

Concentration Units in Gas Analysis

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Concentrations in analytical results are meaningless without affixing associated reporting units. Every methodology has its favorite units, but they must be indicated to make any sense of the answers. Typically measurements of impurities in solid matrices are listed in values of $\mu\text{g}/\text{kilogram}$, and in liquids as $\mu\text{g}/\text{L}$. With gas samples, concentrations can have a variety of units, such as $\mu\text{g}/\text{m}^3$, ppmV/V, $\mu\text{g}/\text{L}$, and others appropriate to a referenced technique.

Many scientific disciplines involved in gas measurements have their choice units for concentrations. Industrial hygienists commonly use the unit of $\mu\text{g}/\text{m}^3$ for health effects with toxic compounds.¹ Chemical engineers are usually distinguished from others by their frequent use of mass ratios ($\mu\text{g}/\text{g}$), or mixed units of $\mu\text{g}/\text{L}$. And atmospheric chemists often use mol/m^3 . The differences between expressing concentrations as mass/mass, mass/volume, moles/volume or volume/volume are quite significant when dealing with gases, and it is very important to specify which is being used to avoid any confusion and possible misinterpretation.

Interconversions among units are possible through the ideal gas volume using 22.710953 ± 0.000021 L/mole (IUPAC) at standard temperature (0°C or 273.15°K) and pressure (**100 kPa**, 1 bar, 0.987 atm, 14,504 psiA, 750.06 torr), **OR** 22.413968 ± 0.000020 L/mole (NIST) at standard temperature (0°C or 273.15°K) and pressure (**1 atm**, 760 torr, 101.325 kPa, 1.013 bar, 14.696 psiA),² and molecular weight of the target analyte. One available on-line converter is www.airtoxics.com/cclasses/unitcalc.html; however, this translator does not compensate for changes in sample temperature, or atmospheric pressure, and uses the NIST standard pressure of 1 atm and 25°C .

Molar Gas Volumes as a Function of Temperature³

Temperature (°C)	Molar Gas Volume (moles/L) at 100 kPa (IUPAC)	Molar Gas Volume (moles/L) at 1 atm (NIST)	Temperature (°C)	Molar Gas Volume (moles/L) at 100 kPa (IUPAC)	Molar Gas Volume (moles/L) at 1 atm (NIST)
15	23.958	23.645	26	24.873	24.547
16	24.041	23.727	27	24.956	24.630
17	24.124	23.809	28	25.039	25.712
18	24.208	23.891	29	25.122	24.794
19	24.291	23.973	30	25.205	24.876
20	24.374	24.055	31	25.288	24.958
21	24.457	24.137	32	25.372	25.040
22	24.540	24.219	33	25.455	25.122
23	24.623	24.301	34	25.538	25.204
24	24.706	24.383	35	25.621	25.286
25	24.790	24.465			

¹ See for examples: www.arb.ca.gov/energy/biogas/documents/FINAL_AB_1900_Staff_Report_&_Appendices_%20051513.pdf, and www.epa.gov/oswer/vaporintrusion/documents/oswer-vapor-intrusion-background-Report-062411.pdf.

² In 1982 the International Union of Pure and Applied Chemistry (IUPAC) re-established the gas volume of at 273.15°K and 100 kPa (14.504 psiA, 0.987 atm, 1 bar), and NIST conditions remain at 273.15°K and 1 atm. The difference in the two values is related to a definition change in standard pressure, and can be readily interconverted by Boyle-Mariotte's Law (en.wikipedia.org/wiki/Boyle%27s_law).

³ physics.nist.gov/cgi-bin/cuu/Value?mvolstd|search_for=ideal+gas+volume, and en.wikipedia.org/wiki/Molar_volume.

Quite often, concentration values in environmental measurements are bantered about without much attention to units. The “ppb” labeling can imply one part per billion in weight per unit volume (W/V), or one part per billion in volume per unit volume (V/V) or even one part per billion per unit weight (W/W). Typically, “ppb” in W/V is $\mu\text{g/L}$ or $\mu\text{g/m}^3$, whereas “ppb” in V/V is nmol/mol. They differ by the molecular weight of the analyte involved and the molar gas volume corrected for temperature.⁴ The conversions are:

$$\text{nmol/mol (ppb V/V)} = \frac{\text{ppb (W/V)} * 22.414 \text{ L/mole} * \text{room temperature (} ^\circ\text{C} + 273.15)}{\text{molecular weight (g/mole)} * 273.15 \text{ } ^\circ\text{K}}$$

As a result, 1 ppb W/V Methane (ng/ml) at 25 °C becomes:

$$\begin{aligned} \frac{1 \text{ ppb (W/V)} * 22.414 * 298.15}{16.04 * 273.15} &= 1.53 \text{ nmol/mol (ppb V/V) (NIST)} \\ &= 1.55 \text{ nmol/mol (IUPAC)} \end{aligned}$$

Or, 1 ppb W/V Tridecane (ng/ml) becomes:

$$\begin{aligned} \frac{1 \text{ ppb (W/V)} * 22.414 * 298.15}{184.36 * 273.15} &= 0.133 \text{ nmol/mol (ppb V/V) (NIST)} \\ &= 0.134 \text{ nmol/mol (IUPAC)} \end{aligned}$$

Common Misuse of “parts per...” for Liquids

Although the notation of “parts per...” is frequently used in results for both gas and liquid samples, the unit is only applicable to gases. This ratio with liquids is not “unitless”, as the numerator is typically weight and the denominator is volume. If the liquid matrix is pure water, with a density of near 1 gram/ml, the ratio could have some meaning, but fails when applied to other solvents⁵ or added salinity⁶, and subtle changes with temperature.⁷

Solvent	Density, ρ (kg/m^3) at 20 °C
Water	998.2
Acetone	786
Chloroform	1,498
Diethylether	713
Hexane	659
Methanol	791
Pentane	626

wt% Sodium Chloride in Water	Density, ρ (kg/m^3) at 20 °C
0	998.2
1	1,075
2	1,159
3	1,249
4	1,348

⁴ Molar gas volumes for NIST and IUPAC differ by 1.325%, and are not significantly different at the same temperature to have much impact on chromatographic results.

⁵ www.wuestgroup.com/Solvent%20Properties.pdf.

⁶ www.csgnetwork.com/h2odenscalc.html.

⁷ www.engineeringtoolbox.com/water-density-specific-weight-d_595.html.

Temperature (°C)	Density of Liquid Water, ρ (kg/m ³)
0	999.8
4	1,000
10	999.7
20	998.2
30	995.7

“Parts-per...” notation may be used appropriately only to express true dimensionless quantities; that is, the units of measurement ***must*** cancel in expressions like "1 $\mu\text{mol/mol}$ ", such that the quotients are pure numbers with values less than one. For liquids, proper labeling for concentrations is to spell out the weight unit and volume unit.⁸

Ratio of Analyte Weight to Total Volume	Proper Units for Liquids	Invalid Reporting Units for Liquids
1:10 ⁶	mg/L	ppm
1:10 ⁹	$\mu\text{g/L}$	ppb
1:10 ¹²	ng/L	ppt
1:10 ¹⁵	pg/L	ppq
1:10 ¹⁸	fg/L	---

Concerns with “parts-per...” Unit for Gases

Another problem with the “parts-per...” notation is that it may refer to either a mass fraction or a mole fraction. Since it is often not stated which quantity is used, it is better to write the unit as $\mu\text{g/kg}$, or nmol/mol , even though they are dimensionless.

The differences between expressing concentrations as mass/mass (W/W) or volume/volume (V/V) are quite significant when dealing with gases. For example, the conversion factor between a **mass** fraction of 1 “ppb” and a **mole** fraction of 1 “ppb” is about 4.7 for the greenhouse gas trichlorofluoromethane in air. It is very important to specify which is being used.

⁸ old.iupac.org/publications/books/gbook/green_book_2ed.pdf.

In addition, most continental European countries use a “long number system” that sets up different scales for “billion” and “trillion” from that for most English-speaking countries with the “short scale”. Confusion sets in especially with the magnitude for “part per billion” for the short [10^{-9}] and long [10^{-12}] scales.

Amplitude	Short Number Scale	Long Number Scale
10^3	Thousand	Thousand
10^6	Million	Million
10^9	Billion	Milliard
10^{12}	Trillion	Billion
10^{15}	Quadrillion	Billiard

And occasionally, one part per thousand is labeled as “ppt”, which conflicts with one part per trillion.

The US National Institute of Standards and Technology (NIST) mandates that “language-dependent terms [...] are **not** acceptable to express the values of quantities.”⁹ Instead, both NIST and the International System of Units (SI)⁸ encourage the use of units based on the mole, as it emphasizes chemical relationships, eliminates artificial variability associated with mass changes due to chemical reactions, and clarifies the labeling difficulties between the short and long number scales. Appropriate units for gases become these as listed:

Ratio of Analyte to Total	Molar Units for Gases	Invalid Reporting Units	Number of Analyte Molecules per Liter
1:100	cmol/mol	%	2.69×10^{20}
1:10 ⁶	μmol/mol	ppm	2.69×10^{16}
1:10 ⁹	nmol/mol	ppb	2.69×10^{13}
1:10 ¹²	pmol/mol	ppt	2.69×10^{10}
1:10 ¹⁵	fmol/mol	ppq	2.69×10^7
1:10 ¹⁸	amol/mol	---	26,867

Because most common bulk gases at atmospheric pressure and ambient temperature are effectively ideal gases,¹⁰ the volume fraction is essentially equal to the mole fraction. For all practical purposes, the two quantities can be used interchangeably and without distinction. Mole fraction is preferable, however, because it does not require an implicit assumption of ideality of the gases and, more importantly, because it is applicable also to condensed-phase species. In a mixture of ideal gases, the mole fraction can be expressed as the ratio of partial pressure to total pressure of the mixture. Most gas analytes obey the Ideal Gas Laws, including Boyle-Mariotte (pressure)¹¹ and Charles-Gay-Lussac Laws (temperature),¹² and the molar gas volume.³ Water vapor is a notable exception.¹³

⁹ physics.nist.gov/Pubs/SP811/sec07.html.

¹⁰ Most gases are ideal at temperatures above their boiling points and near atmospheric pressures (en.wikipedia.org/wiki/Ideal_gas).

¹¹ en.wikipedia.org/wiki/Boyle%27s_law

¹² en.wikipedia.org/wiki/Charles%27s_law

¹³ www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html

Total Hydrocarbons

The flame ionization detector (FID) has been demonstrated as a near perfect carbon counter for all saturated and unsaturated hydrocarbons, including aromatics, except for some enhancement with methane (~+8%).¹⁴ An equal $\mu\text{mol/mol}$ concentration of propane generates a FID response half of the value for the same amount of hexane, since the latter has twice the number of carbons per molecule. Here the concentration for each hydrocarbon is multiplied by the number of carbons in the molecule, and then summed to yield total hydrocarbons (THC). Alternately, the hydrocarbon sample can be directed to a flame ionization detector without chromatography, to generate a single peak related to its total hydrocarbons.¹⁵ The preferred concentration unit is " $\mu\text{mol/mol}$ as methane equivalent", especially when a sample is measured for total non-methane hydrocarbons.¹⁶

Non-Methane Organic Compounds (NMOC) per EPA Method 25¹⁷ and SCAQMD Method 25.1¹⁸ and 25.3¹⁹

Method 25 standard methods measure the total organics in gas samples, including hydrocarbons, organic oxygenates and halocarbons. These protocols separate methane, carbon dioxide and carbon monoxide from the rest of the organics and then directs the non-methane organic group first to an oxidation catalyst to convert them all to carbon dioxide and then to a reduction catalyst for a final conversion to methane, and finally is detected by a flame ionization detector as a single peak. The final concentration represents a total count on the amount of non-methane organic carbon in the sample, and its ideal reporting unit is " $\mu\text{mol/mol}$ as methane equivalent", although it is commonly listed as "ppmCarbon" in the reference methods.

¹⁴ www.arb.ca.gov/testmeth/slb/sop102-103v2-2.pdf.

¹⁵ This operation only applies to both saturated and unsaturated hydrocarbons, and not to samples with heteroatomic molecules, including oxygenates and halogenates, as these do not have the equal-carbon responses as true hydrocarbons.

¹⁶ www.arb.ca.gov/msprog/levprog/cleandoc/clean_nmogtps_final.pdf.

¹⁷ www.epa.gov/ttn/emc/promgate/m-25c.pdf.

¹⁸ www.aqmd.gov/tao/methods/stm/stm-025-1.pdf.

¹⁹ www.aqmd.gov/tao/methods/stm/stm-025-3.pdf.

Silicon in Biogas and Biomethane

Most analytical results for siloxanes are routinely reported as “ppmV” for each analyte, the concentration unit for EPA TO15, or as “ $\mu\text{g}/\text{m}^3$ ”, which is often listed for ambient air concentrations. The silicon atom is what produces silica after incineration to disrupt the efficacy of engines, heat exchangers and emission controls. Although the weight percentage of silicon in most polysiloxanes is relative consistent, the reported value in units of W/V does not represent the potential of silica mass generated from combustion. An alternate reporting unit is “grams of silicon per 1000 standard cubic feet”, or “g Si/MSCF” of fuel.¹³ This anticipates the actual amount of silica build up, independent of the siloxane species. The calculation process is shown below. The multiplying factor for conversion from $\mu\text{mol}/\text{mol}$ to g Si/MSCF is provided in the last column for each siloxane.

Details in Generation of Factors for Conversion of Concentrations from $\mu\text{mol}/\text{mol}$ to “g Si/MSCF”.

Silicone Analyte	Molecular Weight	# of Silicons per Molecule	Atomic Weight of Silicon	Portion of Si by weight	Rel wt of Si	mg/m ³ Siloxanes for 1 $\mu\text{mol}/\text{mol}$	cubic meter to scf	mg/scf	g Si/MSCF for 1 $\mu\text{mol}/\text{mol}$
TMDS	134.32	2	28.09	56.17	0.418	5.49	35.31	193.9	81.1
L2	162.38	2	28.09	56.17	0.346	6.64	35.31	234.5	81.1
D3	222.46	3	28.09	84.26	0.379	9.10	35.31	321.3	121.7
L3	236.53	3	28.09	84.26	0.356	9.67	35.31	341.5	121.7
D4	296.62	4	28.09	112.3	0.379	12.13	35.31	428.4	162.3
DMTVDS	210.42	2	28.09	56.17	0.267	8.61	35.31	304.1	81.2
L4	310.68	4	28.09	112.3	0.362	12.71	35.31	448.9	162.3
D5	370.77	5	28.09	140.4	0.379	15.16	35.31	535.4	202.8
L5	384.84	5	28.09	140.4	0.365	15.74	35.31	555.85	202.8
D6	444.92	6	28.09	168.5	0.379	18.2	35.31	642.73	243.4

²⁰ Bramston-Cook, R.; Bramston-Cook, E; “Online, Direct Measurement of Volatile Siloxanes in Anaerobic Digester and Landfill Gases by Gas Chromatography with Mass Spectrometric Detection,” AWMA Conference on Air Quality Measurement Methods and Technology, Durham, NC, 2012.