

Ozonometer M-124 calibration for the Ukrainian network: method and results

A. Grytsai¹, G. Milinevsky^{1,2*}, O. Evtushevsky¹, M. Sosonkin², V. Kravchenko¹, V. Danylevsky¹

¹Taras Shevchenko National University of Kyiv, 64/13 Volodymyrska St., 01601, Kyiv, Ukraine

²Main Astronomical Observatory of NAS of Ukraine, 27 Akademika Zabolotnoho St., 03143, Kyiv, Ukraine

M-124 filter ozonometers are used for total ozone measuring in Ukraine since 1970s. Recently the need to calibrate several M-124 instruments of the Ukrainian filter ozonometer network is raised to continue ozone observations. The calibration became possible owing to the accurate ozone measurements by Dobson spectrophotometer started in 2010 at the Kyiv-Goloseyev WMO station located at the Main Astronomical Observatory of National Academy of Sciences of Ukraine. For calibration purposes the simultaneous M-124 and Dobson Direct Sun measurements were carried out during the 2013–2016 period by researchers from Taras Shevchenko National University of Kyiv and Main Astronomical Observatory. The M-124 instrument has two spectral channels: first is 305 nm and second is 325 nm. Outgoing signal from M-124 is determined by transparency of the terrestrial atmosphere and filter characteristics. Theoretical description of the solar radiation propagation through the atmosphere is determined by the Bouguer-Lambert-Beer law taking into account ozone absorption, Rayleigh and aerosol scattering. Parameters of the aerosol scattering have been determined from observations with the CIMEL sunphotometer of Aerosol Robotic Network which is also located at the Kyiv-Goloseyev station. The ozonometers optical characteristics were studied after M-124 refurbishment and modernization at the Central Geophysical Observatory of Ukraine that includes a significant part of the whole calibration work. Knowing the spectral dependence of each filter is necessary to calculate signal ratios in two channels. This information allowed solving the inverse problem of determining total ozone content in the terrestrial atmosphere. Comparison of these results with Dobson spectrophotometer data shows their good quality even without an additional correction. These results open a possibility to calibrate M-124 filter ozonometers for future ozone measurements at the observation sites of the Ukraine ozonometer network.

Key words: instruments and techniques, methods: observational, radiative transfer

INTRODUCTION

Ozone in the atmosphere is a minor constituent that is significant due to absorption of solar ultraviolet (UV) radiation and almost nontransparent for light with wavelengths less than 293–295 nm [27]. Importance of that for biological life on the planet brings a lot of attention to spatial and temporal ozone variability. The molecule number of specific constituent in atmospheric column with unit cross-section that normal to the Earth surface is known as total column. Total ozone column (TOC) or total amount of ozone in vertical atmospheric column is expressed in Dobson Units (DU) and is equal to thickness of the pure ozone layer at standard temperature/pressure conditions, 1 DU = 10^{-5} m, or 1 DU is equivalent to 1 m atm cm [22].

The TOC level is measured by remote observations using radiation, which passes through the Earth's atmosphere or scatters in the atmosphere. Preferably, the sunlight intensity with a wavelength longer than 300 nm is measured [28]. In ground-

based measurements, light transfer depends mainly on the absorption by ozone and aerosol as well as Rayleigh scattering. The intensities ratio at different wavelengths can be determined much more accurately than the intensity itself. This causes the application of two-wave methods: first (second) wavelength should be characterised by strong (weak) absorption by ozone [9]. Even better result is provided with measurements in two pairs of wavelengths, as implemented in Dobson spectrophotometer [22]. The latter approach can minimise the aerosol influence.

Global ground-based network of ozone measurements consists mainly of Dobson spectrophotometers and Brewer spectrometers. These instruments isolate the desired range of wavelengths by the spectral decomposition of solar light. The advantage of this approach is the low variability of the instrument properties with time and the possibility of separation of a narrow spectral area, less than 3–4 nm for Dobson spectrophotometer [22]. The latter allows the calculation of the TOC values with monochromatic approach that greatly simplifies the solution.

*genmilinevsky@gmail.com

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In addition to Dobson spectrophotometers and Brewer spectrometers, the global ozone network includes also the filter ozonometers M-124 [15]. The filter ozonometer was developed by Gushchin and Sokolov in 1970s, when 450 instruments have been produced [17]. In Ukraine the filter ozonometers M-124 have been used in last decades since 1970s [16, 18]. The filter instruments M-124 measure solar light at 302 and 326 nm with the spectral band pass of 20 nm and the accuracy is about 4% for zenith blue and up to 6–8% for cloudy observations [15].

Large filter bandwidth prevents monochromatic approach and initiates to use the integral approach. The intercomparisons showed that the discrepancies between the mean TOC values obtained with the ozonometer M-124 and the Dobson spectrophotometer did not exceed 3–5% [17]. In average, the accuracy of the transfer of the calibration scale into the M-124 network is estimated to be about 3% [15].

Comparison with satellite TOMS instrument for the Direct Sun (DS) measurements showed that the standard deviations for Dobson, Brewer and M-124 instruments were about 2.4%, 2.2 and 3.5%, respectively. For less accurate Zenith Sky measurements the standard deviation is 3.8%, 4.0% and 4.7%, respectively [12]. In the later comparisons with satellite observations, filter ozonometers demonstrated also larger mean and median values of the difference, 2.5% and 2.0%, respectively, against 1.3% and 1.6%, respectively, for the Dobson and Brewer instruments [13]. It was concluded that the filter ozonometer network performance is slightly better in 2001–2006 than in 1996–2000.

Historically, the TOC observations with the M-124 filter ozonometers have been started in the Kyiv region since 1973 [7, 23]. These data were archived in the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) database, Global Atmosphere Watch (GAW) website¹ and are available for the observational period 1973–1997. In the same region, analysis was performed using M-124 at Lisnyky station near Kyiv for the time period of 1997–2002. The ozonometer M-124, operated at the Lisnyky station, was calibrated using Dobson spectrophotometer No. 031 at Vernadsky Antarctic station. Its comparison with the Lisnyky station ozone data obtained with TOMS–EP spectrometer measurements showed near zero relative difference (from –0.4% to 0.1%) during 1997–1999 [14]. At the same time, difference was 0.15% for cloudless sky and –3.5% for totally overcast sky. In Ukraine this type of ozone measurements was realised also at the Lviv, Odessa and Feodosia stations since 1973–1974, and at the Kyiv and Boguslav stations since 1990, which all form the Ukraine ozonometer network [7, 23].

In late 1990s the filter degradation of M-124 instruments available in Ukraine, took place. Quality

of filters, used in M-124, becomes much worse during long-term operation and this makes impossible the reliable measurements. In this regard, eight M-124 instruments have been upgraded including filter replacements, electronics modification and thermoregulation installation. In general, M-124 are quite common instruments and still operating at over a third of ozonometric network at wide area between Eastern Europe and Eastern Asia [8]. Calibration of ozonometers is performed traditionally at the Main Geophysical Observatory near St. Petersburg (Regional Centre for calibration of filter ozonometers) using Dobson spectrophotometers. For ozonometers M-124 available in Ukraine the calibration is possible since 2010, when Dobson spectrophotometer was installed at the WMO Kyiv-Goloseyev station [11, 23].

In May 2010, spectrophotometer Dobson No. 040 has been transferred from the Royal Meteorological Institute of Belgium to Taras Shevchenko National University of Kyiv and it operates at the station Kyiv-Goloseyev (Kyiv-Goloseyev, Main Astronomical Observatory (MAO) of National Academy of Sciences building, 50.364°N, 30.497°E, altitude above sea level 206 m, WOUDC Regional station ID 498, GAW ID KGV). During summer months in 2013–2016, parallel observations using Dobson spectrophotometer No. 040 and refurbished instruments M-124 have been made. Along with Dobson spectrophotometer, the CIMEL sun photometer of AERONET (Aerosol Robotic Network² [10, 20]), operates at the same station and allows determining aerosol properties [24, 25]. The development of the calibration method and results of the intercomparison of upgraded ozonometers M-124 with Dobson spectrophotometer data are analysed in this work.

THEORY FOR TOTAL

OZONE COLUMN CALCULATION

To reveal the TOC value in ground-based observations we describe first the monochromatic approach. Total ozone column X can be calculated on the base of two wavelengths measurement [22]:

$$X = \frac{\lg \frac{I_0}{I'} - \lg \frac{I}{I'} - (\beta - \beta') m \frac{p}{p_0} - (\delta - \delta') \sec Z}{\mu(\alpha - \alpha')} \quad (1)$$

Expression (1) is obtained from Bouguer–Lambert–Beer’s law, taking into account ozone, aerosol and Rayleigh scattering influence on the direct solar radiation transfer through the Earth atmosphere. Here I_0 is solar radiation intensity at the top of atmosphere, I is intensity of the solar radiation at the Earth surface in the observation point, μ is ratio of the actual and vertical paths of solar radiation

¹<https://gawsis.meteoswiss.ch/GAWSIS/index.html#/>

²<http://aeronet.gsfc.nasa.gov/>

through the ozone layer, the mean height of the ozone layer is 21 km for Kyiv-Goloseyev station latitude, m is airmass: ratio of the actual and vertical paths of solar radiation through the atmosphere, taking into account refraction and the Earth's curvature, Z is angular zenith distance of the sun (solar zenith angle, strictly speaking, instead of $\sec Z$ should be m_a , which is ratio of the actual and vertical paths of solar radiation through the 'aerosol layer', however, that is not essential), p is atmospheric pressure at the observational station, $p_0 = 1013.25$ hPa is standard pressure at sea level. Variables $\alpha = \tilde{\alpha}/\ln 10$, $\beta = \tilde{\beta}/\ln 10$, $\delta = \tilde{\delta}/\ln 10$, where $\tilde{\alpha}$ is absorption coefficient of ozone when Bouguer–Lambert–Beer's law is written in exponential way (the coefficient dimensionality is inversely proportional to dimension of TOC value X), $\tilde{\beta}$ is Rayleigh scattering coefficient of air or optical thickness of Rayleigh scattering in conditions of vertical path of solar radiation through the atmosphere and standard pressure p_0 ([5]; Table 1), $\tilde{\delta}$ is aerosol optical thickness of vertical path of solar radiation through the atmosphere.

Relationships that include the natural logarithm of ten occur due to the fact that the optical thickness is usually inserted through exponential description, while, in the TOC determination, coefficients on logarithm base 10 are historically used. The longer wavelength corresponding the higher values of absorption and scattering coefficients is designated by prime mark.

Note, that in the real measurement conditions, in addition to $\lg \frac{I_0}{I}$, the term caused by the instrument properties could be included. That, in particular, is demand of a calibration procedure [3]. By marking this generalised constant as L , we have:

$$L = \mu(\alpha - \alpha')X + (\beta - \beta')m \frac{p}{p_0} + (\delta - \delta')\sec Z + \lg \frac{I}{I'}. \quad (2)$$

In the expression (2) p_0 is constant by definition. Standard (tabular) coefficients of absorption due to ozone and Rayleigh scattering are taken from the literature and described in detail in the next section. Solar zenith angle Z may be calculated using ephemerides of the Sun. In practice, it is useful to apply a supporting program from the package for Dobson spectrophotometer that gives also the value μ (its influence is small at a given altitude of ozone layer). The ratio of intensities is measured directly. The TOC value should be taken from parallel intercomparison measurements by Dobson spectrophotometer. Pressure and aerosol optical thickness, in principle, can be measured in parallel with ozone observations. If, as in the case of the AERONET sun photometer, optical thickness is taken at other wave-

lengths, we use relation with Ångström exponent k :

$$\delta = \delta_0 \left(\frac{\lambda}{\lambda_0} \right)^{-k}. \quad (3)$$

Under condition of ozonometer temperature stabilisation, instrument temperature influence is negligibly small. If the instrument heating is determined by external conditions, the temperature coefficient is of quite significant value. According to [1], it is equal 0.87–1.23 as temperature drops from +50 °C to –30 °C.

Important consequences follow from non-monochromatic case. In monochromatic approach, the Bouguer–Lambert–Beer's law can be presented as:

$$I = I_0 \cdot 10^{-\alpha\mu X - \beta m \frac{p}{p_0} - \delta \sec Z}.$$

To move from the intensity to actual spectral sensitivity of the filter instrument M-124 measured value S , it is necessary to take into account the filter transmission curve $C(\lambda)$:

$$S = \int_0^{\infty} I_0 C(\lambda) \cdot 10^{-\alpha(\lambda)\mu X - \beta(\lambda)m \frac{p}{p_0} - \delta(\lambda)\sec Z} d\lambda. \quad (4)$$

Similarly, output signal S' for the second filter could be obtained using spectral sensitivity $C'(\lambda)$. Mark (') is used for channel, which has maximum sensitivity at the longer wavelength:

$$S' = \int_0^{\infty} I_0 C'(\lambda) \cdot 10^{-\alpha(\lambda)\mu X - \beta(\lambda)m \frac{p}{p_0} - \delta(\lambda)\sec Z} d\lambda. \quad (5)$$

In general, it is impossible to calculate X from (5). One of the alternative is to introduce effective absorption coefficient for ozone, which depends on μ and X ([3], Chapter 6). The most appropriate way is to determine X by numerical methods. Variations of coefficients β and δ within the spectral bandwidth of the M-124 filter should be, in general, relatively low, but the including of their dependency on the wavelength is not difficult.

Note that the basic wavelengths for maximum bandwidths of M-124 are 300 ± 2 nm and 326 ± 2 nm ([1], p. 26). Full width at half maximum (FWHM), according to cited work, is 21 nm. In our case, approximate representation for transmission curves of the filters 1 and 2 was first obtained. On this basis, location of maximum bandwidth at 301 nm and 329 nm for the filters 1 and 2, respectively, was estimated. This roughly corresponds to the Aleksandrov's data [1] (in the second case, it is probably a little more). The FWHM is about 19 nanometers (291–310 nm) in the first case and only 13 nm (323–336 nm) in the second case. These are less than the standard values, but too large for monochromatic approach. That is significantly different scale in

comparison to 3–4 nm for Dobson spectrophotometer [3, 22].

As it follows from the described data, in particular, from ([1], p. 57), integral method should be applied for calibration of ozonometer M-124 taking into account the spectrum of extra-atmospheric solar radiation. Actually, this method was used to construct the M-124 nomograms, which serve to reveal TOC values from M-124 observations [16]. Even in this case, the error of the instrument in [1] is given as 7–10% (the second value corresponds to a high aerosol amount).

In the view of some non-triviality of the ozonometer M-124 calibration problem, different approaches are characterised by unequal accuracy and complexity. In particular, they are:

a) the most rough, monochromatic approach ignoring aerosol term and pressure influence;

b) more accurate monochromatic approach, which takes into account the impact of aerosols and, if possible, the pressure variations (calculation method described in detail above). Because of the unreasonableness of measurements at the solar zenith angle $Z > 70 - 75^\circ$, the values m and μ could be assumed as equal to $\sec Z$. Note that approaches (a) and (b) do not provide accurate results, and these methods are not suitable for calibration of M-124;

c) integral approach, which is the most appropriate, but is much more difficult than (a) and (b). Integrals for S and S' in the calculation should be replaced by sum with a step, for example, 1 nm or 0.1 nm. The final goal is to create an algorithm for computing the X -values for a given values of ratio S to S' , Z and p including the dependence $\delta(\lambda)$ (real or approximated from Ångström exponent). For integration/summation, reliable tables for ozone absorption coefficient $\alpha(\lambda)$, Rayleigh scattering coefficient $\beta(\lambda)$, filter transmission curves $C(\lambda)$ and $C'(\lambda)$, extra-atmospheric solar radiation intensity $I_0(\lambda)$ are required. Clearly, some simplifications concerned with ignoring the impact of aerosols and pressure variations are also assumed and reduce the method accuracy.

PRACTICAL ASPECTS OF OZONOMETER M-124 CALIBRATION

We use the available information for the construction of nomograms for M-124 instruments. Taking into account a basic expression for the signal ratio of the two filters according to (4) and (5):

$$\frac{S}{S'} = \frac{\int_0^\infty I_0 C(\lambda) \cdot 10^{-\alpha(\lambda)\mu X - \beta(\lambda)m \frac{p}{p_0} - \delta(\lambda)\sec Z} d\lambda}{\int_0^\infty I_0 C'(\lambda) \cdot 10^{-\alpha(\lambda)\mu X - \beta(\lambda)m \frac{p}{p_0} - \delta(\lambda)\sec Z} d\lambda},$$

we identify the data, which should be included for practical work with this formula. The value $\frac{S}{S'}$ is obtained directly from the measurement. For the solar radiation flux, the data from [2] were used. The spectrum presented in [19] was also used for control and it does not affect notably the results. Data for solar radiation flux between 119.5 nm to 1 mm with variable wavelength step were included. This range of wavelength is apparently sufficient, even with excess. Linear interpolation was made with step of 0.1 nm for the wavelength range 246–629 nm. Note that a change of the Earth–Sun distance does not play any role, because the inverse square of the distance is made outside the two integrals and is cancelled by each other.

Situation with ozone absorption coefficients is rather difficult. In particular, coefficients have significant temperature dependence [26]. We used the scattering cross-sections from the IGACO-3 website³, available for temperatures of 203, 223, 246, 273, 276 and 280 K, which were calculated according to [4]. Based on the definitions of scattering cross-section σ and absorption coefficient α ,

$$\alpha = n\sigma,$$

where n is the concentration of aerosol particles.

Since the TOC value X is defined for gas under normal conditions, the concentration must be equal to the Loschmidt constant $n = 2.687 \cdot 10^{19} \text{ cm}^{-3}$.

The air temperature must correspond to the real conditions in the stratosphere, where the main part of ozone amount is located. Therefore, the typical summer stratosphere temperature value of $T = 223 \text{ K}$ was used for interpolation by wavelength because most measurements for the M-124 intercalibration against Dobson spectrophotometer have been undertaken during summer season. The temperature dependence of Dobson measurements is estimated as 0.13% per degree Celsius [21, 28], which cannot produce in usual stratosphere conditions the discrepancy exceeding typical M-124 uncertainties. Note that the list of the used absorption coefficients is limited by wavelength range of 246–342 nm according to the initial data (absorption at 342 nm is weaker by more than two orders of magnitude than at 300 nm). For Rayleigh scattering, the data from [5] were used. The data of the last column of the Table 4 from cited work (where US Standard Atmosphere, 1962 is presented) were interpolated. Step for the initial data is 10 nm (wavelengths from 200 nm to 800 nm), however, as it is seen, this does not result in significant interpolation errors because of the function smoothness.

For aerosol optical thickness δ , it is useful to include the AERONET Kyiv station data [24]. Spectral dependence $\delta(\lambda)$ is calculated using optical thickness at one of the wavelengths $\delta_0(\lambda_0)$ and Ångström exponent k , see (3). Optimal case is to

³http://igaco-o3.fmi.fi/ACSO/cross_sections.html

use the data for the same day, when the measurements were made or, that is more or less acceptable, to use the annual means. The latter approach, in particular, should be applied for the construction of nomograms, which will be used at the station, where regular aerosol observations are absent. Approximation with Ångström exponent is not ideal, however, it is quite simple and easy. For example, from daily mean data of Kyiv station (data level 1.5): $\tilde{\delta}(\lambda_0 = 340 \text{ nm}) = 0.275$ on 6 August 2013, and $\tilde{\delta}(\lambda_0 = 340 \text{ nm}) = 0.412$ on 7 August 2013 (the first dates of measurements with M-124); $k = 1.603$ on 6 August 2013, and $k = 1.579$ on 7 August 2013.

Ozone layer thickness μ is considered as independent from wavelength value. The data were obtained with the 1-minute step and linear interpolation is sufficient within the 1-minute interval. To control the total ozone content X , we use the value obtained with the Dobson spectrophotometer (the nearest or daily mean), usually, by the Direct Sun measurements at the wavelength pair AD (DSAD). The observation types with the Dobson spectrophotometer are described in detail in [22].

The air mass m is calculated by formula from [22]:

$$m = \sec Z - 0.0018167(\sec Z - 1) - 0.002875(\sec Z - 1)^2 - 0.0008083(\sec Z - 1)^3.$$

The value m depends on the solar zenith angle Z only and approximation as $\sec Z$ can be used for typically applied values.

The importance of pressure p is required to be tested. The variants for substitution may include: a standard value corrected only for altitude above sea level; the average for the MAO weather station (the same place as Kyiv-Goloseyev station); the Kyiv daily pressure value with altitude correction; the current value at the MAO weather station (if operating). These cases are listed from the most rough to the most accurate. The atmosphere pressure $p = 990 \text{ hPa}$ is taken in all calculation cases.

The interval of the TOC changes during the observations in 2013 was 285–325 DU. Usually, measurements in the late winter and spring, when the midlatitude TOC maximum due to the Brewer–Dobson circulation is observed [6, 11], are preferable.

In Fig. 1, the solar spectra at the top of the atmosphere and at the Earth surface are illustrated. In the latter case, the data correspond to 7 August 2013, 7:31 UT ($Z = 45.77^\circ$, $\mu = 1.43$, $p = 990 \text{ hPa}$, TOC = 302.3 DU determined from the Dobson spectrophotometer with DSAD measurements in 7:35, daily aerosol optical thickness at wavelength 340 nm is 0.412, Ångström exponent is 1.579). The transmittance of the atmosphere decreases rapidly with decreasing wavelength, notably at wavelengths close to 300 nm.

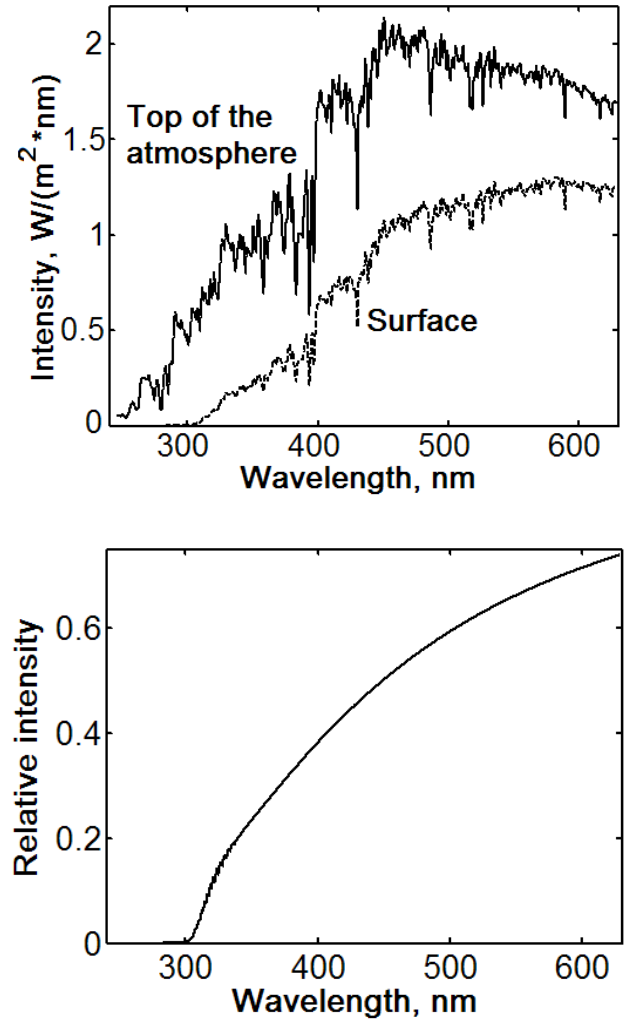


Fig. 1: The spectra of the solar radiation (top) at the top of the atmosphere and at the surface, (bottom) transmittance of the atmosphere.

Rayleigh scattering and scattering by aerosol particles increase with wavelength decreasing. Ozone absorption near 300 nm has the same dependence. Light with a wavelength of about 285 nm and less is barely passed through the ozone layer (Fig. 2, left). Near 300 nm, absorption by ozone also dominates, though, is not as strong. Instead, ozone component at 318 nm gives smaller effect than the others (Fig. 2, right). At a wavelength of 318 nm Rayleigh scattering component dominates. Total ozone value 300 DU and pressure 990 hPa are chosen for the calculations. Aerosol optical thickness at 340 nm is 0.3 and it varies according to a power law with the Ångström exponent of 1.6.

Test calculations for ozonometer No.428 with Gaussian transmission curves were performed and they do not give satisfactory results. The M-124 nomogram quality was significantly improved, when the real curves of transmission have been measured.

In particular, the result for the instrument No. 343 is shown in Fig. 3. Note that no empirical corrections were used at this stage and the calculations were based on the theory and measurement results only. Aerosol optical thickness at 340 nm was taken 0.3, and Ångström exponent was equal to 1.6. The range of values for Dobson spectrophotometer and M-124 ozonometer obtained from calculations is shown in Fig. 4. The standard deviation is $\sigma = 11.2$ DU. Discreteness of the values on the plots in Fig. 4 is caused by a step of 5 DU taken for calculations (if necessary, it is not difficult to reduce a step). Decrease of the step does not influence noticeably the standard deviation, e. g., $\sigma = 10.9$ DU in case of a step of 1 DU.

Similar calculations were performed for several M-124 instruments. In particular, standard deviation $\sigma = 17.7$ DU has been obtained for ozonometer No. 496 with a short series of measurements. In case of ozonometer No. 80 in spite of a relatively large number of values available in 2013, measurements show high dispersion and, as a result, $\sigma = 62.1$ DU. Significantly less measurements were performed for ozonometer No. 188, and the result is clearly unsatisfactory (large systematic underestimation of TOC) and requires further analysis. The range of values for Dobson spectrophotometer and M-124 No. 188 instrument gives a standard deviation $\sigma = 158.1$ DU. Regarding the features of the data, this instrument shows very low values at the transmission maximum for filter 2, no more than 12 units; in other cases, the value are at least twice as much.

Finally, the results for ozonometer No. 428 by both 2013 and 2015 measurements are analysed. Spectral sensitivity in the filters and the corresponding calculation of TOC for the observations in August–September 2013 are presented in Fig. 5. Dispersion of the TOC values for Dobson and M-124 No. 428 in 2013 is characterised by the standard deviation $\sigma = 70.6$ DU. Standard deviation is increased due to the points location far left of the curve for 200 DU (the number of these points is 8 of total point number 123). If the values below 150 DU are considered as very inaccurate, they can be ignored in the calculations. This reduces the deviation more than doubled up to $\sigma = 31.9$ DU.

Dispersion for instrument No. 428 from the data obtained in 2013 is not quite acceptable. Unfortunately, the result obtained from observations in 2015, is even worse in relation to the 2013 data. The standard deviation between the data of Dobson spectrophotometer and M-124 increases to $\sigma = 108.4$ DU. Thus, the discrepancy becomes too large. Examination of the role of aerosol factor shows that with the parameters, typical for Kyiv, it should not be significant.

The latest intercalibration campaign has been provided for M-124 ozonometer No. 496 in 2016. The intercomparison of results for this instrument show correspondence of M-124 data and Dobson spec-

trophotometer data in 15–20 DU discrepancy. Interesting that nomograms for M-124 measurements built by Direct Sun data are appropriate to reveal Zenith Blue observations.

CONCLUSIONS

Calibration procedure for the filter ozonometer M-124 using intercomparison observations with the Dobson spectrophotometer No. 040 has been described. In this work, as a first step, the spectral characteristics of five ozonometers M-124 in each of the two filters have been measured. This improved significantly the calibration of these instruments at the WMO station Kyiv-Goloseyev. It was possible to achieve a qualitative similarity between the total ozone values calculated at least for the two M-124 ozonometers and those observed with the Dobson spectrophotometer.

At the same time, quantitative results for the instruments M-124 are not always satisfactory. The best results were obtained for the instruments No. 343 (standard deviation from the Dobson data DSAD $\sigma = 11$ DU) and No. 496 ($\sigma = 18$ DU). However, even in these cases, there is a need to test the results over the larger TOC range, than that observed in August–September 2013. Besides, it should be also ensured that the instrument characteristics are stable during the observational period. The last factor is important, particularly, with regard to calibration of instrument No. 428. Observations in 2013 showed not very good result ($\sigma = 32$ DU after exclusion of several distinctly unsatisfactory measurements). Moreover, in winter–spring 2015 a very large discrepancy ($\sigma = 108$ DU) has been registered. Therefore, determination of the causes of these distinctions is necessary in future work.

The characteristics of the instruments No. 80 and No. 188 have been also investigated. In the first case, the significant difference with the standard deviation $\sigma = 62$ DU has been obtained. In the second case, the large systematic error (underestimated TOC values) with $\sigma = 158$ DU has been revealed.

Estimation of the aerosol influence on calibration results shows that under conditions of aerosol optical thickness (up to 0.3 at a wavelength of 340 nm) and Ångström exponent (1.4–1.6) typical for the station Kyiv-Goloseyev, this factor can cause only minor differences, which do not exceed 10 DU. It seems that one of possible causes of the large standard deviations could be a variability of weather conditions during the observations. Because the M-124 ozonometer measures the radiation intensities in the two spectral channels with some time intervals, the presence of even subtle moving clouds can critically influence the observational data distorting the value of the intensity ratio. Another group of possible errors is subjective mistakes caused by the inexperienced observer, who made parallel measurements

with the instruments of the two different types, M-124 ozonometer and Dobson spectrophotometer.

The results show that the measurements with each of ozonometers under steadily clear weather are necessary. The calibration should include a large range of the TOC levels, particularly, around the seasonal TOC minimum and TOC maximum observed typically in autumn and spring, respectively. More clear separation of the error sources associated with (1) the weather conditions, (2) observer mistakes and (3) instrument itself should be made in future work.

ACKNOWLEDGEMENT

The work was supported by Ukrainian Hydrometeorological Center, Central Geophysical Observatory of Ukraine and Ukrainian Hydrometeorological Institute, the Special Complex Program for Space Research 2012–2016 of the National Academy of Sciences of Ukraine, project 16BF051-02 of the Taras Shevchenko National University of Kyiv. Aerosol measurements are supported by the grant of the State Fund for Fundamental Research, project F73/115-2016. We thank all observers who provided M-124 ozonometer measurements. Authors also thank referee Dr. Iryna Dvoretzka for useful comments and corrections.

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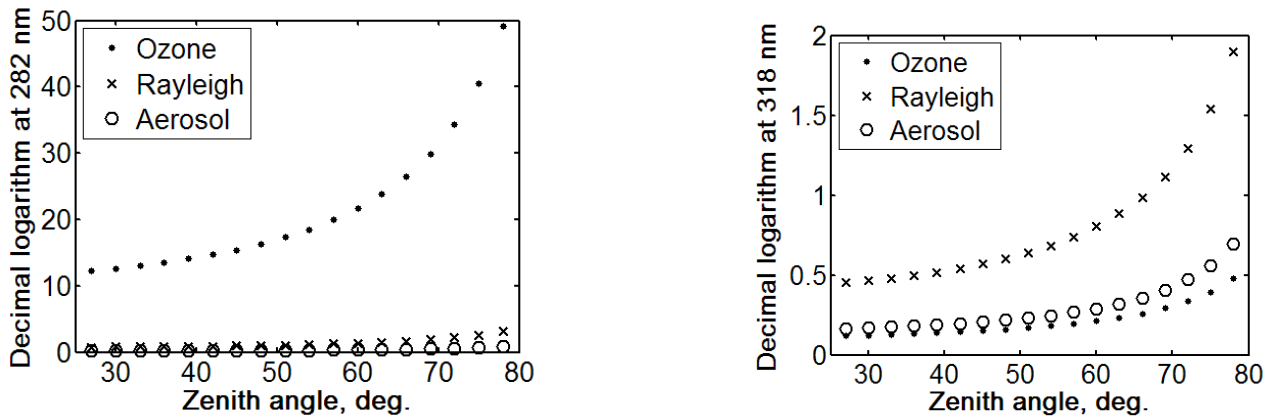


Fig. 2: Dependences on solar zenith angle of decimal logarithm of the ratio of radiation fluxes at the top of the Earth's atmosphere and at the surface, if only one of the factors is taken into account: absorption by ozone, Rayleigh and aerosol scattering. The dependences on the solar zenith angle at the wavelengths of (left) 282 nm and (right) 318 nm are shown.

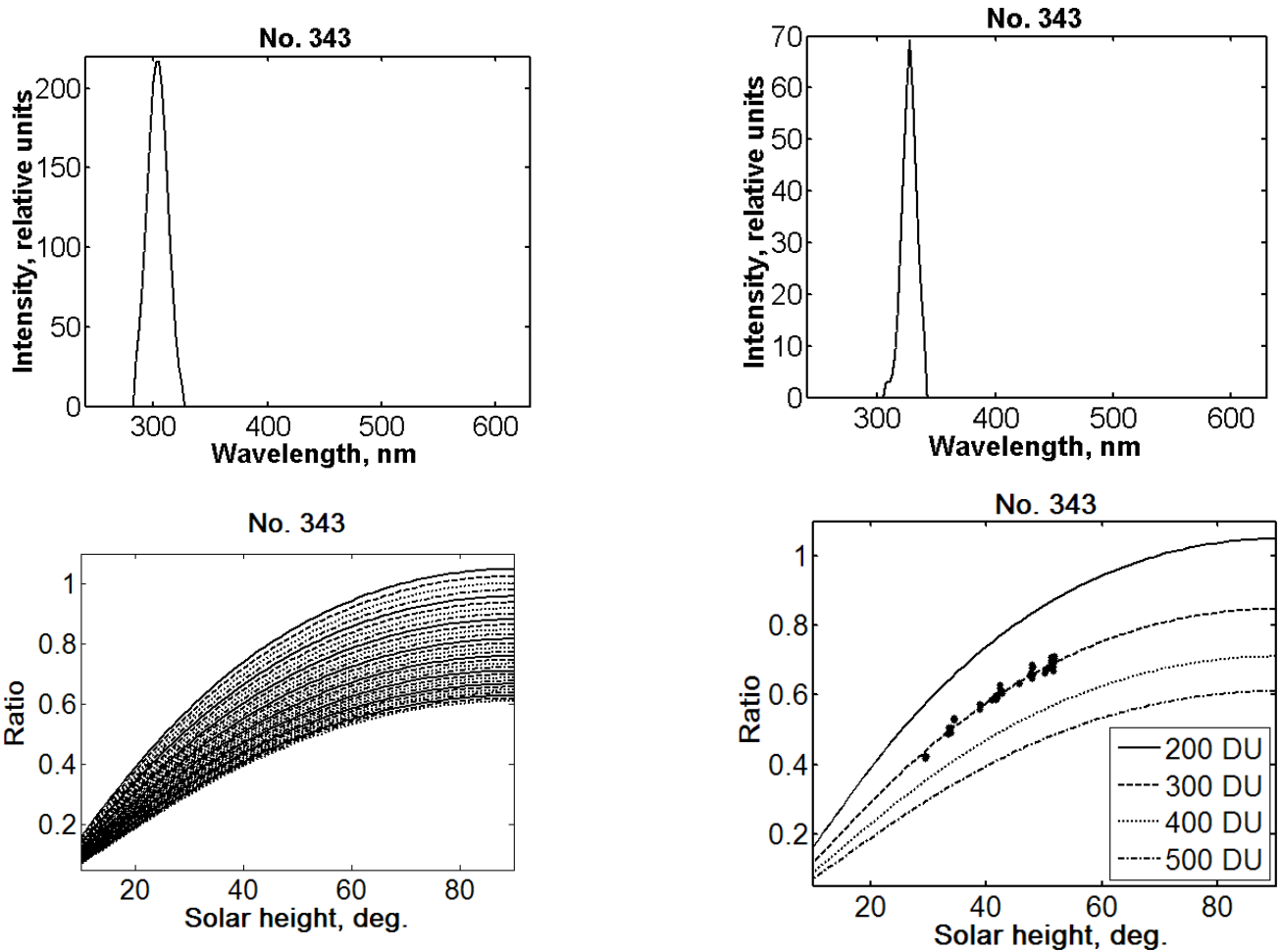


Fig. 3: Spectral transmission curves for (top left) filter 1 and (top right) filter 2, relative units. Nomograms calculated using these curves are shown at the bottom and (bottom right) observational points are superimposed on the nomograms.

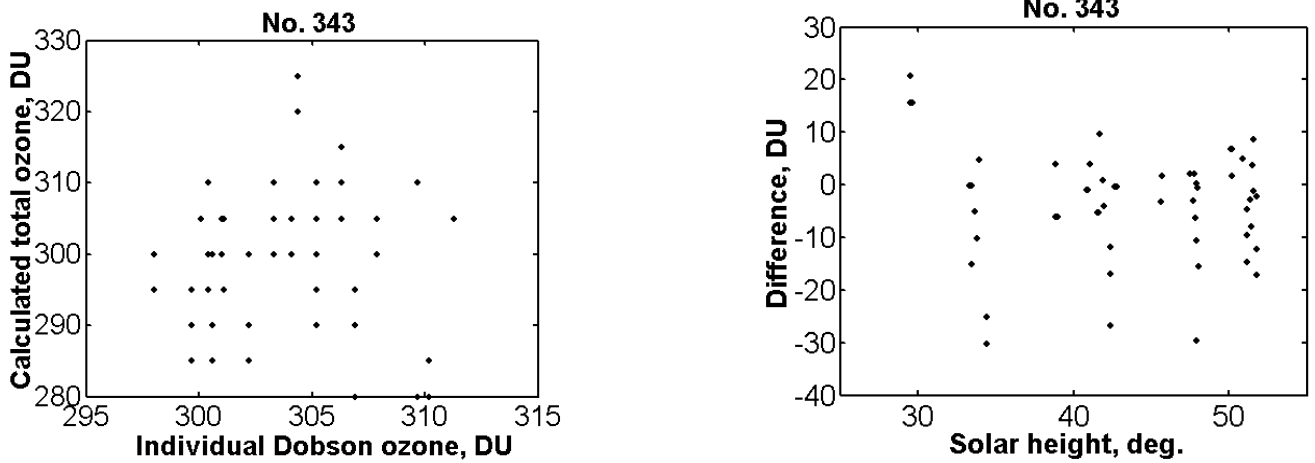


Fig. 4: The TOC values (left) calculated for M-124 in relation to the TOC level determined with Dobson spectrophotometer No. 040 and M-124–Dobson differences (right) in dependence on the Solar height.

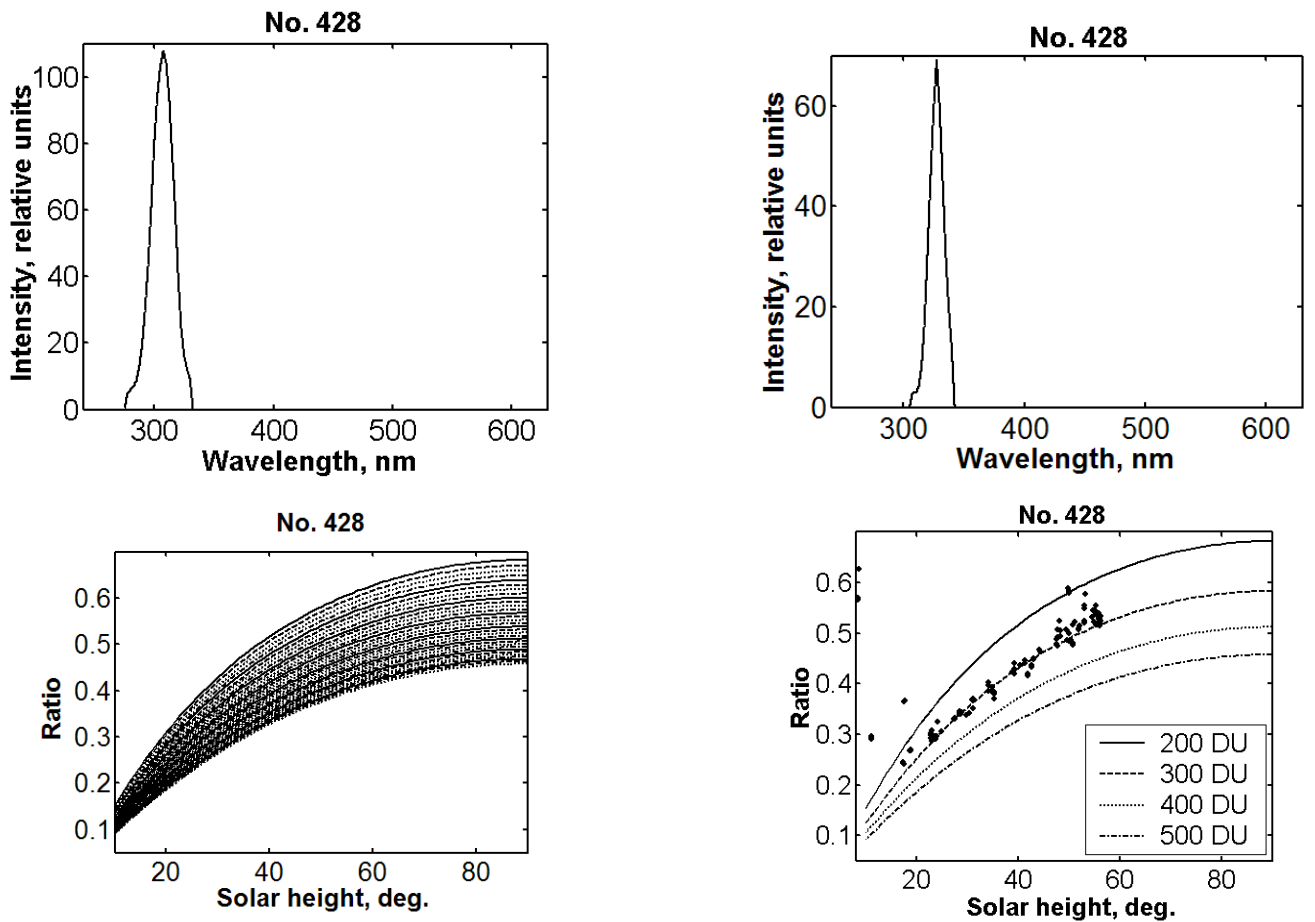


Fig. 5: Spectral sensitivity (top) and calculated nomograms (bottom) for M-124 No. 428. Construction was made similarly to Fig. 3