Spectrophotometric gas analyzer

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A spectrophotometric gas analyzer was developed for real-time (within about 1–60 s) measurements of CH_4, H_2O, CO_2, CO, and C_2H_2 concentrations, as well as of the total content of hydrocarbons in the air. Measurements of products of pyrolysis and burning of deciduous needles were also conducted.

Monitoring of greenhouse gases and pollutants in the atmosphere is one of the most important problems of ecology and climatology. To solve this problem, highly sensitive and reliable measurement techniques and devices are needed. Infrared spectrometers are most reliable and selective devices for gas analysis. At the same time, no small-size and easy to use spectrophotometric gas analyzers are available.

We have developed a spectrophotometric gas analyzer for determining the content of greenhouse gases in atmospheric air from their absorption spectra in the IR region, as well as for real-time qualitative and quantitative analysis and dynamic monitoring of the concentration of gas components in technological cycles.

Gas analyzer

The gas analyzer is a rapid-scanning IR spectrophotometer with a computerized recording and processing of a spectral signal. The photo of the spectrophotometric gas analyzer is shown in Fig. 1.

The recorded absorption spectrum is compared with the absorption spectra of reference samples, which are stored in a computer database. The design of the gas analyzer is simplified to a maximum degree; mechanic instabilities are followed up and taken into account at computerized recording of signals. The general functional block-diagram of the gas analyzer is shown in Fig. 2. For our device, we took the Ebert optical arrangement: lighter L, spherical mirrors M, diffraction grating DG, photodetector Ph, optical slits S.

As known, in the linear case, the absorption of optical radiation by matter is described by the Beer–Lambert–Bouguer law:

$$I(\lambda) = I_0(\lambda) \exp[-K(\lambda)L] = I_0(\lambda) \exp[-\sigma(\lambda)\, nL], \quad (1)$$

which relates the radiation intensity $I(\lambda)$ (where λ is the radiation wavelength) at the exit from an absorbing medium of length L to the spectral absorption coefficient $K(\lambda)$ with the intensity of radiation incident on the medium being $I_0(\lambda)$. The values of $I(\lambda)$ and $I_0(\lambda)$ can be found from experimental data, and after that $\sigma(\lambda)$ can be determined from Eq. (1) and the gas concentration n can be found provided that absorption cross section $\sigma(\lambda)$ is known.

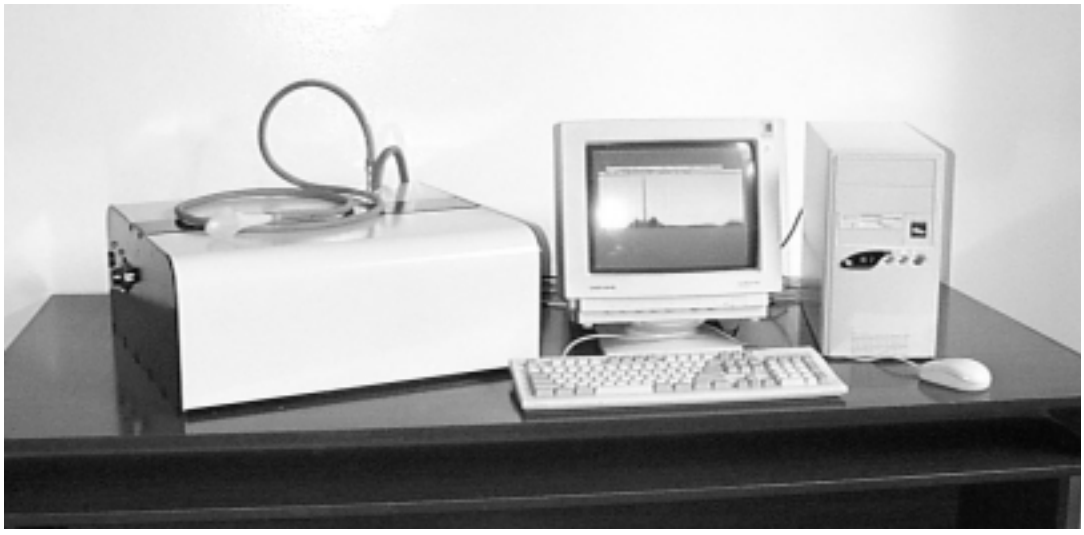

Fig. 1. Spectrophotometric gas analyzer.

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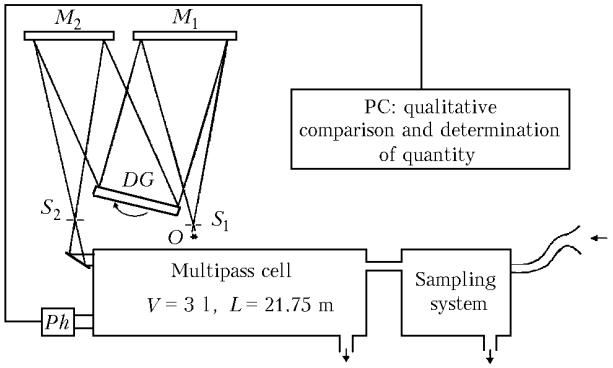

Fig. 2. Functional layout of the spectrophotometric gas analyzer.

This spectrophotometer differs from typical diffraction spectrometers by a rapid control of the diffraction grating rotation and by that a computer is used to correct the spectra obtained. Rotating in the dispersion plane, the grating sequentially tunes radiation within the entire spectral region, however the computer records the data only from the spectral region determined by sensors that are a part of the synchronization unit. Unwanted superposition of the diffraction orders is eliminated with a filter. The synchronization unit serves for generation of signals synchronizing spectral scanning and the sync pulse of a reference signal. Its components are magnetosensitive sensors and a magnet attached to the turntable the grating is placed at.

In the course of measurements, the output signal and the sync pulse come to the computer through the interface including an ADC (analog-to-digital converter). The computer first digitizes the signal, then processes the spectrum using specially developed software, and analyzes it after averaging over 50–1000 realizations of the spectrum.

The spectral range $\Delta\lambda$ of the gas analyzer is 1000–4500 nm, scanning and processing of one realization of the spectrum take 0.5 – 1 s, the photometric sensitivity in transmittance is about $5 \cdot 10^{-7}$ (at L = 2175 cm and 1000 realizations of the spectrum), and the spectral resolution is 10 cm^{-1}.

Computer is a necessary element of the gas analyzer. It performs correction of the rate of spectrum scanning and other unsteady changes in the spectrum at multiple recording of the same spectrum. Statistical processing of the computer-corrected spectra provides for a significant increase in the signal-to-noise ratio. For example, if the signal-to-noise ratio is 100–200 at single recording, then the analyzer noise decreases 10 times at accumulation of 100 spectra, 33 times at accumulation of 1000 spectra, and so on. Besides, the computer recognizes recorded spectra. For this purpose, a database, which also is a part of the gas analyzer, stores absorption spectra of the initial substances, and computer makes the needed operations with the spectra (addition, subtraction, division of spectra, calculating the first, second, etc., derivatives of a spectrum, self-tuning of the frequency scale by reference spectra, etc.).

Differences in spectra of actual multicomponent mixtures do not allow unambiguous determination of the component concentrations and, consequently, parameters of multicomponent mixtures with the use of ordinary regression methods of analysis. Therefore, tools for processing the initial spectral curves aimed at extracting maximum information from them should be combined with the methods of serious logical analysis, including methods of cybernetics and pattern recognition theory, since the problem of interpretation of spectral curves is very much alike the problem of pattern (image) analysis. Therefore, for qualitative and quantitative analysis of hydrocarbons, we applied a new method consisting in mathematical processing of spectral data by the methods of mathematical statistics in combination with the methods of the pattern recognition theory,[1] whose application allows correct analysis of multidimensional data, i.e., extracting maximum possible information from the spectrum analyzed, thus decreasing noise, increasing repeatability of measurements, and so on.

The practical use of this approach significantly improves the sensitivity of spectroscopic devices applied and makes them suitable for various studies: from measurement of concentrations of minor atmospheric constituents to determination of the type of an analyzed substance and various parameters of multicomponent mixtures.

The gas composition of air is analyzed after preparing the database. To determine the concentration of gas components in air, we have developed the technique, algorithms, and computer programs especially for this device.

Experimental results and analysis

1. Although the strongest absorption bands of molecules lie in the mid-infrared region from 3 to 20 μm, the region from 1 to 4 μm also contains some strong fundamental and overtone bands of the greenhouse gases. The centers of the strongest bands, their intensities, as well as gas concentrations are given in Table 1.

Table 1

Molecule	Concentration, ppm (Ref. 2)	Band	Band center	Intensity, cm/mol
1	2	3	4	5
H_2O	3000	100–000	3657.05	$4.95 \cdot 10^{-19}$
		020	3151.63	$7.6 \cdot 10^{-20}$
		001	3755.93	$7.2 \cdot 10^{-18}$
		011	5331.27	$8.04 \cdot 10^{-19}$
		101	7249.81	$5.63 \cdot 10^{-19}$

Table 1 (continued)

1	2	3	4	5
CO		1–0	2143.27	$1.0 \cdot 10^{-17}$
		2–0	4260.06	$7.8 \cdot 10^{-20}$
CO_2	345	02211	3612.84	$1.0 \cdot 10^{-18}$
		10012–00001	3714.78	$1.5 \cdot 10^{-18}$
		20011	4853.62	$8.0 \cdot 10^{-21}$
		20012	4977.83	$3.4 \cdot 10^{-20}$
		20011	5099.66	$1.1 \cdot 10^{-17}$
		11111–01101	3723.25	$1.2 \cdot 10^{-19}$
		00011–00001	2349.14	$9.1 \cdot 10^{-17}$
CH_4	1.7	00011001	3018.92	$1.0 \cdot 10^{-17}$
		02200002	3062.00	$3.4 \cdot 10^{-20}$
		10000111	4223.50	$2.4 \cdot 10^{-19}$
		00011112	4340.00	$4.1 \cdot 10^{-19}$
		01111002	4540.00	$6.2 \cdot 10^{-20}$
		00022002	6004.99	$4.1 \cdot 10^{-20}$
C_2H_2	1	01011110	3281.90	$5.0 \cdot 10^{-18}$
		00100000	3294.84	$4.4 \cdot 10^{-18}$
N_2O	0.3	1001	3480.32	$1.7 \cdot 10^{-18}$
		2000	2563.34	$1.2 \cdot 10^{-18}$
		2110–0110	2577.09	$1.2 \cdot 10^{-19}$
		1111–0110	3473.21	$1.9 \cdot 10^{-19}$
O_3	0.1^{-10}	101	2110.78	$1.2 \cdot 10^{-18}$
		003	3046.09	$1.3 \cdot 10^{-19}$
		103	4021.85	$1.4 \cdot 10^{-20}$
$CFCl_3$	$0.22 \cdot 10^{-3}$		800	
			1100	
			1750	
			2150	
CF_2Cl_2	$0.36 \cdot 10^{-3}$		900	
			1100	
			2200	

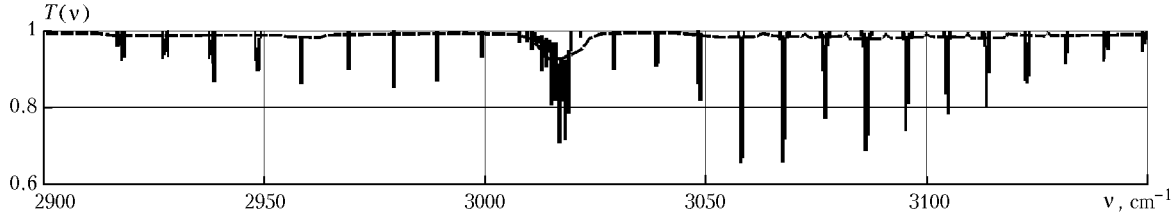

Fig. 3. Fragment of the spectrum of atmospheric air with CH_4 lines: high (——) and low (- - - -) spectral resolution.

The gas methane, CH_4, has a strong ν_3 absorption band with the integral intensity of $1.0 \cdot 10^{-17}$ cm/mol. Figure 3 shows a fragment of the CH_4 spectrum in the region of the ν_3 band near 3 μm with high (~ 0.01 cm^{-1}) and low (10 cm^{-1}) spectral resolution with the apparently seen *R*-, *P*-, and *Q*-branches. The path length was 21.75 m, and the gas concentration was 1 ppm. The *R*- and *P*-branches consist of groups of isolated lines and have a long spectral length ~200 cm^{-1}, whereas the *Q*-branch is a dense group of unresolved lines occupying the range about 10 cm^{-1}. The maximum dips in the transmission function achieve 3049 at the resolution of 0.01 cm^{-1}. At the resolution of 10 cm^{-1}, due to convolution of the methane transmission function features with a triangular instrumental function of the gas analyzer having the halfwidth of 10 cm^{-1}, the dip depth in the region of the *Q*-branch decreases by three times, whereas the dips in the regions of the *R*- and *P*-branches decrease by 10 to 20 times. Consequently, to record CH_4 with low resolution at the same concentration, the path should be three times longer when using analytical lines of the *Q*-branch and 10 – 20 times longer when using the lines of the *R*- and *P*-branches.

The absorption spectrum of atmospheric air was recorded in the region from 1.5–4 μm. As a "background" signal, we took the spectrum of radiation emitted by a halogen lamp and passed through a cell filled with pure nitrogen (Fig. 4). The absorption spectrum of atmospheric air in the region of 3 μm is determined mostly by water vapor. In dried air, the pattern is different – absorption is determined by methane, whose concentration in the atmosphere is ~1.7 ppm (background content of methane in the Earth's atmosphere).

As experiments showed, the gas analyzer can reliably record (for 1–5 min) the main greenhouse gases (H_2O, CO_2, CO, etc.), methane at the level of 0.3–0.5 ppm

(background content of methane in the atmosphere is 1.7 ppm), acetylene (C_2H_2) at the level of 0.5–1 ppm, and the total content of volatile fractions of light hydrocarbons at the level of 1–2 ppm.

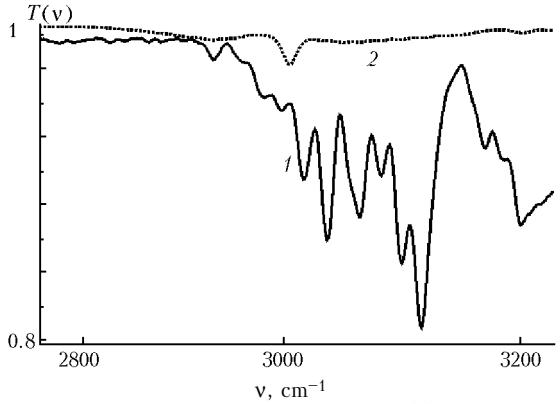

Fig. 4. Absorption spectrum of non-dried (*1*) and dried (*2*) atmospheric air in the region of 3 μm.

2. High sensitivity and high speed of measurements allow simultaneous determination of concentrations of several gases. Therefore, the gas analyzer can be efficiently used to study and monitor products of pyrolysis and burning of forest materials.

The gas analyzer was used for recording the spectra of products of burning of deciduous needles with the water content of 1%. Five 0.4-kg heavy needle samples were burned with the interval of 30 min and gas was sampled from a flame at different height levels. All experiments were conducted within the framework of physical simulation of ground forest fires in the UNLP-2 laboratory setup placed in a Big Aerosol Chamber (BAC) of the Institute of Atmospheric Optics SB RAS. Experiments in the chamber with the volume of 1800 m^3 were conducted under the following conditions: temperature of 19°C, humidity of 60%, and low natural ventilation through an outlet pipe in the upper part of the chamber. The length of optical path in the analyzer cell was chosen to be $L = 825$ cm at five passages inside the cell [$L = (2 + 4N) \cdot 37.5$], and the spectral region used was from 1900–3800 nm. The background signal from the light source $I_0(\lambda)$ was recorded in the nitrogen atmosphere. All the measurements conducted used summing of 100 individual spectra. The absorption spectra in the IR region chosen are mostly determined by water vapor, CO_2, CO, CH_4, and a set of unidentified hydrocarbons both in the upper part of flame – above the glowing zone (region 1) and in the lower part, in the immediate proximity to the flame front – 1–2 cm above the needle layer (region 2).

Figure 5 shows two fragments of absorption spectra for burning products of pine needles at gas sampling from the regions 1 and 2.

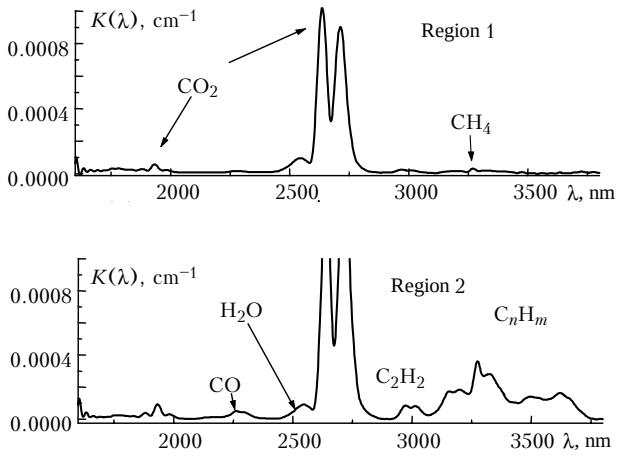

Fig. 5. Fragments of spectra of burning products of deciduous needles in regions 1 and 2.

Table 2 gives the maximum permissible concentration (MPC) and detection limits (DL) for gases analyzed in the experiment along with the measurement error S in gas concentrations.

The quantitative analysis of needle burning products was conducted in the gas samples taken from the regions 1 and 2. Table 3 gives the data on gas concentrations (mg/m^3 = 0.044μ ppm, μ is a molecular weight of a gas).

The experimental technique provided for measurement of the background content of H_2O, CO_2, CO, CH_4, C_2H_2, and C_nH_m vapor in the BAC for the entire measurement cycle. Measurements were conducted after complete burning of each of five needle samples.

Figure 6 depicts the plots of variation of the background concentration of gases in the BAC at sequential burning of five 0.4-kg heavy samples of pine needles.

The numbers of the burned samples are plotted along the ordinate, and the abscissa presents gas concentrations in ppm; Sd is the root-mean-square deviation in ppm, and k is the mean concentration growth in ppm at burning of one sample.

Table 2. Maximum permissible concentrations (MPC) and detection limits (DL) of gases

Parameter	H_2O	CO_2	CO	CH_4	C_2H_2	ΣC_nH_m
MPC, mg/m^3	–	5000–9000	10–15	300	500	300
DT, mg/m^3	50	20	7	2	4	3
Measurement range	10–30000	15–10000	4–700	1–500	20–900	4–3000
S, %	40	15	5	10	20	25

Table 3. Qualitative and quantitative composition of burning products

Region	H_2O*	CO_2	CO	CH_4	C_2H_2	ΣC_nH_m
	Concentration, ppm					
1	19150	6660	110	49	4	73
2	20550	6750	576	384	85	625

* For H_2O, the measurement range is limited from the above by the temperature (dew point) of a sampler.

The composition of gas mixtures in BAC during the experiments is indicative of marked emission of harmful chemical substances at burning of forest materials. Experiment showed that the use of IR spectrophotometers opens up the possibility of obtaining additional information on the quantitative composition of gaseous media at monitoring of the products of pyrolysis and burning of forest combustible materials.

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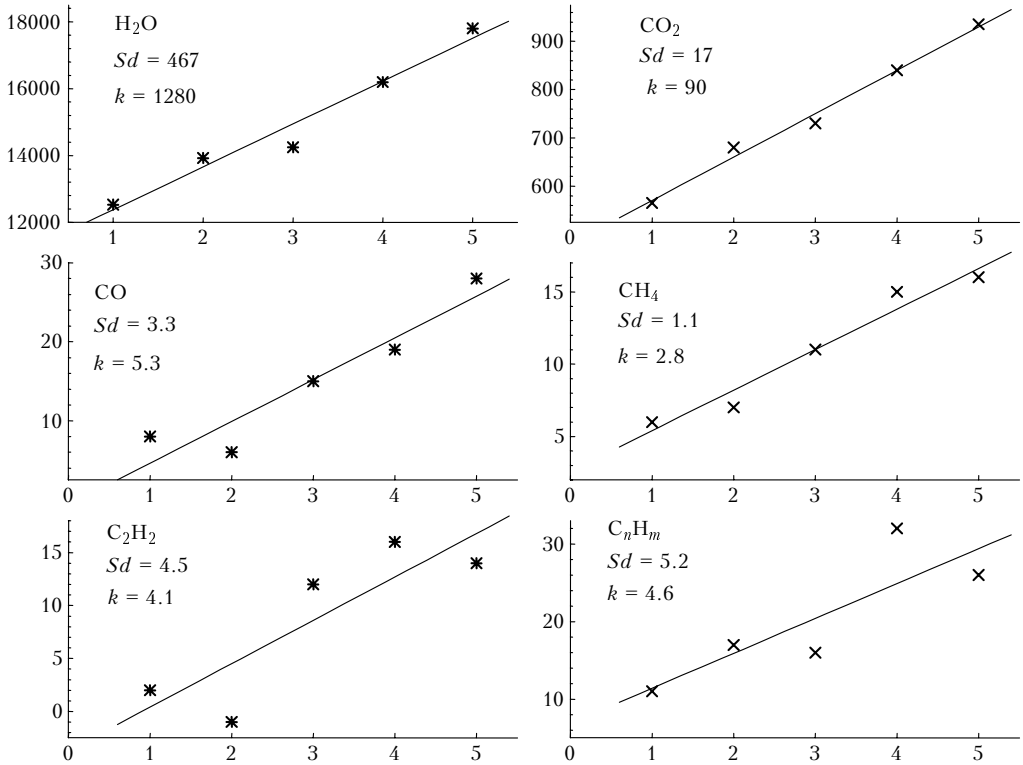

Fig. 6. Dependence of the concentration of burning products in the BAC on the number of weighted samples of pine needles burned.

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