

# Tropospheric ozone. 2. Measurement instrumentation

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Methods and devices for *in situ* measurement of tropospheric ozone: chemical, electrochemical, chemiluminescent, optical, colorimetric, and some others are considered. Ozone measurements with the use of semiconductor metal-oxide film sensors and passive ozone samplers for ozone dose determination are described. Remote methods of ozone measurement are also discussed: optical absorption spectroscopy; laser, and satellite ones. Methods of determination of vertical ozone distribution in the troposphere with the use of ozonesondes, aircrafts, and lidar sensing are analyzed. Different devices and systems are compared. Data on ozone generators are presented.

## Introduction

In analysis of spatiotemporal variations of the tropospheric ozone and identification of its role in interaction with environmental objects, it is important to have information on the instrumentation measuring the gas concentration in the atmosphere (temporal and spatial resolution, errors, etc.).

In this overview, some of the measurement methods are considered. The main attention is devoted to the instrumentation used for the determination of ozone concentration in troposphere. The methods developed for total ozone determination are excluded from the consideration. They were elucidated in detail earlier.<sup>1–5</sup>

C.F. Schönbein, who discovered ozone in the atmosphere, developed the first device and method of the ozone measurement.<sup>6</sup> He suggested to determine ozone in air from the degree of bluing the paper, impregnated with solution of potassium iodide and starch. The ozone concentration was measured visually using a conditional scale. With the help of this chemical method, quite many measurements were performed in Europe and even Africa, which gave first evidences on the spatiotemporal variations of ozone.

Then the chemical method had been refined,<sup>5</sup> which was based of the effect of ozone oxidation of KAsO<sub>3</sub> to yield KAsO<sub>4</sub> in the presence of KI. This method gave first quantitative data on ozone.

Attempts to realize the optical methods of ozone measurement, which were successfully applied for determination of total ozone content have been failed for long time.<sup>1</sup> Only in 1930s they started to develop rapidly.<sup>5</sup>

To date, tens of methods for measuring ozone concentration in the troposphere are created. There exist several approaches to their classification. It is proposed to conditionally divide all methods into chemical, physical, physical-chemical or, alternatively, into the absolute and relative ones.<sup>7</sup>

The absolute methods allow an immediate determination of the measured concentration magnitude. In contrast, the relative methods give the quantity, which is a function of ozone concentration and, hence, requires the calibration.

It was also suggested<sup>2</sup> to divide all methods into two groups: *in situ* and remote. In the first case, the device immediately analyzes the surrounding air; in the second case the measurement is performed at some distance from the instrument. The classification of the methods can be also connected with the location of the measuring device: satellite, rocket, balloon (balloon-sonde), and aircraft.

A close classification is suggested by Karol.<sup>8</sup> In addition to the *in situ* and remote methods, it is suggested to consider the air sampling as an individual method (both with and without concentrating of minor gas constituents).

Use a part of these suggestions and arrange the further description as follows. First, consider the *in situ* methods, relying on some or another physical or chemical principle, variants of their realization, and then pass to remote methods.

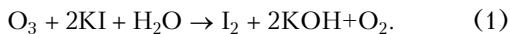
## 1. *In situ* methods of ozone measurement

Each of the variety of modern ozone analyzers is based on a certain physical principle or a chemical reaction.<sup>9</sup> Primarily, they are ultraviolet absorption, chemiluminescence, differential optical absorption spectrometry (DOAS), and electrochemistry. Evidently, there are some devices based on other principles. However, they generally do not find a wide application.

Historically, the chemical methods were first in the application, and then the optical methods in different modifications came into practice. In parallel, some other methods were created. Many of them are the object of this consideration.

### 1.1. Chemical and electrochemical methods of ozone measurement

The iodometric method is most frequently used among chemical ones.<sup>2,7</sup> Ozone interacts with potassium iodide, being in the water solution, to yield free iodine, which is determined through titration by the solution of thiosulfate of a known concentration:

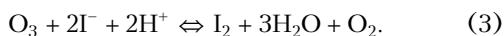


A simple system of analysis, on which this method is based, is described in Ref. 7. This system consists of three bubblers, connected in series, the pump or compressor, and the meter of the gas consumption. The water solution of potassium iodide is poured into these three bubblers, and the ozone-containing gas is pumped through them. Almost all ozone is absorbed in the first bubbler. The second bubbler is used for safety, i.e., to check the ozone escape. The third bubbler is for comparison purposes. After addition of starch and a 2-min pause the measurements are conducted. The ozone concentration is calculated as

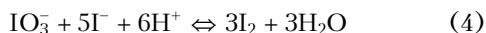
$$[\text{O}_3]_{(\%)} = 100 \frac{22.41 P_0 v TN}{2P T_0 1000 V} \approx 1.12 \frac{vN}{V}, \quad (2)$$

where  $P_0$  and  $T_0$  are the pressure and the temperature under normal conditions;  $P$  and  $T$  are the pressure and the temperature, at which the measurements are made;  $v$  is the number of millimeters of thiosulfate consumed in titration;  $N$  is the normality of the thiosulfate solution;  $V$  is the volume of gas mixture passed through the solution (in liters). The factor 2 in the denominator means that two thiosulfate molecules are consumed for neutralization of one iodine molecule.

This method was studied in detail from the viewpoint of stoichiometry  $\text{O}_3 : \text{I}_2$ , which in the neutral medium was found to be close to unity<sup>2</sup> in accordance with the equation



It was also found that the stoichiometric coefficient in the alkaline medium may change as a result of formation of iodate  $\text{IO}_3^-$ . In this case, iodine (and ozone) determination leads to underestimated (sometimes by 60%) values. The errors can be avoided through oxidation of the solution before measurements. Then, via the reaction



the iodine is formed again and the total stoichiometric coefficient becomes equal to unity.

The simplicity and good reproducibility of results are advantages of the method. It does not require an expensive instrumentation. The sensitivity of the method is 1–2 ppb, and the error in the  $\text{O}_3$  concentration range  $10^{-4}$  ... 0.1% does not exceed 5–10% [Ref. 7].

When using this method, it is necessary to follow the iodometric laboratory calibrations, namely, the composition of air, passed through the bubbler. For instance, the oxidants such as  $\text{NO}_2$  participate in reaction, similar to Eq. (1). In their turn, the reducers ( $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ) cause the opposite effect. This non-selectivity is one of the main shortcomings of the method, when using it in troposphere, especially in the vicinity of large industrial centers. A serious disadvantage of this method is a slow-rate analysis, giving approximately an hour-average concentration. The coagulation of starch introduces an additional difficulty, as well as the human element because of the laborious and monotonous work.

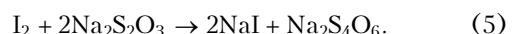
Nevertheless, this method was for a long time a basic tool at the network of ozonometric stations and helped to collect abundant data on the spatiotemporal variations of the tropospheric ozone.

The analysis of the ozone interaction with other compounds<sup>10</sup> has shown that KI is not the only species applicable in ozonometry. It was recommended to use either the solution of methyl oleate in acetic acid or the solution of methyl oleate in tetrachlorated carbon instead of KI. Other variants are possible as well.

The low rate and laboriousness of the analysis, inherent to the chemical methods, have required to refine them, which motivated the development of the electrochemical methods, having played an important role in ozonometry.

The voltamperometric (polarographic) method for determination of ozone was proposed in Ref. 7, based on finding the voltage dependence of current strength in electrolysis of solutions of substances capable of electrochemical oxidation or reduction.<sup>11</sup>

In the installation, where the analysis is performed, the electrolyte consists of the water solution of potassium iodide, to which a small, exactly known amount of sodium thiosulphate is added. The voltage at the electrodes is maintained constant and such that in the presence of depolarizer, the current correspond to the limiting diffusion current. Air is pumped through the solution, the reaction (1) proceeds in the presence of ozone, and



Until sodium thiosulphate is present in the solution, there is no free iodine, and the current in the chain is absent. On expending the thiosulphate, the current rapidly increases. The ozone concentration is determined from formula (2). Here, the electrochemistry role consists in the exact determination of the end of titration process.

There are several modifications of this method. However, nothing aside from the description of laboratory experimental installations<sup>12</sup> was found by us in the literature.

One more electrochemical method, coulometric, was developed to the production of commercial samples.

The coulometric method is based on the Faraday law. In the measurement cell, the total amount of electricity, required for electrolysis, is recorded.<sup>7</sup> The amount of electricity is linearly related to the amount of the determined substance. In this case, all current should be expended in this electrochemical reaction. For ozone, if it is determined from the amount of extracted iodine, it is necessary that:

1) all ozone is expended in the reaction of extraction of iodine, and its decomposition on the cell walls or in the electrolyte in the side reactions should be negligible;

2) all extracted iodine should participate in the electrode process, reducing on the cathode to yield the iodide



and oxidizing on the anode to yield the iodine;

3) stoichiometry of the reaction of ozone with potassium iodide should be known;

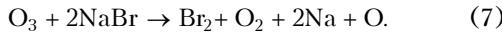
4) electrolyte should be constantly renewed or have the system of regeneration.

One of the successful achievements attained with this method is a flow-free cell, designed by Alperin<sup>13</sup>; it was used as a basis for design of a few commercial samples of the device.<sup>14</sup>

### Gas analyzers "Atmosphere-2" and "Atmosphere -II M"

The developer and manufacturer of these devices is the Smolensk Industrial Association "Analitpribor," currently FSUE "SPO Analitpribor." The gas analyzer is designed for determination of O<sub>3</sub> concentration in air, in which the concentration of the main interfering components does not exceed 0.8 for SO<sub>2</sub>, 0.01 for H<sub>2</sub>S, 0.6 for Cl<sub>2</sub>, and 0.1 mg/m<sup>3</sup> for NO<sub>2</sub>. The ranges of measured variables are: 0–0.2; 0–0.5 mg/m<sup>3</sup>, and the measurement error is 25%.

The ozone determination is based on the measurement of the limiting current, arising in the course of reduction on the platinum electrode of bromine, which is formed through interaction of ozone with sodium bromide:



The reaction proceeds inside the measurement chamber of the electrochemical cell. The experience of exploitation of these gas analyzers has shown that, virtually, the measurement error turns to be much higher than the standard one. This precludes from their use in the atmospheric monitoring as a measurement tool, therefore, they are now considered as indicators. The producing of the gas analyzer "Atmosphere" had ceased in 1990.

### Gas analyzer "Osoka"

This device is produced by Limited Liability Company "NPTO Ekopribor" (Moscow). It is based on the electrochemical principle and is designed to equip personnel, rooms, and working places of

enterprises, where excessive ozone may be observed. The device has no display and ensures a continuous monitoring of ozone concentration. On exceeding a threshold of 1 mg/m<sup>3</sup>, sound and optical signals are sent. On exceeding a second threshold (1 ... 214 mg/m<sup>3</sup>), a signal of other type is sent. The device "Osoka" is certified and registered in the State Registry List of measurement facilities No. 18388-99.

### Stationary gas analyzer "GOZON"

This device with an electrochemical sensor is developed and produced by the Close Corporation "Khromdet-Ekologia" (Moscow). It measures in the range 0–1000 mg/m<sup>3</sup> and presets the threshold for triggering the signalization and sending the control relay signals to the secondary executive devices. The device is certified and registered in the State Registry List of measurement facilities No. 18925-99.

### Gas analyzer MGL-19M-5

The device is developed and produced by Close Corporation "OPTEK" (Saint Petersburg). It is analogous to "GOZON." As a MGL-19.5 modification, this gas-analyzer can be used as a portable leakage detector as well. The device is certified and registered in the State Registry List No. 17541-98.

## 1.2. Chemiluminescent method of ozone measurement

This is one of the most widespread methods of ozone measurement. It is applied in all cases, when a high accuracy, speed, and efficiency of measurements are required. Because of the appropriate instrumental realization, it is used in laboratory conditions, onboard the aircraft, balloon, and rocket, as well as in the near-ground monitoring of ozone.

When ozone interacts with some species, the energy is released in the form of radiation. This forms the physical-chemical basis of the chemiluminescent method. For a finite interval of concentrations, the proportionality between the ozone concentration and the intensity of radiation is experimentally proved.

To produce the device sensor, foreign manufacturers use the impregnation of substrate by rhodamine B [Refs. 15 and 16], while the national ones use the rhodamine C [Ref. 2], luminal, phenosafranine, and eosin.<sup>7</sup>

The photometric measurements of the rhodamine C emission under impact of ozone<sup>17</sup> has shown it to fall within spectral region 0.56–0.7 μm, therefore, it can be recorded with usual PMTs.

The method's drawbacks are relatively fast expenditure of luminophor, used to impregnate the device sensor, and the distortion of linearity in the region of high ozone concentrations. This problem can be partially solved through addition of gaseous ethylene to the analyzed air.<sup>7</sup>

In this case, the problem of the emission stability is eliminated, because the ozone-air-

ethylene mixture is continuously renewed. Data of Ref. 18 show that the chemiluminescent determination of ozone from its reaction with ethylene substantially increases the selectivity of the method. At equal amounts of ozone and other minor admixtures, the error is 0.5 for HO<sub>2</sub>, 0.02 for H<sub>2</sub>CO, 0.03 for NO<sub>2</sub>, 0.01 for NO, 0.006 for SO<sub>2</sub>, and 0.05% for acrolein.

First successful experience of chemiluminescent measurement of atmospheric ozone seems to be dated to 1935 when, under conditions of mountain expedition to Elbrus, the ozone-induced emission of acridine was observed.<sup>19</sup> Later, this method was applied on sondes, balloons, and rockets. The use of this method is reviewed in detail in Ref. 2.

Different opinions exist among specialists on the use of the chemiluminescent methods as applied to problems of atmospheric monitoring: from full rejection because of the difficulty in description of the chemiluminescence mechanism under heterogeneous conditions and poorly studied elementary stages of the process of appearance of electronically excited particles with preset physical and chemical properties to their acceptance as a reliable basis for construction of means of ozone measurement in air of working zone and in the free atmosphere, especially under conditions of the presence of other undetermined gas components of organic and inorganic origin.<sup>14</sup> The elaborated technologic findings in application of high-accuracy, built-in ozone generators, used as internal ozone standards, make it possible to measure reliably ozone in gas mixtures.<sup>14</sup> Just in this case, the main advantages of the method, namely high sensitivity and selectivity in ozone determination, become evident.

Consider examples of present-day realizations of this method.<sup>14</sup>

#### Gas analyzers 652KhL01 and 652KhL04

The gas analyzer 652KhL01 was developed and fabricated in All-Union Scientific Research

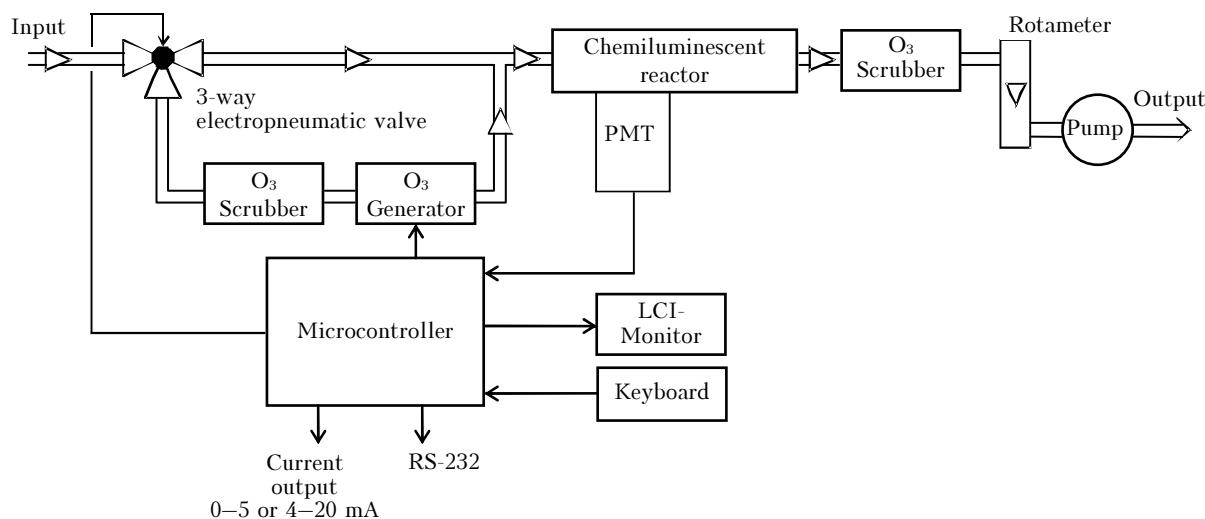
Institute of Analytical Instrument-making Industry, Kiev (currently Ukrainian Scientific Research Institute "Analitpribor"). The reaction of ethylene with ozone is accompanied by the chemiluminescence. By measuring and recording radiation with PMT, the ozone concentration in the analyzed gas mixture is determined. The consumption stimulator is used to create the optimal rarefaction (about 0.2 atm) in order to obtain the maximum sensitivity of the gas-analyzer in the chamber, where the interaction of analyzed ozone with ethylene proceeds.

The gas analyzer 652KhL01 was manufactured as a stationary device and consisted of five modules: analysis, automatic control, electronic block, stimulator of consumption, and gas block. A disadvantage of the device was the need in ethylene-filled cylinder, whose delivery to customer involves exploitation difficulties. A number of other shortcomings, such as low reliability, large measurement error, and difficulties in maintenance made users to refuse from this instrument. At present, the production of the gas analyzer 652KhL04 is ceased.

#### Gas analyzers 3.02P-R and 3.02P-A

The gas analyzer 3.02P-R is a portable device designed for the measurement of ozone microconcentrations in the lower troposphere (near-ground layer) and in the air of working rooms. The device can be employed as a part of mobile laboratories of atmospheric monitoring, at the stations of background monitoring, and in field conditions. The device can be used as ozone measurer to ensure safe conditions of work in industry and agriculture. The block-diagram of the device is presented in Fig. 1.

The device was developed in 1990 at Close Corporation "OPTEK," Saint Petersburg. Since 2002, two new promising models are commercially available. These analyzers show best parameters of selectivity, sensitivity, and reliability.



**Fig. 1.** Schematic view of the chemiluminescent gas analyzer 3.02P-R/3.02P-A.

A distinctive feature of the devices is a strict stabilization of photoreactor of ozone calibrator, ensuring the required meteorological characteristics in exploitation.

Within the dynamic range of measured ozone concentrations of 15–500  $\mu\text{g}/\text{m}^3$ , the reduced measurement error does not exceed 20% for the range 0–100  $\mu\text{g}/\text{m}^3$ , and the relative error does not exceed 20% for the range 100–500  $\mu\text{g}/\text{m}^3$ . The minimal level of recorded ozone concentrations is 1  $\mu\text{g}/\text{m}^3$ . The devices have re-tunable analog output signals 0–5 or 4–20 mA and the digital output RS-232.

The gas analyzer 3.02P-R is designed primarily for measuring the ozone concentration in the atmosphere of working zone in industry. Nonetheless, it is also successfully used in field measurements. The specialized gas analyzer, model KhGO-02A (also produced on the base of 3.02P-R), has two-step block of temperature stabilization, which ensures the safe device operation at the ambient air temperature between –20 and +20°C, and the module of cyclic program control for the gas analyzer operation in automated mode.

The model 3.02P-A is currently the base instrument, used by Russian Committee for Hydrometeorology at the net of automatic stations of monitoring the atmospheric air pollution.

To ensure the required meteorological parameters, the manufacturer produces the sources — standard reference gas mixtures (SRMs) — generators of ozone microconcentrations of the first class and two second class models GS-024-1 and GS-024-21/GS-024-25, respectively.

### Gas analyzer ANKAT-7601

The chemiluminescent gas analyzer of ozone microconcentrations is developed and produced by Smolensk FSUE "ANALITPRIBOR" since 1991. According to the technical specifications, the device is designed for a continuous automated measurement of ozone concentrations in the atmosphere and in industrial indoor air. The working range of the device is 0–1000  $\mu\text{g}/\text{m}^3$ , with division into subranges 0–100 and 0–1000  $\mu\text{g}/\text{m}^3$ . The manufacturer assures the reduced measurement error at the MPC level in the declared range of working temperatures: 0 ...+45°C. However, the used schematic-technical solutions in the gas analyzer design (low-resource stimulator of gas consumption, the absence of active system of temperature stabilization of the built-in ozone calibrator, and the applied construction of the pneumatic system) call into question the declared ozone measurement accuracy. The device is certified and manufactured in accordance with the Technical Regulations 25-7407.039-90.

### 1.3. Optical methods of ozone measurement

These methods are based on the Lambert–Beer law:

$$J_\lambda = J_{0\lambda} \exp[-\sigma_\lambda(\text{O}_3)l], \quad (8)$$

where  $J_0$  and  $J$  are the light intensities at the wavelength  $\lambda$  at the input and output of the measurement cell, in which the absorbing gas (ozone) is located;  $\sigma_\lambda(\text{O}_3)$  is the absorption cross section of the ozone molecule at the wavelength  $\lambda$ ; and  $l$  is the optical pathlength of the absorbing mixture.

Ozone has broad absorption bands in different parts of the spectrum, any of which theoretically can be used. In practice, the Hartley band is used most often. Therefore, the band absorption maximum is usually chosen for work. In cases of too high absorption, shorter cells are used.

Many different modifications of one- and two-beam schemes of ozone analyzers exist. Consider the characteristics of these analyzers and principles of their operation.<sup>14,20</sup>

The ozone concentration in the gas sample is determined through the measurement of intensity of a 0.254  $\mu\text{m}$  radiation absorbed by the analyzed sample during its flow through the optical absorption cell. Since the effective ozone absorption cross section at this wavelength is quite accurately measured in the optical laboratory, no other calibration (via the rate of sample pumping through the cell or the gas sample temperature, etc.) is required. Moreover, the method of UV absorption itself is not the source of atmospheric pollution and, therefore, it does not distort the physical-chemical characteristics of the analyzed medium. This makes it possible to perform simultaneous comparisons with other methods of ozone measurement, that increases the reliability of the obtained experimental data. Generally, the photometer scheme consists of three functional units:

- a source of UV radiation of high stability and brightness;

- one or a few optical flow chambers (absorption chambers) with the corresponding pneumatic system (supplying ducts, pipes, pneumatic valves, filters, ozone destructors, stabilizers of gas consumption, as well as pressure and flow sensors);

- the "solar blind" silicon-carbide photodetectors (one per an optical chamber) with the corresponding electron circuits.

The lamp emits a 0.254  $\mu\text{m}$  radiation, which is directed along the measurement chamber axes to photodetectors. Since ozone strongly absorbs the radiation at this wavelength, the variations of ozone concentration in any of the chambers will lead to a change of the radiation flux intensity at a corresponding photodetector. The ozone-containing air is passed through the ozone destruktur and then is directed to the optical chambers. These commutations of gas flows are performed using four-way valve. The ozone-cleaned air is alternatively directed to one of the chambers. The measured radiation intensities in the photodetectors are used to calculate the ozone concentration in the sample.

The construction of photodetectors, their temperature stabilization, and the construction of electronic blocks should ensure high parameters of sensitivity and stability of operation, which makes it

possible to ensure a technological compromise: a short optical absorption chamber, minimal mass of the optical cell, minimal temperature gradients along the axes of the optical cells (and, as a consequence, elimination of the optical refraction of the light beam), minimal time of the gas sample residence in the cell, their blowing for elimination of the turbulent regime in chambers (and, as a consequence, reduction of the heterogeneous destruction of the ozone molecules at the walls of the gas channels and cells).

Under conditions of precision measurements, photodetectors themselves and all input soldered joints between the operational amplifiers and photodiodes should be temperature stabilized. The experience shows that the absence of insulation of soldered joints against the temperature variations leads to appearance of spurious noises at the inputs of the precision amplifiers. The soldered joints themselves start operating as thermocouples (sources of EMF).

Experiments revealed the following main causes of errors in UV photometer measurements:

1) errors in determination of optical absorption pathlength of photometer, arising as a result of reflection of the optical light beam from the internal side walls of the optical cell. This results in mismatch between the geometrical and effective absorption pathlengths of ozone molecules in the optical cell;

2) multiple light beam reflections from the windows at the cell ends;

3) inaccuracy in determination of the specified effective absorption cross section of the ozone molecule;

4) ozone losses in heterogeneous reactions at the walls of the pneumatic channels of the device;

5) influence of gas mixture temperature and pressure along the length of optical cells;

6) contribution of mercury weak lines of low-pressure quartz lamp near 0.254  $\mu\text{m}$ , recorded with varying efficiency by silicon-carbide (or other type) photodiode (0.27528; 0.28936; 0.29673; 0.29675; 0.31257; 0.31315; and 0.31318  $\mu\text{m}$ );

7) errors arising in analysis of ozone-containing gas mixtures, when the built-in generators of clean air do not ensure the selective removal of non-measurable components of gas mixture, such as the sulfurous anhydride, nitrogen oxides, or aromatic hydrocarbons. These errors are quite typical for operation of UV photometers in the natural atmosphere of industrial cities with high level of anthropogenic emissions;

8) the use of radiation sources with diverging beams.

The use of the double-frequency lasers as a source of radiation is promising for UV photometers, developed presently. The double-frequency argon laser operating at 0.2572  $\mu\text{m}$  is an optimal source (Fig. 2).

Such a source has a number of excellent characteristics:

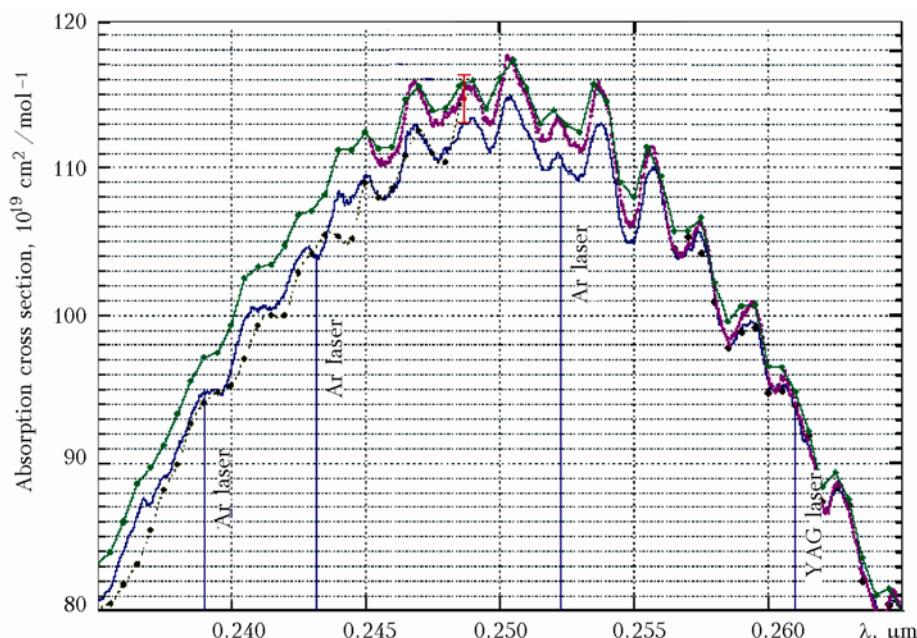
- the light beam is well collimated;

- the use of the laser-based source suggests an accurate measurement of optical absorption pathlength (accuracy is better than 0.001  $\mu\text{m}$ );

- the wavelength is known (it is determined at a level of 0.001  $\mu\text{m}$ );

- there is no need to apply additional special dispersing elements (monochromators, interference filters), because of one-wavelength radiation;

- high-power radiation, ensuring much better signal-to-noise ratio;



**Fig. 2.** Positions of wavelengths of argon laser radiation after frequency doubling in the Hartley band of ozone absorption.<sup>14</sup>

— a possibility of application of technologies of multi-pass array optical systems, ensuring an extended optical absorption path in cells.

Thus, the UV photometers — gas analyzers of ozone of equivalent type, constructed according to the classic scheme with the use of polychromatic source of radiation, can be applied to different analytical problems in industrial and scientific studies. The error of ozone measurements by such facilities is determined by the revealed system uncertainties.

The use of lasers makes it possible to construct a laser UV photometer of ozone, showing the best meteorological characteristics. The use of the laser UV photometers will allow elimination of the most considered uncertainties. The laser UV photometer can be considered as a reference measurement facility of the national standard grade.

Present characteristics of some gas analyzers.<sup>14</sup>

#### Meters of ozone concentration IKO-1 and IKO-2

Meter of ozone concentration of the IKO type is designed for a continuous control of ozone content in a gas mixture, arriving from ozone generator to a customer. The meter is developed by Limited Liability Company "MELP" (Saint Petersburg) and makes it possible to measure the ozone concentrations within 1–30 and 5–150 g/m<sup>3</sup> with a relative error no more than 15%. The devices have the digital liquid-crystal display, 0.1 g/m<sup>3</sup> discreteness of counting. There is an option of connecting the meter to computer via interface RS-232.

The meter of ozone concentration IKO-1 of a similar type is produced by the enterprise "Medozons," Kharkov. The device, also constructed on the principle of the optical UV absorption, measures in the range 1–150 g/m<sup>3</sup> with the relative error within 10%. This instrument is classified as a device of semi-automatic type, because the procedure of ozone measurement requires preliminary manual zeroing of device. Information on certification of this device is not available.

#### Gas analyzer "OZON-PDK"

The optical UV analyzer of ozone "OZON-PDK" is developed and commercially produced by

the Corporation "Angarskoe OKBA". The device is totally automated and has the option of zero drift correction. Because of the use of components of national production, the device shows comparatively modest meteorological characteristics in the measurement range 25...500 µg/m<sup>3</sup> at an absolute error of ± 25 µg/m<sup>3</sup>. The device is constructed on the basis of two-beam optical scheme. Main application of this gas analyzer is the control of air in the working zone. The device is certified and recorded in the State registry list of measurements in Russian Federation.

#### Gas analyzers of UV absorption of OZON-5 series

"Angarskoe OKBA" has developed and commercially produces the optical gas analyzer OZON-5. Under this name, the enterprise produces four types of the device, differing in the range of the measurable ozone concentrations. The ranges are 0–1, 0–2 or 0–5 g/m<sup>3</sup> for OZON-5-1; 0–25, 0–50 or 0–100 g/m<sup>3</sup> for OZON-5-25; and 0–50, 0–100 or 0–200 g/m<sup>3</sup> for OZON-5-200.

The gas-analyzers of the OZON-5 type are designed for measuring the ozone mass concentration in ozone-air, ozone-oxygen, and ozone-nitrogen gas mixtures. It can be used for the control of ozone in gas mixtures at the output of ozonizers, bubble columns, as well as for the research purposes. The analysis of the construction of such devices provides grounds to believe that it is promising in industry, especially at high ozone concentrations. It has a unified current output: 0–5 mA and output discrete signal of the type of "dry contact." The device OZON-5 is classified as the automated measurement facility and can be used in complexes and systems controlling technologic process. The device is certified and recorded in the State Registry List of Measurement Facilities of Russian Federation.

#### Optical gas analyzer Cyclon-5

Under this name, the enterprise OPTEK produces six versions of ozone analyzer, differing in the ranges of measurable ozone concentration (Table 1). All devices of Cyclon-5 type are constructed on the basis of a single-channel optical scheme.

Table 1

Type	Range of concentration measurement		Error	
	1st	2nd	absolute	relative
			1st range	2nd range
Cyclon-5.11	0–1.0 g/m <sup>3</sup>	1–99.9 g/m <sup>3</sup>	±0.2 g/m <sup>3</sup>	±10%
Cyclon-5.21	0–0.5 g/m <sup>3</sup>	0.5–50 g/m <sup>3</sup>	±0.1 g/m <sup>3</sup>	±10%
Cyclon-5.31	0–0.05 g/m <sup>3</sup>	0.05–5 g/m <sup>3</sup>	±1 mg/m <sup>3</sup>	±10%
Cyclon-5.41	0–0.02 g/m <sup>3</sup>	0.02–1 g/m <sup>3</sup>	±2 mg/m <sup>3</sup>	±10%
Cyclon-5.51	0–10 mg/m <sup>3</sup>	10–100 mg/m <sup>3</sup>	±1.0 mg/m <sup>3</sup>	±10%
Cyclon-5.51M	0–2 mg/m <sup>3</sup>	2–10 mg/m <sup>3</sup>	±0.2 mg/m <sup>3</sup>	±10%

The devices are designed for measuring the ozone mass concentration in the technological gas mixtures. The gas analyzer has high measurement stability and a large resource of work. As the high-stability source of UV radiation, a high-frequency portable electrode-free lamp with mercury and argon vapors at a strictly fixed plasma temperature is used. The construction of the device casing provides for its applicability in zones with a high level of industrial noise. The devices have a program-readjustable analog output signal 0–5 mA (or 4–20 mA), as well as the digital output RS-232. The conditions of exploitation of gas analyzers are the following: the temperature within 10–35°C, humidity up to 98% without moisture condensation. The devices are certified.

### Optical analyzer of ozone F-105

The photometer F-105 (optical UV gas analyzer) is developed and commercially produced by the instrument-making enterprise OPTEK since 2002 (Fig. 3).

At present, this gas analyzer shows the best exploitation characteristics (accuracy, stability of work, sensitivity, and a wide range of measurable concentrations up to 10 mg/m<sup>3</sup>) among the ozone analyzers, produced in Russia. Parameters of F-105 are not worse than those of the foreign versions of ozone analyzers of analogous purpose: 1003 AN, 1008-PC models by DASIBI Company (USA); 9810V and 9811V models by Monitor Labs Company (USA) and Monitor Europe Company (UK), PPM-Systems (Finland), SERES (France).

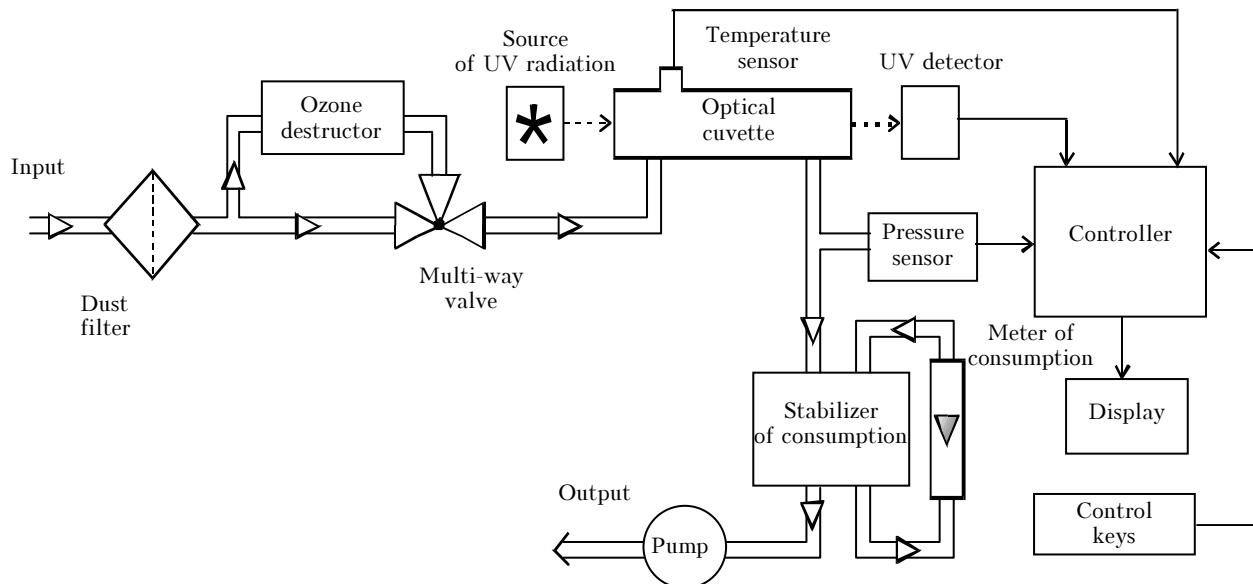
The range of the measurable ozone concentrations is 0–10 000 µg/m<sup>3</sup>. The absolute error

is ±20 µg/m<sup>3</sup> in the range 0–100 µg/m<sup>3</sup>, and ( $\pm 14 + 0.06 C_x$ ) in the range 100–1000 µg/m<sup>3</sup>. The relative error is ±7% in the range 1000–10000 µg/m<sup>3</sup>. The meteorological parameters are realized at ambient air temperatures of 10–35°C, an atmospheric pressure of 630–800 mm Hg, and relative air humidity up to 95% without condensation of moisture. The device incorporates a number of promising technological findings: digital filtering of the optical signal, the system of equalization of temperature field along the length of the optical cell for elimination of the optical beam refraction, application of special catalysts for selective removal of ozone from the analyzed mixture of gases in order to form the base line, the use of high-quality optical elements, application of special construction materials for elimination of the heterogeneous ozone destruction at walls, etc. The analyzer F-105 is certified in Russian Federation.

Characterize briefly the gas analyzers, produced abroad (Table 2). Data are taken from the information materials.

**Table 2**

Model	Manufacturer	Measurement range	Error
1008-PC; 1008-RS	DASIBI	0 ... 1000 ppb	± 1 ppb
ML-9811	Monitor Labs	0 ... 400 µg/m <sup>3</sup>	± 1.3%
TE-49C	Thermo Environmental Instruments Inc.	0 ... 1000 ppb	< 2%
O <sub>3</sub> 41M	ANSYCO	0 ... 200 ppb	< 6%
APOA-360	HORIBA	0 ... 200 ppb	< 5%
MLU	MLU	0 ... 900 ppb	< 2.4%



**Fig. 3.** Schematic view of optical gas analyzer F-105.

#### 1.4. Ozone measurement facilities using semiconductor metal-oxide film sensors

Sensors of this type make it possible to convert the adsorption magnitude of chemically active molecules, atoms and radicals, electronically and vibrationally excited particles on their surface directly to the electric signal.<sup>14</sup> This signal corresponds to the adsorption (chemisorption) rate of molecules and is proportional to the particle concentration in the atmosphere surrounding the detector.

The possibility of conversion of the adsorption magnitude to electric signal (change of photoelectric work function of electron, change of electroconductivity or change of Hall characteristics of thin semiconductor oxide films) stimulated the development of a new field in the analytical chemistry and construction of new-generation gas analyzers.

The principle of operation of most presently used semiconductor detectors is based on the phenomenon of change of the conductivity of the sintered samples of metal oxides as a result of adsorption of active particles. The general requirements to semiconductors of all forms, used as the working elements of the sensors, are the following: a sufficient chemical stability, sufficient mechanical and thermal strength, and impossibility to form stable chemical compounds with the adsorbed particles. Wide-gap semiconductors should be most sensitive to adsorption, primarily because of almost total absence in them of own charge carriers and, hence, a high sensitivity of their electric conductivity to doping of any type. Therefore, the sensors on the basis of metal-oxide semiconductors are presently of most wide use, such as SnO<sub>2</sub>, ZnO, NiO, CdO, In<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and WO<sub>3</sub>.

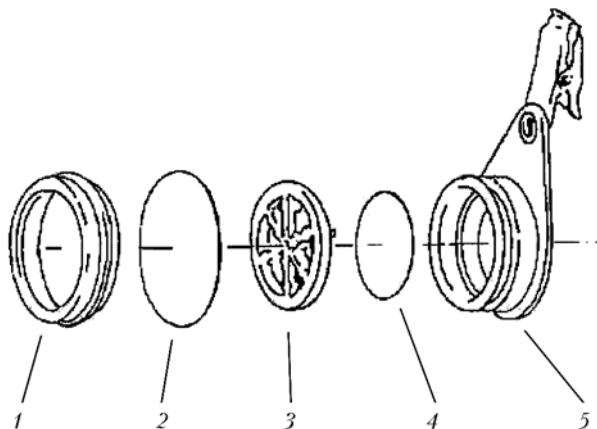
The semiconductor sensors differ in the chemical composition and construction implementation. All they operate at elevated temperatures, that in many cases determines their construction. All sensors have in their composition the insulating carrier, on which all other elements, electrodes, heater, sensitive element, and in certain cases the thermistor are put; silicon or sapphire, as well as insulating membranes are predominately used as the insulating carrier. The sensor elements can be put also on both sides of the carrier. The sensitive element of the sensor may include not only the semiconductor layer, but also other elements. The electrodes may be either of specific design or have many functions; e.g., heating element, arranged in the form of the closed ring, is at the same time the external measuring electrode.<sup>14</sup>

#### 1.5. Passive samplers for determination of ozone dose

Almost one hundred years have elapsed since the time of organization of the network of 300 monitoring stations, equipped with passive sensors controlling ozone and other air pollutants.<sup>21</sup> In recent

two decades, the interest of researchers has returned to these methods of ozone monitoring.<sup>22–24</sup> At present, they are widely used in monitoring of air quality in working places, living apartments, polluted cities, for determination of the effect of dose exposure on plants.

The typical scheme of the passive sampler is presented in Fig. 4.



**Fig. 4.** Scheme of the passive sampler: the input cover (1); the diffusion membrane (2); the laminator (3); the accumulating filter (4); fastening (5).

The principle of operation of the passive sampler is based on accumulation of pollutant in the filter body through chemical or physical absorption. Thus, it provides an integrated (over the entire sampling period) content of a particular gas. Presently, there are quite many constructions of such samplers. A considerable part of them is described in Refs. 21 and 25.

As absorbers of ozone, of most frequent use are the following: 1,2-di(4-pyridyl)ethylene,<sup>26</sup> indigo,<sup>27</sup> indigocarmine,<sup>22</sup> different metals,<sup>28</sup> nitrites, potassium iodide,<sup>30</sup> and caoutchouc.<sup>31</sup>

The theory of the method is quite simple.<sup>21</sup> The gas flow, studied via the carrier gas, is written using the Fick equation

$$F_1 = -D_{12} \frac{dN_1}{dz}, \quad (9)$$

where  $F_1$  is the gas flow,  $\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ;  $D_{12}$  is the coefficient of diffusion of some gas in another gas,  $\text{cm}^2 \cdot \text{s}^{-1}$ ;  $N_1$  is the concentration of the gas in another gas,  $\text{mol} \cdot \text{cm}^{-3}$ ; and  $z$  is the mixing path. The amount of gas  $Q_1$  (mol), passed for the time  $t$  (s) through cylinder of the radius  $r$  is given by the formula

$$Q_1 = F_1(\pi r^2)t. \quad (10)$$

Hence:

$$Q_1 = -D_{12}(N_1 - N_0)(\pi r^2)t/z, \quad (11)$$

where  $N_0$  is the concentration, determined experimentally on the absorbent surface;  $(N_1 - N_0)/z$  is the gradient of concentration along the cylinder of the length  $z$  in case of non-zero absorbent efficiency.

For sampler operating by the adsorption principle, the formulas are even simpler<sup>32</sup>:

$$N = \frac{M}{v_a t} \quad (12)$$

where  $M$  is the adsorbed mass, mg;  $v_a$  is the adsorption rate, ng/(min<sup>-1</sup>·min); and  $t$  is the exposure time, min. The adsorption rate in Eq. (12) is calculated as

$$v = (DA)/L, \quad (13)$$

where  $D$  is the diffusion coefficient in air, cm<sup>2</sup>·s<sup>-1</sup>;  $A$  is the cross section, where the gas diffusion occurs, cm<sup>2</sup>; and  $L$  is the pathlength, along which the diffusion occurs, cm.

In addition to determination of ozone dose, the passive samplers make it possible to analyze the products of reactions, which occur in the adsorbent body or accumulated in the adsorbent. Analysis is made by the usual analytical methods: colorimetry, reflection spectroscopy, spectrophotometry, ion chromatography, and fluorometry.<sup>21</sup>

The method's advantages are the simplicity, low cost, and relatively high sensitivity. The disadvantages are impossibility of determination of current ozone concentrations and relatively large error.

### 1.6. Colorimetric method

This method is based on recombination of active particles and heat release after their *in situ* with the surface of solids. The wire-sensor of the colorimeter is connected into the bridge arm of direct current. From the measurements of wire resistance during heating, it is possible to measure the particle concentration. The sensitivity of the method is 0.1 ... 1 ppb [Ref. 7], and it cannot be raised sensibly through thermal stabilization of the device and stabilization of air consumption. In addition to the requirement of high stability of the device characteristics, the method has a more substantial disadvantage. The sensitivity of the catalyst at a room temperature starts to drop. The work time of the device depends on the mass of catalyst applied and the amount of the destructed ozone.<sup>33</sup> For small ozone concentrations, the actual work time is about 10–20 h without the loss of sensitivity.

These difficulties are eliminated when using the catalytic sensor at an elevated temperature. This allows measurements of high ozone concentrations (0.01 ... 10%) for a long time.<sup>7</sup>

At present, the colorimetric method of ozone determination is applied seldom, primarily because in the course of chemical processes on the body surface, the surface ages, becomes "poisoned," etc. Therefore, the reproducibility of results decreases.

### 1.7. Other *in situ* methods

Besides the above methods, there are some other methods of ozone measurements, also used in practice.<sup>10,34</sup>

### Method of indicator tubes

One of the variants of the method is based on quenching the luminal fluorescence by ozone. On flowing of a given amount of gas mixture through the tube, it is illuminated by the mercury lamp, and the ozone concentration is determined from the length of the quenched portion of the tube.

In other variants, the method employs the effect of change of reagent color during passage of ozone-reached air through the reagent. The ozone concentration is determined from the length of tube segment that changed in color. The method is most often used in express analysis of air of some working zone.

### Method of radioactive mesh

Dried air with ozone is blown through the radioactive layer containing the compounds of quinal groups and radioactive atoms Kr<sup>85</sup>. The reaction



leads to liberation of krypton atoms, recorded by the counter. The method of radioactive mesh is one of the most sensitive. The detection limit<sup>1</sup> is 10<sup>-4</sup> ppb. The method's drawback is its poor selectivity.

### Method of rubber destruction

The method uses the ozone property to exert oxidizing effect on raw or vulcanized natural rubber, whereupon it loses its properties. The exposure results are determined by a simple method, namely tension test. The method is quite old. First results were published in 1951.<sup>35</sup> Nonetheless, however simple, it makes it possible to attain an accuracy of ~10% [Ref. 36].

Thus, the chemical and electrochemical *in situ* methods show good sensitivity and simplicity, however being insufficiently selective. Chemiluminescent and optical ozonometers have a good selectivity, sensitivity, stability, and inertial properties. Therefore, they are most often used in the atmospheric monitoring.

## 2. Remote methods of ozone measurement

In recent years, these methods are actively developed due to many their merits: high selectivity, sensitivity, and accuracy, as well as the absence in many cases of influence on the studied object. An important point stimulating their wide use is the possibility of installation of the corresponding instrumentation on different carriers: automobile, train, aircraft, rocket, and satellite. This makes it possible to obtain data on spatiotemporal variations of ozone concentration in the range from the earth surface to the upper atmosphere all around the globe with sufficient periodicity.

By the way of their implementation, the methods can be divided into two large groups:

1) passive (transparency, thermal radiation, and scattered and reflected radiation); and 2) active, based on the use of the laser radiation. In comparison with *in situ* methods, the passive remote methods have no effect on the characteristics of the studied volume of the atmosphere. This is also true for active (laser) methods, provided the power of the used radiation does not exceed a certain critical value.<sup>37,38</sup>

Extensive information on the use of the optical remote methods for ozone measurement is available in Refs. 9 and 39. They can be grouped into three directions: the remote optical absorption spectroscopy, laser sensing, and a few types of the space sensing techniques.

### 2.1. Differential optical absorption spectroscopy (DOAS)

The DOAS methods were analyzed in Ref. 40. In a broad sense, by the differential methods in the spectroscopy are meant any measurements, based on comparison of spectral characteristics at two or several wavelengths. In recording the spectrum in high-accuracy measurements by the DOAS method, it is important to eliminate any signal variations, not related to the absorption spectrum of the measured gases. Therefore, researchers either rapidly scan the spectrum with the help of the moving slits or simultaneously record all spectral components of the chosen range with the help of multichannel detector.

The DOAS method is based on the Lambert–Beer law<sup>41</sup>:

$$J_\lambda = J_{0\lambda} \exp\left\{-\left[\sum n_i \sigma_i(\lambda) + K_R(\lambda) + K_M(\lambda)\right]l\right\}, \quad (15)$$

where  $J_{0\lambda}$  is the intensity of lamp radiation;  $n_i$  and  $\sigma_i$  are the concentration and absorption cross section of the  $i$ th component;  $K_R(\lambda)$  is the coefficient of molecular scattering,  $K_M(\lambda)$  is the aerosol scattering coefficient; and  $l$  is the optical pathlength.

Minimally, the method uses two wavelengths, one ( $\lambda_1$ ) is chosen at the center of the intense absorption line of the  $i$ th gas, and the second ( $\lambda_2$ ) is chosen near this wavelength, however off the absorption contour. Then,

$$\ln\left(\frac{J_{0\lambda}}{J_\lambda}\right) = \sum n_i \sigma_{\text{diff},i}(\lambda) l, \quad (16)$$

where  $\sigma_{\text{diff},i}$  are differences between absorption coefficients at wavelengths  $\lambda_1$  and  $\lambda_2$ .

Most often, the DOAS-based devices are operated in a wavelength range 0.2–0.46 μm, in which there are absorption lines of many air pollutant gases.<sup>42–45</sup> To date, the detection threshold for individual gases ranges from 0.1 to 1.0 ppb.

The DOAS method has a number of advantages over the usual *in situ* methods. It does not require sampling and application of expendables, a few gas components may be measured simultaneously in automated mode, and the time of a

single measurement is generally 2–3 min. The improvement of the method is continued.<sup>46–48</sup> Noteworthy, a non-standard approach to the measurement of vertical profiles of ozone and other admixtures was reported in Ref. 48, at which the sensing instrumentation was placed at the mast, while the reflectors were located at different separations from the mast close to the ground surface.

### 2.2. Laser method of ozone measurement

The idea of the method of atmospheric laser sensing is quite simple.<sup>49</sup> The laser radiation pulse, propagating in the atmosphere, interacts with the latter, leaving a trace in the form of light, scattered according to a certain law in all directions by the molecules, particles, and inhomogeneities; the trace can be also in the form of the lost energy due to its absorption or in the form of the radiative energy, absorbed by the atoms and immediately reemitted by them. One more form of the trace can be the modified frequency of radiation (due to the Doppler effect or Raman light scattering). In addition, during interaction of light with the medium, the pulse form and the state of its polarization can change as well. The problems of the laser sensing were discussed in many monographs.<sup>49–55</sup>

The differential absorption lidar (DIAL) method is most frequently used in measuring ozone. This method is based on the phenomenon of resonance absorption within the selective absorption line contour of the atmospheric gas. In such narrow spectral interval, the coefficient of resonance molecular absorption suffers maximum variations depending on the spectral frequency, while the extinction coefficient practically does not change due to non-resonance scattering and absorption. This makes it possible, when comparing data of laser atmospheric sensing at two close spectral wavelengths, one of which,  $\lambda_0$ , being at the center of the absorption line, and the second,  $\lambda_1$ , located in the line wing, to extract in the pure form the dependence of the ratio of sensing data only on the resonance absorption along the sensing path. The calculation formula for determination of concentration has the form<sup>50</sup>:

$$N(\Delta z) = \frac{1}{2\Delta\sigma(\Delta\nu, \Delta z)\Delta z} \ln\left[\frac{Q(\lambda_1, \Delta z)Q_0(\lambda_0)}{Q_0(\lambda_1)Q_0(\lambda_0, \Delta z)}\right]. \quad (17)$$

This formula allows the retrieval of the atmospheric gas concentration averaged over entire, sometimes very extended, sensing path  $\Delta z$ .

The method may be realized according to three schemes: on a horizontal path with retroreflector, using the topographic target, and using the radar scheme, which can ensure ozone determination in entire hemisphere.

Some lidars are working already for a few decades, ensuring monitoring of the vertical ozone distribution<sup>56–59</sup>; new lidars are under development.<sup>60</sup>

In its capabilities, the lidar instrumentation is comparable with other systems, and this will be demonstrated below.

### 2.3. Satellite methods of ozone measurement

Most these methods are passive. They are widely used also in aircraft, balloon, and satellite experiments, employing different measurement schemes. Figure 5 shows several schemes of satellite implementation of passive remote methods.<sup>8,61</sup>

When using the transparency method, the transmitted radiation along the tangent path is measured.

In the methods dealing with the thermal and scattered radiation, two viewing geometry types can be used:

a) nadir measurements, which record the outgoing radiation in the vertical or near-vertical directions;

b) measurements toward earth's horizon (limb or tangential paths).

In the transparency method, the initial data for extracting information on the air composition are taken from measurements of radiation, coming from external sources (Sun, Moon, stars, etc.) and transmitted through the atmospheric layer. This method is applied in very wide wavelength range: from ultraviolet to radio.

The scattering method uses the angular and spectral measurements of the scattered (and reflected) solar radiation in the range from ultraviolet to the middle (3–4 μm) infrared.

The method of thermal radiation makes it possible to obtain diurnal information and study the intra-diurnal variations of the atmospheric composition. These measurements use the spectral region from 4 μm to the radio range.

Among the variety of the satellite methods of measurement, of most frequent practical use for the

ozone monitoring are the following<sup>2</sup>: measurements of backscattered UV solar radiation and measurements of intrinsic ozone emission in the band 9.6 μm (solar backscattered ultraviolet (SBUV) and IR methods).

The idea of the use of the scattered radiation for satellite determination of the ozone profile was first suggested in Ref. 62, and its experimental implementation was described in Ref. 8. The first ozone measurements were performed from satellites of the "Kosmos" series in 1965–1966.<sup>64,65</sup>

The total content of ozone molecules  $N_0$  between the device and a certain height in nadir observations is determined by the formula<sup>66</sup>:

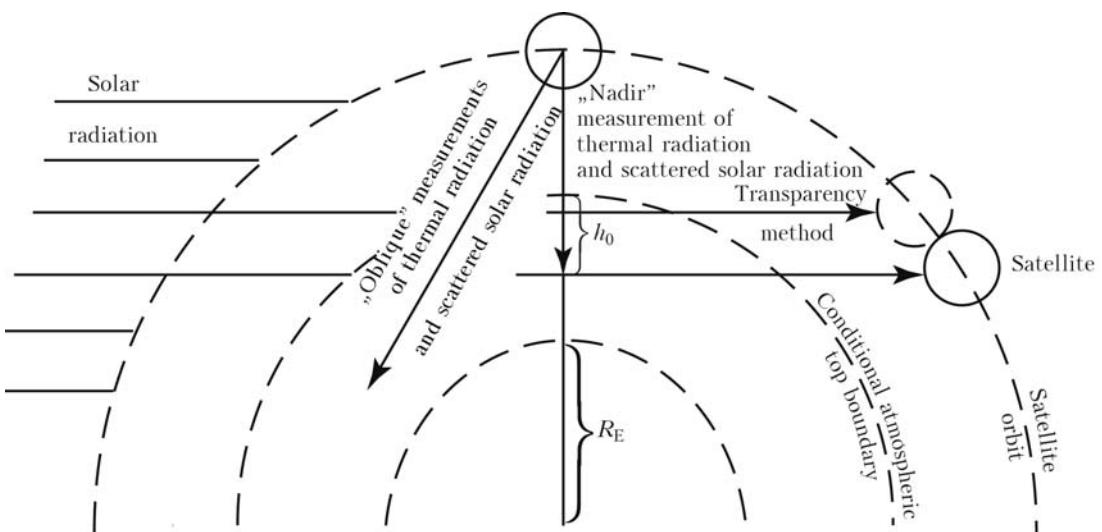
$$N_0 = \int_z^{\infty} N_3 dz \approx \frac{1}{(K_{\lambda 1} - K_{\lambda 2}) \sec Z} \ln \frac{A_{\lambda 1}}{A_{\lambda 2}}, \quad (18)$$

where  $Z$  is the solar zenith angle;  $K_{\lambda 1}$  and  $K_{\lambda 2}$  are the ozone absorption coefficients at different  $\lambda$ ;  $A_{\lambda}$  is a certain function determined by the ratio of direct and scattered radiation, which, in turn, depends on  $Z$ ,  $\lambda$ ,  $Q$ , and  $N_0$ ;  $P$  is the part of the pixels showing clouds or snow, whose albedo is maximal.

Solution of the problem of retrieving the vertical ozone profile relies upon the integral relation

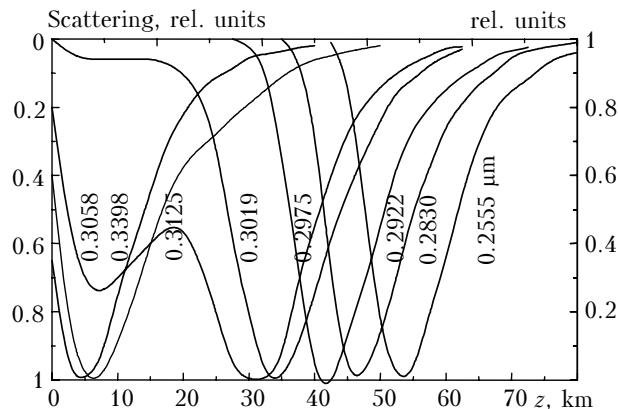
$$J(\lambda, Z) = F_0(\lambda) \frac{3\beta_{\lambda}}{16\pi} (1 + \cos^2 Z) \times \\ \times \int_0^1 \exp[-(1 + \sec Z)(\alpha_{\lambda} X_P + \beta_{\lambda} P)] dp, \quad (19)$$

where  $F_0(\lambda)$  is the extraterrestrial solar radiation,  $\text{W} \cdot \text{m}^{-2} \cdot \mu\text{m}^{-1}$ ;  $J(\lambda, Z)$  is the terrestrial radiation,  $\text{W} \cdot \text{m}^{-2} \cdot \mu\text{m}^{-1} \cdot \text{sr}^{-1}$ ; and  $X_P$  is the amount of ozone in the atmosphere above the level with the pressure  $P$ ,  $\text{atm} \cdot \text{cm}$ . The coefficients of scattering  $\beta_{\lambda}$  and absorption  $\alpha_{\lambda}$ ,  $\text{cm}^{-1}$ , are measured respectively in  $\text{atm}^{-1}$  and  $\text{atm}^{-1} \cdot \text{cm}^{-1}$ . The single-scattering model is used.



**Fig. 5.** The geometry of measurements from satellites ( $h_0$  and  $R_E$  are the target height of measurements along the tangent paths and the Earth's radius).

The determination of ozone profile is based on the idea of sensing different atmospheric depths by radiation of some or another wavelength in such a way that a particular wavelength corresponds to each effective scattering layer depending on the ozone content and solar angle. Figure 6 illustrates this approach.<sup>67</sup>



**Fig. 6.** Effective layers for solar radiation scattered from nadir direction at a solar zenith angle of  $60^\circ$  and a total ozone content of 336 D.U.

The SBUV method has a number of drawbacks, caused by the influence of aerosol and the need to introduce corrections for albedo of the troposphere and underlying surface.<sup>68–71</sup> The basic limitation of the method is the impossibility to obtain information from the non-sunlit atmosphere. These limitations are absent in the infrared method. Technically, it is simpler and provides for nighttime and daytime measurements in any geographic region. In interpretation of results, it allows the neglect of the scattering processes and influence of direct solar radiation.

The extraction of useful information from the satellite-derived signals is based on the radiative transfer equation, introduced earlier in astrophysics.<sup>72</sup> Methodic implementation of the solution of equation and the method itself are substantiated in Refs. 73 and 74.

There are two possible variants in the satellite monitoring: nadir and limb measurements.

In the first case, the detector receives the radiation  $J_{\Delta\nu}$  in the spectral interval  $\Delta\nu$  from the Earth–Atmosphere system:

$$J_{\Delta\nu} = B_v[T(P_0)]\tau_{\Delta\nu}(P_0) + \int_{P_0}^0 B_v[T(P)]d\tau_{\Delta\nu}(P), \quad (20)$$

where  $\tau_{\Delta\nu}(P)$  is the transmission function of the atmospheric layer from the level with pressure  $P$  to the conditional top boundary;  $P_0$  is the near-surface pressure;  $B_v[T(P)]$  is the Plank function of the blackbody.

In the second case

$$J_{\Delta\nu}(h) = \int_{x_2(h)}^{x_1(h)} B_v[T(x)]d\tau_{\Delta\nu}(x). \quad (21)$$

Here the integration is along the  $x$ -direction with boundary points  $x_2$  and  $x_1$  on the line of sight, corresponding to the target heights of  $h$  integration (see Fig. 5).

Solution of equations (20) and (21) refers to the classical methods of inverse problems and is unstable. Therefore, A.N. Tikhonov had constructed the methods of regularization.<sup>75</sup> The method application to the problems of atmospheric optics was described in Ref. 76.

The global ozone measurements by the described methods were initiated on Kosmos-65, Kosmos-121, OGO-4, Nimbus-3, Nimbus-4, and Explorer-E satellites.<sup>77–80</sup> Then the measurements were continued using different devices installed on the TOVS, ERS-2, ADEOS, TERRA, Envisat, AQUA, AURA, and Metop satellites. More detailed information on the instruments and obtained results is available in Refs. 81–109. Below we compare the data, obtained from the satellites, with measurements using other instrument types.

### 3. Determination of the vertical ozone distribution in the troposphere

Attempts to determine the vertical ozone distribution from measurements of the total ozone content were made quite long ago. For instance, Götz<sup>110</sup> determined from measurements in Spitsbergen that the “inversion” effect in the scattered radiation is observed as solar zenith angles increases. It was found that the ratio  $J_{\lambda 1}/J_{\lambda 2}$  ( $J_{\lambda 1}$  is the intensity of shorter-wavelength radiation, which decreases as the Sun approaches the horizon) increases starting from a certain moment. Götz concluded that the “inversion” effect is caused by the vertical ozone distribution. Later, Götz and Dobson<sup>4</sup> suggested two methods for determination of the vertical ozone distribution on the basis of the “inversion” method. A simple method consists in calculation of the mean ozone concentration in the layers 20–35 and 35–50 km from two observed ratios  $J_{\lambda 1}/J_{\lambda 2}$  at two zenith angles  $Z_1$  and  $Z_2$ . More complex method makes it possible to estimate the ozone concentration in eight layers in such a way as to ensure better determination of  $J_{\lambda 1}/J_{\lambda 2}$  at a larger number of increasing solar zenith angles. This method gave first insight into the vertical ozone distribution.

More exact and diverse information was provided by setting remote and in situ means on balloons, rockets, and aircrafts. This was followed by the start of the era of satellites and laser radars (lidars) and, correspondingly, of remote methods.

#### 3.1. Ozonesondes

Ozonesonde is a complex consisting of the measuring device and lifting means whose role is played by the rubber or polyethylene envelope, filled with hydrogen or helium. The obtained data are transmitted via the radio channel.

First experiment of ozone observation above the near ground layer was performed in 1934, when the balloon-borne spectrograph was lifted.<sup>1</sup> An optical device<sup>111</sup> can be considered as a prototype of ozonesondes. It consisted of changeable glass filters for the wavelength range 0.29–0.325 μm and a cadmium photoelectric cell.

Further technical progress has led to advent of other ozonesonde types. Their variety can be divided into two large groups of devices: optical and chemical.

### Optical ozonesondes

One of the first ozonesondes was designed and described by Vassy.<sup>112</sup> Like many other optical sondes, it measures the total content of ozone, contained at a given time above the device reaching the height  $z$ . The ozone density  $\rho_3(z)$  can be calculated for a particular height via the numerical differentiation with respect to  $z$ .

In this ozonesonde, the solar beam is incident on the capsule made of quartz with matted surface on both sides. The capsule is designed for elimination of variations of received solar radiation during swinging the device. The light, scattered by the capsule, passes through the constant glass filter with the maximal transmission at  $\lambda = 0.33 \mu\text{m}$ . The light is perceived by the vacuum antimony photoelectric cell. In the troposphere, this sonde practically does not work, because the variations of ultraviolet radiation are insignificant there.

In the Kulke and Paetzold<sup>113</sup> ozonesonde, the receiver is a hollow quartz sphere with a radius of 2 cm and with magnesium spray-coating inside, therefore, the received solar radiative flux almost does not depend on the incident angle. The light filter has the same characteristics as in the Vassy sonde. It additionally includes a filter with  $\lambda_{\max} = 0.311 \mu\text{m}$ . The second filter combination, switched on alternatively, has a sharp transmission maximum at  $\lambda = 0.37 \mu\text{m}$ . The receiver is the photoelectric cell with a receiving surface area of about 3 cm<sup>2</sup>.

In 1963–1965, a national optical ozonesonde was developed.<sup>114</sup> It included a narrowband light filter at  $\lambda_{\max} = 0.310 \mu\text{m}$ . Additionally, it had a combination of glass filters, switched on alternatively and operating at  $\lambda = 0.34–0.375 \mu\text{m}$ . The receiver was the photomultiplier tube FEU-39A. The ozonesonde was connected to the national radiosonde RCS.

At the same period, a Japanese ozonesonde was also created.<sup>11</sup>

Despite the fact that optical ozonesondes with filters give almost no information suitable for study of the tropospheric ozone, their development continues. Mention some of them.<sup>115–120</sup>

Chemiluminescent ozonesondes turned to be more informative for the troposphere. The method itself is described above. One of the most successful

ozonesondes with the longest service life was described by Regener.<sup>121,122</sup> Production of these ozonesondes was initiated in 1962 and continued till 1965 in North and Central America, Greenland, Hawaiian Islands, and then in South America.

Low persistence of chemiluminescent sensors favored their wide use in rocket sensing.<sup>123–127</sup> Rocket-sensing altitude range lies above the region of our interest.

### Chemical ozonesondes

This type of ozonesondes performs currently the most part of measurements of vertical ozone distribution.

In the electrochemical ozonesonde, liquid-filled coulometric cell is used; in which the piston pump is used for air sample bubbling. The potassium iodide (or other reagent) reacts in solution with ozone to yield free iodine, which nearby cathode forms negative ions. Under influence of electric field between electrodes, I<sup>-</sup> ions move to anode, where they are reduced, while the neutral I<sub>2</sub> molecules react with silver and do not return to the solution.

At present, a few types of electrochemical ozonesondes are in use, which differ only in the construction. For instance, the ozonesonde, patented by A. Brewer and manufactured by the Mast Keystone Corporation firm<sup>128</sup>; the electrochemical cell, suggested by Komhyr W.D.<sup>129</sup>; Japanese ozonesonde (KC79) [Ref. 130]; Indian electrochemical ozonesonde<sup>131</sup>; and electrochemical ozonesonde GPS03, recently developed in China.<sup>132</sup> Earlier, an electrochemical attachment to the Soviet radiosonde was produced in former German Democratic Republic.<sup>133</sup>

To compare data, obtained by ozonesondes of different systems, international intercalibration experiments are performed.<sup>134–137</sup>

Despite the long application of the ozonesonde method, it is under constant improvement.<sup>138–141</sup>

Note that the electrochemical ozonesondes, though providing currently the main information on vertical ozone distribution, have a high persistence being a serious drawback. This leads to smoothing of profiles. However, as was shown by Bol'shakova,<sup>142</sup> the electrochemical sondes in troposphere, besides skipping thin layers, record lower ozone concentrations. One of the reasons of this fact may be the presence of other oxidants (in addition to ozone), which influence the electrochemical cell and have no effect on the chemiluminescent sensor.

### 3.2. Aircraft sensing

The aircraft method of study of the atmosphere profitably differs from others by the ability of the carrier, equipped with the devices, not only to measure the vertical or horizontal distribution of air composition, but also to accompany the atmospheric phenomenon, being of interest to the researcher, for many hundreds of kilometers. The modern research

aircrafts use almost all above-mentioned methods of ozone measurement: *in situ* and remote, passive and active. The equipment of the research aircraft is extensively overviewed in Ref. 143, where the used methods and devices are described.

As an example, the research aircraft AN-30 "Optik-E," owned by IAO SB RAS and used since 1988 to the present time for the atmospheric sensing, can be mentioned.<sup>144</sup>

In contrast to research laboratories, operating within certain programs, there is the MOZAIC<sup>145,146</sup> Program of aircraft sensing, giving a large body of information on the tropospheric ozone. It rests upon the measurements with the use of devices, installed on civil regular aircrafts. The *in situ* devices measure ozone and other air constituents<sup>147</sup> during the taking off and landing, as well as in flight.

### 3.3. Lidar sensing

Lidar methods occupy a firm position in the ozone monitoring system.<sup>56–59</sup>

The progress, reached to date, allows researchers to build joint networks, analogous to the meteorological network operating under auspices of WMO. For example, the GIS-LINET is a lidar network created on the territory of the former USSR,<sup>148</sup> and the Asian lidar network.<sup>149,150</sup>

To date, a large family of lidars is built; they measure vertical profiles of many atmospheric trace gas admixtures, including ozone, as well as meteorological parameters.<sup>151–157,158</sup>

## 4. Comparison of different devices and systems

### 4.1. *In situ* measurement means

In current monitoring systems, the ozone concentration in the atmospheric air is most frequently measured using devices based on chemiluminescence and absorption of UV radiation by ozone. The scientific literature periodically discusses the expedience of application of some or another method. This discussion is quite serious in character because in the atmospheric air many gas admixtures and aerosol particles of different sizes are present simultaneously, contributing to the readings of devices. Therefore, the selectivity of the methods influences the measurement accuracy and, hence, the comparability of results.

Since July, 1997, IAO SB RAS, in collaboration with National Institute for Environmental Studies, Tsukuba, Japan, initiated aircraft monitoring of greenhouse gases, including the tropospheric ozone. In IAO SB RAS, the ozone is measured using the chemiluminescent ozonometer 3-02P, developed and produced in Close Corporation "OPTEK," Saint Petersburg, Russia. The Japan party has chosen the ultraviolet ozonometer, Model-49, Thermo Environment Inc., USA. Already first flights revealed that the data, obtained synchronously by the

two devices, have large discrepancies, exceeding the error corridors of the devices. These discrepancies have no systematic character. Therefore, the laboratory and field tests were undertaken<sup>159</sup> to elucidate the reasons of the discrepancies. Consider briefly the obtained results.

Firstly, the devices were tested using the reference generator GS-2, manufactured in Close Corporation "OPTEK" and certified as a test device in Mendeleev All-Russian Scientific Research Institute of Metrology, Saint Petersburg. Both ozonometers were connected to the T-joint. The generator at the input had a filter, well cleaning the air; therefore, the ozone-rich mixture, admitted then synchronously in ozonometers, was free of additional admixtures. It has been found that when both devices deal with the reference mixture, their readings coincide to the error corridors. The relative error does not exceed 15% for 3-02P and 10% for Model-49. Therefore, when operating with the reference generator, both devices give almost identical results.

Then, both devices were included in instrumentation of TOR-station,<sup>160</sup> which executes now diurnal and annual monitoring of air composition in the region of Tomsk Akademgorodok. The data of synchronous measurements have shown that the ultraviolet ozonometer, Model-49, gives 2–3 times higher concentration than the chemiluminescent ozonometer 3-02P. And, only in individual periods, their readings differ by only a factor of 1.2–1.5. Both devices well reproduce the diurnal behavior of ozone concentration and synoptic-scale and mesoscale ozone variations. These discrepancies in the readings were observed during a few measurement months. The devices were periodically tested using the ozone generator GS-2.

It could be speculated that one of the devices was destroyed; but, its change did not clear the reason of the discrepancies in the readings. It was evident that either Model-49 overestimates the ozone concentrations in the measurements in the real atmosphere by recording one more additional air admixture, or the 3-02P underestimates the concentration by quenching the luminescence of a similar minor component of air in the sensor. Analysis of discrepancies over a few months has shown the amplitude of the discrepancies generally to decrease during day and to increase at night.

The problem was solved with the help of air mass, rich in the smoke of forest fires, which arrived at the region where both ozonometers were located. In such case, generally, the ozone concentration drops to zero due to ozone rapid depletion in reactions with aerosol particles.<sup>161</sup> The ozonometer 3-02P responded to smoke adequately, showing zero readings, while Model-49 began to show very high ozone concentrations (300–400 ppb) in contradict with physical laws. This motivated testing of the Model-49 in the presence of the smoke aerosol.

Further test experiments of the Model-49 with the Diffusion Spectrometer of Aerosol (DSA) of

construction of Institute of Chemical Kinetics and Combustion SB RAS in the aerosol chamber have shown that the response of the ozonometer Model-49 depends on the type of the smoke. The cigarette smoke leads to much more overestimated measurements than the gasper smoke. Since the cigarette and the gasper smokes are formed at different temperatures of the tobacco combustion (700 and 500°C, respectively), they must have different disperse compositions.<sup>162</sup>

Thus, the performed aerosol testing has shown that the ozonometer Model-49, besides ozone, recorded also the fine aerosol fraction. Seemingly, this was due to the imperfection of the input filter of device, which did not catch particles less than 0.2 μm in diameter. After attaching the filter of generator GS-2 to the output of the device Model-49, its readings decreased to zero.

It became apparent why the discrepancies in the device readings in the real atmosphere increased during day. The earlier data suggested<sup>163</sup> that the generation of the microdisperse aerosol fraction occurred mainly at daylight hours. Hence, the enhancement of the readings of ozonometer Model-49 took place at that time.

Thus, the use of Model-49 in the real atmosphere required either to improve the input aerosol filter or correct the readings proportionally to the number concentration of the fine aerosol fraction. Thus, the empirical formula was derived, allowing estimation of the ozonometer response to changes in the concentration of microdisperse aerosol fraction:

$$N_{O_3}(O_3) = 2.5 \cdot 10^{-2} 2r N_a^{1/2}, \quad (22)$$

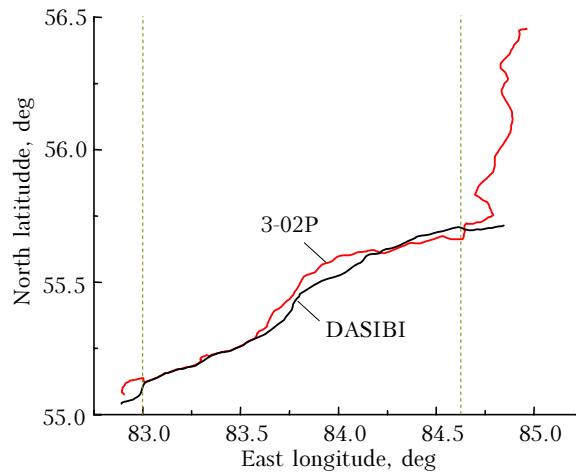
where  $2r$  is the mean geometric diameter of the mode of aerosol particles, μm; and  $N_a$  is their number concentration, cm<sup>-3</sup>.

Note that many research groups studied the excessive ozone concentration with devices, operating on the principle of UV absorption. In a number of papers the distortions in readings of UV ozonometers is associated with the presence of aromatic hydrocarbons in air.<sup>164–167</sup> Huntzicker and Johnson<sup>168</sup> connected the cause with the presence of mercury vapors.

All these facts stimulated a complex experiment on determination of the basic instrument type for the air monitoring network in USA.<sup>169</sup> By the results of this experiment, the devices were suggested, taking into account aerosol, because the aromatic hydrocarbons and mercury were shown to only slightly affect the measurements.

It should be noted that in most situations the aerosol effect is not significant. This was verified experimentally. Since the early 1990s, Russian scientists perform experiment "Troika," in which they study the air composition with the help of researching car-laboratory moving along the Trans-Siberian Railway from Moscow to Khabarovsk.<sup>170</sup> They compared the measurements obtained with UV ozonometers, installed in the researching car, and

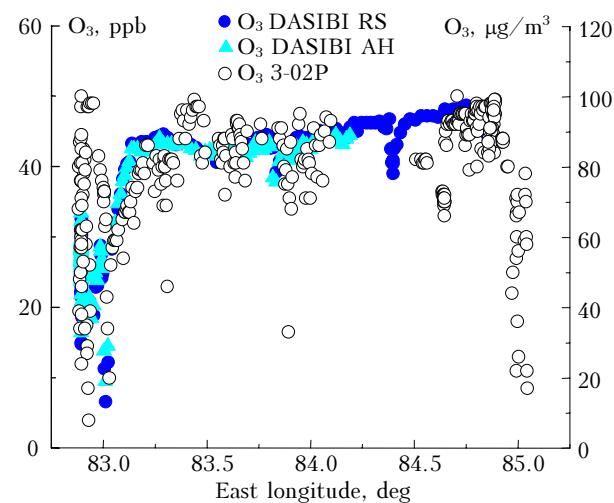
with chemiluminescent devices incorporated into the mobile station of IAO SB RAS.<sup>171</sup> The station and researching car moved in parallel along the railroad segment shown in Fig. 7.



**Fig. 7.** Tracks of the mobile station AKV-2 (path M53) and researching car (March 21, 2004).

It is seen that on the leg from Novosibirsk to the Bolotnaya village (120 km, the distance between the dashed lines), the tracks of both measurement platforms were close.

The data, obtained in the experiment, are presented in Fig. 8. It is seen that the results of the measurements practically do not differ. At least, they are within the corridor of the standard errors of the devices.



**Fig. 8.** Ozone measurements by UV ozonometers (DASIBI RS and AH) and chemiluminescent ozonometer 3-02P.

The obtained results suggest that the use of UV ozonometers for ozone measurements in the real atmosphere, seemingly, requires a continuous control for the fine aerosol fraction or application of the additional filters, not destructing ozone.

At the same time, when *in situ* devices, operating on the basis of one method, are compared,

the results generally coincide to the standard error corridor.<sup>172</sup>

#### 4.2. Comparison of remote methods

In contrast to *in situ* methods, the remote methods are difficult to be calibrated under controlled laboratory conditions. Therefore, the assent of some or another measurement system suitable for atmospheric observations is based on the intercalibration with devices being in operation.

Starting from 1998, for a few years the Southeren Hemisphere ADDitional OZonesondes (SHADOZ) project compared total ozone content, measured by electrochemical ozonesondes and the TOMS sensor, installed on the satellites of the "Nimbus" series.<sup>173</sup> It was found that each instrument has an error about 5%. Average discrepancy between two systems lies in the range 2–7% and varies from 0 to 11%.

In the framework of the SHADOZ experiment, the vertical ozone profiles were compared,<sup>174</sup> measured by ozonesondes, balloon-borne diode spectrometer ZAOZ, satellite sensor of UARS launched within the HALOE Program, and sensor used in SAGE II. Despite the fact that each device measured ozone concentration with an uncertainty no worse than 3.5% in the stratosphere and no worse than 5–6% in the troposphere, the measurements differed by 12% in the stratosphere and by 25% in the troposphere. In addition, systematic discrepancies, up to 400 m, in the height of ozone layers were recorded. Subsequently, Borch et al. extended the list of satellite sensors for the comparison with ZAOZ and SHADOZ. The obtained results are presented in Table 3, borrowed from Ref. 175.

Satellite devices SBUV (Solar Backscattered Ultra Violet), SAGE II, inversion method and ozonesondes are tested in Ref. 176. It is shown that at north midlatitudes, the uncertainty is 8% in a layer of 0–10 km (for altitude-integrated ozone), though the ozonesondes demonstrate a better altitude resolution. In a layer 20–28 km, the uncertainty decreases to 4–6%. Similar estimates are obtained for stratosphere.<sup>177</sup> More recent comparisons can be found in Refs. 178–180.

There is a series of papers on comparison of data, obtained using lidars, with satellite data.

The lidars themselves are calibrated against the *in situ* facilities.<sup>9,181,182</sup>

Results of comparison of laser sensing and measurements of global ozone monitoring experiment (GOME 1) sensor are presented in Ref. 183. They revealed that in the layer 20–40 km, the average discrepancies between the data are 8%. An interesting fact was fixed, unexplained yet. In summer the GOME 1 data are by 6.4% lower than the lidar measurements. On the contrary, in winter (October–March), the lidar-derived ozone concentration is 11.7% higher than that measured from the satellite. Close results are obtained in Ref. 184.

In Kiruna, during SOLVE II and VINTERSOL field experiments, a few instruments were compared<sup>185</sup>: Airborne Raman Ozone, Temperature, and Aerosol Lidar (AROTAL) installed onboard DC-8 (NASA) and differential absorption lidar (DIAL) Polar Ozone and Aerosol Measurement 3 (POAM-3). In the layer 18–24 km, the AROTAL and DIAL measurements coincided to 0.25 ppm or better than with a 10% error, though their readings were higher than POAM-3 and ozonesonde measurements. Below 18 km, the discrepancies exceeded 20%. In this layer, the satellite data were validated against aircraft ones.

Generally, the aircraft method seems to be the most effective tool of satellite instrumentation verification, which is supported by Table 4, summarizing the data of these experiments.

It is seen that for verification of satellite data, different aircrafts were used: Falcon, DC-8, flying only in the troposphere, and high-altitude sensing aircrafts ER-2, M-55 "Geofizika," ascending up to 20–22 km.

A considerable body of comparisons was performed for satellite devices by remote means from the ground.<sup>201–211</sup> At present, the operational satellites have a few devices, measuring the vertical ozone profiles by different methods; therefore, the obtained data should be intercompared, which is already in progress.

It was shown that the discrepancies between measurements are, on average,  $\pm 15\%$  for ASUR – SCIMACHY;  $0...+6\%$  for ASUR – MIPAS; up to 17% for ASUR – OSIRIS ; and  $-6...+17\%$  for ASUR – SMR.<sup>222</sup> By the data from Ref. 213, the tested devices disagree by  $\pm 15\%$ . One more comparison gave a disagreement from 4 to 15% [Ref. 214].

**Table 3**

Device	Recording of height, m	Stratospheric error, %	Stratospheric uncertainty, %	Tropospheric error, %	Tropospheric uncertainty, %
Ozonesondes	+400/600	65	$-1 \dots +5$	10	?
HALOE	$\pm 100$	<3	$4 \pm 1$	n/a	n/a
SAGE II	$\pm 100$	<3	$3 \pm 2.6$	40	–60
SMR	$\pm 100$	20	$7 \pm 10$	n/a	n/a
OSIRIS	–300	15	$0 \pm 3$	n/a	n/a
GOMOS	$\pm 100$	7	$2 \pm 1.5$	n/a	n/a
MIRAS	$\pm 10$	11	$1 \pm 5$	n/a	n/a

Note: n/a indicates that the value is not available.

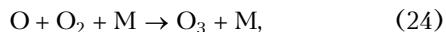
**Table 4**

Instrument	Aircraft	Constituent	Control method	Refs.
ATMOS	ER-2	N <sub>2</sub> O, O <sub>3</sub> , NO <sub>y</sub> , H <sub>2</sub> O, CH <sub>4</sub> , CO	<i>In situ</i>	186, 187
GOME	Falcon	NO <sub>2</sub>	<i>In situ</i>	188
	Falcon	NO <sub>2</sub> , H <sub>2</sub> CO	<i>In situ</i>	189
HALOE	ER-2	H <sub>2</sub> O, CH <sub>4</sub>	<i>In situ</i>	190
ILAS	Falcon	O <sub>3</sub>	<i>In situ</i> , LIR	191
	ER-2	H <sub>2</sub> O, CH <sub>4</sub>	<i>In situ</i>	182
MAHRSI	Falcon	OH	LIR	193
MIPAS	M-55 "Geofizika"	N <sub>2</sub> O, O <sub>3</sub> , HNO <sub>3</sub> , H <sub>2</sub> O, CH <sub>4</sub>	<i>In situ</i> , LIR, MIR	194
	Falcon	H <sub>2</sub> O	lidar	195
SCIMACHY	Falcon	H <sub>2</sub> O, O <sub>3</sub> , NO <sub>2</sub> , N <sub>2</sub> O, BrO, OCIO	<i>In situ</i> , lidar	195
MOPITT	DC-8	CO	<i>In situ</i>	196
	Falcon	CO	<i>In situ</i>	197
POAM-3	DC-8	O <sub>3</sub>	<i>In situ</i> , lidar	198, 199
	MOZAIC	H <sub>2</sub> O, O <sub>3</sub>	<i>In situ</i>	200

## 5. Ozone generators

For calibration of *in situ* devices, as well as for many applications in industry and medicine, it is necessary not only to measure the ozone concentration, but also to generate ozone. In this case, the ozone concentration at the output should be known. The ozone theory on applications of electric-charge and photolysis generators is described most fully in Refs. 7, 10, 215, and 216.

Ozone can be obtained in gas-phase medium which contains the molecular oxygen under purposeful physical and chemical acting in order to obtain dissociation into atoms:



where  $E$  is the definite impact on the initial oxygen molecule; and  $\text{M}$  is the molecule of neutral gas removing the excessive energy.

The reaction can be initiated by thermal effect, electric (glow, spark, corona, barrier, surface, etc.) discharge, radiative flux with a wavelength less than 0.24  $\mu\text{m}$ , as well as other types of the high-energy electromagnetic radiation. In the liquid medium, ozone is obtained via electrolysis.

The methods of ozone generation are quite diverse. The method of electric discharge is most widespread in industry. It provides for a large amount of ozone at high concentrations at a relatively low energy consumptions. The photochemical methods of generation have their advantages, because they ensure generation of particularly pure isotropic ozone-air and ozone-oxygen mixtures. They are free of other admixtures, inevitably arising during electrical discharge with its less chemical selectivity. For this reason, the photochemical ozonizers are more often used in the laboratory studies, medicine, metrology, and chemistry.

Extensive list of patents concerning ozone generators and different installations involving ozone is contained in Ref. 14. Certain industrial generators and their specifications are described in Refs. 174–219.

In period when the overview was under edition, some new publications on the subject have appeared (see Refs. 220–239).

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