Possibility of using a semiconductor ozonometer for monitoring ozone in the atmosphere

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A model of ozonometer based on the semiconductor sensor with ozone sensitivity better than 0.2 ppb has been developed. The device was included in the automated measuring gas complex of Obukhov Institute of Atmospheric Physics and was tested in March–June in 2002 and 2004. Some results of synchronous measurements of the ozone concentration in the atmospheric boundary layer carried out using a DASIBI 1008 AH ozone analyzer based on the ultraviolet photometry method and a semiconductor ozonometer are discussed. The results obtained show that the new device is capable of recording the diurnal variation of the ozone concentration synchronously with the DASIBI 1008 AH.

Recently gas analyzers based on the semiconductor sensors (SCS) have become quite promising devices for measuring concentrations of minor atmospheric gases. Their advantages are high sensitivity, high operation speed, compactness, and low cost.[1,2] Such devices can find a wide application in monitoring of the environment, including the atmospheric sounding from mobile platforms (balloon, airplane, automobile, and railway laboratories), determination of turbulent fluxes of the atmospheric admixtures, and measurements of their dry deposition rate to the ground surface.

Here we present some results obtained with a breadboard of a semiconductor ozonometer in field measurements of the ozone in the atmospheric surface layer. The device has undergone full-scale tests as a component of an automated complex for gas measurements at Obukhov Institute of Atmospheric Physics of the Russian Academy of Sciences[3] in spring–summer of 2002 on the territory of meteorological observatory of Lomonosov Moscow State University.

Instrumentation and measurement procedure

The semiconductor ozonometer has been designed as a portable device, whose basic elements are the semiconductor sensor located under a Teflon cap of 1.5-cm^3 volume, and the electronic board providing the temperature stabilization of a sensor, measurement, amplification, and transfer of the analog signal. The sensor itself is a 3×3 mm substrate of the insulating material on which a radiator, a thermometer, contact pads, and a sensitive layer of a film of the semiconductor metal oxide are mounted. As the sensitive layer substances, the zinc oxide or the indium oxide, modified by the iron oxide were used.

A physical sensor characteristic dependent on the ozone concentration, is the electrical conductivity of the sensitive layer. The output analog signal of a sensor is read out as voltage then it is transferred through an Lcard-154 interface to a computer where it is recorded at a rate of 0.1 to 1 Hz. In measuring ozone content, the sensor was aspirated with air at a rate of 0.4 l/min. The semiconductor ozonometer has passed laboratory tests with a GS-024-1 first-category ozone generator from OPTEK firm. Three specimens of the semiconductor sensor have been tested: the one with a sensitive layer from ZnO, the other two with the sensitive layer of same chemical composition, i.e., In_2O_3 (3% Fe_2O_3), but prepared using different methods. The specimens were tested in a flow of the ozone–air mixture at the ozone concentration of 15 to 80 ppb. A zero level of the sensor signals was determined in a flow of “zero-gas” (the ozone content is below 0.0003 mg/m^3), produced by the GS-024-1 generator.

From March till August, 2002 four measurement sessions have been carried out of the duration from 2 to 4 weeks with the successive replacement of the sensors 1, 2, and 3 in the semiconductor ozonometer. Measurements of the atmospheric ozone by the tested device carried out synchronously with a DASIBI 1008 AH gas analyzer, being a basic ozonometer device of the measurement complex at the Obukhov Institute of Atmospheric Physics. In its turn, the gas analyzer was calibrated under the international standard “ENV O_3-41M” No. 1298 in July, 2002. This calibration, just as previous and the subsequent one, shows high accuracy and operation stability of the DASIBI 1008 AH gas analyzer.

The measuring devices have been installed at the ecological laboratory of the meteorological observatory of Moscow State University. The intake of the analyzed air was carried out at a height of 4 m above the ground level through the Teflon tubes. Each device, was equipped with a separate compressor. The length of 0.4-cm-diameter gas tubes was 500 cm. The DASIBI 1008 AH was operated at a pump rate of 2 l/min while the semiconductor ozonometer at 0.4 l/min.

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The devices connected to two channels of the interface board. Measurements were carried out in parallel with the frequency of 0.1 Hz and were compiled in a computer database.

Results and their discussion

Laboratory tests of the semiconductor ozonometer

The laboratory procedure of the ozonometer testing assumes determination of a shape of the kinetic curve of the sensor signal at variation of the ozone content in the air, the ozone calibration by the stationary sensor signal U_∞, corresponding to the established ozone concentration, the estimation of measurement sensitivity and accuracy at the stationary signal level.

Character of the semiconductor ozonometer signal in the presence of ozone

The presence of ozone in the air reduces the electric conductivity of sensors with a sensitive layer based on the semiconductors of *n*-type ZnO and In_2O_3 that corresponds to an increase in the output analog sensor signal.

In Fig. 1 the kinetic curves are depicted of the semiconductor ozonometer signal, obtained at the exposure of the sensor 2 to a flow of the ozone–air mixture.

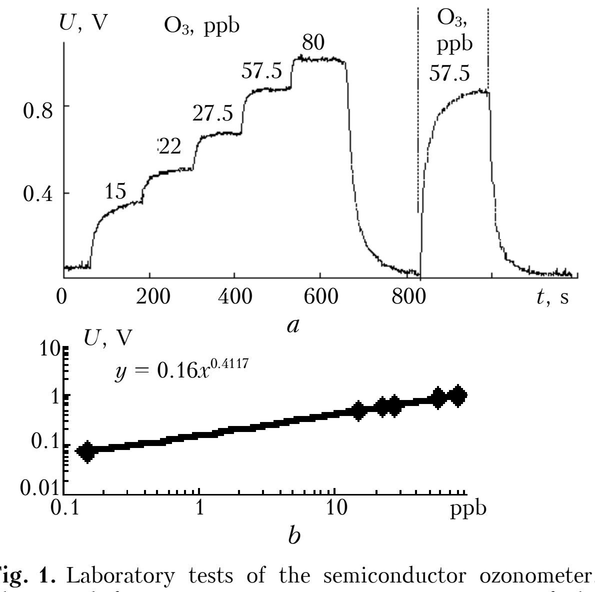

Fig. 1. Laboratory tests of the semiconductor ozonometer. The signal from sensor 2 at a successive increase of the ozone content in the analyzed air, measurement frequency of 1 Hz (*a*); the calibration dependence of the stationary signal from the sensor 2 (*b*).

The first and the last steps of the kinetic curves correspond to "zero-gas". High speed of the forward and backward signals of the semiconductor ozonometer, a complete signal reversibility, and a stable stationary level confirm that the device can be operated under both stationary and kinetic conditions of the ozone measurements.[1]

The kinetic conditions of the ozonometer operation are of interest for measurements in the medium with the varying ozone concentration. However, at the given operation stage the precise calibration of the semiconductor ozonometer can be fulfilled only under stationary conditions of the ozone measurements. The device calibration under kinetic conditions needs for a technique providing, in a model calibration experiment, a controllable and faster than the sensor response variation of the ozone content near the sensor surface excluding the blurring of test gas in the airflow and the ozone destruction on the setup walls and pipe lines.

Calibration of the semiconductor ozonometer

Dependence of the stationary sensor signal U_∞ on the impurity concentration in gas media are frequently described by the power-law function of the form

$$U_\infty = Kc^x, \qquad (1)$$

where c is the impurity concentration (ppb); x is the exponent, dependent on the type of the sensor and gas impurity; K is the constant characterizing the sensor sensitivity and the amplification factor of the analog signal. For sensor 1, the x parameter value is equal to 1.12, for sensors 2 and 3 it is 0.41 and 1.9, respectively.

The possibility of manufacturing sensors with different calibration dependences expands the prospects of their application to solution of various problems. Almost linear calibration dependence of the sensor 1 has obvious advantages at visualization and processing of the measurement data. Small x value in the power-law function means a weak dependence of the sensor 2 signal on concentration. If such a sensor possesses high sensitivity, it is kept high at low ozone concentration as well. At a large x value, sensor 3 can turn out to be useful in measuring small fluctuations, for example, pulsations of the atmospheric ozone, against the background of high ozone concentrations.

Let us evaluate the sensitivity of the semiconductor ozonometer. The ozone content in "zero-gas" makes up about 0.15 ppb. A zero level of the sensor signal is 0.073 V (Fig. 1) corresponds to this concentration. A background noise of the semiconductor ozonometer makes up 15 mV. Using the parameters of equation (1) for sensor 2, we shall obtain, that the signal-to-noise ratio for the stationary signal level becomes equal to 1 at 0.25 ppb and 2 at 0.35 ppb, respectively. Hence, the lowest ozone concentration which can be measured with the tested device, is estimated to be at the level of 0.2 ppb. The relative error of the ozone measurement at the stationary signal level makes up 5–8% (see Fig. 1).

Field tests of the semiconductor ozonometer

In Figs. 2 and 3 the examples of time records of the ozone concentration in the surface atmospheric layer, made using a DASIBI 1008 AH gas analyzer and the tested semiconductor ozonometer, are presented. The gas analyzer readouts are in ppb by volume. The signal from the semiconductor ozonometer is in volts. It is obtained from comparison of the measurement data, including those from Figs. 2 and 3, that, first, a signal of the semiconductor ozonometer follows the time variation of the ozone concentration, measured with the DASIBI 1008 AH.

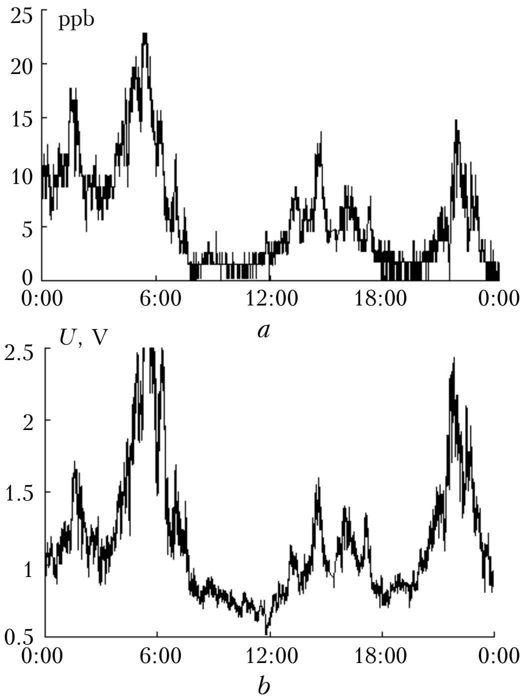

Fig. 2. Diurnal variation of the ozone concentration 04.17.02, measured with the DASIBI 1008 AH gas analyzer (*a*) and with the semiconductor ozonometer (the sensor 1). The data acquisition rate is 0.1 Hz (*b*).

Second, it shows high sensitivity and high time resolution of the semiconductor sensors, namely: all sensors tested trace the atmospheric ozone variations at the level below 1 ppb. For example, in Fig. 3*a* the discrete pattern of the concentration ozone spectrum is limited by the 1 ppb level while in Fig. 3*b* the semiconductor ozonometer gives a continuous signal in this concentration range as well. Note, that time characteristics of the DASIBI 100 AH gas analyzer are limited by the data acquisition rate of 0.1 Hz, and its sensitivity limit in the ozone measurements is about 1 ppb.

The field tests performed have shown, that the semiconductor ozonometer well meets the requirement to it under conditions of long-term monitoring measurements. It can be adapted for use in the automated measuring complexes, has the admissible sensitivity regarding to the atmospheric ozone measurement and a higher frequency characteristics, than the commercial photometric and chemiluminescent gas analyzers of the leading manufacturers in Russia and abroad. These advantages allow one to use the semiconductor ozonometers in solving research problems, for example for measurement of the fast small-scale ozone pulsations in a friction layer to obtain the estimates of the heterogeneous ozone flow in aerosols, the turbulent ozone flows and the rate of dry sedimentation on the underlaying surface.[3–5] Up to now, the research of short-term variations of the ozone concentration caused by the turbulent vortices and heterogeneous processes was rather inconvenient because of the practical absence of the full-scale measurements. The problem of influence of the meteorological parameters on the semiconductor ozonometer's characteristics should become a subject of further research. However, results of the performed tests allow us to believe, that there are no principal restrictions on the use of the device at both high and low temperatures and the variable humidity of the free air. At carrying out of the field tests, the obvious conveniences of technical operation of the semiconductor ozonometer appeared, such as an easy sensor regeneration, possibility of its fast replacement in the operating complex, possibility of a long-term sensor conservation and a break in their use, and small size of the device.

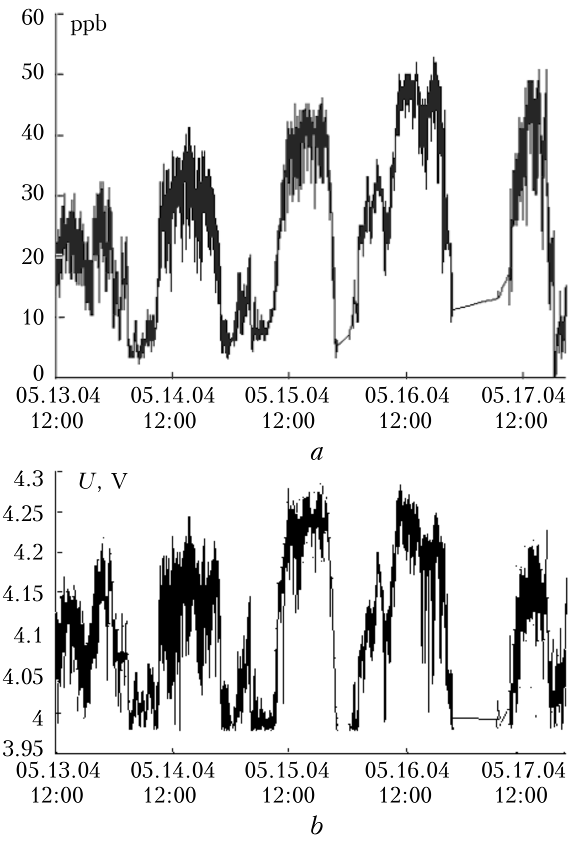

Fig. 3. Diurnal variation of the ozone concentration, measured with the DASIBI 1008 AH gas analyzer (*a*) and with the semiconductor ozonometer at averaging time of 1 min (*b*).

The tests of the semiconductor ozonometer performed have revealed a number of technical and methodical problems. For example, it is a challenge the determination of the time constant of the semiconductor sensor as the quantity, measured in laboratory is the integral characteristic of the entire device including changes of the parameters of the medium analyzed, occurred during measurements, the ozone generation stability, influence of the pipe lines, etc. The other problem connected with the above-mentioned one, is the sensor calibration under conditions of a quickly varying ozone concentration and the retrieval of the ozone concentration spectrum from the dynamic signal of the sensor. It is obvious that increasing the ozonometer sensitivity and accuracy of the measurement can lead to a reduction of the background noise of the device.

Acknowledgments

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