

Technical Note No. 010

Explanation of Temperature and Pressure Corrections in Ozone Measurements of Mixing Ratios

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Background

Some older ozone monitors sold by other companies do not correct for temperature and pressure. The instruments calculate ozone mixing ratios assuming that the cell pressure is one atmosphere and the temperature is some fixed value such as 25 °C. All ozone monitors manufactured by 2B Technologies automatically correct for temperature and pressure. Here, we explain why temperature and pressure correction is required to obtain a true mixing ratio (ppb, ppm or pphm) and how it is achieved in 2B Technologies ozone monitors.

Mixing Ratio

Technically, “concentration” and “mixing ratio” are two different things, although people often use the term concentration when they mean mixing ratio. Concentration, C , has units such as molecules/cm³ or moles/L. Mixing ratio is a ratio of concentrations and is unitless. Mixing ratio, X , is defined as follows:

$$X = \frac{C_{\text{analyte}}}{C_{\text{air}}} \quad (1)$$

This is often a very small number, so mixing ratio is usually expressed in per cent, parts per million, parts per hundred million, or parts per billion (all by volume, not mass) as follows:

$$\begin{aligned}
X_{\%} &= X \times 100 \\
X_{ppm} &= X \times 10^6 \\
X_{pphm} &= X \times 10^8 \\
X_{ppb} &= X \times 10^9
\end{aligned}
\tag{2}$$

Atmospheric chemists often label these units as ppmv, pphmv and ppbv to emphasize that this is a mixing ratio by volume (i.e., mole/mole ratio and not mass/mass ratio). The reason for expressing ozone and other atmospheric measurements in mixing ratio is that a species that is well mixed in the atmosphere has a mixing ratio that does not change with altitude up to about 90 km (where the air composition becomes dominated by atomic species due to photolysis). For example, nitrogen has a constant mixing ratio of 78%, oxygen has a constant mixing ratio of 21% and argon and has a constant mixing ratio of 1% even though their concentrations in molecules/cm³ decrease exponentially with altitude. Similarly, carbon dioxide currently has a mixing ratio of about 370 ppm, and some CFCs have mixing ratios of a few ppb throughout most of the atmosphere.

Temperature and Pressure Dependence of Mixing Ratio

The UV absorbance technique fundamentally measures concentration, not mixing ratio. The concentration, in molecules/cm³, is given by the Beer-Lambert Law:

$$C_{Ozone} = \frac{1}{\epsilon l} \ln\left(\frac{I_o}{I}\right) \tag{3}$$

Here, ϵ is the extinction coefficient for ozone at the Hg emission line at 253.7 nm and is 1.15×10^{-17} cm²/molecule. The parameter l is the pathlength of the absorption cell and is 15 cm for Model 202 and Model 205 Ozone Monitors™. I_o is the light intensity measured by the photodiode for ozone-scrubbed air, and I is the light intensity measured for the sample air. The ratio (I_o/I) is unitless, so the ozone concentration units are molecules/cm³.

In order to obtain a mixing ratio through equation 1, it is necessary to know the concentration of air molecules in the detection cell as well. We can use the ideal gas law to calculate the concentration of air molecules as follows:

$$C_{air} = \frac{nN_A}{V} = \frac{P}{RT} \tag{4}$$

where n is moles, N_A is Avagadro's number, P is pressure, R is the gas constant and T is absolute temperature. Using this equation, the value of C_{air} at 1

atmosphere of pressure and a temperature of 298.16 K is calculated to be 2.46×10^{19} molecules/cm³. Thus, at other temperatures and pressure, C_{air} is given by

$$C_{air} = 2.462 \times 10^{19} \left(\frac{P_{cell}}{760} \right) \left(\frac{298.16}{T_{cell}} \right) \quad (5)$$

where the cell pressure is in torr and the cell temperature is in Kelvin. We may now calculate the ozone mixing ratio in ppb by ratioing C_{ozone} to C_{air} using equation 1:

$$X_{ozone} = \frac{1}{\epsilon I} \ln \left(\frac{I_o}{I} \right) \frac{1}{2.462 \times 10^{19}} \left(\frac{760}{298.16} \right) \left(\frac{T_{cell}}{P_{cell}} \right) \times 10^9 \quad (6)$$

Note that the temperature and pressure correction term, (T_{cell}/P_{cell}) , comes from calculating the concentration of air molecules inside the detection cell. Thus, the temperature and pressure used in the correction are those of molecules inside the cell, not those of outside air. For an instrument with a 15-cm detection cell, the constants in equation 6 can be combined to give

$$X_{ozone} = 6.002 \times 10^5 \ln \left(\frac{I_o}{I} \right) \left(\frac{T_{cell}}{P_{cell}} \right) \quad (7)$$

where, again, the cell temperature is in Kelvin and the cell pressure is in torr. This is the temperature and pressure corrected expression used in the 2B Tech Ozone Monitors.TM

Note that the mixing ratio measured inside the detection cell is the same as the mixing ratio in the outside air being sampled even though the temperature and pressure inside the cell are not the same as outside the instrument. This is because the mixing ratio is a ratio of ozone molecules to air molecules in any given volume. Expanding or contracting that volume by changing the temperature and/or pressure will not change that ratio.