

TECHNICAL NOTE**EFFECTS OF ALTITUDE ON THE DETERMINATION OF AMBIENT OZONE
CONCENTRATIONS VIA UV PHOTOMETRY**

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April 10, 2009

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Summary

Relative quantities of trace gasses in the atmosphere are typically expressed in terms of their volumetric mixing ratio, i.e., parts per million by volume (ppm). For an ideal gas, the mixing ratio is equal to the ratio of moles of trace gas to total moles of air in a sample or, equivalently, the ratio of the partial pressure of the trace gas to the total sample pressure. Mixing ratios are convenient measures of “concentration” because they are independent of the pressure and temperature of the air sample. In some situations, mass per unit volume concentrations, i.e., micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), are used instead of mixing ratios. In particular, measurements of ozone concentration based on the absorption of UV light in a sample cell are a function of ozone mass per unit volume concentration and therefore such measurements must be corrected for sample temperature and pressure to determine the ozone mixing ratio. We derive below the equation used to make this correction.

Determination of the ozone mixing ratio from UV photometric measurements is necessary for comparisons with the level of the National Ambient Air Quality Standard for ozone which is defined as 0.075 ppm. For a fixed mixing ratio (e.g., 0.075 ppm), the mass concentration will vary with the ratio of pressure to absolute temperature. As this ratio decreases with altitude, the mass concentration corresponding to 0.075 ppm also decreases with altitude. Thus, *in terms of $\mu\text{g}/\text{m}^3$ concentrations*, the ozone standard is more stringent at higher elevations. We show below how the ideal gas law is used to calculate ozone concentration ($\mu\text{g}/\text{m}^3$) as a function of ozone mixing ratio (ppm) and illustrate the effect of typical changes in temperature and pressure with altitude on ozone concentrations ($\mu\text{g}/\text{m}^3$) corresponding to a fixed mixing ratio of 0.075 ppm.

Determination of Ozone in Ambient Air by UV Photometry

Routine measurements of ambient ozone concentrations by air quality monitoring agencies rely almost exclusively on the ultra violet (UV) absorption method which has been designated a Federal Equivalent Method for making such measurements by the U.S. Environmental Protection Agency. The UV absorption method is based on the measurements of the absorption of 240 nm wavelength light in an absorption cell of known volume filled with sample air relative to UV absorption in the cell when filled with sample air from which ozone has been removed via a suitable scrubber (usually composed of manganese dioxide coated material or heated silver wool). Absorption of UV light by ozone in the sample cell is a function of the ozone concentration (number of ozone molecules per unit volume or, equivalently, mass of ozone per unit volume) in the sample cell. However, since the National Ambient Air Quality Standard for ozone is stated in terms of the ozone mixing ratio (parts per million by volume or ppm), ambient ozone monitors are configured to output ozone “concentration” in ppm. Mixing ratios have the advantage of being independent of the temperature and pressure of the air sample whereas mass per unit volume concentrations vary with the ratio of temperature to pressure as prescribed by the ideal gas law.

Below we provide a simple derivation of the ozone calibration equation specified in EPA's ozone monitoring regulations (40 CFR 50 Appendix D) which includes terms that correct the ozone mixing ratio output by the UV photometer for sample temperature and pressure.

Derivation of the Ozone Calibration Equation¹

The relative absorption is stated in terms of the transmittance, defined as the ratio I/I_0 , where I is the intensity of 254 nm light passing through the cell as sensed by the photo detector when the cell contains sample air, and I_0 is the intensity of 254 nm light which passes through the cell and is sensed by the detector when the cell contains sample air from which all ozone has been removed. Transmittance is related to ozone concentration via the Beer-Lambert Law. A simple way of deriving the Beer-Lambert Law is to consider the transmittance of light oriented perpendicular to a thin plane of sample air with area A containing n ozone molecules. In this case, the transmittance is equal to

$$1 - \sigma \cdot \frac{n}{A}$$

Where σ is the absorption cross section in units of cm^2 per molecule. For absorption of 240 nm wavelength light by ozone, σ depends only slightly on the temperature and pressure of the sample and these minor variations are assumed to be of no consequence for measuring ambient ozone concentrations. To extend the above relationship to a real, three dimensional sample cell of length l , the transmittance can be rewritten as

$$1 - \sigma \cdot \frac{l \cdot n}{A \cdot l} = 1 - \sigma \cdot l \cdot \frac{n}{V}$$

Where $V = A l$ is the volume of the sample cell. Since sigma is constant, the transmittance depends only on the length of the sample cell and the ozone number concentration in the cell, n/V . To obtain the ozone mixing ratio, we first compute the ozone partial pressure, p , from the number concentration via the ideal gas law:

$$p = R \cdot T \cdot \frac{n}{V}$$

where

p is the partial pressure in atmospheres

T is the temperature in K and

R is the ideal gas constant in $(\text{cm}^3 \text{ atm}) / (\text{molecules K})$.

Using this relationship and defining the absorption coefficient as $\alpha = \sigma / RT$, the transmittance becomes

¹ This discussion is based on the derivation described in *Technical Assistance Document for the Calibration of Ambient Ozone Monitors*. EPA-600/4-79-057, U.S. Environmental Protection Agency, September 1979.

$$\text{Transmittance} = \frac{I}{I_0} = 1 - \alpha \cdot p \cdot l$$

Note that the absorption coefficient, α , is inversely proportional to temperature.

The above expression for transmittance is reasonably accurate for low ozone mixing ratios and/or short cell lengths. For significantly higher ozone concentrations or longer cell lengths, we must take into consideration the possibility of ozone molecules “shading” one another in the cell. To eliminate this error, we integrate the transmittance over each small cell segment, dl , within which there is no shading effect. This integration results in the familiar form of the Beer-Lambert Law:

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha p l} \quad (1)$$

In applying Equation (1), we set:

α = absorption coefficient of O₃ at 254 nm = 308 ± 4 atm⁻¹cm⁻¹ at 0 °C and 760 torr

p = O₃ partial pressure in units of atmospheres

l = optical length through the sample cell in cm

Equation (1) can be used to determine the partial pressure of ozone in a sample at standard temperature (273 K) and pressure (1 atm) or STP:

$$p(\text{atm}) = -\frac{1}{\alpha \cdot l} \left\{ \ln \left(\frac{I_0}{I} \right) \right\} \quad \text{at STP.} \quad (2a)$$

In Equation (2a), $p(\text{atm})$ is equivalent to the (unitless) ozone mixing ratio since the sample is at 1 atm pressure. To obtain the concentration in terms of mixing ratio at arbitrary pressure, P , we must take into account the ratio of the sample pressure to one atmosphere:

$$c(\text{ppm}) = -\frac{760}{P(\text{torr})} \times \frac{10^6}{\alpha l} \{ \ln(I/I_0) \} \quad \text{at } T = 273 \text{ K and pressure } P \quad (2b)$$

where the sample pressure, P is in units of torr (1 atm = 760 torr) and the factor of 10⁶ is introduced to obtain the mixing ratio in parts per million by volume (ppm).

Equation (2b) is only valid at the temperature for which the value of α has been determined ($T = 273 \text{ K}$). Since α is inversely proportional to temperature as shown above, $c(\text{ppm})$ for arbitrary sample temperature, T , is given by:

$$c(\text{ppm}) = \frac{-10^6}{\alpha l} \ln \left(\frac{I}{I_0} \right) \times \frac{760}{P} \times \frac{T}{273}$$

which is identical to equation (4) in Appendix D of 40 CFR 50 with the exception that the Appendix D equation includes a $1/L$ loss term which accounts for the slight loss of ozone within the sample cell due to interaction with the cell walls and other sampler components.

Altitude Effects

Ozone mass concentration $c(\mu\text{g}/\text{m}^3)$ can be related to the ozone mixing ratio $c(\text{ppm})$ via the ideal gas law:

$$c(\mu\text{g}/\text{m}^3) = c(\text{ppm}) * P * MW / (R * T)$$

where P is pressure (Pa), MW is the molecular weight of O_3 (48 g/mole), T is the temperature (K) and R is the ideal gas constant ($8.314 \text{ m}^3 \text{ Pa} / \text{mole K}$). Thus, for a fixed mixing ratio, the mass concentration is a function of the ratio P/T . Since pressure drops more rapidly than absolute temperature with increasing altitude in the troposphere (up to approximately 11 km), this ratio decreases with altitude and the mass concentration corresponding to a given mixing ratio also decreases with altitude. This relationship is illustrated in Table 1 and by the solid line in Figure 1 for mixing ratio fixed at the 0.075 ppm EPA ozone standard as specified in 40 CFR 50. Values of pressure and temperature as a function of altitude shown in this table and figure are based on the U.S. Standard Atmosphere (1976) which serves as a useful set of reference conditions for this calculation.² Mass concentrations corresponding to 0.075 ppm decrease with altitude: an ozone value of 0.075 ppm corresponds to a mass concentration of $152.3 \mu\text{g}/\text{m}^3$ at sea level but just $123.4 \mu\text{g}/\text{m}^3$ at 7,000 ft, a difference of 19%. In other words, *in terms of mass concentration*, the 0.075 ppm standard is more stringent at higher elevation sites. A similar set of results assuming isothermal conditions (with temperature fixed at $25 \text{ }^\circ\text{C}$)³ is provided in Table 2 and by the dashed line in Figure 1. Note that the surface temperature specified in the U.S. Standard Atmosphere is $15 \text{ }^\circ\text{C}$, resulting in a higher $\mu\text{g}/\text{m}^3$ concentration than in the $25 \text{ }^\circ\text{C}$ isothermal case.

² For altitudes below 11 km, the U.S. Standard Atmosphere is based on assumptions of a dry, hydrostatic air mass with a constant (adiabatic) lapse rate of $-6.5 \text{ C}/\text{km}$; see: <http://www.atmoscutor.com/The%20Standard%20Atmosphere.html?>

³ Assumes dry, hydrostatic air mass at a fixed temperature of $25 \text{ }^\circ\text{C}$.

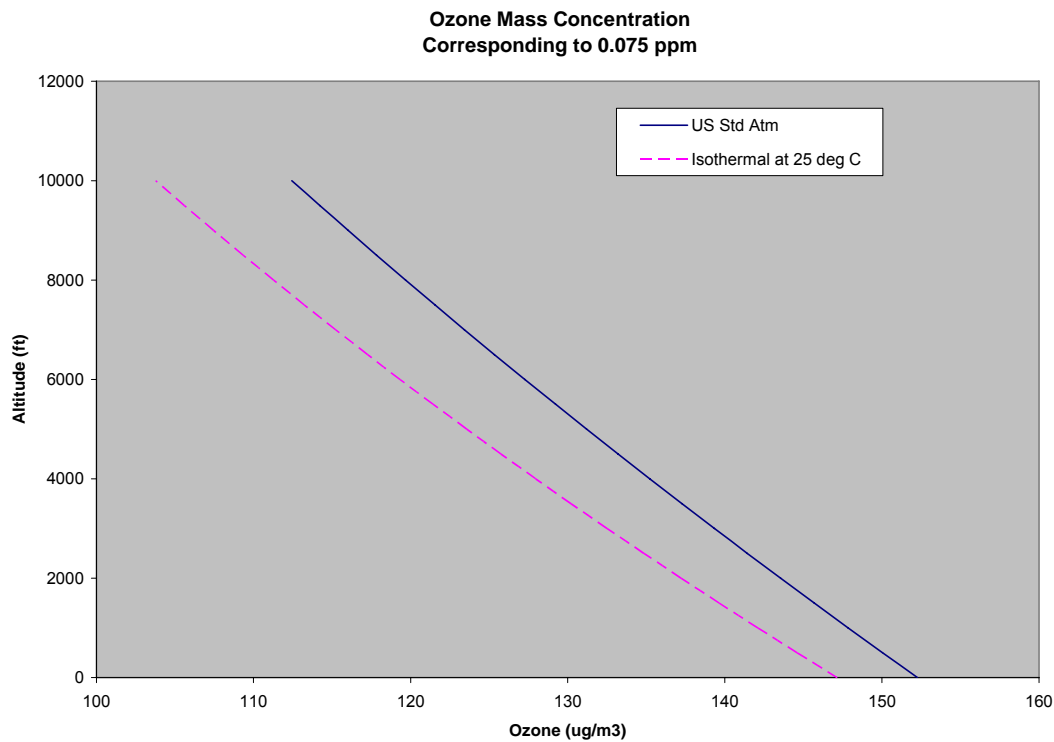


Figure 1. Decrease of ozone mass concentration ($\mu\text{g}/\text{m}^3$) with altitude at constant mixing ratio of 0.075 ppm by volume assuming 1) US Standard Atmosphere (solid line) and 2) isothermal atmosphere at 25 °C (dashed line); note that sea level temperature in the U.S. Standard Atmosphere is 15 °C (see tables 1 and 2).

Table 1. Ozone mass concentration ($\mu\text{g}/\text{m}^3$) corresponding to 0.075 ppm as a function of altitude (based on U.S. Standard Atmosphere).

Altitude (msl) ⁴		Pressure			Temperature		Concentration	
ft	km	torr	hPa	atm	°F	°C	$\mu\text{g}/\text{m}^3$	%Change
0	0.00	760.0	1013.3	1.000	59.0	15.0	152.3	0.0%
500	0.15	746.4	995.1	0.982	57.2	14.0	150.0	-1.5%
1000	0.30	732.9	977.2	0.964	55.4	13.0	147.9	-2.9%
1500	0.46	719.7	959.5	0.947	53.7	12.0	145.7	-4.3%
2000	0.61	706.7	942.1	0.930	51.9	11.0	143.5	-5.7%
2500	0.76	693.8	925.0	0.913	50.1	10.0	141.4	-7.1%
3000	0.91	681.1	908.1	0.896	48.3	9.1	139.3	-8.5%
3500	1.07	668.7	891.5	0.880	46.5	8.1	137.3	-9.8%
4000	1.22	656.4	875.1	0.864	44.7	7.1	135.2	-11.2%
4500	1.37	644.3	859.0	0.848	43.0	6.1	133.2	-12.5%
5000	1.52	632.4	843.1	0.832	41.2	5.1	131.2	-13.8%
5500	1.68	620.6	827.4	0.817	39.4	4.1	129.2	-15.1%
6000	1.83	609.0	812.0	0.801	37.6	3.1	127.3	-16.4%
6500	1.98	597.7	796.8	0.786	35.8	2.1	125.3	-17.7%
7000	2.13	586.4	781.9	0.772	34.0	1.1	123.4	-18.9%
7500	2.29	575.4	767.1	0.757	32.3	0.1	121.5	-20.2%
8000	2.44	564.5	752.6	0.743	30.5	-0.8	119.7	-21.4%
8500	2.59	553.8	738.3	0.729	28.7	-1.8	117.8	-22.6%
9000	2.74	543.3	724.3	0.715	26.9	-2.8	116.0	-23.8%
9500	2.90	532.9	710.4	0.701	25.1	-3.8	114.2	-25.0%
10000	3.05	522.7	696.8	0.688	23.3	-4.8	112.4	-26.2%
10500	3.20	512.6	683.4	0.674	21.6	-5.8	110.7	-27.3%
11000	3.35	502.7	670.2	0.661	19.8	-6.8	109.0	-28.4%
11500	3.51	492.9	657.2	0.649	18.0	-7.8	107.2	-29.6%
12000	3.66	483.3	644.4	0.636	16.2	-8.8	105.5	-30.7%
12500	3.81	473.9	631.8	0.624	14.4	-9.8	103.9	-31.8%
13000	3.96	464.6	619.4	0.611	12.6	-10.8	102.2	-32.9%
13500	4.11	455.5	607.2	0.599	10.9	-11.7	100.6	-33.9%
14000	4.27	446.5	595.2	0.587	9.1	-12.7	99.0	-35.0%
14500	4.42	437.6	583.4	0.576	7.3	-13.7	97.4	-36.0%
15000	4.57	428.9	571.8	0.564	5.5	-14.7	95.8	-37.1%
15500	4.72	420.3	560.4	0.553	3.7	-15.7	94.3	-38.1%
16000	4.88	411.9	549.2	0.542	1.9	-16.7	92.7	-39.1%

⁴ Altitudes above mean sea level (msl) shown here are actually geopotential heights based on a fixed value of the gravitational constant (9.80665 m/s^2). Geopotential altitude differs slightly from actual heights above mean sea level but differences are negligible for purposes of this tabulation.

Table 2. Ozone mass concentration ($\mu\text{g}/\text{m}^3$) corresponding to 0.075 ppm as a function of altitude (assuming isothermal conditions).

Altitude msl ⁵		Pressure			Temperature		Concentration	
ft	km	torr	hPa	atm	°F	°C	$\mu\text{g}/\text{m}^3$	%Change
0	0.00	760.0	1013.3	1.000	77.0	25.0	147.2	0.0%
500	0.15	746.8	995.7	0.983	77.0	25.0	144.6	-1.7%
1000	0.30	733.9	978.5	0.966	77.0	25.0	142.1	-3.4%
1500	0.46	721.2	961.5	0.949	77.0	25.0	139.6	-5.1%
2000	0.61	708.7	944.9	0.933	77.0	25.0	137.2	-6.7%
2500	0.76	696.5	928.5	0.916	77.0	25.0	134.9	-8.4%
3000	0.91	684.4	912.5	0.901	77.0	25.0	132.5	-9.9%
3500	1.07	672.6	896.7	0.885	77.0	25.0	130.2	-11.5%
4000	1.22	660.9	881.1	0.870	77.0	25.0	128.0	-13.0%
4500	1.37	649.5	865.9	0.855	77.0	25.0	125.8	-14.5%
5000	1.52	638.2	850.9	0.840	77.0	25.0	123.6	-16.0%
5500	1.68	627.2	836.2	0.825	77.0	25.0	121.4	-17.5%
6000	1.83	616.3	821.7	0.811	77.0	25.0	119.3	-18.9%
6500	1.98	605.7	807.5	0.797	77.0	25.0	117.3	-20.3%
7000	2.13	595.2	793.5	0.783	77.0	25.0	115.2	-21.7%
7500	2.29	584.9	779.8	0.770	77.0	25.0	113.2	-23.0%
8000	2.44	574.7	766.3	0.756	77.0	25.0	111.3	-24.4%
8500	2.59	564.8	753.0	0.743	77.0	25.0	109.4	-25.7%
9000	2.74	555.0	740.0	0.730	77.0	25.0	107.5	-27.0%
9500	2.90	545.4	727.1	0.718	77.0	25.0	105.6	-28.2%
10000	3.05	536.0	714.6	0.705	77.0	25.0	103.8	-29.5%
10500	3.20	526.7	702.2	0.693	77.0	25.0	102.0	-30.7%
11000	3.35	517.6	690.0	0.681	77.0	25.0	100.2	-31.9%
11500	3.51	508.6	678.1	0.669	77.0	25.0	98.5	-33.1%
12000	3.66	499.8	666.4	0.658	77.0	25.0	96.8	-34.2%
12500	3.81	491.2	654.8	0.646	77.0	25.0	95.1	-35.4%
13000	3.96	482.6	643.5	0.635	77.0	25.0	93.5	-36.5%
13500	4.11	474.3	632.3	0.624	77.0	25.0	91.8	-37.6%
14000	4.27	466.1	621.4	0.613	77.0	25.0	90.2	-38.7%
14500	4.42	458.0	610.6	0.603	77.0	25.0	88.7	-39.7%
15000	4.57	450.1	600.1	0.592	77.0	25.0	87.1	-40.8%
15500	4.72	442.3	589.7	0.582	77.0	25.0	85.6	-41.8%
16000	4.88	434.6	579.5	0.572	77.0	25.0	84.2	-42.8%

⁵ Altitudes above mean sea level (msl) shown here are actually geopotential heights based on a fixed value of the gravitational constant (9.80665 m/s^2). Geopotential altitude differs slightly from actual heights above mean sea level but differences are negligible for purposes of this tabulation.