CHAPTER 16 — MEASUREMENT OF OZONE

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16.1 General

Ozone comprises more than half a part per million of the total atmosphere. The radiation properties of this gas make it a significant contributor to the radiative energy balance of the atmosphere and an important regulator of net radiation received at the Earth's surface. Most of the atmospheric ozone is located in the stratosphere, where its presence causes stratospheric temperature inversion and results in maximum temperature at the stratopause. In addition to its radiation properties, ozone reacts photochemically with many other trace species, some of which are anthropogenic in origin. The meridional and vertical distributions of ozone in the atmosphere are determined by a complex interaction of atmospheric dynamics and photochemistry.

Ozone near the ground is monitored because it is a product of industrial and urban pollution. Measurements of tropospheric and stratospheric ozone occurring naturally are used for verification of model atmospheres which simulate the photochemistry or general circulation of the real atmosphere. Ozone is also measured to determine whether man-made gases are perturbing the stratospheric ozone layer as predicted by photochemical theory and model studies.

16.1.1 *Definitions*

There are basically three characteristics of atmospheric ozone that are routinely measured and reported by the stations of the Global Ozone Observing System:

(*a*) Surface ozone;
(*b*) Total ozone; and
(*c*) The vertical profile of ozone.

Surface ozone expresses the concentration of local ozone to a few metres (3–10 m) above the ground at a particular site on the Earth's surface. Surface ozone measurements are commonly given in units of partial pressure or mixing ratio (by either mass or volume).

Total ozone refers to the total amount of ozone contained in a vertical column in the atmosphere above the ground. Commonly used units of total ozone are column thickness at standard temperature and pressure (STP) and vertical column density.

The vertical profile of ozone expresses the ozone concentration as a function of height or ambient pressure. The amount of ozone at each height or pressure level in the atmosphere is commonly expressed as partial pressure, mixing ratio (either by mass or volume), or local concentration. The integral of the ozone profile from the ground to the top of the atmosphere is the total column amount of ozone.

The following are definitions of other terms used frequently in this context:

Aerosols: A suspension, in a gaseous medium, of solid particles, liquid particles, or solid and liquid particles, having negligible falling velocity.

Air mass: The ratio of the path of solar radiation through the atmosphere to the vertical path.

Dobson unit (DU): A measure of total ozone equalling a thickness of 10^{-5} m of pure ozone at STP (commonly used but not a unit in the International System of Units).

Milliatmosphere centimetre (matm cm): A measure of total ozone equal to 10^{-3} cm of pure ozone at STP (one milliatmosphere centimetre is equivalent to one Dobson unit).

Ozone (O_3): An unstable blue gaseous allotrope of oxygen and a strong oxidant. It absorbs radiative energy in the 0.1–0.34 and 0.4–0.65 μm bands of the solar spectrum and at 4.7, 9.6, 10.5 and 14.1 μm in the infrared.

Spectrophotometer: An instrument for producing a spectrum and measuring the radiance at selected wavelengths.

Total ozone: The thickness of a layer of pure ozone which would result if all the ozone in the atmosphere were reduced to STP.

Ultraviolet (UV): Electromagnetic radiation in the range 100–400 nm which may be divided into UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (200–280 nm).

Umkehr: A method utlizing an optical effect appearing through a series of zenith sky radiance measurements at various UV wavelengths to infer the vertical distribution of ozone. These ground-based measurements are performed using a spectrophotometer as the solar zenith distance changes from 60° to 90°.

16.1.2 *Units and scales*

A complete description of the units is given in Annex 16.A and a brief summary is given in the table below:

Local ozone	*Units*	*Column ozone*	*Units*
Partial pressure	nanobar millipascal	Total ozone	matm cm 10^{-3} cm ozone at STP Dobson unit (DU)
Mass mixing ratio Volume mixing ratio	$\mu g\ g^{-1}$ ppmv		
Local concentration	molecules cm^{-3} molecules m^{-3}	Column density	matm cm km^{-1}
Local density	$g\ m^{-3}$ $\mu g\ cm^{-3}$		

NOTE: In honour of the pioneering work of G. M. B Dobson, the unit of the vertical column of ozone, the milliatmosphere centimetre may also be called Dobson unit (DU). One Dobson unit defines the amount of ozone in the vertical column which, when reduced to a temperature of 0°C and a pressure of 101 325 Pa will occupy a depth of 10^{-5} m. Therefore, we have:

$$1 \text{ Dobson unit} = 1 \text{ DI} = 1 \text{ matm cm} =$$
$$2.141\,4\ \mu g\ cm^{-1} = 2.687 \cdot 10^{16} \text{ molecules } cm^{-2}.$$

16.1.3 *Methods of measurement*

Atmospheric ozone is measured both by remote sensing and *in situ* techniques. *In situ* measurements of ozone are made by analysing a sample of air to determine its ozone content by optical, chemical, or electrochemical techniques. Remote sensing measurements are made by differential absorption techniques. Ozone has a strong and variable absorption spectrum for UV wavelengths shorter than 340 nm, a weaker broad absorption peak centred at 600 nm in visible light, and many absorption and thermal emission lines at infrared (IR) and microwave wavelengths. By measuring spectral irradiance from a natural (Sun or Moon) or man-made source after it has passed through atmospheric ozone, it is possible to determine the amount of ozone in the optical path. The amount of thermal radiation emitted by atmospheric ozone is also measured and used to determine ozone amounts.

Errors in the knowledge of the ozone absorption spectrum could affect the accuracy of virtually all types of routine ozone measurement. The ozone absorption coefficient (α) in equation 16.1 (section 16.2.2) is the basic absolute calibration for all surface ozone measurements. All ground-based total ozone measurements depend on the ozone absorption coefficient (α) in equation 16.2 (section 16.3.2.1). Umkehr and ozonesonde measurements of the ozone profile are normalized to a nearly coincident ground-based total ozone measurement. Absorption coefficients are used in the inversion algorithms for light detection and ranging (LIDAR) and for satellite measurements of total ozone and the ozone profile.

Several groups have made a significant effort to measure the ozone-absorption spectrum in the laboratory. Measurements have been made over a wide range of temperatures because there is a strong temperature dependence of the absorption. The International Ozone Commission recommended, and WMO adopted, a standard ozone spectrum effective 1 January 1992 based on measurements provided by Bass and Paur (1985). The absolute accuracy of the standard ozone-absorption spectrum is estimated to be between 3 and 5 per cent. This uncertainty affects all types of ozone measurement equally. The precision of the standard ozone-absorption spectrum is estimated to be about 1 per cent. This uncertainty will arise as a bias error when one instrument using one set of wavelengths is compared with another instrument using different wavelengths.

There are a number of other sources of error in the measurement of ozone that depend on what is being measured and the method used to make the measurement. These are discussed below.

16.2 Measurements of surface ozone

16.2.1 *Instruments for measuring surface ozone*

Surface ozone is routinely measured by ozone analysers, which measure the concentration of ozone in ambient air near the ground. The most commonly used instruments for measuring surface ozone are the UV photometric ozone analyser and the Dasibi-type ozone monitor. These instruments measure ozone by UV absorption photometry in a narrow wavelength interval (≈ 0.5 to 1 nm) and are the most commonly used instruments for the measurement of ambient ozone.

The dry chemical analyser — which applies the chemiluminescence method — and the wet chemical analysers have been in routine operation, but their use is becoming less common because these methods are not as reliable as the UV absorption method. Technical information regarding ambient ozone-monitoring instruments is given by Paur and McElroy (1979). Intercomparisons of surface ozone instruments have been made. (Attmannspacher and Hartmannsgruber, 1982).

16.2.2 *Methods for measuring surface ozone*

Surface ozone is routinely measured by *in situ* techniques, while ozone near the ground is sampled by an ozone analyser. The most commonly used method is that of UV photometry, where ambient air is drawn through a cell in which the absorption of UV radiation is measured at the 254 nm emission line of a mercury-vapour lamp. The strong absorption by ozone at this wavelength produces a detectable absorption measurement when ozone is present in the cell. Other atmospheric gases do not cause significant absorption.

The absorption cell alternately samples ambient air coming directly from the atmosphere and ambient air diverted through a manganese dioxide "scrubber" that converts ozone catalytically to oxygen and leaves all other trace gases intact. The UV irradiance is measured when ozone is present in the ambient air and when it is not. The measured irradiance with ozone present I is related to the measured irradiance without ozone present I_o by the following expression:

$$I = I_o \exp(-\alpha CL) \qquad (16.1)$$

where α is the absorption cross-section of ozone at 254 nm (cm^2), C is the concentration of ozone in the cell (molecules cm^{-3}), and L is the length of the cell (cm).

By comparing the two irradiance signals it is possible to determine the concentration of ozone in the cell, provided the length of the cell and the absorption cross-section for ozone are known. Ozone measurements are reported as part per million volume (ppmv) or partial pressure. The range of detectability is from .001 to 1 ppmv.

There are other types of field measurement in use. These include wet chemical, chemiluminescent, electrochemical, and gas titration methods. These methods are becoming less common because they are less practical and not as accurate as the UV photometric method and, hence, will not be described.

16.2.3 *Exposure of instruments for surface ozone*

The *in situ* instruments for measuring surface ozone usually operate in an indoor laboratory, with the ambient air pumped to the analyser through a clean teflon tube. The intake of the tube is mounted so that the air being sampled is representative of the local atmosphere. The intake should be at a height of at least 3 m above the ground (usually on a rooftop). The inlet should be inverted and protected by a funnel to avoid the intake of rain-water and to minimize the intake of large particles and dirt. All potential causes of a perturbation in the composition of the local atmosphere (e.g. a roadway, chimney, ventilation fan, etc.) should be avoided. There should be a small particle filter at the intake in order to prevent large particles and dirt from contaminating the transfer tube and the filter should be changed when required (about once a week depending on the atmospheric conditions). The inlet tube must be kept clean and as short as possible to ensure that ozone is not destroyed before it is measured. A compromise between a high intake height and a short tube usually results in the length of the tube being between 3 and 5 m.

If background (non-polluted) surface ozone values are being measured, then the site should be located away from major pollution sources (cities). The stations should satisfy the regional and/or global station criteria of the Global Atmosphere Watch, as specified in WMO (1988) and approved by the forty-fourth session of the Executive Council in July 1992 (WMO, 1993).

16.2.4 *Errors in measuring surface ozone*

The main source of error for all *in situ* ozone analysers measuring surface ozone is the loss of ozone along the inlet tube. This error can be minimized by ensuring that the tube is kept clean and dry.

Some other trace gases absorb radiation at the 254 nm wavelength that is used to measure ozone absorption. The differential method of comparing between ambient air with ozone and with ozone removed avoids the problem of other absorbing gases because they are present during both measurements. However, should the concentration of another gas change between the ozone and non-ozone sampling periods, an erroneous ozone measurement will result.

In general, the measurement of ozone with the UV photometer method is quite stable because it is a relative measurement (comparing absorption in a cell with ozone to that without ozone present). The output of the lamp and the sensitivity of the detector may drift without affecting the ozone absorption measurement. Other ozone analysers (chemiluminescence, wet chemistry) are also subject to drifts, and periodic checks are required.

16.2.5 *Comparison, calibration, and maintenance of instruments for surface ozone*

UV photometric instruments are recognized as standard instruments. The absolute calibration of a UV photometric analyser depends on the accuracy of the value of the absorption cross-section of ozone at 254 nm. This measurement is made by measuring the absorption in a cell containing a known amount of ozone. The amount of ozone in the cell must be determined by a chemical or physical process which yields the number of ozone molecules in the cell. These absolute concentration measurement methods include passing ozone through a potassium iodide solution, titrating ozone with nitric oxide, and measuring pressure change as oxygen is converted to ozone. The ozone cross-section is estimated to be accurate to within ± 5 per cent.

The UV photometric measurement is recognized as a reliable method to transfer the primary calibration to the field. A field instrument is calibrated by measuring a sample of ozone (generated either in the laboratory or in ambient air) by both the field instrument and the standard.

16.3 Measurements of total ozone

16.3.1 *Instruments for measuring total ozone*

Total ozone is routinely measured with ground-based remote sensing instruments which measure the intensity of UV or visible light at wavelengths in the absorption spectrum of ozone. The most commonly used ground-based instruments in the Global Ozone Observing System are the Dobson (Dobson, 1957; WMO, 1980) and Brewer (Evans, *et al.*, 1987) ozone spectrophotometers, and the M-83 (Gushchin, 1963) and M-124 ozonometers (Gushchin, Sokolenko and Kovalyev, 1985). Other UV, visible ground-based total ozone measuring instruments have been developed recently but their use has been limited to special experimental applications rather than to routine monitoring and data reporting.

Total ozone is also measured routinely by remote sensing instruments from satellites. Ozone is measured from its emission of infrared radiation or its absorption of backscattered solar UV radiation. Most of these satellite instruments have been experimental and have limited lifetimes. The longest total ozone records from satellite instruments are from the Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscatter Ultraviolet (SBUV) instruments which have been operational on board the NIMBUS-7 satellite since 1978 (Heath, Krueger and Park, 1978). Both these instruments measure the radiance of solar UV which is scattered by the Earth's atmosphere to the satellite sensors. Global daily maps of total ozone are made from the TOMS data.

16.3.2 *Methods for measuring total ozone*

Total ozone is measured by remote sensing techniques using ground-based and satellite instruments which measure irradiances in the UV absorption spectrum of ozone between 300 and 340 nm. In this spectral region, the absorption due to ozone decreases by about a factor of two for every increase of 5 nm in wavelength. Total ozone is measured from the ground using the direct Sun, direct Moon, and zenith sky methods and from space by measuring the solar UV radiation scattered back to space by the Earth's atmosphere.

16.3.2.1 DIRECT SUN MEASUREMENTS

The most accurate and best-defined method to measure total ozone is that of measuring direct solar radiation from the ground at UV wavebands between 305 and 330 nm. In its simplest form for an ozone-only atmosphere, the technique would comprise measurements at one wavelength made at different times during the day. The measured irradiance reading I would be given by:

$$I = I_o \exp(-\alpha X \mu) \qquad (16.2)$$

where I_o is a constant identified as the reading of the instrument if it were above the atmosphere (the extraterrestrial constant), α is the laboratory-measured ozone absorption coefficient at the specified wavelength (nm), X is the total amount of ozone in the atmosphere (m at STP), and μ is the ratio of the path through the atmosphere to the vertical path.

The expression above contains two unknowns, I_o and the total ozone amount X. With several measurements made during a day — necessarily spanning a range of values for μ, and assuming that the amount of ozone remains constant — both I_o and X can be determined by least-square methods. After establishing a value for I_o, just one measurement of I would be sufficient to give a value for total ozone in a column.

In practice, using just one wavelength can give inaccurate results because other atmospheric constituents, such as aerosols, affect the measurement of UV and because instruments are unstable. These effects are significantly reduced by considering the relative irradiance of UV measured at two or more wavelengths with different ozone-absorption coefficients. A complete description of the multi-wavelength direct Sun measurement and the method used to calibrate an instrument for its extraterrestrial constants is given in Annex 16.B.

Direct Sun measurements are limited to daylight hours at times when the direct solar beam is not obscured by clouds for a period of at least two to three minutes. The apparent solar zenith distance must be less than 75°.

16.3.2.2 DIRECT MOON MEASUREMENTS

Total ozone is also measured by the direct Moon method where the Moon is used as the UV source instead of the Sun. This method is similar in principle to the direct Sun measurement but is less accurate because of the reduced amount of available UV and the difficulty in making measurements. The measurement period is limited to within five days of the full Moon, so complete coverage on a daily basis is not possible. Also, the direct beam from the Moon must be clear of clouds and the apparent zenith distance of the Moon must be less than 75°. The direct Moon measurements are very useful during polar nights when there would otherwise be no information from ground-based measurements.

16.3.2.3 ZENITH SKY MEASUREMENTS

The zenith sky measurement has been developed for use on days when the Sun is obscured by clouds in order to satisfy the desire to measure total ozone on a daily basis. Empirically, evidence shows that the information content of UV scattered from the zenith sky to the Earth's surface is sufficient to provide a reasonable measurement of total ozone. The measurement of the relative magnitude of UV at a pair of wavelengths is dependent both on total ozone and on the μ value. Many near-simultaneous sets of zenith sky and direct Sun observations are used to develop empirical sky charts which are graphical or functional representations of the dependence of total ozone on the zenith sky measurement and the μ value. Computer models which simulate multiple scattering atmospheres have been used to verify and improve the empirical results.

The zenith sky measurement is limited to daylight hours when the Sun is at an apparent zenith distance less than 80°. It is less accurate than the direct Sun measurement because the path of light through the atmospheric ozone depends on other variables, such as the vertical distribution of ozone and the presence of clouds. Studies comparing direct Sun with zenith sky measurements suggest that the uncertainty of the blue sky measurement is ±1.5 per cent and degrades with cloudiness. The inclusion of zenith sky total ozone measurements from blue and cloudy days are essential for keeping continuous ozone records especially at mid- and high-latitude stations in winter. However, each station should prepare its own sky chart.

16.3.2.4 BACKSCATTER ULTRAVIOLET MEASUREMENTS

The spectral solar UV radiation which is scattered by the atmosphere into space contains sufficient information to obtain a measurement of atmospheric ozone. Solar UV backscattered to space is absorbed by atmospheric ozone along the solar path to the scattering level and on the return path to space. A satellite-borne instrument measures the radiance of backscattered solar UV and the direct solar UV irradiance before it enters the atmosphere. The amount of absorption due to atmospheric ozone is determined by comparing these two measurements.

The solar UV irradiance outside the Earth's atmosphere is determined once each day by measuring solar UV falling on a diffuser plate which is exposed to the direct solar beam. Calibrations of the diffuser plate are necessary to determine its diffusing characteristics as a function of wavelength.

Measurements are made at five wavelengths between 312 and 380 nm. Radiation at the longest wavelength is not absorbed by ozone and is used as a measure of ground or cloud reflectivity. Radiation at the other four wavelengths absorbs ozone by varying amounts. The amount of absorption depends on the local solar zenith angle, the instrument viewing angle, the effective scattering level, the ozone-absorption coefficient, and the amount of ozone in the atmosphere. Results of multiple-scattering model atmospheres are required to develop the appropriate algorithms for determining atmospheric ozone amounts. These inversion algorithms also incorporate the results of extensive intercomparison with ground-based direct Sun measurements. Different algorithms have been developed for different seasons and latitudes.

The measurement of total ozone is limited to periods of daylight when the solar zenith distance is less than 88°. It is, therefore, not possible to measure ozone by this technique at high latitudes during polar nights.

The Total Ozone Mapping Spectrometer (TOMS) is an example of such an instrument on board the NIMBUS-7 satellite, which was launched in late 1978 in a polar orbit. TOMS provides a daily map of the total ozone above all parts of the globe except at high latitudes during winter. The instrument's field of view scans across the atmosphere below the satellite perpendicular to the direction of travel. Total ozone is measured with a horizontal resolution that varies from 50 km for nadir viewing to 250 km for non-nadir extremes. At least one measurement is made each day above all parts of the Earth where the solar elevation is greater than 2°.

The Solar Backscatter Ultraviolet (SBUV) instrument is also on board the NIMBUS-7 satellite and uses a spectrometer similar to that used in TOMS; however its primary objective is to measure the vertical profile of ozone. Total ozone is also measured in a 200 km path directly below the satellite. The data algorithms are identical to those for TOMS. The horizontal coverage is not as extensive as TOMS but the redundancy of the total ozone measurement in the nadir is useful to verify instrument performance. The TIROS Operational Vertical Sounder (TOVS) experiment of the National Oceanic and Atmospheric Administration (NOAA) satellites also provides total global ozone data (Planet, *et al.*, 1984).

16.3.3 *Exposure of instruments for total ozone*

The ground-based remote sensing instruments for measuring ozone in the stratosphere are exposed according to their viewing requirements. In general, an observatory with a clear view of the Sun, Moon, and zenith sky is required. The measurement site should avoid sources of local pollution or other contaminants which may affect the optical properties of the local atmosphere, particularly their rate of change.

The Dobson, M-83 and M-124 instruments are stored indoors and must be transported outside to take a measurement using sunlight or zenith skylight. The requirement to move the instrument outdoors is avoided at several observatories by use of a roof hatch or observation dome which may be opened to take a measurement.

The fully automated Brewer instrument is permanently mounted outdoors at a location allowing a good view of the Sun and Moon above an elevation of 15° on all days of the year. The instrument is levelled and its alignment is fixed to the Sun in order to allow automatic pointing at the Sun and Moon.

Light detection and ranging (LIDAR) instruments as well as microwave instruments operate from inside a laboratory, and measurements are usually made on the zenith sky through a roof hatch or dome. In some instances, LIDAR measures in other directions by pointing the laser beam and detector. LIDAR instruments must be located in such a way as to avoid interference from other UV sources, and microwave instruments must avoid interference which may come from microwave and radio transmitters.

16.3.4 *Errors in measuring total ozone*

Equation 16.B.4 in Annex 16.B is the fundamental physical basis for the direct Sun total ozone measurement. Some of the errors in the measurement of total ozone by the direct Sun method are demonstrated by considering the uncertainties in the individual terms in this equation.

The extraterrestrial constant for an instrument (F_o in equation 16.B.4) is the reading that the instrument would register about Sun radiation outside the Earth's atmosphere with no ozone in the path. This value is not measured directly; it is determined either from a number of air-mass extrapolation measurements or by calibrating an instrument against a standard with a known F_o. Errors in F_o may arise from uncertainty of the initial calibration or from a change (either a gradual drift or an abrupt shift) in the optical properties of the instrument. Uncertainties in the initial calibration generally result in measurement errors of less than 0.5 per cent. However, errors due to changes with time can result in measurement errors as large as 20 per cent. Variability of the radiation spectrum emitted from the Sun would also cause an error in F_o. It is believed that errors from solar variability are less than 0.25 per cent.

There are errors in the reading that an instrument registers (F in equation 16.B.4). One potential source of error is non-linear response of the instrument to the variable it is measuring. In the case of the Dobson instrument, an unavoidable non-linearity arises because of irregularities in the optical "wedge". A Brewer instrument's non-linearity is due to the dead time of the photon counting system. Both of these effects are corrected by linearity calibration measurements. However, for the Dobson instrument, the non-linearity may change with time due to changes in the optical wedge. This uncertainty is generally less than 0.3 per cent for the Brewer instrument and generally less than 0.5 per cent (WMO, 1982) for the Dobson instrument. There is also error in the measured value (F) arising from the random uncertainty (noise) with which a signal is measured. For both the Brewer and Dobson instruments, this error is generally less than 0.3 per cent for a typical direct Sun measurement. Another error in F

arises when irradiance from the wrong wavelength is measured. This error is less than 0.5 per cent for air-mass (μ) values that are less than 3.5.

Another source of error in the determination of total ozone is the air-mass (μ) value in equation 16.B.4. This value is calculated from time and from the geographical location of the instrument (latitude and longitude). Errors of 1′ latitude or longitude or 10 seconds in time can result in an error of 0.1 per cent in the μ value. Calculations of the μ value assume that the ozone layer is optically centred at 22 km above the station. A deviation of a 2-km height from this assumption could result in an 0.25 per cent error in the μ value.

Uncertainty of the absorption coefficient (α in equation 16.B.4) of a specific instrument arises from uncertainty of the slit transmission functions. An uncertainty of about 2 per cent is typical for a Dobson instrument and about 0.5 per cent for a Brewer instrument. An additional error in the ozone absorption coefficients arises from their temperature dependence. If, for example, the actual temperature of the ozone layer is 10° colder than the assumed temperature of –55°C, then the effective absorption coefficients for the Dobson instrument are about 1.2 per cent for AD and about 3 per cent for CD smaller than those valid for –45°C. Such a temperature effect can produce additional error. AD and CD are differences between the absorption of pairs of wavelengths which are most commonly used for the total ozone calculations, where the wavelengths (in nm) are:

A: 305.5/325.4
C: 311.4/332.4
D: 317.6/339.8.

Other absorbing gases (such as sulphur dioxide and nitrogen dioxide) in the atmosphere can cause errors in ozone measurement. These errors are generally less than 3 per cent for a Dobson instrument and less than 2 per cent for a Brewer instrument.

The effect of haze, aerosols, and thin clouds on direct Sun measurements for the Brewer and Dobson instruments is less than 0.5 per cent. For zenith sky measurements and direct Sun measurements with M-83 and M-124 instruments, the effects of turbidity are considerably larger.

The effects of thick clouds can cause errors as large as 10 per cent on the zenith sky measurements and 3 per cent on the TOMS and SBUV satellite measurements.

Variations of the height of the ozone layer may cause errors of up to 5 per cent for the zenith sky and satellite total ozone measurements.

The measurement of total ozone by the solar backscatter method is not as physically well defined as the ground-based direct Sun measurement. The inversion is based on results of computer model atmospheres and several assumptions are required regarding seasonal and latitudinal dependence of the vertical ozone profile. The measurement of tropospheric ozone is quite inaccurate because the absorption by this lower-level ozone is hidden by the stronger absorption signal from stratospheric ozone. Reflectivity from the ground or tropospheric clouds also affects the measurements and must be considered. A drift in the reflectivity of the diffuser plate which is used for determining the incoming solar radiation has been a serious source of error for the TOMS and SBUV total ozone measurement.

16.3.5 *Comparison, calibration, and maintenance of instruments for total ozone*

16.3.5.1 CALIBRATION OF A PRIMARY STANDARD INSTRUMENT

The calibration of a field instrument is ultimately traced to a reference standard. The Dobson reference consists of the WMO-recognized primary standard instrument Dobson No. 83, which is maintained at NOAA in Boulder, Colorado. The Brewer reference (consisting of a trio of primary standard instruments) is maintained at the Atmospheric Environment Service in Toronto, Canada. All M-83 and M-124 field ozonemeters are referenced to a regional Dobson standard instrument and are maintained in St. Petersburg, Russia.

It is necessary to use the well-defined direct Sun measurement method in order to determine the amount of total ozone on an absolute basis with small uncertainty. This method in outlined in equation 16.2 and described in Annex 16.B. The value for total ozone is given if equation 16.2 is rewritten as follows:

$$X = \frac{1}{\mu\alpha} \cdot \log\left(\frac{I_o}{I}\right) \qquad (16.3)$$

The absolute accuracy of the total ozone measurement depends on the accuracy of all the variables in equation 16.3 above. The μ value is determined from geometry, solar elevation, and the altitude of observations; its uncertainty is nominally less than ±0.2 per cent. Instrumental properties affecting the accuracy of the ozone measurement are:

(*a*) The instrumental response (linearity) to absolute or relative irradiance (I);
(*b*) The effective ozone absorption coefficient (α) applicable to the instrument; and
(*c*) The instrumental extraterrestrial constant (I_o).

An instrument with a non-linear response would produce a non-linear random error for the ozone measurement. An error in the value of the absorption coefficient results in an inverse error for the absolute measurement of ozone. An error in the extraterrestrial constant results in fictitious diurnal and annual variations of total ozone.

Another important consideration affecting the accuracy of the total ozone measurement is the spectral purity of the instrument. This is the ability of the instrument to detect irradiance at a discrete wavelength and to reject it at all other wavelengths. Irradiance measured from undesired wavelengths affects the values of I, I_o, and α in equation 16.3. For example, the lack of spectral purity prevents the ozonemeter from being calibrated absolutely because the sharp gradient in the ozone absorption spectrum across the broad bandpass filters results in a value for α that is not constant over the measured range of ozone concentration.

The linear response of the Dobson instrument is determined by calibrating the optical wedge. This calibration is necessary to scale the mechanical setting of the wedge to the log of the ratio of irradiance signals at the short and long wavelengths. It is carried out by using two lamps of equal output and by measuring the balanced wedge position when the lamps are on individually and together. This measurement gives the incremental wedge setting required to reduce the irradiance by a factor of two at each position of the wedge. The procedure is carried out at about 50 wedge settings over the entire length of the wedge for all four of the wavelength pairs. This calibration should be done every four years, or more often, if there is reason to suspect degradation of the optical properties in the wedge.

The response of the Brewer instrument is fundamentally linear except at high irradiances. In operation, this small correction is accurately applied and larger corrections are avoided by reducing measured irradiances with neutral density filters.

The Dobson instrument absorption coefficients have been calculated by applying the measured wavelength transmission characteristics of a primary standard instrument of the United States National Bureau of Standards to a laboratory measurement of the ozone absorption spectrum at –46.3°C (a temperature considered representative of the stratosphere) made by Bass and Paur (1985). The absorption coefficient for the AD double pair was recommended by the International Ozone Commission (IOC) and adopted by WMO on 1 January 1992 as the standard for all Dobson instruments.

Absorption coefficients for a primary Brewer standard instrument are determined by measuring the instrument's wavelength transmission functions and by applying measurements of the ozone absorption spectrum at –46.3°C. It has been observed that Brewer instruments differ slightly in wavelength transmission and each instrument has a unique set of values for the absorption coefficient which vary by about 1 per cent from instrument to instrument.

Extraterrestrial constants for the Dobson and Brewer standard instruments are determined by the airmass extrapolation method outlined in Annex 16.B. Many measurements are made on clear days when ozone remains constant. A good site for making these measurements is at the Mauna Loa Observatory in Hawaii because of the high proportion of ideal days. In general, good extraterrestrial values can be determined from extrapolation data taken on several days. Such calibrations are routinely carried out on the primary standard Dobson No. 83 every two or three years.

16.3.5.2 CALIBRATION TRANSFER AND MAINTENANCE

The absolute calibration determined for the primary reference must be transferred to all field instruments and the calibration must be carefully maintained.

Two methods are used to transfer the calibration of the primary Dobson standard to a field instrument: the travelling standard lamp method and the simultaneous direct Sun method. For the lamp method, the primary Dobson instrument measures the relative irradiance from a well-regulated lamp source at the four wavelength settings. The lamp is then shipped to a field station where its output is measured by the field Dobson instrument and the extraterrestrial constants are adjusted by an amount determined from the lamp measurements. The accuracy of the calibration transfer using the standard lamp method does not cover the entire range of the wedges and, therefore, while useful has only limited application.

The simultaneous direct Sun method requires the standard and the field instrument to take a series of simultaneous direct Sun total ozone measurements at the same site. Measurements should be made on at least one half-day with an adequate range of μ value and good observing conditions. The extraterrestrial constant of the field instrument is adjusted to provide the best fit for total ozone values with the reference instrument. It is not practical to bring all field instruments to the same site as the standard instrument on a routine basis. Therefore, eight regional secondary standards are used to transfer the primary reference to the field. Periodic intercomparisons are held to calibrate several secondary standards against the primary. The secondary standards are then used to calibrate the field instruments.

Calibration constants are transferred to a field Brewer instrument by direct intercomparison with the primary reference at Toronto or by using a secondary travelling standard at the field site. Both the standard and the field instruments take simultaneous direct Sun ozone measurements throughout a day with good observing conditions over a sufficient range of values. Values of absorption coefficient and extraterrestrial constants for the field instrument are determined by fitting the data from the field instrument to the ozone data measured by the standard. Calibration of the secondary travelling standard is checked at Toronto prior to departure to the field and on its return to ensure that the calibration has not altered in transit.

An M-83 or M-124 field ozonemeter is recalibrated, on average, every two years by direct intercomparison with a Dobson instrument. The field instrument is replaced by a recently calibrated instrument and brought to the calibration site where it takes simultaneous direct Sun readings with the Dobson instrument. Instrument readings as a function of solar zenith angle and total ozone (as measured by the Dobson instrument) are determined. The calibrated instrument is, then, returned to the field at a different site.

Routine checks and tests are required to maintain the calibration of all reference and field instruments. These checks verify that an instrument is operating properly and, if not, alert the operator of a problem or potential problem. Results of the tests are used to correct an instrument calibration, if necessary, and to help determine whether an instrument requires recalibration.

Checks for the wavelength settings, response to relative irradiance signals, and wedge calibration are carried out twice a month on the Dobson instrument. The wavelength setting is measured and adjusted by measuring the emission lines from a mercury vapour lamp. The instrument's response to relative irradiance is checked at all four wavelength settings by measuring the output of a quartz halogen standard lamp. This measurement is used to adjust the instrument's extraterrestrial constant, if necessary. Calibration of the optical wedge is done by means of rhodium-coated quartz plates with standard lamp measurements enabling standard lamp measurements to be made at more than one position along the wedge.

Checks for the wavelength setting, response to irradiance levels, and dead time are made daily for the Brewer instrument. Emission lines from a mercury vapour lamp are used for wavelength calibration and setting. A quartz halogen standard lamp is measured to monitor the instrument's response to irradiance and to adjust the extraterrestrial constants, if necessary. Linearity is checked by measuring the dead time.

16.4 Measurements of the vertical profile of ozone

16.4.1 *Instruments for measuring the vertical profile of ozone*

The vertical profile of ozone is measured with an ozonesonde, which is an ozone analyser coupled to a radiosonde. The ozonesonde measures the concentration of ozone as a function of height by sampling ambient air during its balloon-borne ascent to an altitude typically between 30 and 40 km. Ozonesondes in routine use are the Brewer-Mast and Electrochemical Concentration Cell (ECC) sondes (Komhyr, 1986), or modified variations of these instruments.

Ground-based instruments measure the ozone profile on a routine basis by using remote sensing techniques. Measurements of solar UV light from the zenith sky during twilight made by a Dobson or Brewer ozone spectrophotometer are used to determine ozone profiles using the Umkehr inversion method. Ultraviolet LIDAR (optical radar) systems have recently been developed and are now in operation at some sites.

The ozone profile is also measured routinely by satellite instruments. The SBUV instrument uses backscattered solar UV from the nadir to determine profiles. The Stratospheric Aerosol and Gas Experiment (SAGE) measures the ozone profile by the solar occultation method. Other satellite instruments using infrared and microwave emission techniques have obtained ozone profile measurements but their operating lifetimes have been relatively short.

16.4.2 *Measurement of the vertical profile of ozone*

Balloon-borne ozonesondes are used to take *in situ* measurements of the vertical distribution of ozone. Remote sensing measurements of the profile are made from the ground by the Umkehr and LIDAR techniques and from space by the solar backscatter UV and solar occultation methods.

16.4.2.1 OZONESONDE MEASUREMENTS

The vertical profile of ozone is routinely measured by a balloon-borne ozone analyser which operates with a radiosonde. Typically, it is carried to an altitude between 30 and 40 km by a large-volume radiosonde balloon. The signal from the ozone analyser is read by the radiosonde and transmitted by telemetry to the ground receiver. Ozone is sampled continuously during the balloon ascent and a profile is obtained from the ground to the top of the ascent with a vertical resolution of about 200 m. There are also techniques that sample ozone during the descent of the ozonesonde on a parachute (De Muer and Malcorps, 1984). Its merits are questionable, however.

The Brewer-Mast and Electrochemical Concentration Cell (ECC) analysers utilize the reaction of ozone with potassium iodide, which produces free iodine. In effect, every molecule of ozone introduced into the cell results in the generation of two electrons. Ambient air is "bubbled" through the solution in the reaction cell by a small battery-powered pump and the signal output is proportional to the number of ozone molecules present in the air sample. With the appropriate conversion, a measurement of ozone in units of partial pressure or mixing ratio is determined.

It is necessary to apply a total ozone correction factor to ozonesonde profile measurements because the accuracy of the analyser is difficult to maintain. The correction factor for the profile makes its integral agree with a representative ground-based total ozone measurement and they usually came close to ±5 per cent. However, the sonde should exceed 15 hPa pressure height. Some assumptions (e.g. constant mixing ratio) are necessary regarding the distribution above the top of the measured profile.

16.4.2.2 UMKEHR MEASUREMENTS

The vertical profile of ozone is measured remotely from the ground by the Umkehr technique. The basis for this method is the dependence on the vertical distribution of the ozone of the differential absorption of solar UV light at two wavelengths passing through atmospheric ozone and scattered to the Earth's surface from the zenith sky. This dependence is enhanced as the Sun nears the horizon. The ratio of zenith clear sky radiation at two UV wavelengths is measured for solar zenith angles between

60° and 90°. The log of the ratio is plotted as a function of zenith angle; the slope of this curve changes sign at a particular zenith angle. This curve is called an Umkehr curve (from the German word meaning 'turn around').

The standard Umkehr technique was developed and put in operation a number of years ago to analyse measurements made by the Dobson spectrophotometer. Zenith blue sky measurements at several solar zenith angles between 60° and 90° are compared with results from a multiple-scattering radiation model. It is assumed that the vertical ozone profile is uniform in the horizontal and remains constant for the duration of the measurement period. A representative total ozone measurement is required as part of the data input. The analysis is based on a climatological first guess and an iterative solution is reached. The resulting profile is reported as mean partial pressure values for the following nine pressure layers:

Layer number	*Pressure range (hPa)*
1	500 – 250
2	250 – 125
3	125 – 62.5
4	62.5 – 31.2
5	31.2 – 15.6
6	15.6 – 7.8
7	7.8 – 3.9
8	3.9 – 1.96
9	1.96 – 0.98

The short Umkehr technique was recently developed for the Dobson and Brewer instruments and is in operation at some sites. The short Umkehr is of similar accuracy to the standard Umkehr and has several operational advantages because the required range of solar zenith angles is reduced to between 80° and 90°. The measurement period is significantly shorter so the probability of obtaining a cloud-free observation period is increased. The observing season is also extended for high latitudes because there are more days in the year when the sun rises to a 10° elevation. Also, effects of ozone changes are not as likely for the shorter observation period. A measurement of total ozone is still required as data input.

16.4.2.3 LIGHT DETECTION AND RANGING MEASUREMENTS

Ground-based measurements of the ozone profile are made with a LIDAR (optical radar) system. A short laser pulse at a wavelength in the UV ozone absorption spectrum is emitted toward the zenith. Backscattered radiance is measured as a function of time after the pulse emission. The time of arrival gives the scattering height and the variation of the radiance as a function of time gives a measurement of the amount of ozone absorption. With appropriate calibrations, the ozone profile is determined.

The LIDAR technique is limited to operating at night when there is not an appreciable amount of cloud cover. A profile measurement is derived from the integration of many laser shots taken over a period of about four hours. Atmospheric aerosols interfere with the measurement, which is less reliable at heights where aerosols are present from sources such as volcanic eruptions.

16.4.2.4 SOLAR BACKSCATTER ULTRAVIOLET MEASUREMENTS

The vertical profile of ozone is measured from space by the SBUV method with the SBUV satellite instrument. Measurements of solar radiation scattered from the atmosphere back to space are made at several UV wavelengths between 250 and 400 nm. The effective scattering height in the atmosphere is determined by the amount of ozone above the scattering height and the ozone absorption coefficient. Because the ozone absorption coefficient varies by several orders of magnitude between 250 and 340 nm, the effective scattering layer is a function of the wavelength. Measurements made at several wavelengths are sufficient to determine an ozone profile. The ozone profile is determined by comparing the measurements of a scattering atmosphere which result from a computer model. The inversion algorithm requires a seasonal and latitudinal a priori first-guess profile and a solution is computed by iteration. The vertical resolution of the SBUV profile measurement is comparable with that of the Umkehr measurement.

16.4.2.5 SOLAR OCCULTATION MEASUREMENTS

The ozone profile is measured on a routine basis from space by the solar occultation technique with the SAGE II satellite instrument. Direct solar irradiance is measured during the sunrise and sunset occultation periods from an orbiting satellite and the absorption by the atmosphere is determined from the 600 nm ozone absorption band at visible wavelengths. During occultation, the measured solar beam rapidly ascends or descends through the atmosphere. The path length of the tangential ray passing through the lowest 1-km thick layer is more than 200 km, so absorption due to ozone in the tangential layer is significantly enhanced.

The measured absorption curve is inverted to yield the vertical ozone profile assuming uniform horizontal distribution. The amount of absorption due to atmospheric ozone is measured as a function of time; the path length of light through each atmospheric layer is well defined by the satellite orbit and geometry.

16.4.2.6 OTHER MEASUREMENT TECHNIQUES

There are a number of other techniques which have been used to measure the vertical ozone profile. These specialized methods do not yield data on a routine basis and are made by instruments which are located on the ground, balloons, rockets, or satellites. These methods include:

(*a*) Microwave thermal emission;
(*b*) *In situ* UV absorption photometry;
(*c*) Differential UV solar absorption;

(*d*) Infrared thermal emission;

(*e*) Infrared absorption.

The ozone profile can be measured from the ground using the microwave thermal emission method. Measurements of the 109.559 or 110.836 GHz thermal emission lines of ozone are made. It is possible to determine the vertical profile of ozone from the shape of the emitted line, which is a function of pressure.

The *in situ* UV absorption photometer normally used to measure surface ozone has been modified to measure ozone from a balloon platform. Ozone concentration is measured as a function of altitude as the instrument ascends (or descends) through the atmosphere.

The differential UV solar absorption technique measures total ozone from an ascending platform (balloon or rocket) as a function of altitude. The ozone profile is determined from the differential of the total ozone versus altitude curve.

Infrared and microwave radiation, which are thermally emitted by ozone, are measured from a balloon or satellite instrument scanning the Earth's limb. The radiance signal as a function of viewing angle can be inverted to give the vertical distribution of ozone.

Infrared absorption measurements are made of solar radiation during sunrise or sunset from a balloon platform. The vertical profile of ozone is determined by inverting the signal as a function of tangential path through the atmospheric layers below the balloon.

16.4.3 *Comparison, calibration, and maintenance of instruments for the vertical profile of ozone*

The siting and exposure of these instruments are described in section 16.3.3.

16.4.4 *Errors in measuring the vertical profile of ozone*

There are a number of error sources for the ozonesonde measurement of the ozone profile. The potassium iodide solution could contain contaminants which would affect the sensitivity of the sonde to ozone. An error in the measurement of the flow rate of air generated by the pump would result in a systematic error in the measurement of ozone at all levels. It is also possible that the pumping characteristics may change during flight.

The absolute accuracy of the integrated profile (total ozone) for an ozonesonde profile is given by the absolute accuracy of the ground-based total ozone measurement because the integrated profile is normalized to a total ozone measurement. This is estimated to be between 3 and 5 per cent. The accuracy of a measurement at a particular height in the atmosphere varies as a function of altitude. In general, the accuracy for the measurement is estimated to be ±10 per cent in the troposphere and ±5 per cent in the stratosphere below 10 hPa. Above 10 hPa, increasing uncertainties in the pump efficiency and flow rate cause the estimated error to increase to 15 per cent at 5 hPa.

There are a number of error sources for the Umkehr inversion technique. Errors result when the horizontal distribution of ozone is not uniform or when changes occur either in total ozone or in the vertical distribution of ozone during the measurement period. The Umkehr measurement is affected by stratospheric aerosols which are present at times when there has been volcanic activity. An error in the a priori first-guess profile causes errors in the final inversion. The overall accuracy of the Umkehr method is estimated to be ±50 per cent for the troposphere (layers 1 and 2), ±10 per cent for the lower stratosphere (layers 3 to 6) and ±20 per cent for the upper stratosphere (layers 7 to 9).

For LIDAR measurements, the accuracy of the ozone profile measurement is estimated to be ±3.0 per cent and is a function of uncertainty in the absolute accuracy of the ozone absorption coefficient. The random error is estimated to be ±2.0 per cent for heights up to 30 km and increases to ±18.0 per cent at 45 km. The measurement uncertainty increases with the presence of haze or aerosols.

There are several sources of error for the SBUV profile measurement. This measurement is affected by the presence of stratospheric aerosols. Uncertainties in the model simulations and in the first-guess profile result in potential error. Instability of the diffuser plate's optical properties could cause measurement error. The overall accuracy of the SBUV profile measurement is estimated to be similar to that of the Umkehr in the lower stratosphere and somewhat better than the Umkehr in the upper stratosphere.

16.4.5 *Comparison, calibration, and maintenance of instruments for the vertical profile of ozone*

The procedures for spectrophotometers and ozonemeters are covered in section 16.3.5. Ozonesondes are disposable instruments which are usually flown only once unless they are recovered and refurbished. There is no requirement to maintain calibration standards for an individual sonde over a long period of time and there is no standard ozonesonde which is used to calibrate others. There are standard procedures which are followed to prepare individual ozonesondes prior to their launch. Detailed preparation procedures are given in Komhyr (1986) for the Electrotechnical Concentration Cell (ECC) sonde and in WMO (1992) for the Brewer-Mast sonde.

16.5 Corrections to ozone measurements

Ozone data made at stations in the World Ozone Monitoring Network are submitted to the World Ozone Data Centre (WODC) in Toronto where the data are archived and reported in the bi-monthly publication entitled *Ozone Data for the World*. The WODC is operated by the Atmospheric Environment Service of Canada in cooperation with WMO. Measurements of surface ozone, total ozone (direct Sun, direct Moon and zenith sky), and vertical distribution of ozone (Umkehr, ozonesonde, and LIDAR) are submitted and published.

The instrumental characteristics which affect a measurement of surface ozone and total ozone (such as temperature response and non-linearities) are generally corrected in the observation procedure or when determining ozone values from the instrument's reading. In some situations, the direct Sun measurement of total ozone is corrected for spectral impurity in order to extend the range of measurements to air-mass values greater than 3.5 (effects of spectral impurity are usually negligible for an air mass of less than 3.5). This would occur at high latitudes during winter. The corrections are empirical and are based on data from days when the measurement from large air mass values (about 6) may be compared with those measurements made at smaller values (<3).

Umkehr measurements are submitted to the WODC where they are processed to yield vertical distributions of ozone, which are then published together with the raw data. All other types of data are processed at the station and the resulting total ozone or ozone concentration values are submitted.

Ozonesonde measurements of the vertical profile of ozone are corrected by normalizing the integrated profile to a ground-based measurement of total ozone. Assumptions must be made regarding the amount of ozone in the atmosphere above the measured profile. If there is no total ozone measurement available, the correction factor is 1.

Individual stations are responsible for ensuring that their data are correct. Questionable data are flagged by the WODC so that a station may check and correct the data, if necessary. The Umkehr data processed at the WODC must pass a quality-control process to be published. Quite often a station may correct previous data by resubmitting the data for publication at a later date. The requirement to correct earlier reported data is usually based on new information regarding an instrumental constant or the discovery of an error or an improvement in the data-reduction process. Corrected data are published in the same format but are usually identified with a "Corrected" comment. Corrected data are also identified in the annual catalogue which summarizes all submitted data.

Data from the TOMS/SBUV and SAGE satellite instruments are processed and archived by NASA. The data are available from the National Aeronautics and Space Administration (NASA) on request. The inversion algorithms and calibration methods for the TOMS/SBUV measurements have improved with time and corrected data based on the most recent version of data analysis are available.

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ANNEX 16.A

UNITS FOR TOTAL AND LOCAL OZONE

Micrometre at STP 1 μm at STP = 0.1 DU
= $2.687 \cdot 10^{19}$ molecules m^{-2}
= $2.687 \cdot 10^{15}$ molecules cm^{-2}
= 1 part per million metre (= 1.0 ppmm at STP)

Dobson unit 1 DU = 1 milliatmosphere centimetre (matm cm)
= 10^{-5} m of ozone at STP

TABLE 16.A.1
Quantities specifying local ozone, units of the International System, and vertical integration

Quantity by	*Density*			*Concentration relative to local air [mixing ratio]*		*Partial pressure*
	Number density	*Density*	*Relative to STP [differentiated total]*	*By mass*	*By volume*	
	m^{-3}	$kg\ m^{-3}$	/[STP]	/	/	Pa
	n	ρ	s	m	v	P
Number density	////	$n \cdot \frac{\rho^o M}{L}$	$n \cdot \frac{1}{L}$	$n \cdot \frac{M}{L} \cdot \frac{T^*}{P^*}$	$n \cdot \frac{1}{L} \cdot \frac{T^*}{P^*}$	$n \cdot \frac{P^o}{L} \cdot T^*$
Density	$\rho \cdot \frac{L}{\rho^o M}$	////	$\rho \cdot \frac{1}{\rho^o M}$	$\rho \cdot \frac{1}{\rho^o} \cdot \frac{T^*}{P^*}$	$\rho \cdot \frac{1}{\rho^o M} \cdot \frac{T^*}{P^*}$	$\rho \cdot \frac{P^o}{\rho^o M} \cdot T^*$
Density relative to STP	$s \cdot L$	$s \cdot \rho^o M$	////	$s \cdot M \cdot \frac{T^*}{P^*}$	$s \cdot \frac{T^*}{P^*}$	$s \cdot P^o \cdot T^*$
Mixing ratio by mass	$m \cdot \frac{L}{M} \cdot \frac{P}{T^*}$	$m \cdot \rho^o \frac{P^*}{T^*}$	$m \cdot \frac{1}{M} \cdot \frac{P^*}{T^*}$	////	$m \cdot \frac{1}{M}$	$m \cdot \frac{P^o}{M} \cdot P^*$
Mixing ratio by volume	$v \cdot L \cdot \frac{P^*}{T^*}$	$v \cdot \rho^o M \cdot \frac{P^*}{T^*}$	$v \cdot \frac{P^*}{T^*}$	$v \cdot M$	////	$v \cdot P^o \cdot P^*$
Partial pressure	$P \cdot \frac{L}{P^o} \cdot \frac{1}{T^*}$	$P \cdot \frac{\rho^o M}{P^o} \cdot \frac{1}{T^*}$	$P \cdot \frac{1}{P^o} \cdot \frac{1}{T^*}$	$P \cdot \frac{M}{P^o} \cdot \frac{1}{P^*}$	$P \cdot \frac{1}{P^o} \cdot \frac{1}{P^*}$	////
Typical concentration at 25 km	$4.97 \cdot 10^{18}$	$3.96 \cdot 10^{-7}$	$1.85 \cdot 10^{-7}$	$10 \cdot 10^{-6}$	$6.03 \cdot 10^{-6}$	$1.51 \cdot 10^{-2}$
Vertical integration (z in metres)	$\int n \cdot dz = L \cdot x$	$\int \rho \cdot dz = \rho^o M \cdot x$	$\int s \cdot dz = x$	$\int m \cdot dP = -Mg \cdot x$	$\int v \cdot dP = -g \cdot x$	$\int p \cdot d(\ln P) = -g \cdot x$

$P^* = P/P^o$, $T^* = T/T^o$	Normalized local temperature and pressure	
P^o, T^o	Standard pressure and temperature (STP)	$1.013\,25 \cdot 10^5$ Pa, 273.15 K
ρ^o	Density of air at STP	1.293 kg m^{-3}
L	Loschmidt number	$2.687 \cdot 10^{25}$ m^{-3}
g	Gravity acceleration	9.807 m s^{-2}
M	Molecular ratio: ozone/air	1.657
x	Total ozone	unit m [at STP]
P, T	Local air pressure, temperature	units Pa, K

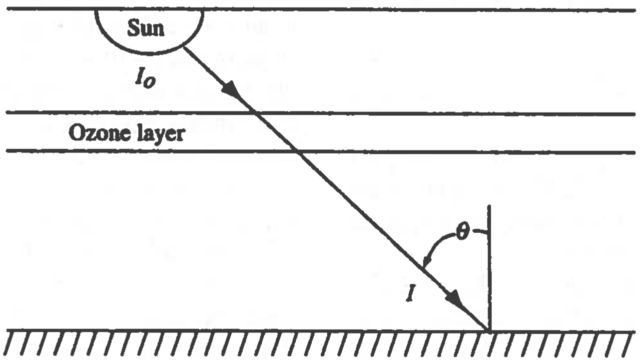
TABLE 16.A.2
Commonly used units for local ozone and their conversion

Unit	*Density*			*Mixing ratios*		*Pressure*
	(10^{11} mol cm^{-3})	*(µg m^{-3})*	*(DU km^{-1})*	*(µg g^{-1})*	*(ppmv)*	*(hPa)*
10^{11} mol cm^{-3} [10^{17} mol m^{-3}]	—	7.97	0.371	$0.022\,9 \frac{T}{P}$	$0.013\,8 \frac{T}{P}$	$0.013\,8\,T$
1 µg m^{-3} [10^{-9} kg m^{-3}]	0.125	—	0.046 7	$0.002\,87 \frac{T}{P}$	$0.001\,73 \frac{T}{P}$	$0.001\,73\,T$
1 DU km^{-1}	2.69	21.4	—	$0.061\,4 \frac{T}{P}$	$0.037\,0 \frac{T}{P}$	$0.037\,0\,T$
1 µg g^{-1} [10^{-6} by mass]	$43.7 \frac{P}{T}$	$348 \frac{P}{T}$	$16.3 \frac{P}{T}$	—	0.603	$0.603\,P$
1 ppmv [10^{-6} by volume]	$72.4 \frac{P}{T}$	$578 \frac{P}{T}$	$27.0 \frac{P}{T}$	1.657	—	P
1 hPa [10^{-4} Pa]	$72.4 \frac{1}{T}$	$578 \frac{1}{T}$	$27.0 \frac{1}{T}$	$1.657 \frac{1}{T}$	$\frac{1}{P}$	—

NOTE:
Pressure (P) in hectopascal.
Temperature (T) in kelvin.
Numbers in square brackets give the equivalent value in units of the International System.

ANNEX 16.B

MEASUREMENT THEORY



Total ozone by spectrophotometer.

The geometry for the path of sunlight passing through the ozone layer in the Earth's atmosphere is illustrated in the figure above. The solar irradiance at wavelength λ (I_λ) measured at the Earth's surface is given by:

$$\log (I_\lambda) = \log (I_{o\lambda}) - \alpha_\lambda X\mu - \alpha'_\lambda X'\mu' - \beta_\lambda m - \delta_\lambda \sec(\theta) \qquad (16.B.1)$$

where: I_o is the irradiance outside the Earth's atmosphere (extraterrestrial value) at wavelength λ;

α_λ is the ozone absorption coefficient at wavelength λ (nm);

X is the amount of total ozone in the atmosphere (m at STP);

μ is the effective geometric enchancement of the solar path through the ozone column;

α'_λ is the sulphur dioxide absorption coefficient at wavelength λ (nm);

X' is the amount of sulphur dioxide in the atmosphere (m at STP);

μ' is the effective enhancement through the sulphur dioxide column;

β_λ is the molecular scattering coefficient at wavelength λ;

m is the number of molecular atmospheres along the incident light path;

δ_λ is the particulate scattering coefficient at wavelength λ; and

θ is the apparent solar zenith angle.

In practice, an accurate measurement of ozone cannot be made by measuring the irradiance at one wavelength because it is difficult to maintain the absolute sensitivity of an instrument over a long period of time. Also, particulate scattering due to haze and thin clouds significantly affect the amount of transmitted irradiance.

It is, therefore, necessary to measure the irradiances at more than one wavelength; ozone is determined from the differential absorption. Measurements of irradiances made at N wavelengths are expressed by N equations of the form given in equation 16.B.1 with different values for $I_{o\lambda}$, α_λ, α'_λ, β_λ and δ_λ. These N equations may be linearly combined to give the following:

$$\Sigma w_\lambda \log (I_\lambda) = \Sigma w_\lambda \log (I_{o\lambda}) - (\Sigma w_\lambda \alpha_\lambda) X\mu - (\Sigma w_\lambda \alpha'_\lambda) X'\mu' - (\Sigma w_\lambda \beta_\lambda) m - (\Sigma w_\lambda \delta_\lambda) \sec(\theta) \qquad (16.B.2)$$

where Σ represents the summation from 1 to N and w_λ is a set of N weighting values, one for each wav length.

The weighting values at each wavelength (w_λ) are selected to minimize the effects of other atmospheric constituents. Weighting values for the Dobson AD measurement reduce the effects of haze. The effect of sulphur dioxide on the Dobson ozone measurement is ignored although the presence of sulphur dioxide adds between 1 and 2 per cent false ozone for some stations. The weighting values for the Brewer standard ozone measurement minimize the effects due to haze and sulphur dioxide. The wavelengths for the Dobson AD and Brewer standard measurements with the appropriate values for w_λ are given in the following table:

Wavelengths and the effective weighting values used for the Dobson and Brewer standard ozone measurement

DOBSON AD MEASUREMENT			BREWER STANDARD MEASUREMENT	
Wavelength (λ) (nm)		Weighting value (w_λ)	Wavelength (λ) (nm)	Weighting value (w_λ)
305.5	A pair	1.0	310.1	1.0
325.4		−1.0	313.5	−0.5
317.6	D pair	−1.0	316.8	−2.2
339.8		1.0	320.0	1.7

If the effects of sulphur dioxide and haze are neglected, then equation 16.B.2 can be rewritten in the following form:

$$F + \beta m = F_o - \alpha X\mu \qquad (16.B.3)$$

where: $F = \Sigma w_\lambda \log (I_\lambda)$
$F_o = \Sigma w_\lambda \log (I_{o\lambda})$
$\beta = \Sigma w_\lambda \beta_\lambda$
$\alpha = \Sigma w_\lambda \alpha_\lambda$

It follows from equation 16.B.3 that the value for total ozone is given by:

$$X = \frac{(F_o - F - \beta m)}{\alpha\mu} \qquad (16.B.4)$$

Here the term F is measured, F_o is a constant which is equal to the value of F outside the Earth's atmosphere (extraterrestrial constant for the instrument), and βm and $\alpha\mu$ are values which are calculated.

In order the determine the amount of total ozone, it is necessary to know F_o, a value which is unique for each instrument. This constant is determined for most field instruments by direct intercomparison with the primary standard instrument Dobson No. 83. The primary standard instrument is calibrated for its extraterrestrial value by the zero air-mass extrapolation technique. It is evident from equation 16.B.3 that there is a linear relation between $(F + \beta m)$ and μ, the air mass. Measurements are made throughout a day over a sufficient range of air mass and the $(F + \beta m)$ are regressed against μ. The slope of the resulting line is αX and the intercept is F_o, the extraterrestrial constant. It is necessary that ozone and other atmospheric constituents remain constant during the day.

In practice, zero air-mass extrapolation measurements are made at a site where good observing conditions are common. The Mauna Loa Observatory in Hawaii has proved to be an ideal site for these measurements because it is at sufficient altitude to avoid most tropospheric aerosols and the weather is usually clear. Also, it is located in the tropics where daily variations of ozone are small.