Comparison of ultraviolet and chemiluminescent ozonometers

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In this study we have compared Model-49 (Thermo Environmental Instruments Inc., USA) and 3-02P ozonometers that employ different principles of operation. It is shown that Model-49 overestimates by two to three times the ozone concentration in the atmosphere because of the contribution from fine aerosol fraction. Therefore, in using this ozonometer, an additional filter or correction of ozonometer readouts for the effect of fine aerosol fraction is needed.

Biological and medical investigations showed[1] that tropospheric ozone is a virulent poison producing the general toxic effect and causing some other harmful consequences, such as mutagenesis, carcinogenicity, radiomimetic effect (effect on blood similar to that of ionizing radiation). In the degree of toxicity at direct effect on humans and animals, ozone exceeds such well-known poison as prussic acid. It is also a very strong oxidizer decomposing rubber and caoutchouc and oxidizing many metals, even from the platinum group.[2] Such a variety of possible negative consequences from the increase in the concentration of tropospheric ozone both for human beings and for the environment call for continuous monitoring of the ozone, especially, in the surface atmospheric layer.

To measure the ozone concentration in atmospheric air, current monitoring systems widely use devices based on chemiluminescence and absorption of UV radiation by ozone. At the same time, appropriateness of using these methods is periodically discussed in the literature, and followers of the UV and chemiluminescent methods form roughly equal groups. This discussion is rather principle, since other gases and aerosol particles of different size may present in the air simultaneously with the ozone, and they may distort device readouts. Consequently, the selectivity of the methods determines correctness and accuracy of measurements and, as a result, comparability of the data on the ozone content.

In July 1997 the Institute of Atmospheric Optics SB RAS in cooperation with the National Institute for Environmental Studies (Tsukuba, Japan) began airborne monitoring of greenhouse gases, including tropospheric ozone. For ozone measurements, the Institute of Atmospheric Optics has been employing a 3-02P chemiluminescent ozonometer developed and manufactured by OPTEK (St. Petersburg, Russia). Our Japanese colleagues decided to use a Model-49 UV ozonometer manufactured by Thermo Environmental Inc. (USA). Already in the first flights, we found rather large discrepancy between the synchronously recorded readouts of both ozonometers that exceeded their declared errors. This discrepancy had no systematic character. That is why we undertook an attempt to compare in laboratory and field tests these ozonometers to reveal causes for the discrepancy in their readouts. In this paper we present the results obtained in such experiments.

Both ozonometers were first tested with a reference GS-2 ozone generator manufactured by OPTEK and certified by the D.I. Mendeleev Research and Development Institute of Metrology (St. Petersburg). The ozonometers were connected through a tee-pipe connector as shown in Fig. 1.

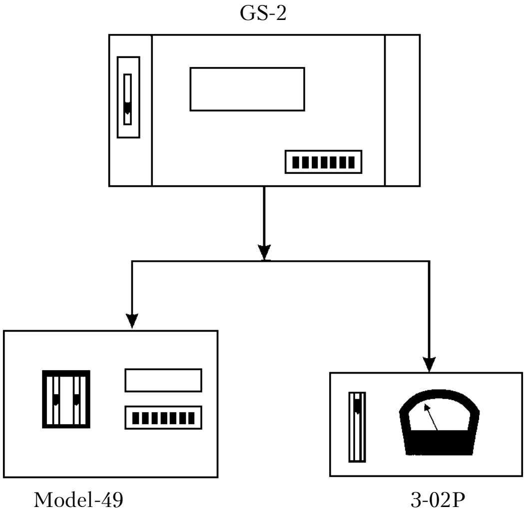

Fig. 1. Calibration of the ozonometers.

The generator was equipped with an input filter that cleans the air, therefore the ozone-enriched mixture coming synchronously to the ozonometers contained no additional admixtures. The results of synchronous measurements in the range of 0–250 $\mu g/m^3$ are shown in Fig. 2. The ozonometers' readouts were in different units: $\mu g/m^3$ for 3-02P and ppb for Model-49, and the plots are given in the initial units. Recall that 1 ppb $\approx 2\ \mu g/m^3$.

It can be seen from Fig. 2 that while operating with the reference mixture, the ozonometers' readouts coincide within their declared errors. The relative errors did not exceed 15% for 3-02P and 10% for Model-49. Consequently, both of the ozonometers in this case gave almost identical results.

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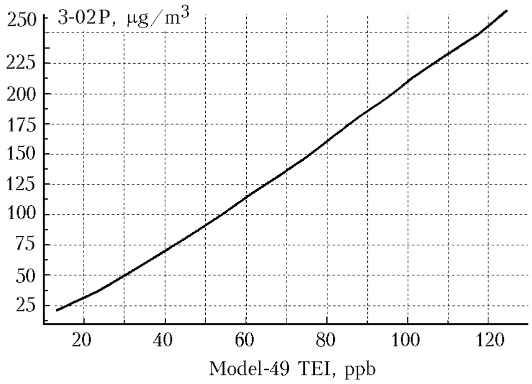

Fig. 2. Readouts of 3-02P and Model-49 ozonometers vs. concentration of the mixture generated by GS-2.

Then both ozonometers were put into operation at the TOR station,[3] which conducts 24-hour round-the-year monitoring of the air composition in the region of Tomsk Akademgorodok. A fragment of the ozone concentration measurements by both of the ozonometers conducted in March of 2001 is shown in Fig. 3 (Model-49 data are converted into μg/m^3).

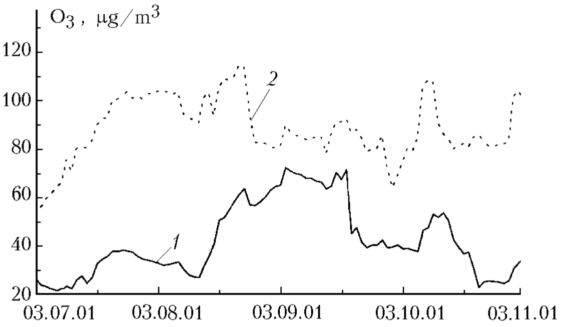

Fig. 3. Ozone concentration measured by chemiluminescent (*1*) and UV (*2*) ozonometers.

It can be seen from Fig. 3 that the Model-49 UV ozonometer gives two to three times higher ozone concentrations than the 3-02P chemiluminescent ozonometer. Only in some periods (daytime of March 9 of 2001), their readouts differ by 1.2–1.5 times. It is also seen from Fig. 3 that both ozonometers well reproduce the diurnal behavior of the ozone concentration, as well as its synoptic and mesoscale variations.

The differences in the ozonometers' readouts demonstrated in Fig. 3 were observed for several months of operation. The ozonometers were periodically tested with the GS-2 ozone generator by use of the test arrangement shown in Fig. 1, and in all the cases they gave the results close to that plotted in Fig. 2. The first assumption was that one ozonometer failed, but replacement with the other of the same type gave no any positive result. It became clear that either the Model-49 ozonometer overestimated the ozone concentration in measurements conducted in the atmosphere through additional measurement of some other admixture or the 3-02P ozonometer underestimated the ozone concentration due to quenching of the luminescence sensor by some other minor atmospheric constituent. Analysis of differences in the readouts for several months showed that the amplitude of the discrepancy usually increased in daytime and decreased in nighttime. However, no answer to the question which ozonometer correctly measured the ozone concentration was obtained.

On one of day, an air mass with a smoke from forest fires invaded the measurement site. In this case, the ozone concentration usually decreases down to zero, because it is quickly consumed in reactions with aerosol particles.[4] The 3-02P ozonometer adequately reacted to smoke income: its readouts fell down to zero. On the contrary, the Model-49 UV ozonometer, began to show very high ozone concentration (300–400 ppb) that couldn't take place according to physical laws. This initiated Model-49 testing with smoke aerosol.

To check the ozonometer reaction to smoke, we have assembled a setup shown in Fig. 4, where DAS is a diffusion aerosol spectrometer designed at the Institute of Chemical Kinetics and Combustion SB RAS. The setup was placed in an aerosol chamber. Cigarette smoke was used as an aerosol. Figure 5 shows the ozonometers' readouts in μg/m^3 versus the number concentration of aerosol particles in the chamber.

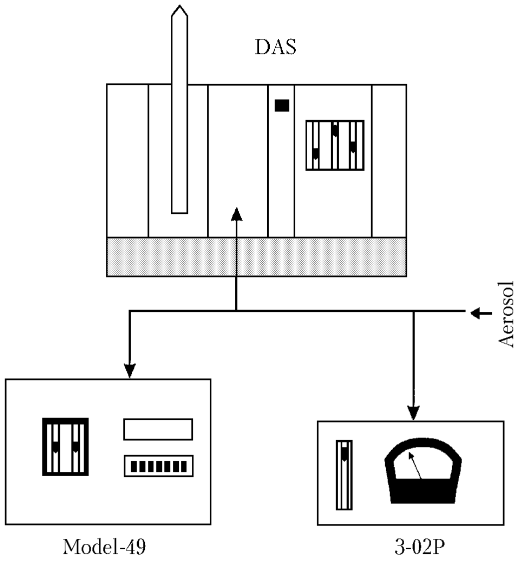

Fig. 4. Setup for ozonometer testing in aerosol chamber.

It can be seen from Fig. 5 that Model-49 readouts were nonzero, when the chamber contained no ozone, but cigarette smoke (aerosol). The higher was the aerosol particle number concentration, the higher were the Model-49 readouts. At the same time, the 3-02P ozonometer stably showed zero readouts regardless of the aerosol concentration. It also follows from Fig. 5 that the response of the Model-49 ozonometer depends on the type of smoke. Curve *1* in Fig. 5 corresponds to the cigarette smoke produced at the tobacco burning temperature of 700°C, while curve *2* is for the smoke produced at 500°C. These two types of smoke have different size spectrum,[5] as is confirmed by the data shown in Fig. 6.

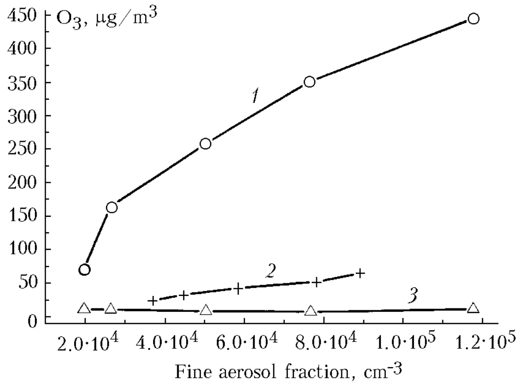

Fig. 5. Model-49 (*1*, *2*) and 3-02P (*3*) readouts in a cigarette smoke.

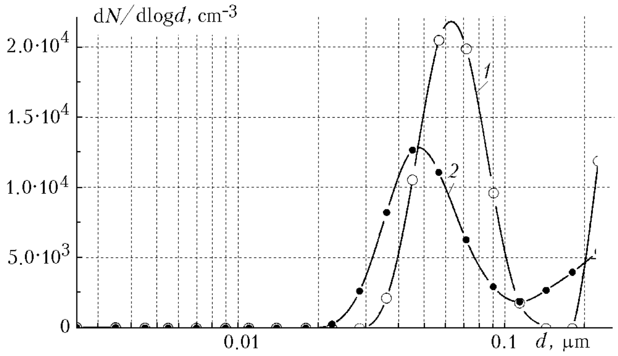

Fig. 6. Size spectrum of smoke particles produced at 700 (*1*) and 500°C (*2*).

It can be seen from Fig. 6 that both types of smoke have a bimodal size-distribution shape. The first, basic, modes lie in the range $d = 60$–70 nm for the higher-temperature smoke and $d = 40$–50 nm for the low-temperature smoke. The second modes lie in the range $d > 200$ nm and thus they are beyond the measurement range. Since Model-49 is a spectral device operating in the UV region, its reaction should be proportional to the aerosol extinction factor, which, in its turn, depends on the wavelength of radiation used in the ozonometer and on the size of aerosol particles.[6] In these experiments, we had no complete technical specification of the Model-49 ozonometer available, therefore now it is impossible to obtain more accurate estimates.

Thus, the aerosol testing demonstrated that the Model-49 ozonometer records, besides the ozone, fine aerosol fraction, likely, because of imperfection of its input filter, which does not filter out particles with the size smaller than 0.2 μm in diameter. When we connected a filter of the GS-2 generator to Model-49 in the aerosol chamber, its readouts decreased down to zero.

It also became clear why the discrepancy between the ozonometers' readouts in the atmosphere increased in daytime. According to earlier data,[7] the fine aerosol fraction is mostly generated in daytime and, consequently, the addition to Model-49 readouts increased in daytime too.

Thus, to use a Model-49 ozonometer for atmospheric measurements, one should either improve its input aerosol filter or correct its readouts proportionally to the number concentration of the fine aerosol fraction.

Based on the results of Model-49 tests in the aerosol chamber, we obtained an empirical equation for calculating the ozonometer response to the change in the number concentration of fine aerosol:

$$[O_3] = 2.5\cdot10^{-2}\, dN^{1/2},$$

where d is the geometric mean diameter of the mode of aerosol particles; N is the number concentration of aerosol particles, in cm^{-3}.

By applying this equation, we plotted the curves in Fig. 7: the readouts of the 3-02P ozonometer from Fig. 3 and the readouts of the Model-49 ozonometer corrected for the contribution coming from the fine aerosol. It can be seen that the readouts of both ozonometers become closer due to correction of the Model-49 data. In this case no discrepancies by two to three times were observed as was in the case with data presented in Fig. 3. At the same time, application of this equation does not completely remove the discrepancy, possibly, because the size spectrum and chemical composition of aerosol particles vary during a day.[7]

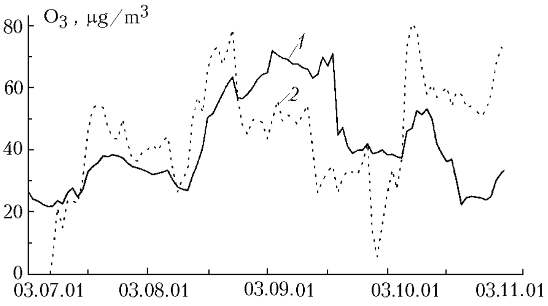

Fig. 7. Readouts of the 3-02P ozonometer (*1*) and corrected readouts of the Model-49 ozonometer (*2*).

Summarizing the results obtained, we would like to note that if a Model-49 ozonometer is used in atmospheric measurements, it is necessary to continuously monitor the fine aerosol fraction in the atmosphere or apply extra filters non-destroying the atmospheric ozone.

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