OZONE-GENERATING SETUP WITH SPECTROPHOTOMETRIC CONTROL OVER O_3 CONCENTRATION

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Described is the setup for ozone generation and measurement of elevated ozone concentration. Excessive O_3 *concentration is produced in air flowing about UV gas-discharge mercury lamp.* O_3 *concentration is measured in air at atmospheric pressure using the spectrophotometric method by absorption of mercury lamp radiation at* 254 nm *wavelength.*

In recent years, interest of researchers in effect of high O_3 concentration (> 40 ppb) upon plants of different types has quickened.[1,2] In contrast to the hypothetical problem of "ozone holes" in the stratosphere, the problem of elevated O_3 concentration in the ground layer is well actual. Anthropogenic compounds destroying the ozone layer in the stratosphere (for example, NO) take part, at the same time, in O_3 generation in the troposphere.[3,4] Elevated concentrations of O_3 in most cases are caused by anthropogenic sources that also give rise to additional stress factors for plants. Therefore, performance of correct study of O_3 impact upon plants under controlled laboratory conditions will serve to solution of many problems.

The setup developed by us comprises a dynamic ozone generator, fumigation chamber for placing plants under study in the ozone-enriched atmosphere, and spectrophotometric measurer of ozone concentration (Fig. 1).

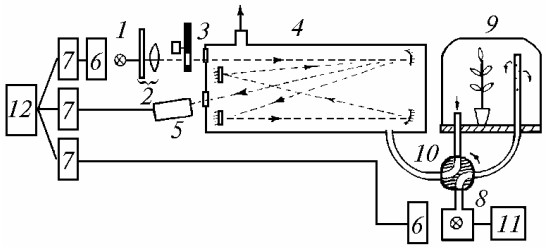

FIG. 1. Experimental setup. VSB-1 lamp (1); UV filter (2), illuminating system; obturator (3); six-path analytic cell (Chernin scheme) (4) ; FEU-142 (5); photodiodes (6); pre-amplifiers (7); VSB-2 lamp (8); fumigation chamber (9); gas-distribution device (10); microprocessor (11); personal computer (12).

The operation principle of ozone generator is based on the well-known photochemical method of O_3 generation from air oxygen under effect of UV radiation quantum:

$$O_2 + h\nu \Rightarrow 2O; \quad (1)$$

$$O + O_2 + M \Rightarrow O_3 + M, \quad (2)$$

where l is any molecule.[5,6]

We used, in the generator, the high-frequency spectral electrode-free lamp VSB–2 with mercury filling widely applied in spectroscopy as a source of UV radiation. The lamp was placed in the quartz bottle of half-liter capacity with air blown through it with the help of the PR–7 microprocessor. O_3 concentration in air flow outcoming from the bottle can be regulated by changing the VSB–2 lamp radiation intensity. The rate of air flow was changed with the needle valve set at PR–7 output and measured with the gas counter GSB–400.

To measure the O_3 concentration in air flow created by generator, we have modified the mercury analyzer RGA–11 produced in Design and Technology Institute "Optika".[7,8] Modification consisted in replacement of a photoelastic polarization modulator with the mechanic obturator modulating radiation from the mercury lamp VSB–1 at a frequency of 120 Hz and, correspondingly, in change of the resonance frequency of selective amplifier from 50 kHz to 120 Hz. The Chernin open six-path optical system[9] used in RGA–11 to enlarge the ray path in an absorbing medium up to 2.7 m was placed in the hermetic enclosure, through which the analyzed air-ozone mixture was blown. When measuring higher concentrations, we used the quartz single-path cell 120 mm long being a part of RGA–11 complement for analysis of solid and liquid samples.

O_3 concentration is estimated from measured transmittance T of the air-ozone mixture at the mercury radiation line $\lambda = 254$ nm (emitted by the VSB–1 lamp). Calculations are performed by the equation of the Bouguer law of absorption

$$I = I_0 \, e^{-\sigma n l}, \quad T = I / I_0, \quad (3)$$

where I_0 is the intensity of radiation passing through the cell with pure air; I is the intensity of radiation

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attenuated by the air-ozone mixture; l is the ray pathlength in the cell; n is concentration; σ is O_3 absorption cross-section at 254 nm. Average value of σ estimated from the data of Refs. 10–13 and recalculated from common logarithms to natural ones is equal to $2.65 \cdot 10^{-17}$ cm^2. (rms deviation of results obtained by different authors, Refs. 10–13, in the period from 1933 to 1961 is 5.6%).

$$n = -\ln T/(\sigma l) \text{ cm}^{-3}. \quad (4)$$

We can pass from ozone concentration n to other often used units. Density ρ can be found as

$$\rho = n \cdot 7.97 \cdot 10^{-14} \text{ mg/cm}^3. \quad (5)$$

Relative concentration of ozone molecules is:

$$C = n \cdot 3.72 \cdot 10^{-14} \text{ ppm}. \quad (6)$$

The analyzer allows measurements of O_3 concentration in air in the range 0–600 ppm, the detection limit is 0.06 ppm.

The analytic cell of the concentration measurer with the gas-distribution device *10* (see Fig. 1) can, if necessary, be connected to both the O_3 generator and output of the fumigation chamber. This allows estimation of the ozone decay rate in both the chamber and the analyzer cell. Figures 2 and 3 show the O_3 concentration change in the analytic cell at changing operation mode of the setup.

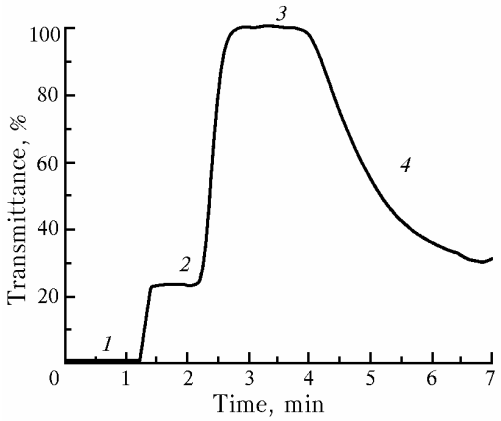

FIG. 2. Transmittance of the analytic cell at different modes. Analytic ray is interrupted by the damper, and the air-ozone mixture is blown through the cell (1); the damper is open, the air-ozone mixture is blown through the cell (2); the cell is pumped out with the forevacuum pump (3); the pump is turn off, the cell is filled with the air-ozone mixture (4). Noise level is 0.5%.

In addition to the spectrophotometric method for monitoring of O_3 content in the air-ozone mixture, we used the method based on relation between the O_3 concentration and the intensity of UV radiation from the ozonizer mercury lamp. Smoothly increasing the voltage of power supply of the high-frequency generator from 150 to 250 V, we obtained the continuous increase in radiation intensity a three times as compared to the minimum intensity (Fig. 4).

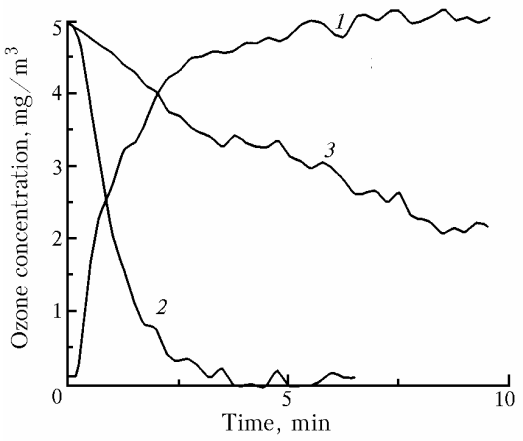

FIG. 3. Ozone concentration in the analytic cell: filling of the cell with the air-ozone mixture (1), following blowing of the cell with air (2), ozone self-decay in the closed cell (3).

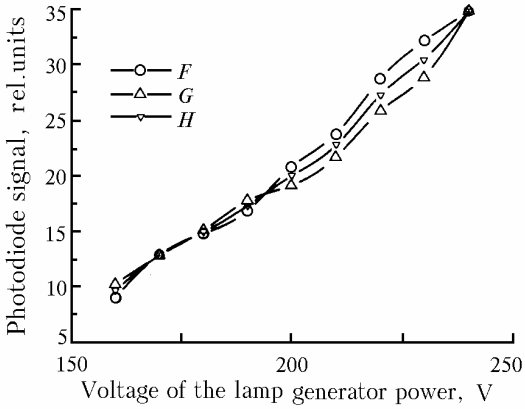

FIG. 4. Photodiode signal (intensity of the VSB-2 lamp of the ozone generator) versus voltage of the generator power supply. G is increase in voltage, F is decrease in voltage, H is average value.

To monitor the intensity of mercury lamps, we used the photodiodes FD–24K working in the visible spectral range. Using the data from Ref. 4, we have shown that the ratio of the sum of intensities of visible lines to the intensity of the line at 254 nm keeps constant at varying power of the generator initiating the discharge in the lamp. Therefore, change in the intensity of UV line can be monitored by change in a signal from visible lines. The authors of Ref. 14 call the density of photon flow measured in units photon/(cm^2·s) as the absolute intensity of a spectral line. Since the energy of photons in the spectral range of 254–546 nm varies more than twice, for convenient comparison we recalculated the intensities presented in Ref. 14 to the relative energy units (Fig. 5). It follows from the figure that the ratio of intensity of visible lines to intensity of the

line at 254 nm is practically constant in the wide range of intensity. When intensity changes a three times, the ratio is within 0.33–0.37.

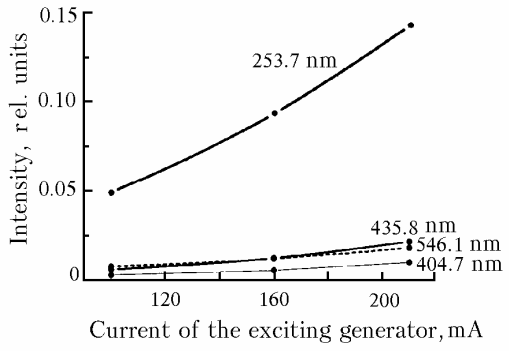

FIG. 5. Intensities of mercury spectral lines emitted by the VSB lamp at different current of the exciting generator. The lamp is filled with saturated mercury vapor + Ar *up to* 2 mm Hg, t = 22°C *(according to the data of Ref. 14 recalculated to energy units).*

Personal computer with multi-channel ADC was used to control operation of the experimental setup and to estimate concentration. The following signals come to ADC input: 1) signal from the solar photomultiplier FEU–142, proportional to I, 2) signal from the photodiode measuring the intensity of a sounding source (VSB–1 lamp), proportional to I_0, and 3) signal I_1 from the photodiode used to monitor intensity of radiation from the lamp (VSB–2) of the ozone generator. The corresponding program allows us to observe, at the monitor screen, all three signals, as well as density or concentration of ozone in the analyzer cell simultaneously in the recorder mode with sweep time from several minutes to several hours. In such cases, when high accuracy in ozone concentration estimation is not necessary, it can be estimated by the concentration characteristic stored in computer memory by inputting only the parameter I_1.

The fumigation chamber is a glass hood 6.5 liter in volume set at a glass foundation. Air-ozone mixture is admitted and discharged through holes in foundation. All communications for passage of air-ozone mixture are made of Teflon hoses. The time constant of the fumigation chamber (parameter determining the time at that the concentration comes to a steady state) at air-ozone mixture blow-down rate of 1 liter/min is 5 min. Therefore, variability of O_3 concentration in the chamber at the expense of intensity fluctuations of the ozonizer lamp manifests itself only at fluctuation period of the same order of magnitude.

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