

UV GAS ANALYZERS FOR INDUSTRIAL GASES

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Design of gas analyzers for monitoring the oxygen and water vapor in industrial gases of high purity and the nitrogen oxide in flue gases from fuel burning installations is described. The operation of gas analyzers is based on the method of differential absorption in the UV spectral range. No laser sources are used. The gas analyzers developed are efficient for continuous monitoring of gases under industrial conditions.

Monitoring of the industrial gases is of great importance for a number of technological processes. In our case, "industrial gases" means as the gases that are necessary for technology as the gases that are produced in the technological processes. The first type of gases are high-purity gases since their purity influences the quality of products to substantial degree. The second type of gases have normally complex composition. Monitoring of their components enables one to control the technological process and exhaust of dangerous gases to the atmosphere. This causes the growing interest in the development of automatic gas analyzers for continuous monitoring of the industrial gases in technological processes.

Among numerous physical and chemical methods of gas analysis the absorption method in the UV range is one of the most promising since it exhibits sufficiently high sensitivity^{1,2} and it is relatively simple.

This paper describes the design of two automatic gas analyzers for industrial gases based on the UV absorption method.

Production of semiconductor units requires high-purity gases, specifically rare gases, nitrogen, and hydrogen. The main impurities in these gases are components of the air, among them the microadmixture of oxygen and water vapor with high reaction ability being of the most importance. According to industrial requirements, the content of oxygen and water vapour in the gases used must be lower than $10^{-4}\%$. Therefore, the sensitivity of gas analysis is to be sufficiently high.

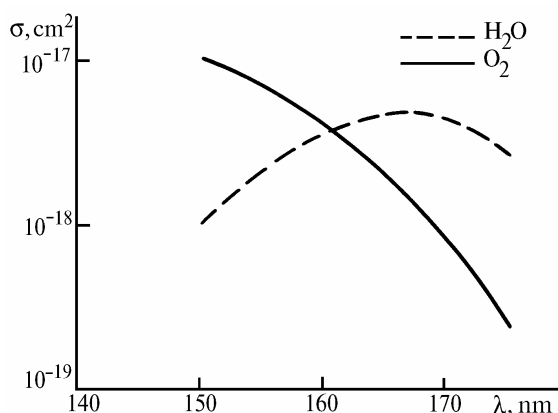


FIG. 1. Absorption cross section of O_2 and H_2O molecules in the spectral range from 150 to 175 nm.

In order to solve this problem, we have developed and manufactured a gas analyzer based on UV differential absorption method. The device operates in the spectral range from 150 to 175 nm. In this range the industrial gases are transparent whereas oxygen and water vapor absorb strongly. The absorption cross sections of O_2 and H_2O molecules³ are presented in Fig. 1. Figure 1 shows that both gases have absorption continuum but there is appreciable difference in their spectra. Hence, it is possible to calculate the concentration of O_2 and H_2O molecules using absorption data measured at several wavelength within the above mentioned spectral range.

The scheme of gas analyzer is shown in Fig. 2 where the figures denote the following: 1 – tunable UV source; 2 – gas cell; 3 – detector; 4 – control unit. The tunable UV source is a specially manufactured vacuum monochromator with gas-discharge hydrogen tube (L) inside. This tube provides both continuous and line spectrum in the range from 150 to 175 nm.⁴ The intensity ratio of these spectra depends on gas mixture filling the tube. A concave diffraction grating (R) with variable period is used as dispersive element. It is firmly mounted on the axis of a stepper. Two apertures with ~ 1 -mm wide slits are set inside the monochromator. A spherical mirror (M) directs the radiation at a separate wavelength to the MgF_2 output window. The monochromator is pumped off through a special valve. The gas cell is a cylinder (of 30-cm optical length) hermetically coupled to the output window of monochromator. It has several branch-pipes for gas replacement.

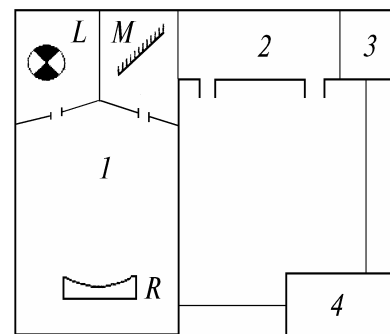


FIG. 2. Block diagram of a gas analyzer for oxygen and water vapor monitoring in rare gases, hydrogen, and nitrogen.

A photomultiplier FÉU-170 coupled to another end of the gas cell is used as UV detector. Control unit contains a microprocessor system including processor unit based on K 1801 VM2, stepper control unit, photon counter unit, and unit of conjugation with digital indicator panel and built-in key control desk. Method of electronic step splitting based on digital-analog converter is used in the stepper control unit, so the spectral step of monochromator was approximately equal to 0.4 nm. The vacuum system and power supplies for the tube and the photomultiplier are included in the control unit as well.

The gas analyzer operates in the following way. When it is switched on, the hydrogen tube lights up, the voltage is applied to photomultiplier, and previously pumped off monochromator (the residual pressure is less than $3 \cdot 10^{-3}$ Torr) is adjusted by a control code. The same ensures turning on a small size incandescent tube whose zero order spectrum is used for inspection of space position of the grating. Next, the stepper rotates the grating till the image of the tube falls on a photodiode placed inside the monochromator. Then the spectral adjustment of the monochromator is over and the incandescent tube goes out. Next, the cyclic algorithm of the control code works. First of all the gas cell is pumped off. The intensity of the radiation at different wavelengths passed through the cell I_j^0 is measured. The j index indicates the number of spectral range whose position is determined by the number of steps made by the stepper from a certain initial wavelength. Then the gas cell is filled by an industrial gas, and the radiation intensities I_j passed through the cell are measured at the same wavelengths. Calculation of the number density of oxygen $N(\text{O}_2)$ and water $N(\text{H}_2\text{O})$ molecules is carried out using the method of least squares from the system of j linear equations

$$\ln \frac{I_j^0}{I_j} = l \sigma_j(\text{O}_2) N(\text{O}_2) + l \sigma_j(\text{H}_2\text{O}) N(\text{H}_2\text{O}),$$

where l is the length of the cell; $\sigma_j(\text{O}_2)$ and $\sigma_j(\text{H}_2\text{O})$ are absorption cross sections in the j th spectral range for O_2 and H_2O , respectively. The values of O_2 and H_2O number density are indicated on the digital panel. The duration of one cycle of measurements is approximately 1 min for conventional operation mode of the gas analyzer ($j = 6$). The cycles are repeated till switching gas analyzer off. The built-in key control desk allows one to change the operation mode (changing the spectral regions or their number or reading storage time).

The operation of gas analyzer was tested for model gas mixtures with O_2 and H_2O molecule number densities within the range from $3 \cdot 10^{14}$ to $6 \cdot 10^{15} \text{ cm}^{-3}$. The results of tests are presented in Table I. The second column of the table shows O_2 and H_2O molecule concentrations in the model gas mixtures measured by Raman scattering spectrometer in the cell at a pressure of approximately 100 atm. The accuracy of the measurements is about 10%. Third column of the table represents readings taken from a gas analyzer operating in the conventional mode ($j = 6$). The central points of the spectral regions chosen as operating ones are the following: $\lambda_1 = 151.4 \text{ nm}$, $\lambda_2 = 154.7 \text{ nm}$, $\lambda_3 = 159.2 \text{ nm}$, $\lambda_4 = 162.9 \text{ nm}$, $\lambda_5 = 165.7 \text{ nm}$, $\lambda_6 = 169.8 \text{ nm}$. The following values of absorption cross section were used in the calculations³:

$$\begin{aligned} \sigma_1(\text{O}_2) &= 1.0 \cdot 10^{-17} \text{ cm}^2, & \sigma_1(\text{H}_2\text{O}) &= 1.1 \cdot 10^{-18} \text{ cm}^2, \\ \sigma_2(\text{O}_2) &= 8.3 \cdot 10^{-18} \text{ cm}^2, & \sigma_2(\text{H}_2\text{O}) &= 1.6 \cdot 10^{-18} \text{ cm}^2, \\ \sigma_3(\text{O}_2) &= 4.0 \cdot 10^{-18} \text{ cm}^2, & \sigma_3(\text{H}_2\text{O}) &= 2.6 \cdot 10^{-18} \text{ cm}^2, \\ \sigma_4(\text{O}_2) &= 2.4 \cdot 10^{-18} \text{ cm}^2, & \sigma_4(\text{H}_2\text{O}) &= 3.0 \cdot 10^{-18} \text{ cm}^2, \\ \sigma_5(\text{O}_2) &= 1.7 \cdot 10^{-18} \text{ cm}^2, & \sigma_5(\text{H}_2\text{O}) &= 3.9 \cdot 10^{-18} \text{ cm}^2, \text{ and} \\ \sigma_6(\text{O}_2) &= 0.8 \cdot 10^{-18} \text{ cm}^2, & \sigma_6(\text{H}_2\text{O}) &= 3.5 \cdot 10^{-18} \text{ cm}^2. \end{aligned}$$

The relative errors of measurements indicated in the last column of the table are somewhat overestimated since they include the errors of Raman scattering spectrometer and uncertainties in $\sigma_j(\text{O}_2)$ and $\sigma_j(\text{H}_2\text{O})$ values. The data presented in the table prove the adequate variation of the readings of gas analyzer with O_2 and H_2O concentrations. The reading fluctuations observed by the repeated measurements at the constant O_2 and H_2O concentrations and caused by short duration instabilities of the monitoring channel did not exceed 10^{14} cm^{-3} . In fact, this value indicating the lowest O_2 and H_2O molecule concentrations that can be still measured is an estimation of sensitivity of such a gas analyzer. If the industrial gas at a pressure of 10 atm is examined the sensitivity of the given gas analyzer is $\sim 3 \cdot 10^{-5}\%$.

TABLE I.

Mixture number	O_2 and H_2O number density, 10^{15} cm^{-3}	Readings of the gas analyzer, 10^{15} cm^{-3}	Relative error, %
1	$\text{O}_2 - 0.3$	$\text{O}_2 - 0.4$	33
	$\text{H}_2\text{O} - 4.9$	$\text{H}_2\text{O} - 4.4$	10
2	$\text{O}_2 - 0.9$	$\text{O}_2 - 1.1$	22
	$\text{H}_2\text{O} - 0.4$	$\text{H}_2\text{O} - 0.5$	25
3	$\text{O}_2 - 1.5$	$\text{O}_2 - 1.3$	13
	$\text{H}_2\text{O} - 3.0$	$\text{H}_2\text{O} - 3.6$	20
4	$\text{O}_2 - 2.3$	$\text{O}_2 - 2.1$	9
	$\text{H}_2\text{O} - 1.6$	$\text{H}_2\text{O} - 1.9$	19
5	$\text{O}_2 - 2.9$	$\text{O}_2 - 3.2$	10
	$\text{H}_2\text{O} - 6.2$	$\text{H}_2\text{O} - 5.8$	6
6	$\text{O}_2 - 5.6$	$\text{O}_2 - 5.4$	4
	$\text{H}_2\text{O} - 0.7$	$\text{H}_2\text{O} - 0.9$	29

Monitoring the flue gases of fuel burning installations is needed for optimization of the process of combustion as well as for ecological control. However, gas analyzers of 344 KhL-01 and 344 KhL-04 type do not ensure the long-term operation under industrial conditions.

An automatic gas analyzer was developed and manufactured for measurements of concentration of nitrogen oxide in exhaust of natural gas burning installations.^{5,6} The gas analyzer developed uses the differential absorption method. The optical fluxes at two different wavelengths passed through cell with flue gas are compared, one of them falling within absorption band of nitrogen oxide, and another one corresponding to the region of transparency. The spectral range from 225 to 230 nm is selected for operation of our gas analyzer as wide absorption band ${}^2\Pi(v=0) \rightarrow {}^2\Sigma^+(v=0) \sim 1.5 \text{ m}$ in half-width falls within this region.³ It should be pointed out that among the flue gases only nitrogen oxide absorbs at $\lambda \sim 227 \text{ nm}$. The absorption spectra of nitrogen oxide and nitrogen dioxide in the spectral range from 220 to 240 nm are presented in

Fig. 3. Since the concentration of nitrogen dioxide in the exhaust is relatively low (the ratio of NO to NO₂ concentration is about 20:1 according to measurements made by portable TESTO-33 gas analyzer manufactured in Germany) the error of our gas analyzer caused by presence of nitrogen dioxide does not exceed 2%.

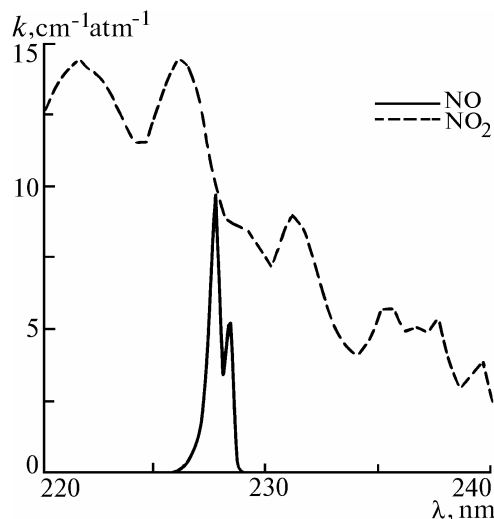


FIG. 3. Absorption coefficient of NO and NO₂ gases in the spectral range from 220 to 240 nm.

The block diagram of such a gas analyzer is shown in Fig. 4, where the figures denote the following: 1 – broadband UV source (discharge deuterium tube LD2(D)); 2 – thermostatic cell (optical length is 50 cm) with branch-pipes for input and output of the flue gas; 3 – tunable interferometric filter (the transmission band halfwidth is 2 nm, peak transmittance is 7–10%); 4 – detector of the UV radiation (photoelement F-29); 5 – control unit; 6 – key desk that is complied to control unit only for calibration and tests.

The radiation source, gas cell, filter, and photodetector are included in one unit. The control unit contains microprocessor system that is composed of a 1821VM85 based processor with memory that is independent of power supply; analog input with resolution of 16 bits; controller of filter transmission band; analog output with coupling to standard recorder for continuous data fixing, and conjugator with digital indicator panel and key desk. The control unit includes also power supplies of the tube and the photoelement.

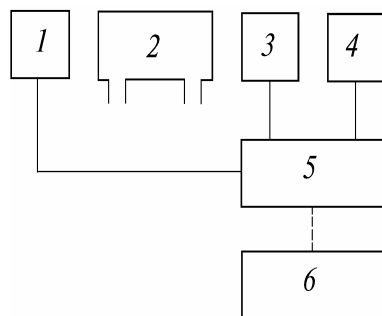


FIG. 4. Block diagram of a gas analyzer for nitrogen oxide monitoring in flue gases of fuel burning instalments.

The gas analyzer operates in the following way. When it is switched on the LD2(D) tube lights up and UV radiation is directed in the cell with flue gas. The spectral adjustment of the filter is carried out simultaneously by the control code. In doing so, the stepper rotates the filter till it holds a certain position. The cyclic algorithm is started. First, the filter is tuned to $\lambda = 227$ nm corresponding to the absorption band of nitrogen oxide (see Fig. 3). The radiation from the tube passes the cell, the filter and reaches the photoelement. The electric signal formed by the photoelement is transformed by the analog input into digital code. This signal I_1 relates to the intensity of radiation for the case when the transmission band of the filter coincides with the absorption band of nitrogen oxide. Then the filter is tuned to $\lambda = 230$ nm and I_2 signal is recorded that relates to the case when the above-mentioned bands do not superimpose each other. Based on I_1 and I_2 values the processor calculates the concentration of nitrogen oxide using the following equation:

$$N(\text{NO}) = A + B I_1 / I_2 + C (I_1 / I_2)^2 + D (I_1 / I_2)^3,$$

where A , B , C and D factors are found in the process of calibration of the gas analyzer. When calibrating the device, I_1 and I_2 values are measured at different known concentration of nitrogen oxide, and the above-mentioned factors are determined by the method of least squares. The value of NO concentration is displayed on the indicator panel and recorded by the recorder. The duration of one measurement is 4 s. The cyclic algorithm of the operation is repeated till the gas analyzer is switched off.

Industrial tests of gas analyzer of this type were carried out at Tyumen' heat and power station under conditions of round-the-clock performance. A gas analyzer was placed on a landing near the exhaust fans and the flue gas circulated through the cell of the device. The sampling system consists of porous filter for protection from mechanical particles, water cooler of KhN-1 type with hydroshutter to promote the condensate flow and consumption prompter MPR-1.

TABLE II.

Vapor productivity, tons per hour	O ₂ content, %	NO content	
		TESTO-33, ppm	Our device, ppm
208	2.5	342	310
208	1.1	256	242
188	2.6	313	302
188	1.9	227	209
188	1.4	210	202
188	1.2	207	199
Standard mixture, ppm	260±10	280	261

The reliability of readings obtained with the gas analyzer was tested in different operation modes of the boiler. For this purpose, simultaneous measurements of the concentration of nitrogen oxide in flue gas were carried out with the gas analyzer being under examination and a portable gas analyzer of TESTO-33 type. Table II presents the findings on concentration of nitrogen oxide in flue gas under variation of vapor productivity of the BKZ-210-140 boiler and of the excess of oxygen in its furnace. The content of oxygen was inspected by conventional oxygen-finder UKARSK-1. It is evident from the Table II that the values of concentration

obtained using two different gas analyzer are in agreement within 10% error. However, it should be noted that TESTO-33 gas analyzer gave higher values in all cases. The test of both gas analyzers using the standard mixture of nitrogen with nitrogen oxide produced and certified at Bakashikha oxygen plant demonstrated that the readings of TESTO-33 gas analyzer are somewhat overreaded.

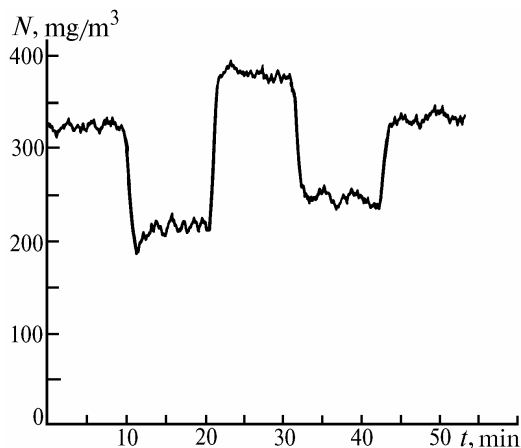


FIG. 5. Variation of NO concentration in flue gases for different boiler operation mode.

The time of reading establishment when the boiler operation mode changing was estimated for our gas analyzer as well. Figure 5 shows the variation of concentration of nitrogen oxide in exhaust gas when the boiler operation mode changing. Five operation modes are evident in Fig. 5. The error of measurement does not exceed 5% for a mode

established with the time of establishment no more than 1 min (from readings of our gas analyzer) caused by transport delay of exhaust gas.

The industrial tests of the gas analyzer were performed continuously during eight months, and they demonstrated high reliability of the device and simplicity of its maintenance. During the tests the adequate and high-rate variations of the readings of gas analyzer with change of boiler operation mode were found demonstrating the possibility to employ such gas analyzer in burning control systems.

Thus, in this paper we show that basing on UV absorption method the automatic gas analyzers can be developed. Besides high sensitivity, selectivity, and high speed of response they exhibit such important features as reliability, durability, simplicity of the maintenance, and relatively low cost. These features enable one to employ these gas analyzers for round-the-clock gas monitoring in order to control and inspect the technological processes under industrial conditions.

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