

MULTICOMPONENT GAS ANALYZER BASED ON DIODE LASERS FOR MONITORING OF GASEOUS POLLUTANTS IN THE OPEN ATMOSPHERE

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A multicomponent gas analyzer based on tunable diode lasers operating in the middle infrared is described. The analyzer is designed to detect trace concentrations of some gaseous pollutants in the open atmosphere. The open-path optical arrangement with a corner cube retroreflector is used. The diode lasers are based on the A4B6 semiconductor compounds fabricated using both the methods of molecular beam epitaxy and by the diffusion technology. The gas analyzer has been tested by measuring trace concentrations of CO, NH₃, and C₂H₄ in the atmosphere. The following concentration sensitivities were achieved: 10 ppb for CO, 2 ppb for NH₃, and 2 ppb for C₂H₄.

1. INTRODUCTION

The easy controllable electronically lasing frequency and a wide spectral range of tunable diode lasers (TDLs) operation are among the basic factors attracting attention to the development of such application as gas analysis using TDLs.¹⁻³ In the monitoring of gaseous substances, diode lasers occupy specific area of detecting quite simple and light molecules in various gas mixtures, including the atmosphere. The TDL-based detection techniques successfully compete with the traditional analytical methods because of their high performance characteristics such as sensitivity, selectivity, and fast recording rate.

High concentration sensitivity of TDLs is caused by high spectral brightness of laser radiation, by the possibility of choosing optimal analytical spectral regions in a wide range from 0.7 to 20 μm , and, third, by the possibility of using fast modulation of the lasing frequency using electronic methods.

The monochromaticity of TDL's radiation combined with the continuously controlled frequency tuning over a sufficiently wide spectral range allows recording of the fine rotational-vibrational structure of molecular absorption spectra to be performed. The resolution of such recording is limited by the collisional broadening of spectral lines. As a result, high selectivity of the analysis is achieved, what is important for detection of trace concentrations in gas mixtures.

At present, multicomponent gas analyzers are designed to incorporate several TDLs in a single device thus providing for several spectral channels to be operated simultaneously. Every spectral channel in this case uses separate laser tuned to detect one or two gases. Such an integration is needed for complex multicomponent measurements needed to solve most of the today's analytical problems.

This work was aimed at construction of three-component gas analyzer based on TDLs for detecting gaseous pollutants in the open atmosphere. The list of molecules to be detected with such a gas analyzer is dictated by current needs of the atmospheric pollution monitoring near oil and gas fields in the West Siberia. This list includes carbon monoxide (q_n), ammonia (NH_3), and ethylene (q_{2m_4}). Ethylene may be replaced with methane (q_{m_4}) if necessary.

2. SELECTION OF THE SPECTRAL RANGES FOR DETECTION

The natural background concentration of q_n in the atmosphere is $\sim 130\text{--}150$ ppb. This value is caused by photochemical processes in the atmosphere, as well as metabolism of plants, animals, and soil bacteria.^{4,5} Anthropogenic sources, associated mostly with the combustion processes, may change the relative q_n content in the urban atmosphere or in the atmosphere of an industrial zone from 0.2 to 20 ppm. The daily mean maximum permissible concentration (MPC) of q_n is 3 mg/m^3 (2.3 ppm) (Ref. 6).

For detecting q_n in this range of concentrations, the fundamental rovibrational 1-0 band has been chosen. This band lies in the spectral range about $4.7 \mu\text{m}$. q_n spectral lines of both branches from this band with the quantum number J varying from 2 to 15 have the integral intensity from $\sim 1.6 \cdot 10^{-19}$ to $\sim 4.4 \cdot 10^{-19} \text{ cm} \cdot \text{mol}^{-1}$ and the coefficient of air collisional broadening from 0.056 to $0.088 \text{ cm}^{-1} \cdot \text{atm}^{-1}$ (Ref. 7). As a result, the concentration sensitivity to q_n is over 5 ppb ($6.25 \mu\text{g/m}^3$) under normal atmospheric conditions with the path length of $\sim 200 \text{ m}$ and the signal-to-noise ratio in the optical channel about $5 \cdot 10^3$. The main factor, which limits the use of some q_n absorption lines, is the interference, i.e., very close proximity to or

overlapping with H_2n and qn_2 absorption lines. To avoid the interference, our preference was given to the $R(5)$ – $R(10)$ lines of the R -branch, which lie in the range from 2164 to 2184 cm^{-1} .

The natural background concentration of NH_3 in the atmosphere is very low (less than 100 ppt). Among the anthropogenic sources of NH_3 there are chemical plants, oil production and refining plants, and agriculture. The required concentration sensitivity and dynamic range for detecting ammonia are determined by the value of daily mean MPC, which is 40 $\mu g/m^3$ (Ref. 6).

For detection of NH_3 , we have chosen the fundamental rovibrational band v_2 with the center near 10.5 μm . The absorption lines in this band have integral intensity of $\sim 4 \cdot 10^{-19}$ $cm \cdot mol^{-1}$, which provides for the sensitivity to NH_3 at the level of ~ 1 ppb (0.76 $\mu g/m^3$). The v_2 band of NH_3 strongly interferes with the spectral bands of some molecules, which may present in the industrial or urban atmosphere. That is why we have chosen the several multiplets of the R -branches of NH_3 absorption spectrum: $aR(4)$, $sR(4)$, $sR(6)$, and $sR(7)$, which lie near 1033, 1065, 1103, and 1122 cm^{-1} , respectively.⁷ Their fine structure is not resolved at the atmospheric pressure because of collisional broadening. The use of these multiplets for NH_3 detection provides for the sensitivity of ~ 0.5 ppb (~ 0.4 $\mu g/m^3$) under normal conditions and the above-indicated parameters of recording.

The natural background methane concentration in the atmosphere is ~ 1.3 ppm (Ref. 8). The anthropogenic component is caused by methane leakage from gas pipelines and generation of biological gas in rotting processes. It may reach several tens of ppm. The maximum permissible concentration for methane is not established. The sensitivity at the level of 50 ppb, i.e. 0.035 mg/m^3 , is sufficient for detecting both natural concentrations and variations in the anthropogenic component.

For qm_4 detection in the concentration range required, the fundamental rovibrational band v_4 with the center at 7.8 μm has been chosen. In order to operate in the same dynamic range determined by the electronic system in use, we used weak qm_4 absorption lines from the P -branch. The lines with large values of the quantum number J , having the intensity below 10^{-21} $cm \cdot mol^{-1}$, were selected. Besides, these lines lying near ~ 1220 cm^{-1} are situated far from the lines of intense absorption by water vapor.⁷

The presence of qm_4 in the atmosphere is due to anthropogenic activity. It is caused by leakage at oil production and chemical plants. The daily mean MPC for qm_4 is 3 mg/m^3 (Ref. 6). The sensitivity of the gas analyzer must be sufficient to provide for minimum detectable concentration of qm_4 in the atmosphere at the level of 30 $\mu g/m^3$.

The analytical spectral range, optimal for qm_4 detection, has been selected on the basis of previous model calculations of its spectrum in the middle

infrared range. The preference was given to the v_7 fundamental rovibrational band with the center near 10.5 μm . Spectral lines in this band have the integral intensity up to $1.3 \cdot 10^{-18}$ $cm \cdot mol^{-1}$. The chosen v_7 band strongly interferes with the absorption spectra of other atmospheric gases. That is why the particular attention has been paid to selecting individual analytical lines. The use of any qm_4 spectral line with the mean intensity of $\sim 2 \cdot 10^{-20}$ $cm \cdot mol^{-1}$ in the spectral range near 9.5 μm provides for the required sensitivity, what allows an easy choice of a suitable laser diode.

3. LASERS

The TDLs based on A4B6 compounds were used as sources of frequency-tunable IR radiation. The TDLs used were fabricated using the methods of molecular beam epitaxy⁹ and the diffusion technology. The main characteristics of the tunable Pb-salt-based diode lasers are presented below.

The feasible operation spectral range, μm	3–20
	(3300–500 cm^{-1})
Typical relative width of a lasing line, cm^{-1}	10^{-4}
Frequency tuning range, cm^{-1}	50–100
Continuous tuning range within a mode, cm^{-1}	0.5–3.0
Distance between modes, cm^{-1}	1–3
Threshold current, A	0.5–2
Current tuning, cm^{-1}/A	< 70
Tuning rate (during a pulse), cm^{-1}/s	50– 10^4
Output power (integral), mW	0.3–1.0
Power per mode, mW	0.1–0.5
Operating temperature, K	4–140

At a fixed temperature, the lasing spectral range is determined by the chemical composition of a working compound. Fine frequency tuning of lasing and tuning to an analytical absorption band of a gas under study are performed by smoothly changing temperature of a laser crystal and by varying parameters of the current pumping. If pulsed current pumping is used, such parameters as amplitude, duration, repetition frequency, and shape of current pulses are being varied, as well as the zero level bias. Laser heating during a single pump pulse results in a periodical piecewise continuous tuning of the radiation wavelength. The spectral length of a lasing mode, alternated by a silence gaps, is from 0.5 to 3 cm^{-1} . That type of the frequency sweeping of TDL radiation, when propagated through a gas medium under study, leads to the envelope of a laser pulse that contains information on the medium transmission spectrum. The accuracy with which the lasing spectrum is reproduced from pulse to pulse and, thus, the accuracy of the recorded transmission spectrum depends on the accuracy of maintenance of the laser crystal temperature as well as on the parameters of pump current.

To measure concentration of a particular gas, a separate laser was used, which was previously selected by the lasing wavelength. The Table I presents the

types of lasers and the spectral ranges for every molecular species under study.

TABLE I. Spectral ranges and types of laser used for monitoring

Molecule	Spectral range, cm^{-1}	Type of a TDL
CO	2164–2184	PbSSe Diffusion
NH ₃	1033; 1065 1103; 1122	PbSeSn l be
CH ₄	1210–1230	the same
C ₂ H ₄	1030–1080	the same

4. OPTICAL ARRANGEMENT OF THE MULTICOMPONENT GAS ANALYZER

As a basis for optical arrangement of the multicomponent gas analyzer, we took the Cassegrainian telescope, as it was earlier done for a qn analyzer.¹⁰ The telescope optical axis was the main optical axis of the gas analyzer (Fig. 1). A cryostat filled with liquid nitrogen, containing the lasers and photodetectors, was set behind the primary mirror of the telescope. The transmitting and receiving channels were separated in height owing to the use of a periscope. The corner-cube retroreflector has been used to form an open optical path in the atmosphere.

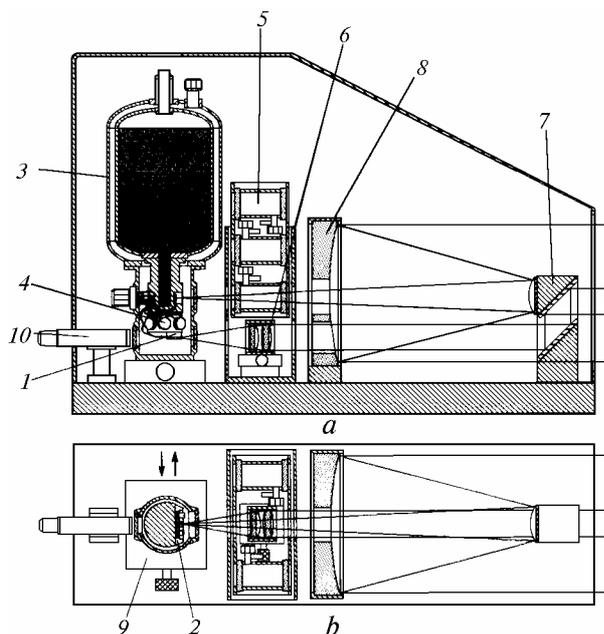


FIG. 1. Optical arrangement of the multicomponent gas analyzer based on TDLs: side view (a), top view (b); diode lasers (1); photodetectors (2); cryostat with liquid nitrogen (3); system for thermostabilization (4); turret with reference cells (5); collimating objective lens (6); periscope (7); primary mirror of the Cassegrainian telescope (8); unit for switching between channels (9); sighting device (10).

In the emitting channel, the set of three lasers (each for one gaseous component under study) was set opposite the cryostat window along the horizontal axis normal to the main optical axis of the analyzer. The output laser beam was collimated with an objective lens made from BaF₂. Then the periscope directed the laser beam to the atmospheric path. The set of three photodetectors was correspondingly set opposite the entrance window of the cryostat. Each photodetector records the radiation of the corresponding spectral channel. A cryostat can be moved in the horizontal direction along the laser positions. This movement was performed with the precise electronically controlled mechanism. In such a way, the lasers and the corresponding photodetectors were aligned with the main optical axis in turn. Thus, the analyzer was switched from one frequency channel to another.

The parameters of the receiving channel were selected such, that the aperture (60 mm) of the corner-cube retroreflector installed at a distance of 100 m corresponded to the size of the photodetectors. In the channels for radiation with the wavelength from 7 to 10 μm , CdHgTe photodetectors with the photosensitive area of $1 \times 1 \text{ mm}$ were used. In the CO channel, the InSb photodetector was used, whose photosensitive zone had the diameter $d = 2 \text{ mm}$.

The optical arrangement of the analyzer also included the turret with three reference cells 50 mm long. The cells were filled with the gases under study. They served for calibration of the gas analyzer. To point the analyzer at the retroreflector, the sighting device set behind the cryostat was used.

5. RECORDING OF SPECTRA, ESTIMATION OF GAS CONCENTRATIONS, AND METROLOGY

Once the analyzer has been pointed at the retroreflector, the envelope of a laser pulse was recorded in one spectral channel. This envelope contains the transmission spectrum of the atmospheric air, including the gas under study. The analyzer was tuned to an analytical absorption line, optimal for recording, by varying the temperature at the cryostat cold exchanger and the pump current. The cryostat temperature needed for each laser was adjusted as the analyzer was switched to a given channel. Then it was maintained automatically by the thermal control system accurate to $\sim 10^{-2} \text{ K}$. The position of a chosen analytical line inside a laser pulse was set by the correspondingly chosen parameters of the pump pulse. The particular attention has been paid to preventing occasional overlap of the analytical line with the weak absorption lines of water vapor or carbon dioxide. The characteristic time shapes of laser pulses propagated through different gases are shown in Fig. 2 along with the absorption lines used.

The Bouguer law was used to estimate the concentration of the gas under study from the recorded transmission spectra. According to this law, the gas concentration q can be found as

$$q = \{-\ln [A_0(\nu_0)/A(\nu_0)]\} / \{K(\nu_0) L\},$$

where $A(\nu_0)$ is the signal from a photodetector at the center of an analytical line; $A_0(\nu_0)$ is the signal corresponding to zero absorption; $K(\nu_0)$ is the gas absorption coefficient at the maximum resonance absorption; L is the path length.

The algorithm for estimation of the concentration of a gas under study consisted of the following steps: (1) recording of the shape of a laser pulse passed through the atmosphere; (2) calculation, by the

approximation methods, of the envelope simulating the absence of resonance absorption by the gas under study in the atmosphere; (3) identification of the analytical line used and determination of its parameters using tabulated or calculated data; (4) recording of the optical zero with the help of a reference cell giving the saturated absorption for making corrections to $A_0(\nu_0)$ and $A(\nu_0)$; (5) measurement of the path length in the atmosphere; (6) calculation of the concentration by the above expression.

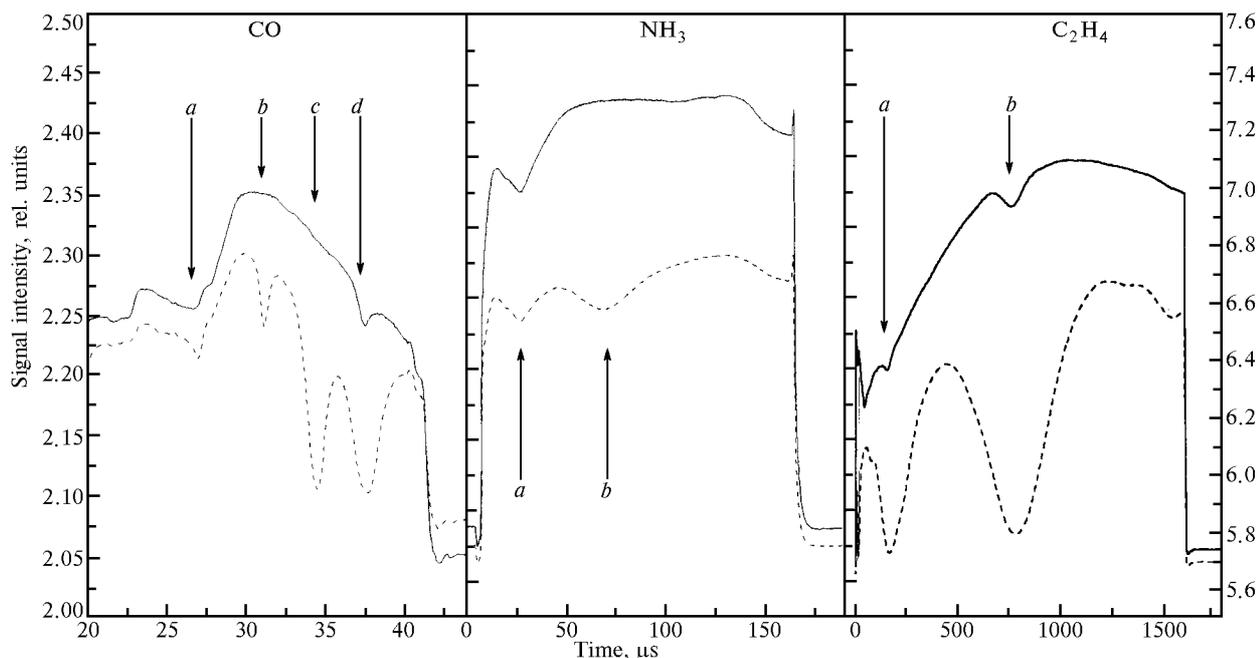


FIG. 2. TDL transmission spectra used for detection of the gases under study along with the absorption lines identified; the q_{n_2} channel: atmospheric q_{n_2} (a); $q_{^{12}n^{18}R(10)}$, 2130.228 cm^{-1} (b); $q_{^{13}n^{16}R(9)}$, 2131.005 cm^{-1} (c); $q_{^{12}n^{16}P(3)}$, 2131.632 cm^{-1} (d); the NH_3 channel: atmospheric q_{n_2} , 00⁰1–02⁰ band, 1053.923 cm^{-1} ; NH_3 $aR(5.2)$, 1054.252 cm^{-1} (b); the q_{2m_4} channel: ν_7 $R(9.9.0)$, 1056.186 cm^{-1} (a); ν_7 $R(15.8.7)$, 1056.186 cm^{-1} (b); the solid curve is for the atmospheric transmission spectrum; the dashed curve is for the transmission of spectra of reference cells.

The concentration sensitivity of the analyzer depends on the absorption coefficient at the analytical line, the length of the optical path in the atmosphere, and the level of minimum detectable variations in the optical density, i.e., the quality of the system for IR signal recording. In our case, having selected the analytical line in every channel and with fixed optical path, the sensitivity of the gas analyzer was determined by the capabilities of the data acquisition system. For signal digitizing, a fast 50-ns 8-bit ADC was used. It limited the signal-to-noise ratio by the level of $2.5 \cdot 10^2$ because of its discreteness. To increase the sensitivity, the instrumental amplitude sweeping of a signal was applied during signal accumulation. Owing to this fact, the signal-to-noise ratio was increased up to $\sim 4 \cdot 10^3$ (Ref. 11). This level of sensitivity to variations in the optical density allowed achievement of the following concentration sensitivity

regarding the gases to be detected: 10 ppb for q_{n_2} , 50 ppb for q_{m_4} , and 2 ppb for both NH_3 and q_{2m_4} . These minimum detectable concentrations of the listed gases allow real-time monitoring of atmospheric pollution starting from the level, which is far lower than allowed by safety standards.

At a fixed path length, the dynamic range of the system was more than $5 \cdot 10^4$. Such a value results from saturation of the resonance absorption at high concentrations of a studied gas. Higher concentrations can be studied with shorter path length or with the use of weaker absorption lines.

The analyzer was controlled with an IBM-compatible computer.¹¹ The specially developed algorithms and software provided for the control over the parameters of laser radiation, selection and stabilization of temperature in the cryostat, automated tuning of a laser to an analytical line, visualization of

spectra and service information, control over the processes of data storage, automated calibration, tuning, and data processing.

6. RESULTS OF FIELD TESTS OF THE GAS ANALYZER IN MOSCOW AND SIBERIA

The three-component analyzer of pollutants in the open atmosphere has been tested under laboratory and field conditions. Figure 3 demonstrates the results on qn content recorded in the atmosphere of Moscow on Vavilova Street. The CO content was monitored at the level of the third floor of the Institute of General Physics. The data obtained on two days correspond to significantly different meteorological situations. A considerable excess over the MPC level is clearly seen for

the day with the temperature inversion layers in the atmosphere, when pollutants are capped in lower levels. At windy weather, the obtained level of qn concentration in the atmosphere was rather low. During this day, the background concentration of qn practically did not exceed 2 ppm. Separate outbursts of the qn concentration, which are clearly seen in Fig. 3, correspond to atmospheric pollution by the automobile traffic along the Vavilova Street.

Figures 4 and 5 demonstrate the results of qn, NH₃, and q_{2m4} monitoring under field conditions in the West Siberia near the Maiskneft' oil field conducted in August of 1995. As seen, the background level of concentrations of these gases does not exceed MPC on the dates of measurement, and this corresponds to the standards of the clean atmospheric air.

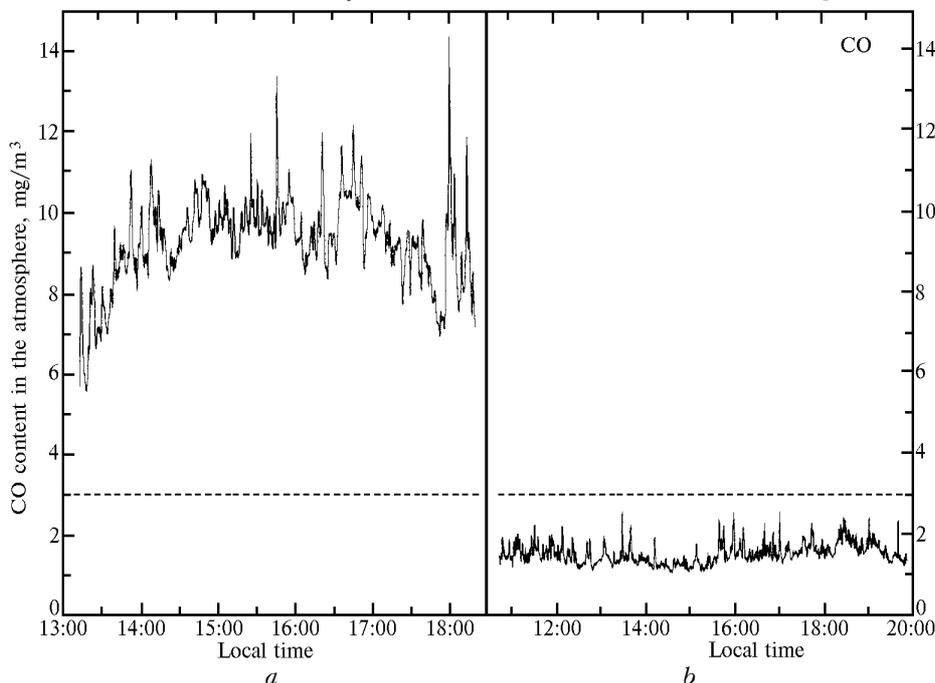


FIG. 3. The data of qn monitoring in the atmosphere over Moscow, Vavilova Street: January 20, 1995 (a), January 25, 1995 (b); the dashed straight line shows the level of MPC for qn.

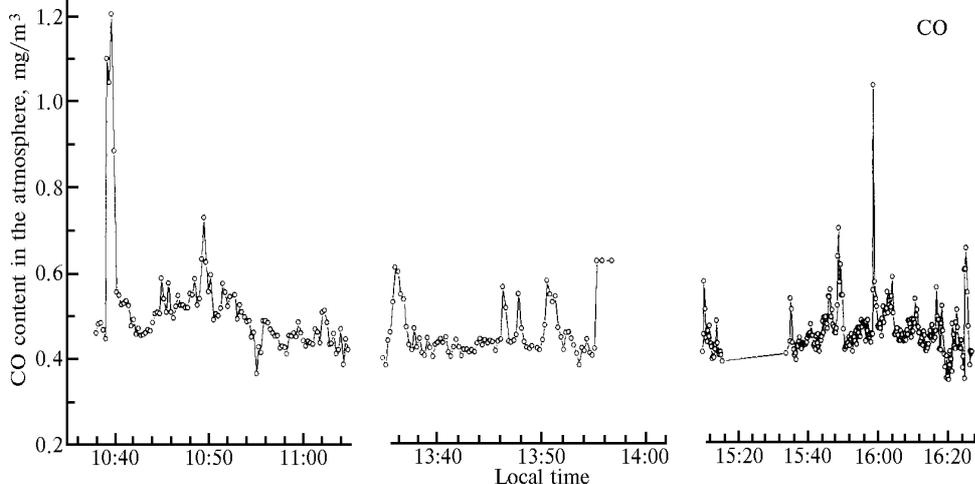


FIG. 4. The data of field experiments on qn monitoring in the atmosphere near Nefteyugansk on August 7 of 1995. The single-Path length is 170 m.

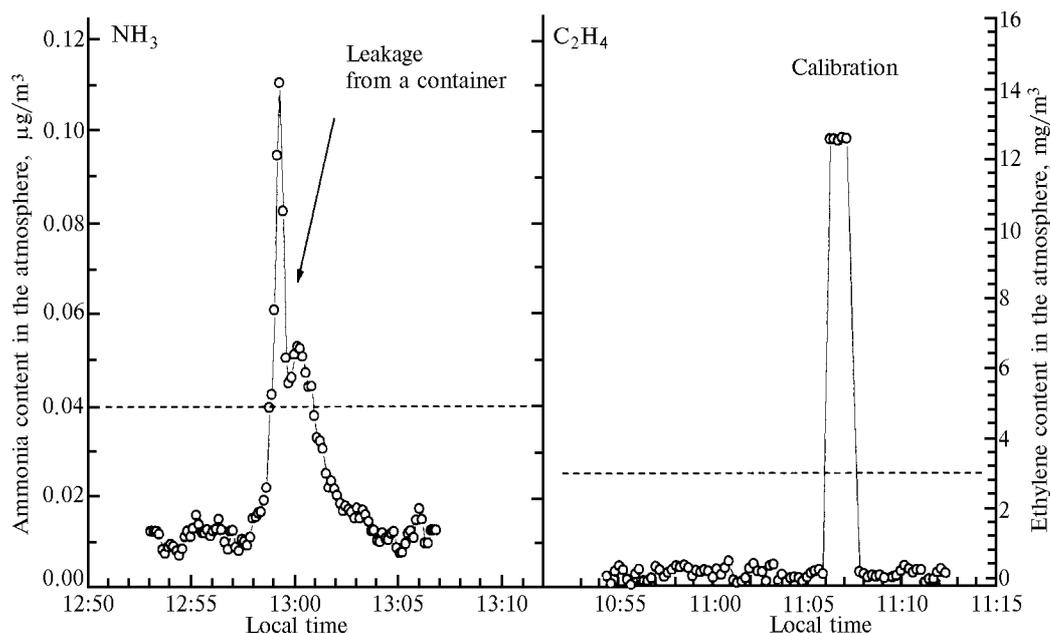


FIG. 5. The data of field experiments on NH_3 and q_2m_4 monitoring in the atmosphere near Nefteyugansk on August 7 and 3 of 1995. The single-path length is 170 m; the dashed straight line indicates the MPC level.

7. CONCLUSION

The multicomponent gas analyzer based on tunable diode lasers operating in the middle infrared range with the open-path optical arrangement with a corner-cube retroreflector has been designed for detecting trace concentrations of gaseous pollutants in the open atmosphere. The analyzer provides for high concentration sensitivity (10 ppb for q_2m_4 , 2 ppb for NH_3 , and 2 ppb for q_2m_4) thus allowing real-time monitoring of the atmospheric pollution.

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