \frac{\ln \tau_c(\lambda_2) - \ln \tau_c(\lambda_1)}{(\sigma(\lambda_1) - \sigma(\lambda_2)) \cdot N_0 \cdot 10^{-6} \cdot d} \qquad (3)$$

Where $N_0=2.69\cdot10^{19}$molecules per cm^3
d= a cuvette thickness being expressed in cm

In Table 1 are given the concentrations of nitrogen dioxide in cuvettes fabricated in the Mendeleev Research Metrology Institute (VNIIM).

Table 1. Nitrogen Dioxide Concentrations and Cuvettes' Transmittance.

Gas	Cuvette #	C_{PPM}	U (atm.cm)	τ_g	S
NO_2	1	3056	0.003057	0.65	0.07
	2	17972	0.017972	0.67	0.137

There is a known technique for the evaluation of gas exhausts based of the measurements of the spectral brightness of a plumage of nitrogen dioxide emitted from an enterprise's chimney by means of a one-channel spectrometer. The spectrometer was mounted on to a motor vehicle that was passing under the plumage cloud, and meanwhile the measurements were done in the zenithal direction in which the instrument viewer was oriented. In this case, the chimney exhaust can be estimated as

$$Q = \int_0^L \int_0^{h_0} C(l,h) \cdot V_w \cdot Cos\gamma \cdot dh \cdot dl \qquad (4)$$

Where Q = the value of the emission from a source
$C(l,h)$ = the concentration of the gas at an altitude of h and at a distance of l from the starting point of the plumage cross-section
L = the length of the vehicle drive while which the signal's exceeding the background is observed

V_w = the wind speed

h_0 = the top boundary of the pollutant gas plumage spreading area.

The angle γ, which allows us to determine the length of the vehicle drive in the direction perpendicular to that of plumage moving from the source is

$$\gamma = 90^\circ - (\beta - \alpha) \qquad (5)$$

where β = the azimuth of the wind vector

α = the azimuth of the vehicle movement.

In the case of measurements with the VSR-GV instrument the plumage was being observed against the sky background under a zenithal angle of the viewing line passing via the centre of the shot, which is 25°. Z-axis of the coordinate system OXYZ goes along the chimney whereas the observation is conducted from point P located at a distance of 350m from the chimney. The plane ZOX is perpendicular to the instrument viewing plane, which goes through the centre of the shot scene frame. The axial line of the plumage is oriented in the vertical plane where the wind vector W is also located. In Fig. 3 are presented the vectors' projections on to the horizontal plane XOY. As it was in the previously considered case, the angle γ between the normal to the viewing plane and the wind direction will be defined by formula (5), but here α is the azimuth of the vertical plane of viewing the plumage. So, the vehicle drive length L at shooting with the VSR-GV instrument means the width of the plumage in metres in the monitored vertical cross-section, which is determined by the shot of the plumage, and the value of

$$CL(l) = \int_0^{h_0} C(l,h) \cdot dh \qquad (6)$$

is equal to NO_2 contents in a unit section at a distance l from the starting point of the plumage section (in $g \cdot m^{-2}$). The latter quantity can be determined by the signal from the VSR-GV with a reference to the contents of NO_2 in the calibration cuvettes (in atm.cm).

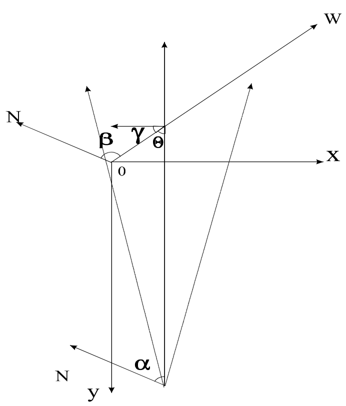

Fig. 3. Observation scheme.

In the formula (6) h_0 means the border of the plumage area in the direction of VSR-GV. Since

$$\int_0^{L} CL(l) \cdot dl = CL_{av} \cdot L \qquad (7)$$

then the equation (4) can be written as

$$Q = V_w \cdot CL_{av} \cdot L \cdot Cos\gamma \qquad (8)$$

where CL_{av} = the average gas content in a unit section (in $g \cdot m^{-2}$) determined by the vertical cross-section of the plumage.

Establishing a correlation between the gas content in a unit section expressed in $g \cdot m^{-2}$ and in atm.cm. can be done basing on the consideration of the measurement units of gas concentration. One can see that

$$CL_{av} = \frac{12.04 \cdot U_{av} \cdot M_g \cdot T_l \cdot P_0}{M_a \cdot T_0 \cdot P_l} \qquad (9)$$

Where U_{av} = the average gas content in a unit section (in atm.cm.)

M_a = the molecular masses of the air

M_g = the molecular masses of NO_2

P_l = the pressure in the gas layer column

T_l = the temperature in the gas layer column

P_0=1 atm. and T_0=293ºK.

Parameters necessary for the assessment of the gas concentration in a plumage and of the amount of exhausted NO_2 are listed in Table 2.

Table 2. Meteorological Parameters.

Wind speed, V_w, $m \cdot s^{-1}$	8
Wind vector azimuth, β, angular deg (°)	112
Vertical viewing plane azimuth, α, angular deg (°)	62
Plumage width in the direction monitored, L, m	50
Pressure, P_l, atm	0.98
Temperature, T_l, Kº	285
Molecular mass, $g \cdot mol^{-1}$ M_a M_g	 29 46

As a signal registered in the GV-VSR, a dimensionless parameter is used

$$S = S_g - S_f \qquad (10)$$

$$S_g = \frac{B_2 - B_1}{B_2} \qquad (11)$$

$$S_f = \frac{B_{2f} - B_{1f}}{B_{2f}} \qquad (12)$$

where B_1 and B_2 are the radiation brightnesses detected in the 1st and the 2nd VSR channels, respectively, in the presence of gas under monitoring and B_{1f} and B_{2f} are the respective brightnesses in the background conditions, when the pollutant gas is absent in the observation track. The background concentration of nitrogen dioxide in the atmospheric air is considerably lower than the ambient air standard and the sensitivity threshold of the instrument. It can be deemed that signal *S* is linearly correlated with the contents of the gas under analysis in the track.

Fig. 4 presents signal S_g distribution in the shot picture of a gas plumage exhausted from the heat power plant chimney, obtained on 17.09.04. As a background, an area F of clear sky was chosen. On the exhaust plumage, an area G was chosen in the middle of the shot picture. The angular size of this area amounts to 7.4°, and the distance from the viewing point to the plumage axis is 375 m, which allows the determination of the plumage width in the vertical cross-section *L* under monitoring. The magnitudes of dimensionless signals are: S_g=0.186, S_f=0.105, and S=0.081. Using the calibration data given in Table 1, coefficients for a linear calibration equation were found and the content of NO_2 was determined in a unit section of G area, which was 31 $g \cdot s^{-1}$.

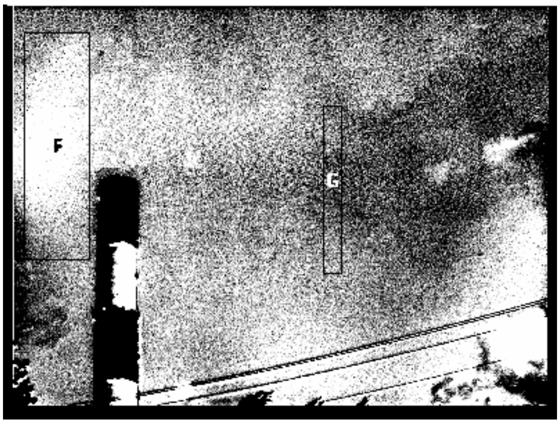

Fig. 4. Visualization of a gas exhaust.

Since the angle is γ=40° and the viewing angle is small enough, (Θ=50°, see Fig. 3), the increment of the gas concentration in the plumage cross-sections to the right is just apparent and is connected with a large increase of the track in the plumage along the VSR-GV viewing line. Besides that, one can see a strong air turbulence in the picture, which had led to the plumage rise in the upper right part of the shot picture. The detection of the space area to the right off the picture confirmed that the plumage cone due to the turbulence was going mainly up and to the side from the observer. In general, the camera angle at the shooting should be chosen close to 90°, but, in this trial case such a result was obtained because there was no possible choice of a spot for shooting.

It should be noted that at the formation of spectral brightness observed by VSR-GV both air constituent molecules and aerosol particles take part, whose diffusion indicatrices are characterised by pronounced angular dependencies. Therefore, there should be observed a dependence of spectral brightness vs. the zenithal angle of the Sun and also vs. the zenithal viewing angle of the instrument. The above angles' influence was analysed for a contrast ratio equal to signal *S* at a given NO_2 concentration of 10ppm in the atmospheric boundary layer of 200 m related to the signal corresponding to the background concentration value. Calculations have shown that utmost changes in the contrast ratio about ~25-30% are connected with the Sun zenithal angle (15-70°), whereas the dependence on the viewing zenithal angle and on the azimuth to the solar vertical plane is weak. At a variation of the Sun altitude the spectral distribution of the diffuse radiation brightness changes considerably, which requires an experimental study of the signal dependence vs. the Sun altitude during the calibration of the VSR-GV instrument using gas-containing cuvettes against sky background.

3. CONCLUSION

The results of the full-scale experiment are in agreement with accepted evaluations of nitrogen dioxide contents in heat power plant chimney exhausts, which corroborates the possibility of operative remote monitoring of nitrogen dioxide exhausts emitted by industrial enterprises.

4 ACKNOWLEDGEMENTS

The work was carried out with the support granted from ISTC Project 2274.

5. REFERENCES

[a]A.V. Afonin, V.S. Davydov, T.A. Vinogradova, V.V. Kazansky, "Spectral filtering system in videospectroradiometer gas viewers for recording NO2 and SO2 in the near-earth atmosphere", Journal of Optical Technology, vol 68, №12, p.p. 908-912, December 2001.

[b]A.V. Afonin, V.V. Kazansky, "Suppressing background radiation in spectral filtering systems in videospectroradiometer-gas viewers for recording NO2 and SO2 in the near-earth atmosphere", Journal of Optical Technology, vol 68, №12, p.p. 913-915, December 2001.

[c]A.V. Afonin, N.M. Drichko, I.N. Sivyakov, "Wide-angle interference polarizing filter for videospectroradiometer gas viewer for detecting nitrogen dioxide", Journal of Optical Technology, vol 71, №11, p.p. 776-779, November 2004.

W.C. Schneider et al, "Absorption cross-sections of NO_2 in the UV and visible region (200-700 nm) at 298K", Journal of photochemistry and photobiology, vol 140, #223, p.p. 195-217, 1987