Surface ozone DOAS measurements comparison with the instrument measuring local ozone concentrations

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Abstract

National ozone monitoring and education centre (NOMREC) of Belarus has engineered a trace meter of surface ozone concentration, which has been exploited at Minsk ozonometric station since 2004. The method of differential absorption in spectral area 260 -290 nm is utilized. The instrument provides obtaining absolute concentrations of surface ozone and does not require any calibration under condition of exact preliminary adjustment of optics. Otherwise data observed contain a systematic additive and constant error. A generalized source of error is the incongruity of spectra of sounding radiation along a route with ozone and along a zero path route without ozone. It is shown, that usage for calibration of padding dishes with a known concentration of ozone does not solve the problem. To eliminate a systematic error of measurements, the procedure grounded on detection and elimination of differences in both spectra is offered. Unknown exact ozone concentration does not hinder solving the problem, it will be found simultaneously with the sought difference in the spectra. Some examples of applying the method are described.
We have investigated differences between measured local ozone concentrations and concentrations averaged over the route by means of natural simulation of local atmosphere circulation generated by thermal convection. Results clearly indicate that local vertical air movements are the main source of surface ozone variability.

1. Introduction

Trace systems on the basis of differential optical absorption spectrometry (DOAS) are widely used to monitor atmosphere gas concentrations including ozone. The trace technique provides measurement of surface ozone concentration averaged over a rather long trace without taking and delivering air samples into the measurement system. This technique substantially decreases errors of measurements of such unstable substance as ozone.

The surface ozone concentration optical trace meter has been engineered, obtained metrological certification, and is currently operating at National ozone monitoring research and education centre (NOMREC) of the Belarus state university. The instrument meets the principles of DOAS technique. Errors of calculated ozone concentration induced by almost all possible sources (i.e. by shortcomings of system elements and by errors in preliminary optical adjustment of the device) may be expressed generally in terms of discrepancy of source spectra emitted to the basic trace (trace of reference) and to the sounding trace. Regarding this discrepancy a multi-wave technique of ozone concentration measurement is proposed. This technique also allows to estimate the degree of influence of signal errors on results of calculations, to assess acceptable period of radiation source stability, etc. The theory of multi-wave DOAS technique simply explains the effectiveness of OPSIS method of gas concentration measurements.

Evidently, averaged over rather long trace ozone concentrations should differ from local ones. To demonstrate possible natural sources of such differences a special experiment has been carried out at Minsk ozonometric station. It has been shown that local vertical air movements induced by thermal convection are among possible sources of discrepancies in local and averaged over the trace surface ozone concentrations.

2. Description of the device

A schematic diagram describing the DOAS system is shown in fig. 1. A quartz halogen lamp in combination with the parabolic reflector (1) is used as a source of sounding radiation in the range of 260 – 290 nm. The moving mirror 6 allows to register radiation alternatively passing through a so-called basic trace (reference trace) or sounding trace. Despite a rather high intensity of probing UV radiation, according to our estimations, it does not cause essential additional formation or destruction of ozone molecules in the irradiated volume of the atmosphere.
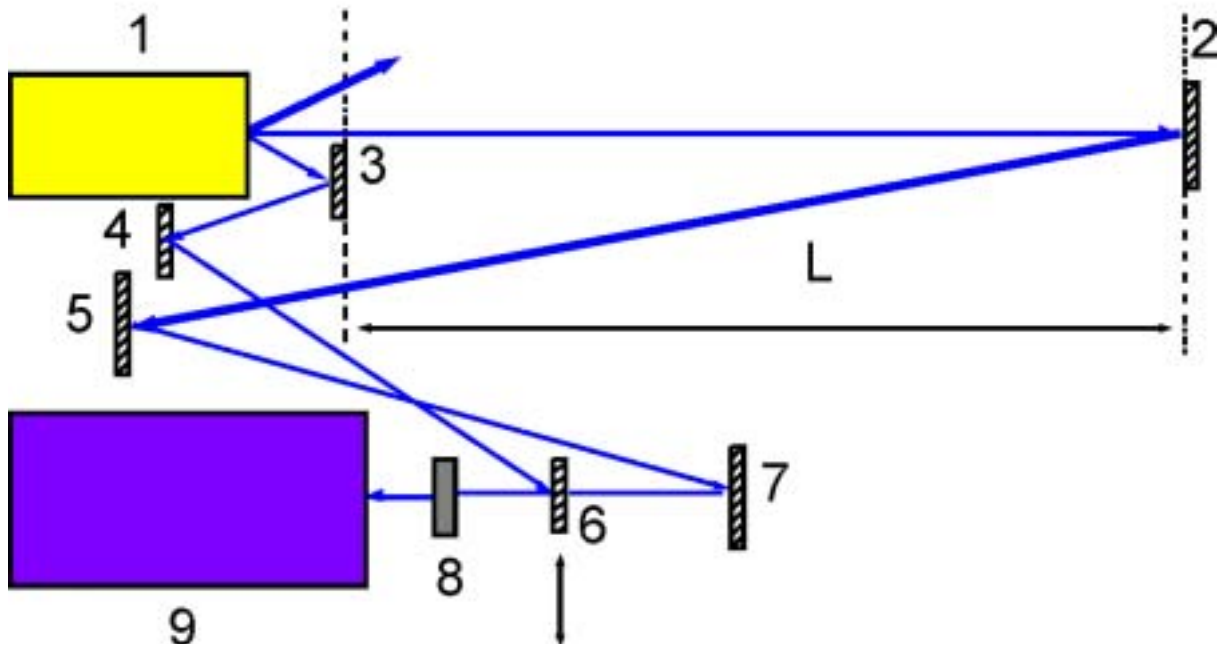
Figure 1. Schematic diagram describing the DOAS system: 1 - source of probing radiation; 2 - reflecting mirror; 3,4,6 - mirrors forming basic trace; 2,5,7 - mirrors forming sounding trace;
6 - moving mirror; 8 - interference filter; 9 - detection device.

A more uniform spectral distribution of the intensity in a range 280-350 nm is achieved with the use of a special interference filter 8 to damp the intensity at the long-wave border of the range. The maximum of the corrected spectrum is located near 285 nm in the long-wave region of the ozone absorption spectrum. The detecting system consists of a double monochromator (a dispersion of 1,3 nm/mm) and a photomultiplier tube. After amplification the signal is averaged for about seconds, digitized, and stored. A computer with the intermediate microprocessor operates the instrument as well as processes the results of measurement. Applying a reflecting mirror 2 allows to place the source of radiation and the detecting unit in the immediate proximity; this provides convenience in service and control. Multi-wave technique is used to measure surface ozone concentration. If being correctly aligned the device appears to be an absolute ozone concentration meter.

3. Theory of multi-wave technique of measurement surface ozone concentration

The signal registered at a wavelength λ can be presented in the form of

$$S_\lambda = g\gamma_\lambda R_\lambda I_\lambda \exp(-\tau_\lambda), \qquad (1)$$

where

g is a "geometric factor" to regard weakening of radiation passing through a trace owing to a divergence of radiation, restricted sizes of mirrors, not selective weakening of radiation being on a trace, etc. "Geometric factor" does not depend on a wavelength of radiation by definition, however differs for different traces being used;

γ_λ is the absolute spectral sensitivity of the instrument - the value of a registered signal from unit intensity of monochromatic radiation coming at an input of registration system;

R_λ is the reflectivity of the returning mirror;

I_λ is the spectral density of the radiation intensity emitted to a trace. Basically, it depends on a selection of the trace;

τ_λ is the optical distance of a trace. Essentially differs for used traces. In case of the basic trace $\tau_{\lambda 0} \equiv 0$ (we will mark with the second index the basic trace (0) and the trace of sounding (l) where it is necessary).

The optical distance of the trace of sounding includes an optical distance of ozone absorption $\tau_{oz\lambda}$, an optical distance of the molecular scattering along a trace $\tau_{mol\lambda}$ and an optical distance of weakening of radiation by aerosols and sediments τ_{aer}. The last one will be considered independent from a wavelength in a narrow enough (260-290 nm) spectral range of sondage. Thus,

$$\tau_{\lambda l} = \tau_{oz\lambda} + \tau_{mol\lambda} + \tau_{aer}. \tag{2}$$

The addend τ_{aer} may be transformed in a sort of component of the "geometric factor" for the sounding trace in view of τ_{aer} spectral non-selectivity hypothesis. However, in such situation the "geometric factor" ceases to be a constant of the instrument and begins depending on conditions of measurements. This condition is not essential as the offered procedure of calculation of ozone concentration admits a variability of the "geometrical factor". On the other hand, it would be desirable to have a permanent "geometric factor" to monitor stability of the measurement system adjustment. The contribution to an optical distance due to molecular scattering is calculated by means of known semi-empirical formulas [1] and depends on the length of the trace and air pressure in a place of measurements. A high accuracy is not obligatory for an estimation of this contribution as the error of ozone concentration calculation if completely ignoring molecular scattering normally does not exceed 2-3 %. The addend due to ozone absorption is determined by average concentration of ozone along the sounding trace n and by the trace-length l:

$$\tau_{o3\lambda} = \sigma_\lambda n l, \tag{3}$$

where σ_λ is the cross-section of radiation absorption by ozone at a wavelength λ.

In eq. (2) contributions due to absorption of radiation by other small gas components, for example, SO2 and NO2 are ignored. Estimates show, that these contributions from practically observed concentrations of the named components in the selected spectral range are small in comparison with the absorption by ozone.

Let's introduce denotations

$$z_\lambda = \ln(S_{\lambda 0}) - \ln(S_{\lambda l}) - \tau_{mol\lambda}, \tag{4}$$

$$G = \ln(g_0 / g_l) + \tau_{aer}, \tag{5}$$

$$X = nl. \tag{6}$$

Then in view of eqs. (1), (2), (3) and assuming that spectra of radiation emitted to both traces coincide we have

$$z_\lambda = G + X\sigma_\lambda. \tag{7}$$

Here the value of z_λ is a little bit transformed observed signals from the basic and sounding traces at a given wavelength and includes errors of different nature. As a matter of fact, this value is equal to the optical distance of ozone absorption along the sounding trace shifted on an ordinate axis by the logarithm of g-factors ratio and "spoiled" by errors of measurements. Parameters G and X are subject to definition. Actually, the equality (7) is never achieved precisely for all wavelengths with the fixed values of parameters G and X because of errors of signal measurements. In this connection it is necessary to regard the expression (7) as the equation of the straight line led through flock of experimentally measured values z_λ for predefined values σ_λ (which are unambiguously defined by the selected set of fixed wavelengths). In particular, to solve (7) it is enough to measure signals at two wavelengths, characterized by different values of the absorption cross-section σ_λ. As it will be shown below, such approach, however, is not optimal, if signals measured include errors of nonrandom nature.

To solve the problem approximately we will take advantage of the least squares method leading to minimization of the quadrates sum of deviations of the eq. (7) right-hand members from really measured values z_λ. As a result we receive

$$X = D_{z\sigma} / D_{\sigma\sigma}, \tag{8}$$
$$G = \bar{z} - \bar{\sigma}X, \tag{9}$$

where $D_{ab} = \overline{(a-\bar{a})(b-\bar{b})}$; upper line means averaging over all set of wavelengths. The covariance D_{ab} in the case of $a = b$ reduces to the common variance of the variable a.

The above mentioned relations are a basis for the analysis of various approaches to the problem of solving and estimating influence on results (calculated concentrations of atmosphere components) caused by possible errors.

4. Influence of an incongruity of spectra of radiation emitted to the basic trace and the sounding trace

Let's consider now a case when spectra of the source of radiation emitted to the basic trace and to the sounding trace differ. Such situation is not incredible, it is to be found rather often, serves as a source of systematic error of calculated ozone concentrations, and testifies to poor-quality preliminary adjustment of the instrument, as actually the same source of radiation is used for both traces. Distinction in spectra can appear as a result of beams usage from different parts of a extended emitter with different temperatures, as a result of distinction in spectral reflectivities of the mirrors used for creation of traces, etc. The task is to define the quantitative criterion of the adjustment quality and to define the possibility of calculation of corrections to measured ozone concentrations when distinction in spectra is sufficiently small.

Let the difference of logarithms of spectral radiation intensities emitted to the basic trace and sounding traces be described by a function $\varphi(\lambda)$:

$$\ln I_{\lambda 0} = \ln I_{\lambda l} + \varphi_\lambda. \tag{10}$$

Then instead of observed data (4) we receive

$$z'_\lambda = z_\lambda + \varphi_\lambda. \tag{11}$$

Using these data in procedure of calculation of X and G values(formulas (8), (9)) leads to

$$X' = X - D_{\sigma\varphi} / D_{\sigma\sigma}, \tag{12}$$

$$G' = G - \overline{\varphi} - \overline{\sigma} D_{\sigma\varphi} / D_{\sigma\sigma}. \tag{13}$$

Thus, results of calculations lead to constant shift of the calculated concentrations and the "geometric factor" when spectra of radiation emitted to the basic trace and sounding trace are different. The value of the shift is proportionate to covariance $D_{\sigma\varphi}$ and does not depend on actual concentration of ozone. Here it would be well to underline the mistake of popular opinion that an optical gas analyzer can be calibrated by means of the calibration cell filled with gas of known concentration and placed in an optical path of sounding radiation. As it follows from eq. (12), a systematic error in calculated gas concentration can not be detected in such way.

A set of values φ_λ can be represented as a sum of two addends:

$$\varphi_\lambda = \frac{D_{\sigma\varphi}}{D_{\sigma\sigma}} \sigma_\lambda + q_\lambda, \text{ where } D_{\sigma q} = 0. \tag{14}$$

Such representation is a discrete analogue of picking out contributions to the initial function $\varphi(\lambda)$ from the function $\sigma(\lambda)$ and an orthogonal to it function $q(\lambda)$. Here the equality $D_{\sigma q} = 0$ serves as an analogue of the orthogonality condition. In statistics this means a non-correlatedness of two sets of random variables. However, here we deal with nonrandom variables if abstracting from presence of accidental errors in z_λ. Therefore the term "orthogonality", despite its obvious inaccuracy, appears to be more suitable.

Let's consider the value $\Delta z_\lambda = z'_\lambda - G' - \sigma_\lambda X'$,which describes deviation of experimentally measured values z'_λ from ones calculated theoretically on the basis of the estimated values X' and G'. Assuming $z_\lambda - G - \sigma_\lambda X \equiv 0$ (i.e. errors of measurements are absent), we have

$$\Delta z_\lambda = \overline{q} - q_\lambda, \tag{15}$$

that is, the visible difference between the measured values of an optical distance of ozone absorption and their theoretical estimates is completely defined by the function $q(\lambda)$ (an orthogonal to $\sigma(\lambda)$ part of $\varphi(\lambda)$). In particular, quite obvious equalities $\overline{\Delta z} = 0$ and $D_{\Delta z \sigma} = 0$ follow from expression (15).

Thus, the value of Δz_λ shows an orthogonal to σ_λ part of difference of logarithms of radiation emitted to both traces. This difference can be revealed in the form of distinction from zero of some values Δz_λ, only if the function $\varphi(\lambda)$ *is not strictly proportional to the dependence* $\sigma(\lambda)$ (having in mind discrete analogues of these functions).
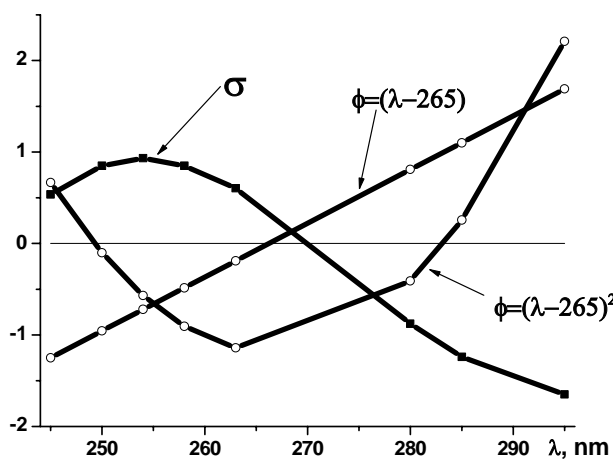
In particular, if only two wavelengths are used for measurements, such proportionality is always ensured, and distinctions in spectra of radiation cannot be revealed in fact. Therefore, systematic error in ozone concentration calculation cannot be revealed. If many wavelengths are used for measurements allowing to reproduce adequately enough peculiar spectral dependence of the ozone

absorption cross-section in the region of 260-290 nanometers, the situation mentioned above should be considered improbable. It is possible to expect that the function $\varphi(\lambda)$ will always include a noticeable component of $q(\lambda)$, "killing" of which by means of preliminary adjustment of the optical system will lead to simultaneous "killing" of the component proportional to $\sigma(\lambda)$.

Nevertheless, the absolute confidence of such outcome is inconceivable. Therefore, the measurement method loses the absoluteness if coincidence of spectra of radiation emitted to the basic trace and to the sounding trace is not ensured by instrument design features and by a procedure of its preliminary adjustment.

As a rule, discussed discrepancy in spectra of sounding radiation is represented by a rather smooth functional dependence on wavelength not holding essential fine-structure details. Therefore, it is intuitively clear, the more complicated shape the ozone absorption cross-section for the selected set of wavelengths is, the smaller the influence of distinction in spectra of emitted radiation on results of measurements will be.

This conclusion is above proved by mentioned example of the extremely unsuccessful case of two wavelengths (a linear dependence of the cross-section on a wavelength), by materials of following section and by the following model example.

To analyze the influence of used wavelengths number on accuracy of gained ozone concentration in conditions of different spectra of radiation emitted to the basic trace and to the sounding trace we have studied two models:

1. $\varphi_\lambda = \lambda - 265$,

2. $\varphi_\lambda = (\lambda - 265)^2$,

where the wavelength is set in nanometers.

Various sets of wavelengths have been used from the list of 245, 250, 254, 258, 263, 280, 285, and 295 nm. The data brought along and information about ozone absorption cross-section at the selected wavelengths allow to define the systematic error in ozone concentration calculation under the given conditions and to restore a form of a "visible" part of distinction in spectra - functions $q_\lambda = \varphi_\lambda - (D_{\sigma\varphi} / D_{\sigma\sigma})\sigma_\lambda$.

Figure 2. Functions σ_λ and φ_λ for the selected wavelengths. The ordinate scale is changed and shift along ordinate axis is used for clarity. Evidently, the shift does not affect the precision of the calculated ozone.

Table 1. Relative changes in contribution to a systematic error of ozone concentration induced by distinction in spectra of emitted radiation

Number of wavelengths	Contribution to a systematic ozone error (variant 1)	Contribution to a systematic ozone error (variant 2)
2	1.00	1.00
3	0.79	0.71
5	0.55	0.21
8	0.65	0.14

Values of ozone absorption cross-sections and both functions φ_λ are given in fig. 2 (scales for convenience have been changed). Relative changes of the systematic error of ozone concentration at usage of various sets of wavelengths are shown in table 1. The value of the error received by using a pair of wavelengths 295, 285 nm is accepted as unity. It is seen that increasing a number of wavelengths reduces the systematic error in the first case not more than twice. Similar lowering in the second case is almost the order. Graphs of the normalized functions q_λ (divided by $\sqrt{D_{qq}}$) for sets of three (295, 285, 280 nm), five (295, 285, 280, 263, 258 nm), and all eight wavelengths, and for both variants of distinction in spectra of emitted radiation are given in fig. 3a, 3b.
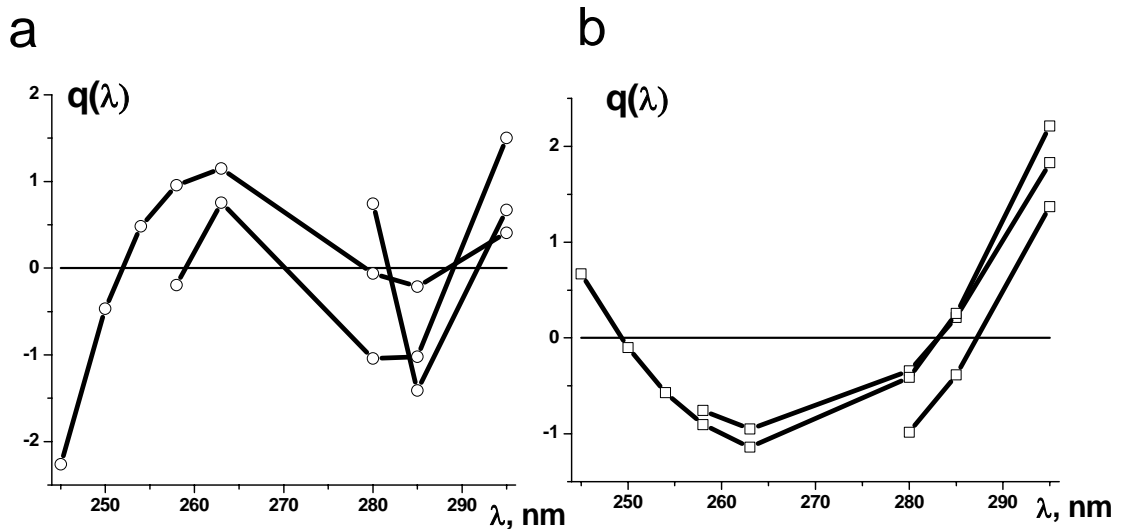
Figure 3. Normalized values of the "visible" part of used distinction in spectra for cases of 3, 5, and 8 wavelengths to calculate ozone concentration. a – distinction is described by linear dependence on wavelength, b – by quadratic one. Remember that in the case of two wavelengths "visible" part vanishes, although the systematic error in ozone concentration is still present.

It is convenient to use the quantity $D_{\Delta z \Delta z} = D_{qq}$ describing a degree of distinction of a set of values $\{\Delta z_\lambda\}$ from zero for estimating the quality and stability of preliminary adjustment. Obviously, the requirement $D_{\Delta z \Delta z} = 0$ is a necessary, but an insufficient condition of coincidence of spectra of emitted radiation to both traces. As mentioned above, it is possible to reveal only the part of distinction in spectra that does not influence measured concentration of ozone. The most essential part remains "invisible" in the sense that it is impossible to estimate its influence on an error of ozone concentration calculation and to introduce appropriate correction.

Taking into account an incongruity of spectra it is possible to correct results of calculations, if possibility to register and to compare spectra of emitted radiation is ensured.

5. OPSIS technique

It is reasonable to discuss a case when rather wide spectral interval is used for measurements, the detailed spectrum is registered, and then observed data are processed. For final calculation of concentrations the transformed data in a sufficiently narrow spectral interval are used where fine-structure details of absorption coefficients of atmosphere components appear.

The procedure used in OPSIS trace atmosphere gas meters [2] is actually drawn upon to such case. The named procedure is based on the presence of narrow absorption spectral lines for gases

being analyzed. The spectral distribution of the source radiation in zero approximation is supposed to be practically constant within the each absorption band .

Actually, the spectral distribution of the source radiation is used in calculations, however it is measured extremely rare. Within the OPSIS technique a polynomial approximation of the logarithm of the registered spectrum is used, normally through a polynomial of 5-th order .

With the purpose of more rigorous substantiation of a procedure, we will extend the approach, having replaced such approximation with a procedure of smoothing which will be viewed as convolution of input data with a non-negative curve of finite width. It is one of the variants of signal filtering standard procedure. An application of OPSIS technique requires lack of structured details in a spectrum of the radiation source with width comparable to linewidths of an absorption cross-sections of gases to be analyzed.

In view of mentioned, function φ_λ (eq. (10)) that possesses a high degree of smoothness (as well as the emitted spectrum of sounding radiation) plays an essential role in equality (11). Immediate usage of eq. (11) for calculation of gas concentration, obviously, will lead to the noteciable systematic error.

Let's take on smoothing of the values z'_λ measured with a small wavelength step (a requirement of procedure OPSIS applicability), and then subtract the smoothed spectrum from raw data z'_λ. The outcome of smoothing will be marked by the upper sign of a wave. Then in view of eqs. (1-10) and equality $\widetilde{\varphi}_\lambda = \varphi_\lambda$ being achieved with a high accuracy owing to adopted suppositions we have

$$ z'_\lambda - \widetilde{z}'_\lambda = z_\lambda - \widetilde{z}_\lambda = X(\sigma_\lambda - \widetilde{\sigma}_\lambda). $$

Thus, spectrum of sounding radiation and the parameter linked to "geometric factors" are eliminated from the data used to calculate ozone concentration. Obviously, two requirements should be satisfied to apply the approach: $\widetilde{\varphi}_\lambda = \varphi_\lambda$, $\sigma_\lambda \neq \widetilde{\sigma}_\lambda$ in the range of wavelengths being used to measure gas concentration. Meaningfully, the half-width of the smoothing filter should exceed half-widths of absorption spectral lines, and there should be no structural details in the spectrum of the source radiation with width, comparable to linewidth of absorbing gas components.

More precisely, there should be no such details in a difference of logarithms of the sounding radiation real spectrum and of a source spectrum (possibly, registered earlier and under other conditions). In the case of ozone two variants of applying the procedure are possible: to use low-intensity spectral structural features of ozone absorption close to its maximum, and to use all range of wavelengths, occupied by Hartley band. Clearly, in the first case the procedure will be weakly sensitive to ozone because of a smallness of differences $\sigma_\lambda - \widetilde{\sigma}_\lambda$, in the second case the problem is how to measure signals for a wide enough interval of wavelengths with small wavelength step. These complexities lead to a lowering of a measurement accuracy of ozone concentration within OPSIS procedure [2].

6. Influence of random errors of signals measurements

Let's accept a quite natural hypothesis, that errors of signals measurements δS_λ at each working wavelength have random nature, and observed data at different wavelengths are not correlated with each other. It means equalities $\overline{\delta S_\lambda} = 0$, $\overline{\delta S_\lambda \delta S_{\lambda'}} = 0$ occur, if $\lambda \neq \lambda'$. Here summation in averages calculation is made (unlike the previous cases) over a set of repeatedly measured signals at a wavelength λ or over a set of repeatedly measured pairs of signals at wavelengths λ and λ'. Obviously, this is valid (according to eq. (4)) in relation to values z_λ: $\overline{\delta z_\lambda} = 0$, $\overline{\delta z_\lambda \delta z_{\lambda'}} = 0$, if $\lambda \neq \lambda'$. We will mark the dispersion of a random variable δz_λ as $d_\lambda = \overline{\delta z_\lambda \delta z_\lambda}$. Then for the

dispersion of X induced by fluctuations of δz_λ it can be received

$$D_{XX} = \frac{1}{N^2 D_{\sigma\sigma}^2} \sum_\lambda (\sigma_\lambda - \overline{\sigma_\lambda})^2 d_\lambda .$$

Here N is amount of wavelengths. If dispersions d_λ are of one order for all wavelengths, it is possible to write down

$$D_{XX} \approx \frac{d}{N D_{\sigma\sigma}},$$

where

$$d = \frac{1}{N} \sum_\lambda d_\lambda \qquad\qquad (16)$$

is an average value of the dispersion of z_λ. For the relative standard deviation of the measured ozone concentrations one can have

$$\varepsilon = \frac{\sqrt{D_{XX}}}{X}.$$

It is necessary to express only a random error in z_λ through relative errors of signals $\varepsilon_{\lambda 0} = \delta S_{\lambda 0} / S_{\lambda 0}$ and $\varepsilon_{\lambda l} = \delta S_{\lambda l} / S_{\lambda l}$, and to connect a dispersion d_λ with the dispersion of signals. According to (4), (6) and in view of a smallness of errors in signals, the error in z_λ is equal to

$$\delta z_\lambda = \frac{\delta S_{\lambda 0}}{S_{\lambda 0}} - \frac{\delta S_{\lambda l}}{S_{\lambda l}} = \varepsilon_{\lambda 0} - \varepsilon_{\lambda l}, \qquad\qquad (17)$$

i.e. it is equal to the difference of relative errors in signals. From here by quite natural assumption about a non-correlatedness of errors $\varepsilon_{\lambda 0}$ and $\varepsilon_{\lambda l}$ it is found

$$d_\lambda = s_{\lambda 0} + s_{\lambda l},$$

where

$$s_{\lambda 0} = \overline{\varepsilon_{\lambda 0}^2}, \; s_{\lambda l} = \overline{\varepsilon_{\lambda l}^2}$$

are relative dispersions of signals which are being estimated during direct measurements. Therefore,

$$d = \frac{1}{N}\sum_{\lambda}(s_{\lambda 0} + s_{\lambda l}). \qquad (18)$$

The brought equations attach relative dispersions of signals at all wavelengths to the dispersion of calculated ozone concentration.

Here it is reasonable to return to a problem of a possible incongruity of spectra of radiation emitted to the basic trace and to the sounding trace. Earlier it has been noted, that the value $D_{\Delta z \Delta z}$ is a convenient quantitative assessment of quality of a trace meter preliminary adjustment and of stability of preliminary adjustment in time. In fact, this value can be never reduced to a zero due to presence of random errors in signals. In particular, if $\varphi_{\lambda} \equiv 0$ (spectra are congruent), according to (16) - (18) we have

$$D_{\Delta z \Delta z} = d. \qquad (19)$$

Thus, random errors of measurements give a contribution to the value $D_{\Delta z \Delta z}$ and make it positive even under conditions of coincidence of spectra of radiation emitted to the basic and to the sounding traces. Therefore, realization of equality (19) corresponds to ideal preliminary adjustment of the measurement system.

7. Interval of radiation source stability

The technique of ozone concentration is based on the hypothesis about enough high temporary stability of the radiation source . Therefore, measurements of signals from the basic trace are being conducted rather rare. At the same time, a source radiation practically always varies in time. Not only absolute intensity of radiation is changing, but its relative spectral distribution as well. Therefore usage for calculations of source radiation spectrum registered from the basic trace in earlier instants actually leads to the discussed above problem of distinction of emitted spectra. That's why it is reasonable to define a period during which the spectrum of emitted radiation may be considered unchanged. After such a gap signal measurements from the basic trace should be iterated. Time intervals between measurements from the basic trace are being defined below.

Suppose there has been a modification of a source spectral distribution during time Δt for unknown reasons. Then the signals measured from the sounding trace, will correspond to a current state of the source at time t, and the signals measured from the basic trace, according to a procedure of measurements will correspond to the moment of their registration - $t - \Delta t$. We will denote

$$\varepsilon_{\lambda}(\Delta t) = \ln[I_{\lambda 0}(t + \Delta t)/I_{\lambda 0}(t)] = \ln[S_{\lambda 0}(t + \Delta t)/S_{\lambda 0}(t)].$$

This value is approximately equal to the relative variation of spectral intensity of the source at a wavelength λ for a period Δt. It is easy to conclude, that the absolute error of the calculated ozone concentration is defined in this case by the ratio

$$\delta X_{\Delta t} = \frac{D_{\sigma \varepsilon}}{D_{\sigma \sigma}}.$$

In the particular case, when $\varepsilon_{\lambda} = \mathrm{const}(\lambda)$ (a proportional modification of source spectrum at all wavelengths has been occurred), we come to an obvious result $\delta X_{\Delta t} = 0$.

The received equation allows to estimate a time interval during which instability of the source

generates an absolute error of ozone concentration, which does not exceed the given value. Let this value be equal to E. Then the admissible time interval T_{stabil} between measurements of signals from the basic trace under the assumption of a linear dependence δX on Δt is defined by expression

$$T_{\text{stabil}} = \frac{\Delta t E}{\delta X_{\Delta t}}.$$ (20)

In an operating procedure time T_{stabil} is restricted by a requirement $T_{\text{stabil}} \leq 30 \min$. In other words, signals from the basic trace are being measured not rare, than after half an hour, despite great values T_{stabil} derived from (20). E value corresponds to 3 ppb, value Δt is equal to the value T_{stabil} defined at the previous stage. New value T_{stabil} is calculated after the next basic trace measurements. At the beginning of operation the value T_{stabil} is set equal to duration of one series of ozone concentration measurements.

8. Comparison of surface ozone data averaged over the route with ones measured at a local point
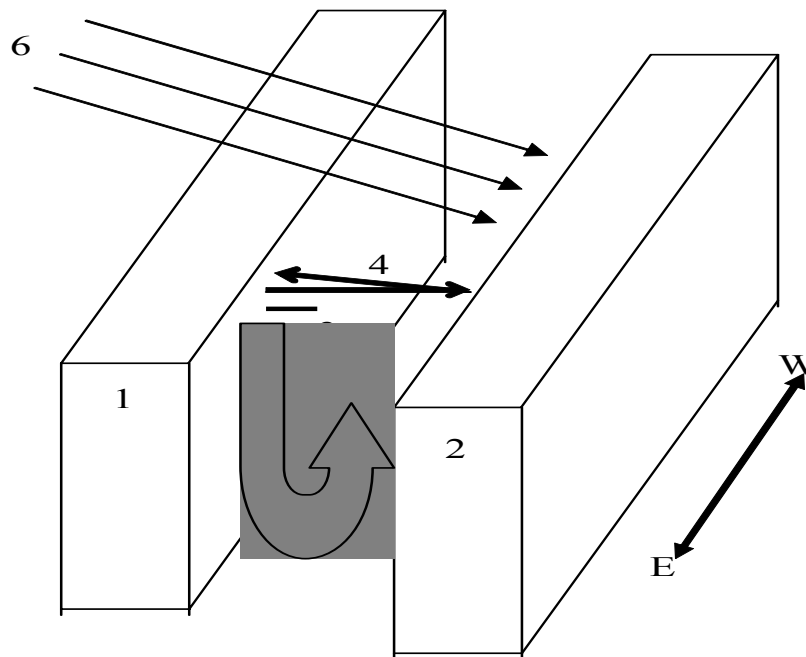
Figure 4. The plan of installation of devices, the sounding trace, and local air circulation arising in clear windless weather. 1- the first building, 2 - the second building, 3 - an air inlet for the TEI-49C device; 4 –the sounding trace; 5 - motion of air in area between buildings; 6 - direction of sunlight slope.

Two types of instruments are usually used to monitor surface ozone concentration. These are: instruments that measure ozone concentration at a local point, and instruments that measure ozone concentration averaged over a rather long route of sounding radiation.

There should be a discrepancy between values measured by the instruments of different types. First, the discrepancy may be caused by inhomogeneous surface, which serves as the destroyer of ozone. Second, the difference in results may be caused by local vertical movements of the atmosphere in the boundary layer. If such movements change the direction along the route of sounding radiation a discrepancy between local ozone concentrations and ones averaged over the route is guaranteed despite the fact that homogeneity of the earth surface is being provided.

We have investigated differences between measured local ozone concentrations and concentrations averaged over the route by means of natural simulation of local atmosphere circulation generated by thermal convection. Results clearly indicate that local vertical air movements are the main source of surface ozone variability.

8.1. Description of the experiment

TEI-49C ozonometer has been used for local point s. A self engineered device described in section 2 has been used to measure ozone concentration averaged over the route.
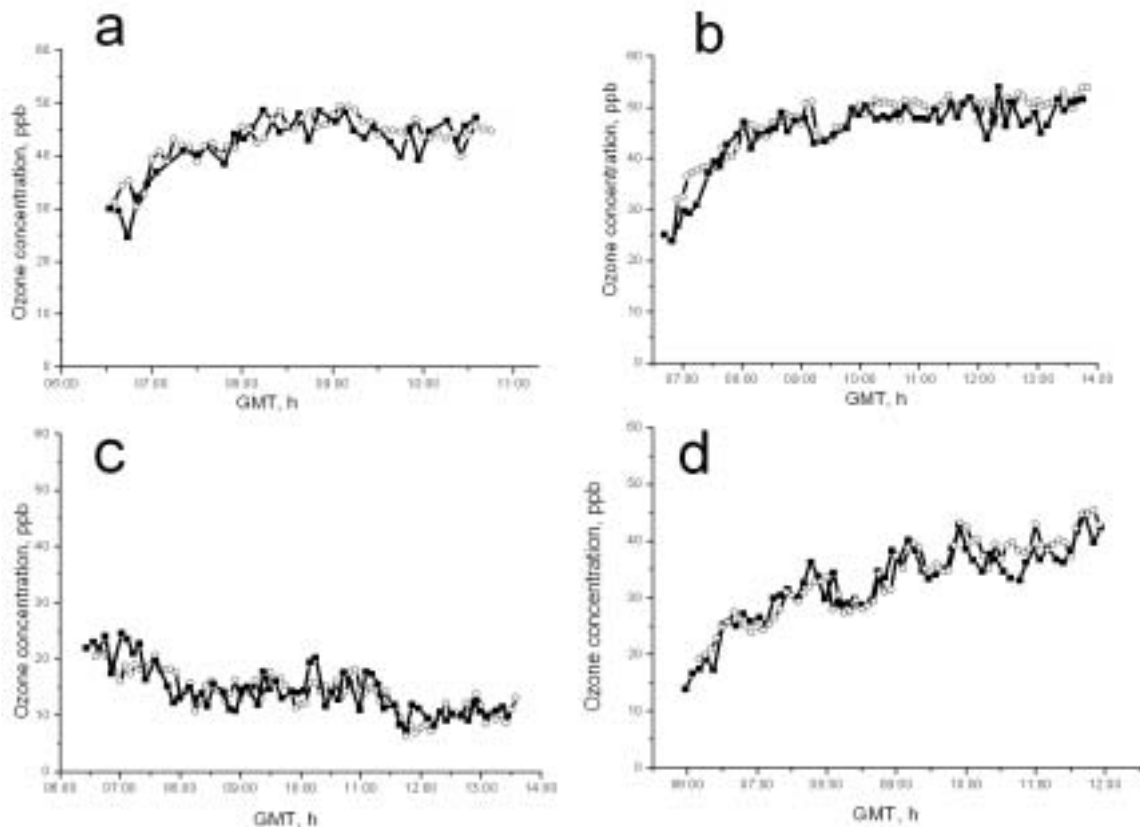
Figure 5. Daily variations of surface ozone concentration measured by TEI-49C (circles) and by NOMREC ozone concentration trace meter (squares). "a" – 2.08.2005, clear in the morning , in the afternoon variable cloudiness; "b" – 3.08.2005, variable cloudiness, fresh enough western wind; "c" – 8.08.2005, continuous cloudiness, precipitates; "d" – 17.08.2005, clear in the morning, almost continuous cloudiness in the afternoon.

The trace for the sounding ultraviolet radiation is fixed between tops of the two parallel long buildings of about 30 m height and at a distance of 50 m (see fig. 4). Buildings have approximately East-West orientation. Direct sun rays have no access to the back side of the first building and always heat the front side of the other one if clouds are absent. This leads to a local atmosphere circulation generated during clear sky days due to differences in temperatures of neighboring sides of the buildings. An upper air with relatively high ozone concentration falls

down along the cold side of the first building, ozone is being destroyed at the surface of the ground, and impoverished air then lifts up along the warm side of the second building.

Evidently, averaged ozone concentration between the buildings should be smaller than the local one near the cool side and greater than ozone concentration near the warm side.
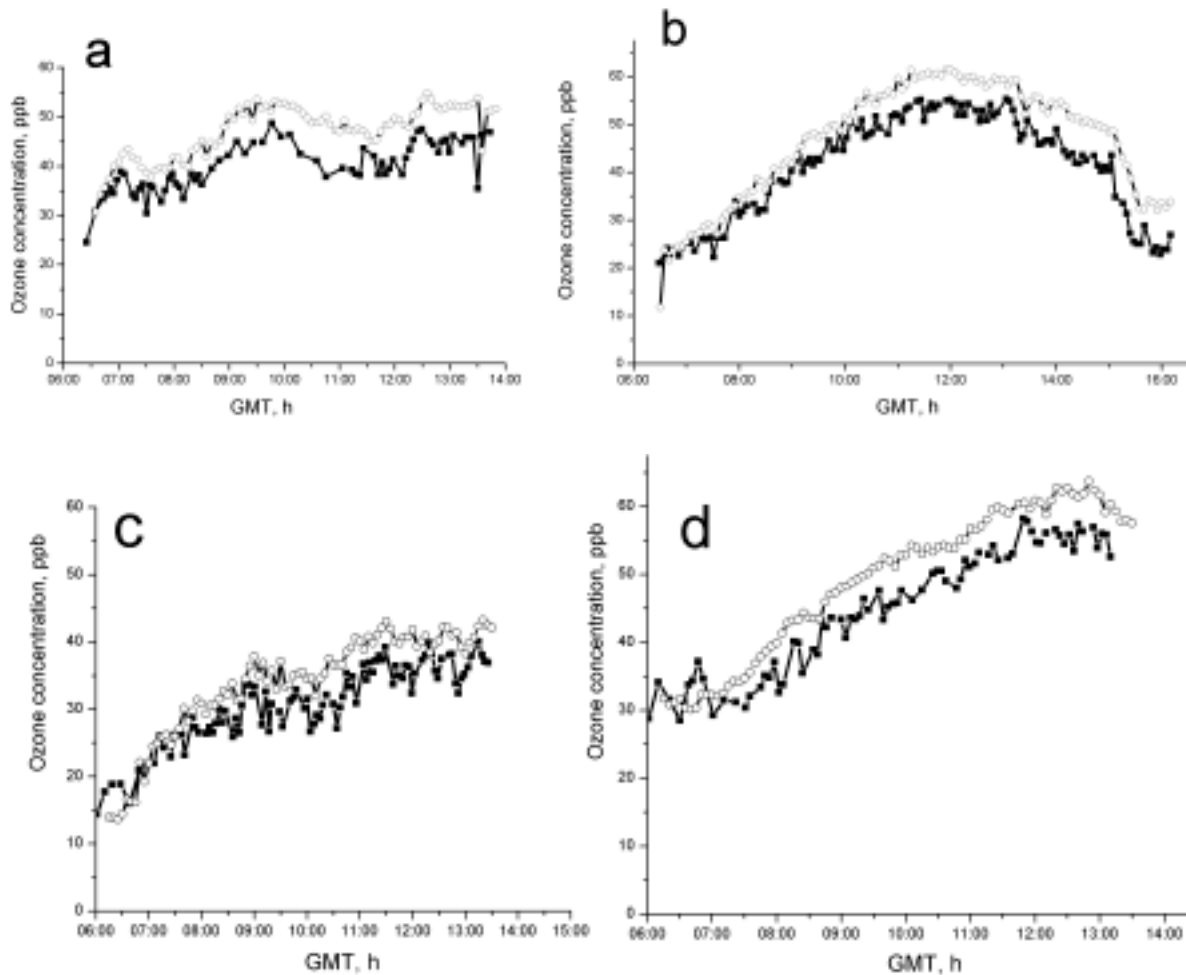
Figure 6. Daily variations of surface ozone concentration measured by TEI-49C (circles) and by NOMREC ozone concentration trace meter (squares). "a" – 25.08.2005, clear day; "b" – 30.08.2005, feeble variable cloudiness; "c" – 6.09.2005, cloudy with clearings; "d" – 8.09.2005, morning cloudiness disappears by the midday.

Clouds or strong eastern (western) winds between the buildings diminish the differences between ozone concentrations. Also the effect should not be detectable in the morning until the south side of the second building becomes significantly warmer than the north side of the first one.

8.2. Results of measurements

General conclusions given in the previous section are confirmed by direct s made in August-September 2005 (see figs 5-6). Fig. 5 shows good conformity of ozone concentrations due to the dumping of local vertical air circulation by specific weather conditions. These are: no direct sun heating of the front side of the second building (figs 5a, 5c, 5d), or rather strong wind in the West-East direction destroying the vertical convection started near the local noon (fig. 5b). Fig. 6 demonstrates another situation when developed local circulation induces discrepancies in local and averaged over the sounding route ozone concentrations.

8.3. Conclusion

An unusual settlement of instruments providing different types of surface ozone measurements leads to a discrepancy of results which is generated mainly by local vertical air flows.

The settlement has been designed in order to show that local vertical air exchange is responsible for the most of surface ozone variability. Despite an artificial design of settlement, the conclusion may be spread to a case of generally accepted settlement which satisfies WMO requirements.

Coincidence of results from the two types of instruments may be expected only in conditions of stable atmosphere when vertical air convection is frozen.

The results may be directly generalized to a case of an ordinary phenomenon - alternation of lowering and rising local convective air flows over a homogeneous surface.

Thus, our experiments clearly indicate that coincidence of ozone concentrations at a local point with ones averaged over the sounding trace can not be achieved in general case, even if requirements of WMO to the arrangement of surface ozone measurements have been met. Methods based on of concentration averaged over the route are preferable for purposes of surface ozone monitoring.

9. Summary

Optical trace meters of surface ozone concentration are widely spread nowadays. They have certain advantages comparing to local point surface ozone meters. In particular, results of trace measurements are less sensitive to influence of features 2 of the equipment arrangement and local air circulation. At the same time, a serious obstacle to widely apply the trace technique is the problem of ensuring absoluteness of measurements, i. e. creating conditions when regularly operating device produces adequate results without previous calibration to a reference meter. As shown above, such problem cannot be solved completely in general case. The theory of multi-wave trace measurements shows that in the particular case of OPSIS procedure the absoluteness of measurements occurs. Indexes of correctness of optical system adjustment and its change in time are defined within multi-wave technique of measurements.

By means of comparative measurements in special conditions it is shown, how local circulation of the atmosphere influences a discrepancy in local and trace measurements of surface ozone concentration.

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