OPTICAL ABSORPTION GAS ANALYZER FOR NITROGEN OXIDE

L.E. Khvorostovskaya, I.Yu. Potekhin, Zh.V. Pogrebnyakova, S.N. Khvorostovskii, I.P. Makarchenko, and E.V. Loginova

St. Petersburg State University, Scientific Research Institute of Physics
Received May 28, 1993

Results are considered of laboratory and field tests of an experimental model of optical absorption gauge for nitrogen oxide. Design features are described of the instrument with a selective gas discharge emitter, which is a part of a balloon complex. Measurement data are presented on the concentration of anthropogenic nitrogen oxide in the stratosphere.

The concentration of pollutants in the atmosphere is determined against the background of noticeable masking gaseous components. For this reason the development of an optical absorption gas analyzer (GA) with a selective resonant emission source, whose frequency characteristic completely coincides with the shape of the absorption band of examined substance, holds much promise. In this case the probability for frequencies of separate rotational lines in the vibrational band of emitted radiation to coincide with those of the fine structure lines of the background components does not exceed several per cent. It was demonstrated[1,2,3] that substitution of the electrically heated emitter in the optical absorption IR GA by a selective resonance gas–discharge emitter improves such characteristics of the instrument as its sensitivity and selectivity by two orders of magnitude.

The use of the gas discharge selective resonance emitters with hollow cathodes makes it possible to abandon complex dispersive optical systems and cooling systems, to reduce the overall dimensions of the instrument, to simplify its basic circuit design, and to provide a multi–component system. The authors of Refs. 3 and 4 studied the optical characteristics of a pulsed gas–discharge emitter with hollow cathode in the vibrational band of nitrogen oxide centered at 5.25 μm and identified the optimal operating conditions for an unsealed radiation source. The radiation intensity in the examined band for an unsealed radiation source remained stable to within the measurement accuracy for several months. The external surface of the emitter under optimal operating conditions remained practically at a temperature of the environment.

In the present paper we experimentally investigate the possibility of using a modified gas–discharge analyzer being developed as part of an optical absorption gauge of ambient concentration of nitrogen oxide placed on a balloon platform. We present results of preliminary testing of an experimental model together with the measurement data on the anthropogenic concentration of nitrogen oxide in the stratosphere.

To investigate the effect of variations in the ambient temperature on the operating regime of the experimental model of the gauge of nitrogen oxide concentration, we used the "Figera" heat chamber and continuously controlled the stability of output signal and discharge current of the emitter. Our test regime included the following stages: (1) lowering the temperature in the heat chamber from room to minimum (–60°C) in 2.5 h, (2) holding this minimum temperature constant for 1 h, and (3) raising the temperature to its initial value in 2.5 h in the open chamber. Such an experiment showed that the intensity of emission recorded by a pyroelectric detector in the 5.25 μm band remained constant as the temperature in the chamber was lowered to –30°C. As a result of further cooling of the chamber from –30°C to –60°C, we observed variations within 10% of the initial intensity, resulting from variations of the discharge current amplitude up to 2 mA, most probably produced by jumps in temperature in the chamber. In operation, with temperature in the chamber remaining at a stable level of –60°C, both the optical and electrical parameters of the emitter stabilized rapidly.

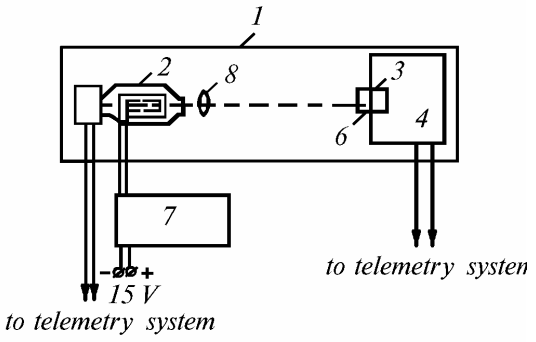

FIG. 1. Block diagram of the experimental model of gas analyzer: 1) housing of the gauge; 2) emitter; 3) pyroelectric detector; 4) amplifier; 5) zero signal control unit; 6) interference filter; 7) power supply unit of the source; and, 8) lens.

The gauge (Fig. 1) was an optical axisymmetric system enclosed in a cylindrical duralumin housing 70 cm long and 10 cm in diameter with longitudinal perforation. The gas discharge emitter was a discharge tube with coaxial electrodes and symmetrical optical windows. Supply voltage was fed to the emitter from a meander–pulse generator producing square 800 V pulses at 100 Hz frequency. During in–flight testing the generator was placed in a tight module of the balloon platform and fed from an onboard 15 V source. The working current of the emitter was 10 mA. The IR radiation flux from the gas discharge emitter passed through the column of examined gas, freely entering the irradiated volume due to circulation of the ambient air, and was recorded by the MG–30 pyroelectric detector. The optical beam path was 40 cm long. Both the focusing lenses and the optical windows of the emitter were fabricated from fluorite. The dispersive unit was an interference filter that had a band half–width of 0.05 μm and a 45% maximum

0235-6880/94/01 50-03 $02.00

transmission at a wavelength of 5.25 μm. The output signal from pyroelectric detector entered a wideband amplifier built around one channel of the K548UN1 two–channel low–noise amplifier. Another channel of the same microchip was used to build a band amplifier with peak amplification at 100 Hz frequency, corresponding to the feeding frequency of the gas discharge emitter. The band amplifier was connected in a circuit with the Wien circuitry in its negative feedback loop. The amplifier was fed from the onboard 15 V battery. Output signal from the amplifier entered the synchronous detector built around the K561KP1 chip. The reference signal from the emitter feeding circuit was fed into the converter of the reference signal level in which its amplitude increased up to 12 V. The total amplification factor of the recording system was $2.5 \cdot 10^4$. For background concentration of the nitrogen oxide in the atmosphere the output signal of the telemetry recording system was 4 mV. Its noise amplitude did not exceed ±0.5 mV. The time constant of the recording system was 30 s. To monitor the operating stability of the emitter, we measured the intensity in the 5.25 μm band directly through the back optical window of the emitter, using an interference filter, an MG–30 pyroelectric detector, and a synchronous detector, hermetically sealed to the outer surface of the window. That output signal reached 130 mV with noise amplitude of ±10 mV. The total power supplied by the gauge did not exceed 10 W at start and dropped to 7 W in operating mode. The mass of the gauge was 6 kg. Its overall dimensions were 70×12×12 cm, and that of the external power supply unit were 20×15×10 cm.

The instrument was initially calibrated under laboratory conditions against radiation absorption in a cell, the partial pressure of nitrogen oxide in that cell varying from 0.1 to 100 Torr, to an accuracy not worse than 10%. The results of measurements in the cell were compared to line–by–line calculations of the transmission function R of the gauge of the following form[5]:

$$R = \frac{\sum_{j=1}^{\infty} I_j}{\sum_{j=1}^{\infty} I_{0j}} = \frac{\sum_{j=1}^{\infty} \upsilon_{0j}^3 S_j \int_0^{\infty} F(\upsilon) \exp\left(-N S_j L\, e^{-\omega_j^2}\right) d\upsilon}{\sum_{j=1}^{\infty} \upsilon_{0j}^3 S_j}, \quad (1)$$

$$\begin{cases} I_j = \int_0^{\infty} I_j(\upsilon)\, d\upsilon \\ I_{0j} = \int_0^{\infty} I_{0j}(\upsilon)\, d\upsilon \end{cases}, \quad \omega = 2\sqrt{\ln 2}\,(\upsilon_0 - \mathrm{t})/\Delta\upsilon_d,$$

where I_j and I_{j_0} are the powers of the jth rotational line emitted by the source before and after absorption in the gas column, S_j is the line intensity,[6] $F(\mathrm{t})$ is the transmission function of the interference filter, N is the concentration of molecules of the examined gas, L is the optical length of the gas column, $\Delta\upsilon_d$ is the half–width of the Doppler profile, $\Delta\upsilon_v$ is the half–width of the Voigt profile, υ is the radiation frequency, and υ_{0j} is the frequency of the center of the jth line.

Expression (1) holds for the Doppler profiles of both the emission and absorption rotational lines (that is, when gas pressure in the cell remains low enough). For the mixed Voigt profiles of the absorption lines (i.e., when the pressure of the absorbing gas is high enough), when the emission lines still have the Doppler profiles, the transmission function is expressed as follows:

$$R = \frac{\sum_{j=1}^{\infty} I_j \exp\left(-\int_0^{\infty} K_j(\upsilon)\, d\upsilon\, L\right)}{\sum_{j=1}^{\infty} I_{0j}}, \quad (2)$$

where $K_j(\upsilon)$ is the absorption coefficient for the line described by the Voigt profile: $K_j(\upsilon) = K_{0j} \times f(a, \omega)$, K_{0j} is the maximum absorption coefficient for the line with the Doppler profile, $a = \Delta\upsilon_d/\Delta\upsilon_v$. Calculations were performed at NO pressures increasing from 0.1 to 1000 Torr, $T = 300$ and 223 K, and the column lengths 0.4 and 40 cm. To within the measurement accuracy the results of our calculations agree with measurement data and are presented in Fig. 2.

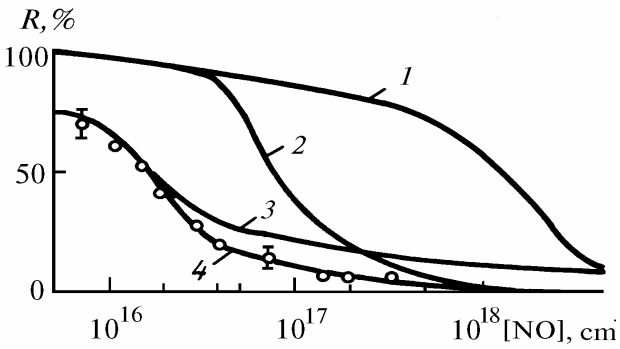

FIG. 2. Transmission function R of nitrogen oxide vs pressure of the absorbing layer at the temperature T = 223 K: 1) L = 0.4 cm, Doppler line profile; 2) L = 0.4 cm, Voigt line profile; 3) L = 40 cm, Doppler line profile; and, 4) L = 40 cm, Voigt line profile. Dots show experiment results.

Nighttime balloon field tests of the experimental model of the gas analyzer for NO were conducted in Ryl'sk within the 15–17 km altitude ranges when the balloon was descending at 5.5 km an hour at ambient temperatures around –50°C in August last year. In tests the NO concentration was artificially increased by injecting the nitrogen oxide into air at prescribed times. Each injection from a cylinder lasted 5 s. The initial and final pressures of nitrogen oxide in the cylinder were recorded (see Table I). Gas entered the working volume of the gauge through perforated housing.

The balloon platform was an open metalwork to which the sensors of the instruments were attached, the tested gas analyzer among them. The tight module for power supply sources and recording units was attached at the center of the metalwork.

Table I lists the amount of nitrogen oxide measured by the gauge and averaged over the optical path.

Since the time constant of the recording system (30 s) exceeded the injection period (5 s), the values thus obtained should be lower than the peak concentration at the instant of release of gas: it diffused rapidly through the air. To estimate the maximum concentration of NO which could be

recorded by the gauge after injection, we denote by p_1 the pressure drop of gas in the cylinder, whose volume is $V_1 = 2$ dm^3, before and after injection of NO, and by p_2 the atmospheric pressure at current flight altitude. Expanding adiabatically, the injected gas would occupy the volume $V_2 = V_1(p_1/p_2)^{1/\gamma}$, where γ is the adiabatic exponent.

Estimates indicate that after injection the injected gas formed a spherical cloud of the volume $V_2 = 20$–30 dm^3, depending on flight altitude and the serial number of injection. These volumes correspond to the NO concentration of about 10^{18} cm^{-3}, which then decreases by the law of diffusion. The telemetry system recorded the maximum concentration at 15 s intervals after the injection start. By that time the NO concentration in the cloud decreased by a factor of 10–15, i.e., to about $5 \cdot 10^{16}$ cm^{-3}, that is in good agreement with the measurement results (Table I).

TABLE I.

Injection No.	Flight altitude, km	Inject. start, s	P_{init} in cylinder, Torr	P_{fin} in cylinder, Torr	Signal in the basic channel, mV	Signal in the second channel, mV	Average concentration in the basic channel$\times 10^{16}$, cm^{-3}	Average concentration in the second channel$\times 10^{16}$, cm^{-3}
0	0.0	00	–	–	4.0	108.0	0.0	0.0
1	16.98	6880	1000	536	0.4	94.0	7.4	5.2
2	16.75	7220	536	423	1.6	100.0	2.2	2.5
3	16.21	7560	423	255	1.8	101.0	1.9	2.2
4	15.20	8220	255	220	3.0	105.0	0.5	0.65

The second channel of the gauge was originally intended to test the in–flight stability of the emitter. However, apparent relaxation of the system back to its initial signal level between NO injections practically excluded the need for additional check of the stability of operation of the gas discharge emitter. In tests the recording system of the second channel broke away from the optical window of the emitter. The design of the system made possible for that system to be displaced only along the optical axis. That displacement from the optical window reached 0.4 cm. Ambient air was freely entering the gap so that the second channel actually operated as the first, except that its optical path length differ. Since the distance between the emitter and the pyroelectric detector in that channel increase, the initial signal decreased down to 108 mV. No experimental calibration was made for this configuration; however, theoretical estimates of the transmission are given in Fig. 1. To within the measurement accuracy the results of measurements of the concentration are close to those in the main channel. The maximum error in measuring the concentration reached 50% in the first channel and 25% in the second channel.

Thus in–flight balloon tests of an experimental model of nitrogen oxide gauge have demonstrated both its concept and design are promising for further development which should be pursued to improve the measurement accuracy due to advanced element base of the gauge and shorter response time of its recording system. Tests have also indicated that the long optical path length which results in large overall dimensions of the gauge is not needed for measurements of the concentration of the anthropogenic nitrogen oxide.

REFERENCES

1. I.V. Dubashinskaya, L.E. Khvorostovskaya, and S.N. Khvorostovskii, Prib. Tekhn. Eksp. **3**, 174 (1984).
2. L.E. Khvorostovskaya, V.A. Tsvetkov, and A.I. Utyashev, Tr. Gl. Geofiz. Obs., No. 492, 82 (1982).
3. L.E. Khvorostovskaya, I.Yu. Potekhin, and S.N. Khvorostovskii, *Photochemical Processes in the Earth's Atmosphere* (Nauka, Moscow, 1990), 194 pp.
4. L.E. Khvorostovskaya, I.Yu. Potekhin, Zh.V. Pogrebnyakova, and S.N. Khvorostovskii, Zh. Prikl. Spectrosk. **53**, 711 (1990).
5. I.Yu. Potekhin, A.I. Utyashev, and L.E. Khvorostovskaya, Zh. Prikl. Spectrosk. **50**, 728 (1989).
6. Z.S. Rothman et al., Appl. Opt. **26**, No. 19, 4058 (1987).