Influence of light absorption by atmospheric water vapor in the UV-range on the determination of the total ozone content

M.M. Makogon, L.I. Nesmelova, and O.B. Rodimova

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received September 12, 2003

The method of determination of the total ozone content (TOC) from measurements of the differential attenuation of solar radiation by the atmosphere in the near UV spectral range (300–350 nm) is, in fact, a standard method being one of the most common in use. In this case, the aerosol and molecular scattering are taken into account and it is conventionally believed that the ozone exclusively determines the molecular absorption in this spectral range. The investigations carried out in the 1980–1990s at the Institute of Atmospheric Optics SB RAS have shown that there exists a weak absorption by water vapor in this region. The total water content in the atmosphere is large enough to contribute to the measured difference of the atmospheric optical depths and to result in a systematic error. In this case the TOC value, determined without the account of water vapor, may appear to be overestimated. The estimates made in the paper indicate that the correction value can reach tens of percent.

Many monographs and hundreds of papers are devoted to the problems of atmospheric ozone and, in particular, to the techniques of ozone measurements.[1–6] Ozone is one of the most important components of the atmosphere, its regular monitoring is performed at more than 100 ozonometric stations throughout the world. The total (integral over the whole atmospheric thickness) ozone content (TOC) is measured by the absorption of direct, scattered in the atmosphere, or reflected by the moon solar radiation. In some cases bright stellar radiation was used. The spectrophotometric technique of TOC determination is based on the Bouguer law. Using this law, the attenuation of solar radiation in the atmosphere is taken into account occurring due to molecular (Rayleigh) scattering, extinction by aerosol, and due to absorption by ozone.

As a rule, the optical thickness of the atmosphere is measured at two adjacent wavelengths, one of which is in the region of local maximum, and another is in the region of local minimum of the ozone absorption spectrum. Such a differential procedure enables one to substantially suppress negative effects of different factors interfering the measurement accuracy. The greatest amount of measurements have been conducted in the near UV range (305–340 nm, the Huggins absorption band of the ozone), very seldom – in the visible (470–722 nm, the Chappuis band), and in the IR-range (band – 9.59 μm).

For the operation in the UV-range different instruments were designed: the Dobson spectrophotometer, which is the basic instrument for TOC measurements at the world ozonometric network, the Bruer spectrophotometer, filter instruments like M-83 and M-124, different spaceborne spectroradiometers, and so on.[3,6] Without analyzing the differences in the instruments, it should be noted that for all the instruments one and the same "technology" is used.

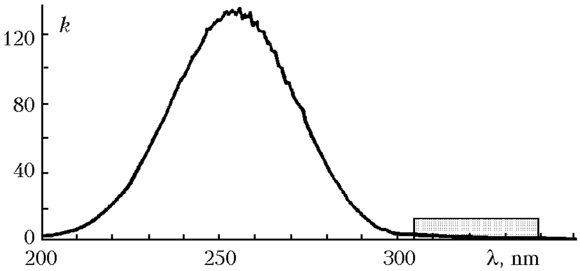

Fig. 1. The ozone absorption spectrum.[7] The Huggins absorption band is marked. The value of k is given in units $\mathrm{cm^{-1} \cdot atm^{-1}}$, the logarithm base is 10.

We can safely assume that the differential optical thickness $\Delta\tau_{12}$ of the atmosphere measured at the wavelengths λ_1 and λ_2 consists of the differential optical thickness of ozone $\Delta\tau_{O_3}$, the differential molecular scattering $\Delta\beta_{12}$, and differential attenuation by aerosol $\Delta\delta_{12}$:

$$\Delta\tau_{12} = \Delta\tau_{O_3}\,\mu + \Delta\beta_{12}\,m + \Delta\delta_{12}\,m'$$

(where μ, m, and m' are the masses of the ozone, air and aerosol in relative units taking into account the direction toward the sun).

For the sake of simplicity assume that the TOC is measured along the zenith direction and therefore there is no need for taking account of the relative masses of ozone, air, and aerosol; total ozone content X is calculated from the expression

$$X = (\Delta\tau_{12} - \Delta\beta_{12} - \Delta\delta_{12})/\Delta\alpha_{12},$$

where $\Delta\alpha_{12}$ is the difference of the ozone absorption coefficients at the wavelengths λ_1 and λ_2. In the Dobson spectrophotometer four pairs of wavelengths A, B, C, D are used,[1] in which the differential

0235-6880/03/11 891-05 $02.00

absorption coefficient differs approximately by a factor of 5.

The dependence $\beta(\lambda)$ for atmospheric air has been studied in detail in Ref. 8. In the simplest case, $\Delta\delta$ can be taken zero ("gray" aerosol scattering), but this result in significant errors. Most often, the spectral dependence of aerosol attenuation in the wavelength range, used for TOC determination, is described by a linear law. Then at simultaneous data processing based on 2 (or more) pairs of wavelengths the dependence on aerosol disappears.

Analysis of measurement errors in TOC measured using the Dobson spectrophotometer by two pairs of lines *AD* was conducted by the experts of the World Meteorological Organization,[9] and the result is given in Table 1.

Table 1. Estimation of relative measurement errors in TOC made by experts from the WMO [see Ref. 9]

Type of error	Estimation, %
Systematic errors	
Ozone absorption	±0.7
Temperature of the stratosphere	±0.5
Instrument drift	±3
Aerosol effect	±1
Pollution of the troposphere:	
a) ozone	±1
b) other absorbers (SO_2, NO_2, HNO_3, CH_2O, N_2O, N_2O_5, H_2S)	±2
Cloudiness	±1
Random errors	
Direct solar radiation, pair *AD*:	
optimal	±1
average	±3
Radiation from the sky zenith:	
optimal	±2.5
average	±5

In the literature[5] one can find a detailed analysis[10] of the effect of surface sulfur and nitrogen dioxides on the accuracy of TOC measurements using Dobson spectrophotometers. For maximum possible concentrations of the above-mentioned impurities the error they give in TOC measured using the *A* pair of lines is 29.5 and 14.5%, and 25.6 and 5.4% if using two pairs of lines, *AD*, for SO_2 and NO_2, respectively. However, in non-industrialized regions, where, as a rule, the ozonometric stations are located, the atmospheric pollution is 1 or 2 orders of magnitude lower and hence the measurement error in TOC due to the influence of the above species will be 1 or even 2 orders of magnitude smaller.[5]

Direct comparisons of different prototypes and types of ground-based instruments have shown[2,6] that the maximum discrepancy is about 8% at its mean value of 4.8%, which is in a good agreement with the estimates by the experts from the WMO.

However, it was many times pointed at the discrepancies in TOC determined from the readouts of Dobson instruments taken using different pairs of wavelengths.[11–13] Filter ozonometers that use several bands are also characterized by stable differences in estimating *X* if using various pairs.[14,15] A pronounced (up to 14%) discrepancy between the results takes place in determining TOC over oceanic regions[16] and over sea waters.[3] The authors of Ref. 3 believe that it is the aerosol that is responsible for this discrepancy.

A possible effect of the atmospheric water vapor on the determination of TOC in the near UV spectral range has not been discussed in the above-mentioned papers and the papers published in 2003.[17] The investigations carried out at the IAO SB RAS in the 1980–90s,[18–25] have shown that water vapor has a weak nonselective absorption in the range from 265 to 350 nm (Fig. 2).

The absorption spectrum in this range was measured using a multipass gas cell with the distance between mirrors of 2.2 m, and in more narrow intervals – using a cell with the distance between mirrors of 110 m, using a photoacoustic method. The values of the absorption coefficients measured in Refs. 19 and 21 exceed those obtained in Ref. 24 by 20 times (a detailed analysis of combined data is given in Ref. 26 as well as the possible causes of such a significant discrepancy).

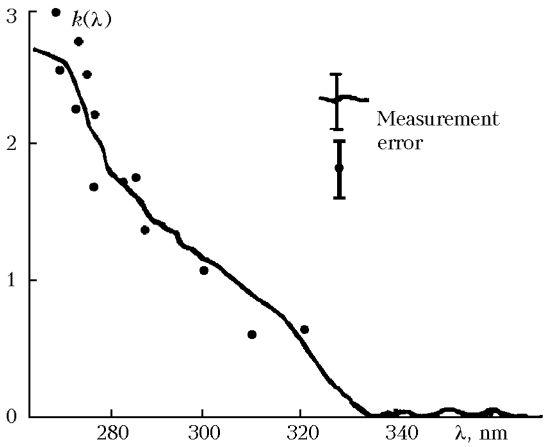

Fig. 2. The water vapor absorption according to literature[19,21] data. The value of k is given in units of $cm^{-1} \cdot Torr^{-1} \cdot 10^{-6}$, the logarithm base is e.

At present, no any comprehensive physical concept or theoretical description exists of the nature of absorption by water vapor in the near ultraviolet range discussed. The vibration-rotation H_2O absorption spectrum in the near UV-range is traditionally considered to be very weak and the strongest bands may be connected only with high overtones of the stretching vibrations.

The most recent model calculations[27,28] have shown that for vibrational states near the dissociation limit, whose wave functions are localized near the linear HOH configuration, nonadiabatic effects strengthen the corresponding transitions due to the intensity transfer from the strong electron band B^1A_1. This interaction of states occurs due to a strong centrifugal distortion of a rotating molecule having nearly linear configuration. The portion of transferred intensity is 10^{-4}–10^{-6} of the *B* band intensity that results in the absorption coefficients of the order of 10^{-6}–10^{-7} $cm^{-1} \cdot Torr^{-1}$, which agree with the experimental data. Because the excited electron state B^1A_1 is decomposing, then due to the predissociation the “intensified” band must be diffuse (that fully corresponds to the experimental observations).

It should be noted that earlier Tennyson and Mussa[29] calculated the vibrational states of H_2O up to the energy of dissociation. According to their analysis of wave functions, among 200 highest H_2O states, the states are available (with the power about 4.5 eV (278 nm)), whose wave functions are highly localized in the bending coordinate. This implies that such states must be considered as high overtones of bending vibration, for which the above-mentioned effect should be observed.

The first attempt to take account of the absorption by water vapor in the near UV range, as a factor with the atmospheric-optical manifestation, was done in Ref. 30. The authors evaluated the effect of water vapor on the measurement of ozone by the lidar sensing technique. The use of absorption values from Refs. 19 and 21 (it is well known now that the values are overestimated) has resulted in the “corrections” that changed the value of the ozone concentration by a factor of up to 8. However, special measurements made by researchers from the USA[31] did not support the conclusions drawn in Ref. 30.

The data[19,21] on the spectrum of absorption by water vapor were used with much success in Ref. 32 to fit the atmospheric transmittance spectrum to the calculated one. The measurement error of spectral atmospheric transmittance in the UV range did not exceed 1% in the range near 310 nm and 0.2% in the range near 400 nm. To explain the obtained data, the authors had to take into account the H_2O contribution to the extinction of UV radiation, which at the wavelength of 310 nm was about 3% from the total attenuation value. To fit the data, the authors had to decrease also the measured[19,21] absorption coefficients by a factor of 20. Therefore there are strong grounds to believe that this corrected water vapor absorption spectrum is quite realistic (Fig. 3).

We used the spectral dependence of water vapor absorption corrected in this way to assess the value of differential optical thickness $\Delta\tau_{H_2O}$ and a possible contribution of water vapor absorption to the measurements of TOC.

Let us estimate the effect of atmospheric water vapor on the determination of TOC as follows. First, we determine the water vapor column density using different models of the atmosphere, then we find the differential optical thickness of water vapor at different lines and the correction in ΔX to the determined TOC value by the formula:

$$\Delta X = X_{\text{true}} - X = -\,\Delta\tau_{H_2O}/\Delta\alpha_{12}$$

(here X_{true} is the true value of TOC). The spectral behavior of the H_2O absorption coefficient is similar to the behavior of the ozone absorption coefficient, therefore the correction should be negative, and the values of TOC, determined without the account of the effect being studied, turned out to be overestimated. The values of the quantities of $\Delta\alpha_{12}$ used are standard for the ozone measurements.[1]

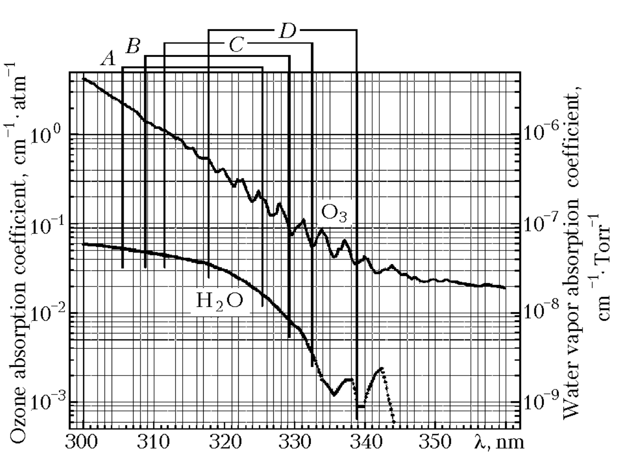

Fig. 3. The ozone and water vapor absorption spectrum[7] (corrected data[21]); the ozone absorption coefficients are taken using the logarithm base 10, and in case of water vapor – for the base *e*. *A–D* denote pairs of lines used for determining TOC in the Dobson spectrophotometer.

Thus assessed values of systematic correction when measuring TOC in different models of the atmosphere are given in Table 2.[33]

It should be noted that in the region of weak ozone absorption the water vapor absorption coefficients were determined with a great error and the assessments given are not reliable. In view of this fact the result in the last column of the table cannot be considered to be optimistic. Nevertheless, from Table 2 it follows that the discussed systematic correction to the TOC value, whose mean value is 370 Dobson units, in some cases far exceeds other possible measurement errors of TOC (see Table 1). In case of determining TOC by the instrument placed on top of a hill, the optical thickness of water vapor decreases and the value of a systematic error also decreases.

The comparison of data of the spaceborne ozonometric (system TOMS, USA) and ground-based instruments in Lerwick (Great Britain) and in Yakutsk[6,34] may serve a definite indication of the necessity of introducing such a systematic correction. In Lerwick the Dobson spectrophotometer was used and in Yakutsk a modernized M-83 ozonometer was used. Data obtained during two years, in 1981 in Yakutsk and in 1982 in Lerwick, were compared. The discrepancy between the readouts varied from +10% to –15% and on the average the values of TOC, measured by the spaceborne instrument, are lower than those measured with the ground-based instruments by 3–4% (Yakutsk) and 5–8% (Lerwick). Lower values obtained with the spaceborne instrument appear explicable because an observation path does not go through the lower levels of the atmosphere where water vapor is concentrated.

Table 2. Estimation of the systematic correction in the determination of TOC

Pairs of wavelengths		*A*	*B*	*C*	*D*	*AD*
λ_1, nm		305.5	308.8	311.4	317.6	
λ_2, nm		325.4	329.1	332.4	339.8	
$\Delta\alpha_{O_3}$, $cm^{-1} \cdot atm^{-1}$ (according to base 10)		1.748	1.140	0.800	0.360	1.388
$\Delta\alpha_{O_3}$, $cm^{-1} \cdot atm^{-1}$ (recalculated according to the base *e*)		4.026	2.625	1.842	0.829	3.197
$\Delta\alpha_{H_2O}$, 10^{-8} $cm^{-1} \cdot Torr^{-1}$ (according to logarithm base *e*)		3.64	3.95	4.07	3.44	0.20
Atmospheric thickness H_2O, 10^6 cm · Torr	tropics			4.238		
	mid-latitude summer			2.936		
	mid-latitude winter			0.786		
	subarctic summer			2.011		
	subarctic winter			0.388		
$\Delta\tau_{H_2O}$	tropics	0.1543	0.1675	0.1726	0.1459	0.0085
	mid-latitude summer	0.1069	0.1160	0.1195	0.1010	0.0059
	mid-latitude winter	0.0286	0.0310	0.0320	0.0270	0.0016
	subarctic summer	0.0732	0.0794	0.0818	0.0692	0.0040
	subarctic winter	0.0141	0.0153	0.0158	0.0134	0.0008
Correction to *X*, Dobson units	tropics	38	64	94	176	2.7
	mid-latitude summer	26	44	65	122	1.8
	mid-latitude winter	7	11	17	33	0.5
	subarctic summer	18	30	44	83	1.2
	subarctic winter	3	6	9	16	0.2

Note from the literature[35] that for correcting the satellite measurements of TOC in the infrared range and for achieving the agreement with the results measured in the ultraviolet spectral range the effect of atmospheric water was taken into account. The edge of the water vapor absorption band is at $\lambda = 9.59$ μm.

Corrections for the determined values of TOC due to the discussed effect may appear to be significant because many atmospheric processes depend on the ozone content. Thus, if the ozone concentration in the atmosphere changes, the radiation fluxes undergo changes and, as a consequence, the atmospheric temperature profile changes too, see, for example Refs. 36 and 37. Then, the variation of TOC results in the variation of the ultraviolet radiation intensity reaching the Earth's surface. The optical thickness of the atmosphere in the region of maximum ozone absorption is about 40, therefore a 10% decrease in TOC results in the increase of the radiation flux in this spectral range by more than ten times that should be taken into account by biologists. Thus the effect put forward for discussion cannot be ignored and should be analyzed in detail based on carefully arranged special measurements of absorption by water vapor.

Acknowledgments

The work was carried out under support from the Russian Foundation for Basic Research (Grant No. 01–05–65338) and the Ministry of Industry and Science of the Russian Federation Grant No. 373. 2003.5 (Scientific School).

References

1. A.Kh. Khrgian, *Physics of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1973), 291 pp.
2. S.P. Perov and A.Kh. Khrgian, *Present-Day Problems of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1980), 287 pp.
3. A.Kh. Khrgian and G.I. Kuznetsov, *Problem of Observations and Investigations of Atmospheric Ozone* (MSU Press, Moscow, 1981), 215 pp.
4. G.P. Gushchin, *Investigation of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1963), 267 pp.
5. G.P. Gushchin and N.N. Vinogradova, *Net Ozone in the Atmosphere* (Gidrometeoizdat, Leningrad, 1983), 238 pp.
6. G.P. Gushchin and A.M. Shalamyanskii, eds., *Atmospheric Ozone. Proceedings of VIth All-Union Symposium* (Gidrometeoizdat, Leningrad, 1987), 304 pp.
7. Kh. Okabe, *Photochemistry of Small Molecules* (Mir, Moscow, 1981), 500 pp.
8. K.Ya. Kondratyev, ed., *Radiation Characteristics of the Atmosphere and the Earth's Surface*, (Gidrometeoizdat, Leningrad, 1969), 384 pp.
9. G.P. Gushchin, in: *Atmospheric Ozone. Proceedings of the VIth All-Union Symposium* (Gidrometeoizdat, Leningrad, 1987), pp. 22–36.
10. W.D. Komhyr and R.D. Evans, Geophys. Res. Lett. **7**, No. 2, 157–160 (1980).
11. D. Strants, in: *Ozone in the Earth's Atmosphere* (Gidrometeoizdat, Leningrad, 1966), pp. 138–144.
12. A.D. Losiowa and C.D. Walshaw, Publ. Inst. Geophysics, Polish Acad. Sci. **89**, 3–59 (1975).
13. J.B. Kerr, C.L. Mateer, C.T. McElroy, and D. Wardle, in: *Proc. Joint Symp. Atm. Ozone* (Dresden, 1977), Vol. 1, pp. 109–120.
14. W.A. Matthews, PAGEOPH **112**, 938–939 (1974).
15. E. Farkas, in: *Proc. Joint Symp. Atm. Ozone* (Dresden, 1977), Vol. 1, pp. 121–128.
16. G.P. Gushchin, in: *Abstracts of Papers at the Second All-Union Symposium on Problems of Atmospheric Ozone*, Tbilisi (1978), pp. 4–6.

17. Yu.M. Timofeev and A.V. Vasil'ev, *Theoretical Foundations of Atmospheric Optics* (Nauka, St. Petersburg, 2003), 425 pp.
18. V.M. Klimkin and V.N. Fedorishchev, Atm. Opt. **2**, No. 2, 174–175 (1989).
19. S.F. Luk'yanenko, T.I. Novakovskaya, and I.N. Potapkin, Atm. Opt. **2**, No. 7, 579–582 (1989).
20. Yu.N. Ponomarev and I.S. Tyryshkin, Atmos. Oceanic Opt. **6**, No. 4, 224–228 (1993).
21. S.F. Luk'yanenko, T.I. Novakovskaya, and I.N. Potapkin, Atm. Opt. **3**, No. 11, 1080–1082 (1990).
22. V.M. Klimkin, S.F. Luk'yanenko, I.N. Potapkin, and V.N. Fedorishchev, Atm. Opt. **2**, No. 3, 258–259 (1989).
23. V.A. Kapitanov, B.A. Tikhomirov, V.O. Troitskii, and I.S. Tyryshkin, Proc. SPIE **3090**, 204–207 (1997).
24. B.A. Tikhomirov, V.O. Troitskii, V.A. Kapitanov, G.S. Evtushenko, and Yu.N. Ponomarev, Acta Phys. Sin. **7**, No. 3, 190–195 (1998).
25. S.F. Luk'yanenko, S.E. Karmazin, V.M. Klimkin, et al., in: *Abstracts of Papers at IXth All-Union Symposium on High Resolution Molecular Spectroscopy*, Tomsk (1989), p. 50.
26. M.M. Makogon, Atmos. Oceanic Opt. **14**, No. 9, 696–706 (2001).
27. A.D. Bykov, S.S. Voronina, and M.M. Makogon, Atmos. Oceanic Opt., **16**, No. 4, 288–291 (2003).
28. A.D. Bykov, S.S. Voronina, and M.M. Makogon, Atmos. Oceanic Opt. **16**, No. 11, 912–915 (2003).
29. H.Y. Mussa and J. Tennyson, J. Chem. Phys. **109**, No. 24, 10885–10892 (1998).
30. V.V. Zuev, A.A. Mitsel, and I.V. Ptashnik, Atmos. Oceanic Opt. **5**, No. 10, 675–680 (1992).
31. V.V. Zuev, Private report.
32. N.F. Borisova and V.M. Osipov, Atmos. Oceanic Opt. **11**, No. 5, 382–386 (1998).
33. M.M. Makogon, S.I. Nesmelova, and O.B. Rodimova, in: *Abstracts of Papers at Joint Int. Symp. on Atmospheric and Ocean Optics and Atmospheric Physics*, Tomsk (2003), p. 52.
34. *Ozone Data for the World. Catalogue of Ozone Stations and Catalogue of Ozone Data for 1980–1983* (Downsview–Ontario, Canada), 141 pp.
35. V.B. Kashkin, A.A. Gomonov, and A.I. Sukhinin, Atmos. Oceanic Opt. **15**, No. 2, 148–150 (2002).
36. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, Vych. Tekhnol. **7**, Special issue, 71–77 (2002).
37. E.P. Gordov, O.B. Rodimova, and A.Z. Fazliev, *Atmospheric-Optical Processes: Simple Nonlinear Models* (IAO SB RAS Press, Tomsk, 2002), 248 pp.