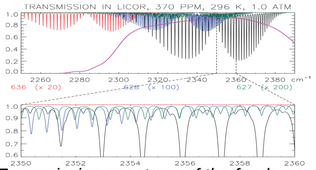
TRACE GAS STANDARDS IN NATURAL AIR

Duane R. Kitzis[1], Pieter Tans[2], Brad Hall[2], Thomas Mefford[1], Dan Endres[2]
[1] CIRES, University of Colorado, Boulder, CO., [2] NOAA/ESRL/GMD, Boulder, CO.

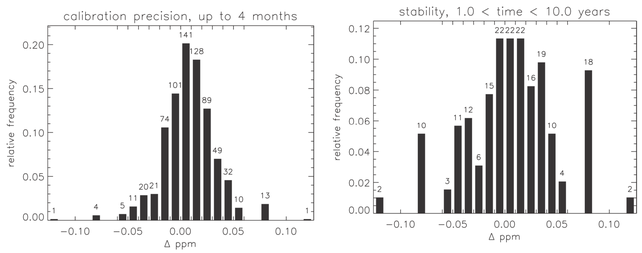
Abstract

Designated by the WMO/GAW as the Central Calibration Laboratory for ambient CO_2, CH_4, CO, N_2O, and SF_6, atmospheric natural air standards are prepared and calibrated. Standards preparation can purposefully alter CO_2, CH_4, CO, N_2O, SF_6 mole fractions and the isotopic ratios of CO_2, to provide sets of differing mole fraction of standards for measuring ambient variability.

For long-lived, well-mixed gases we need high accuracy standards in natural air

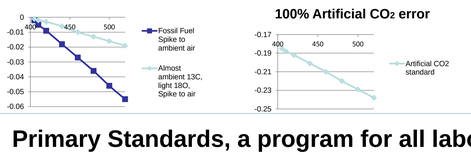


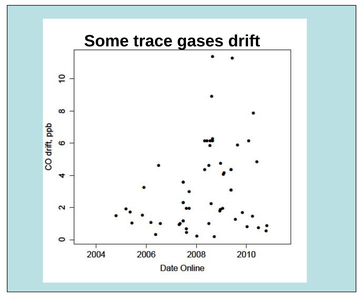
Above: Transmission spectrum of the fundamental CO_2 absorption bands; $^{16}O^{12}C^{16}O$ (black), $^{16}O^{13}C^{16}O$ (Red, enhanced 20 times, to make it visible), $^{16}O^{12}C^{18}O$ (blue, enhanced 100 times), and $^{16}O^{12}C^{17}O$ (green, enhanced 200 times). The band pass filter of LICOR (overplotted pink line) type analyzers (NDIR) differ in sensitivity to the isotopologues of CO_2. ***We strive to make reference gas mixtures as identical to ambient natural air as possible, so that bias effects of measuring ambient air nearly cancel out.***



Standard's stability over time. The above plot shows that the reproducibility is almost Gaussian. Repeat calibrations more than 1 year apart includes potential drift of CO_2 in cylinders. Known conditions leading to CO_2 mole fraction drift include leaks, improper regulator flushing, high flow rates, >5ppm H_2O or gas use to low internal pressure. Rarely some cylinders exhibit unstable characteristics for no apparent reason. **We recommend recalibration at least once every three years.**

Some newer single line isotopologue measurement instrument's error offsets made by adding fossil fuel CO_2 to background CO_2 air or with 100% artificial CO_2 standards.

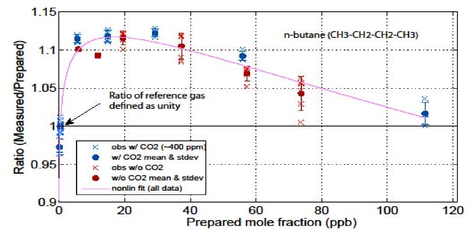




59 CO standards, used at the CCGG towers, with pre and post deployment calibration.
49% cylinders < 2ppb, 80% cylinders < 5 ppb
3.3% > 10 ppb, 5% > 8 ppb
Mean: 3.2 ppb, Std. Dev. 2.6 ppb

Carbon Monoxide is not perfectly stable in aluminum cylinders. There is no perfect container for all compounds we study. **Drifts are quantified with recalibration and then time based data correction can be applied.**

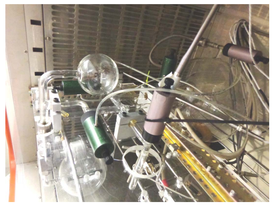
We cannot assume that instruments are linear



Non-linearity curve for n-butane: The sensitivity of this GC-MS varies with the mole fraction of n-butane (up to 12% at 20 ppb). The non-linear behavior of this instrument was characterized by analyzing standards over a wide range of mole fractions prepared by GMD using gravimetric techniques.

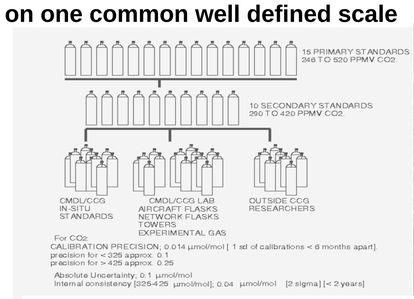
Reference gas mixtures are needed not only to provide long-term traceability, stability, and compatibility between different measurement programs, but also to characterize instrument response over the full range of atmospheric values that can be expected.

Primary Standards, a program for all laboratories to compare on one common well defined scale



CO_2 manometric calibration

We developed a method to separate the CO_2 from a volume of air and determine the CO2 mole fraction directly from pressure, temperature, volume. The absolute uncertainty of this system is 0.07 ppm for CO_2. For more than 2 decades we have been measuring our 15 primaries, spanning 246 to 520 ppm, thus improving the definition of the WMO CO2 Mole Fraction Scale. **The WMO/GAW CO_2 reference scale is defined by these 15 primary standards.**



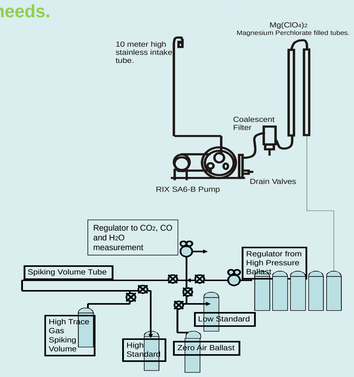
Primary standards are used to calibrate the secondary set CO2 mole fraction on the calibration transfer system.

The CO_2 calibration transfer method is used for all CO_2 standards, has a precision of 0.02 ppm. Each calibration of tertiary standards uses the 4 closest bracketing secondaries. Last year we prepared about 500 tertiary standards for our own program and the global community. To date more than 50,000 measurements were made on CO_2 standards alone. For all our gas standards, the best suited systems and methods are optimized for each specific trace gas species.

Sealing a known mass of pure compound in a capillary tube, used in making gravimetric standards.

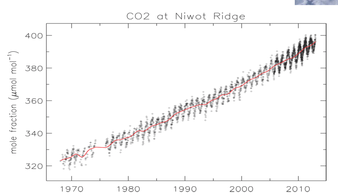
Non-CO_2 gases:
We make gravimetric standards by injecting known quantities of trace gases into a cylinder and then filling with synthetic air or scrubbed real air. The amount of each component added is determined by mass. Standards from ppm to ppt level can be made by serial dilution. Scale stability is confirmed by preparing new gravimetric standards every few years. This is especially important for CO, which is known to drift at ppb levels in aluminum cylinders. **This process is repeated periodically to confirm mole fractions of past gravimetric standards and present secondary, in house, sets used for the calibration transfer.**

Air filling system;
Air is drawn from a 10 m. height and compressed using a RIX SA6(tm) oil-less compressor. Ballasts can be filled during clean air vectors [avoiding urban air intrusion] or air can flow directly into the cylinder. Below ambient standards are first partially filled with hydrocarbon free air, then pressurized to 135 bars with natural air. **Mole fractions can be adjusted to meet ambient air analytical needs.**

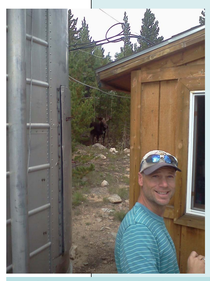


Conclusions; We make our own real air standards. Gas companies and most national metrology institutes provide trace gas air standards composed of mixtures of pure components (not air). The gas matrix and source components (ex. fossil-fuel CO_2) can influence measurement of some greenhouse gases. We discovered that differences in reference gas standards from natural ambient air can lead to apparent offsets and other errors when calibrating instrument measurement of ambient air. Most of these problems are almost cancelled out when the reference gas used has a composition very close to ambient air. For this purpose and our ability to maintain unchanging primary reference scales for these trace gas species, we have been entrusted to provide the very high level of accuracy standards, required for studying long-lived greenhouse gases, as formulated in the WMO Global Atmosphere Watch program goals.

Natural Air standards made at the Niwot Ridge facility, a remote site west of Boulder (elev. ~3000m)



Some trace gas species do not vary over relatively short time frames and can be made into standards with little targeting error. After measuring ambient air CO_2 and CO, their targeting in background air can be corrected. Standards are filled here year round for CO_2, CH_4, CO, N_2O, SF_6 and many other climate change related species.



Resident Moose visits the site