NOAA Technical Memorandum ERL CMDL-14

DEPARTMENT OF COMMERCE ★ UNITED STATES OF AMERICA ★

CMDL/CARBON CYCLE GASES GROUP STANDARDS PREPARATION AND STABILITY

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Boulder, Colorado
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Duane Kitzis and Conglong Zhao

Abstract

The NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) Carbon Cycle Gases Group (CCGG) methods and materials for air standards preparation are presented in detail. Atmospheric natural air standards are prepared in aluminum cylinders as reference gases for trace gas measurement systems by CCGG and others. The trace gas carbon dioxide (CO_2) is primarily discussed, with some mention of common processes for carbon monoxide (CO) and methane (CH_4) where applicable. Cylinders are conditioned with natural air and then pressurized to 135 atmospheres using an oil-free compressor. The mixing ratios of CO_2, CH_4, CO, and the isotopic ratios of CO_2 can be altered by spiking the cylinder with low or high concentration gas prior to filling with a balance of natural air. The air is dried to a dew point of -80°C by passing the air through a very strong desiccant. The calculations and spiking methods for CO_2 are presented for targeting CO_2 mixing ratios to within 2 μmol/mol. The stability of CO_2 and CH_4 in aluminum high-pressure cylinders is better than the present analytical precision.

1. Introduction

High precision measurements of the trace gases CO_2, CH_4, and CO are being undertaken by many laboratories of various nations in order to better understand the biogeochemical cycles of these gasses. There can be no integration of all these various measurement projects unless the data are all referenced to common well-defined calibration scales. The consistency required for optimally usable atmospheric CO_2 measurements and intercomparison must be no worse than 0.1 μmol/mol for the northern hemisphere and 0.05 μmol/mol in the southern hemisphere [*World Meteorological Organization (WMO)*, 1993]. Because of stringent quality controls necessary for the measurement of long-lived trace gases, stable reference gas standards are an integral part of any long-term measurement program. The Carbon Cycle Gases Group (CCGG) of the Climate Monitoring and Diagnostics Laboratory (CMDL) has been involved with making CO_2 standards since the early 1970s [*Miller*, 1974] and over the years has expanded to include methane, carbon monoxide, and the stable isotopes of CO_2. Currently the CCGG standards preparation facility at the Mountain Research Station makes more than 200 standards per year and has enabled many laboratories world wide to be on the same comparable CO_2 and CO [*Novelli et al.*, 1991, 1994] scales as designated by the World Meteorological Organization [*WMO*, 1995]. Most of the discussion in this paper is focused on CO_2.

The need for natural air standards was recognized when standards were measured using different nondispersive infrared (NDIR) analyzers. The comparative work done by *Komhyr et al.* [1985] was prompted by calculations of CO_2 pressure broadening in nitrogen and natural air presented by others [e.g., *Bischof,* 1975; *Griffith et al.*, 1982]. Because of the difference in pressure broadening of the CO_2 absorption lines by nitrogen and by natural air, considerable corrections need to be applied to NDIR measurements when using CO_2-in-nitrogen reference standards to calibrate CO_2-in-air measurements. These corrections are strongly analyzer dependent and may not be constant in time. From these comparisons it became apparent that standards of wholly natural air needed to be created. Efforts started in 1979 [*Thoning et al.*, 1987] and have continued through the present. All standards are calibrated in the central calibration laboratory at CCGG in Boulder, Colorado. The CMDL secondary standards, to which all other NOAA standards are tied, were measured approximately every 3 years against the WMO designated primaries maintained by the Scripps Institution of Oceanography (SIO). In 1995 the WMO designated the CCGG as the central calibration laboratory. The world network is currently tied to the 15 CCGG primary standards now designated as the new WMO primaries. The Boulder primary standards are calibrated at regular intervals on our own manometric system [*Zhao*, 1997] and were intercompared with the previous WMO calibration scale maintained at SIO. As of today, there appears to be no significant offset between the CMDL scale and the SIO scale in the range of ambient concentrations.

2. Site Description

The air standard preparation facility is located in a biosphere preserve at 3040 m altitude, 40°02'N, 105°32'W. This subalpine forested area has very limited vehicle access and usually provides nonurban continental air. A record of the CO_2 mixing ratio and its seasonal variations can be seen at the CCGG network site at Niwot Ridge (NWR) (Figure 1).

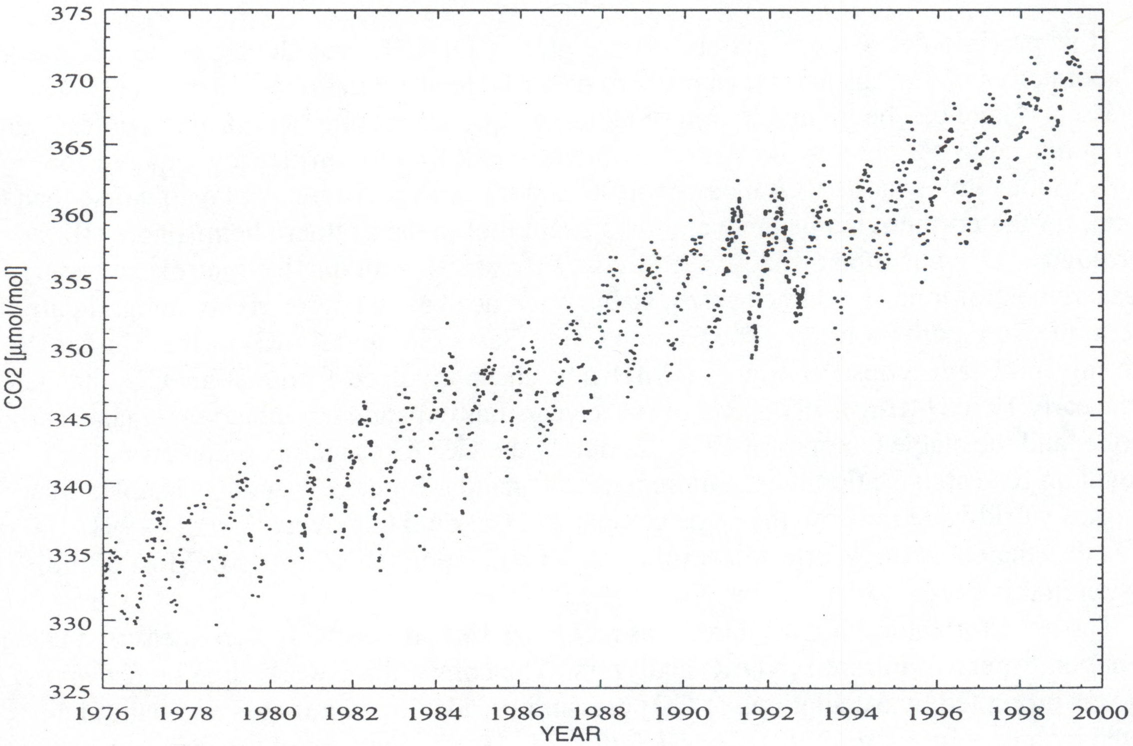


Figure 1. Ambient CO_2 concentration at the Niwot Ridge sample site.

The network site is located just to the west of the preparation facility at 40°03'N, 105°35'W at 3475 m. An aerial picture looking west over the area can be seen at the CCGG Web site (www.cmdl.noaa.gov/cccg/index.html). The biosphere preserve is maintained by the National Forest Service and the University of Colorado, Mountain Research Station. The nearest paved road is approximately 10 km away at a much lower elevation.

Summer and winter transportation to the site over the last 3 km varies due to snow coverage and conditions. The site is unreachable in winter except via snow-tracked vehicles or skis. To the east of the site is the urban front range of Colorado, 25 km away. The densely populated Denver metropolitan area is 45 km to the southeast, and to the south is the city of Boulder watershed, which is closed to all human traffic. To the north and west is the Arapahoe National Forest and wilderness area. Basically south, west, and north is very sparsely populated for 100 km or more.

3. Weather and Wind Trajectories

In general the site experiences clean well-mixed air from the western continent of North America and beyond from the North Pacific Ocean. The daily-averaged wind speed and direction from 1990 to 1997 (Figure 2) show that wind direction is predominantly from the west with a more variable direction and weaker winds during the summer months. Some spring and summer days have short periods of local upslope easterly sourced air with a component of relatively polluted metropolitan air. This is very evident from high concentrations of correlated CO and CO_2. It is common for winter winds to average 5-10 m s^{-1}.

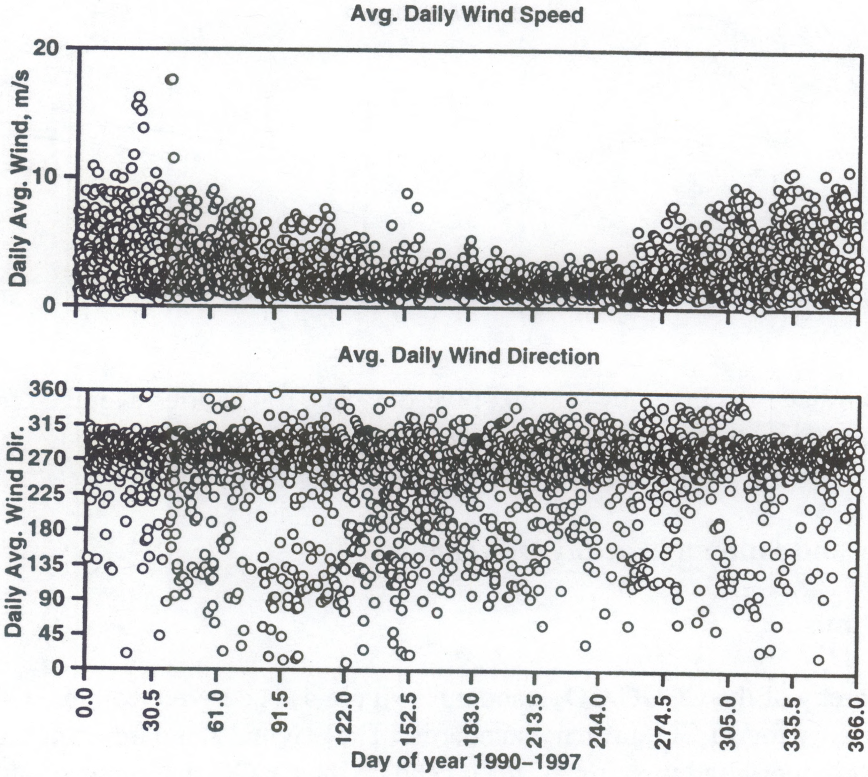


Figure .2. Eight-year daily average wind speed and direction at Niwot Ridge, Colorado, filling facility.

Figure 3 shows back trajectories at the filling site. These trajectories are averages from 1993 to 1997 divided into six of the most common patterns, and all are predominantly from the west with spring and summer showing more continental air as compared with the longer winter trajectories. Currently trajectories can be observed on the CMDL web site (www.cmdl.noaa.gov).

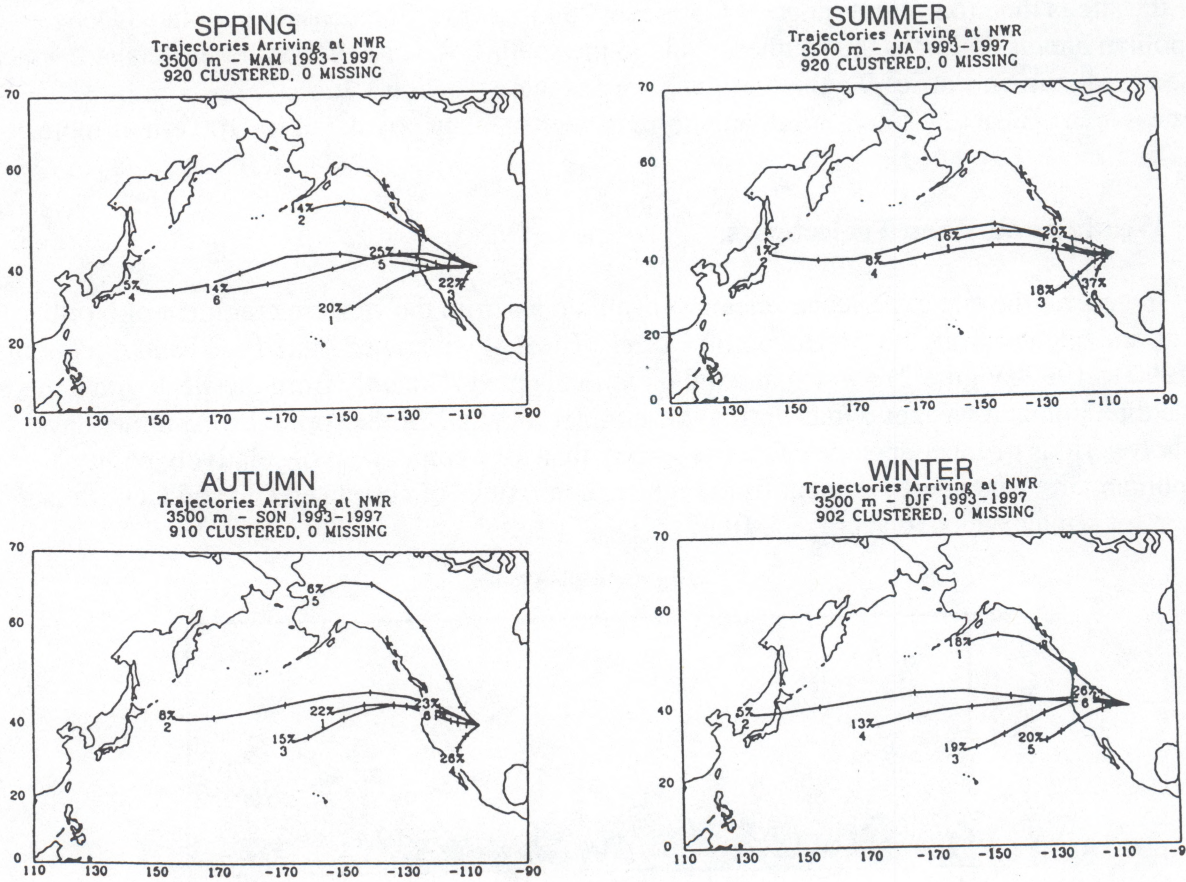
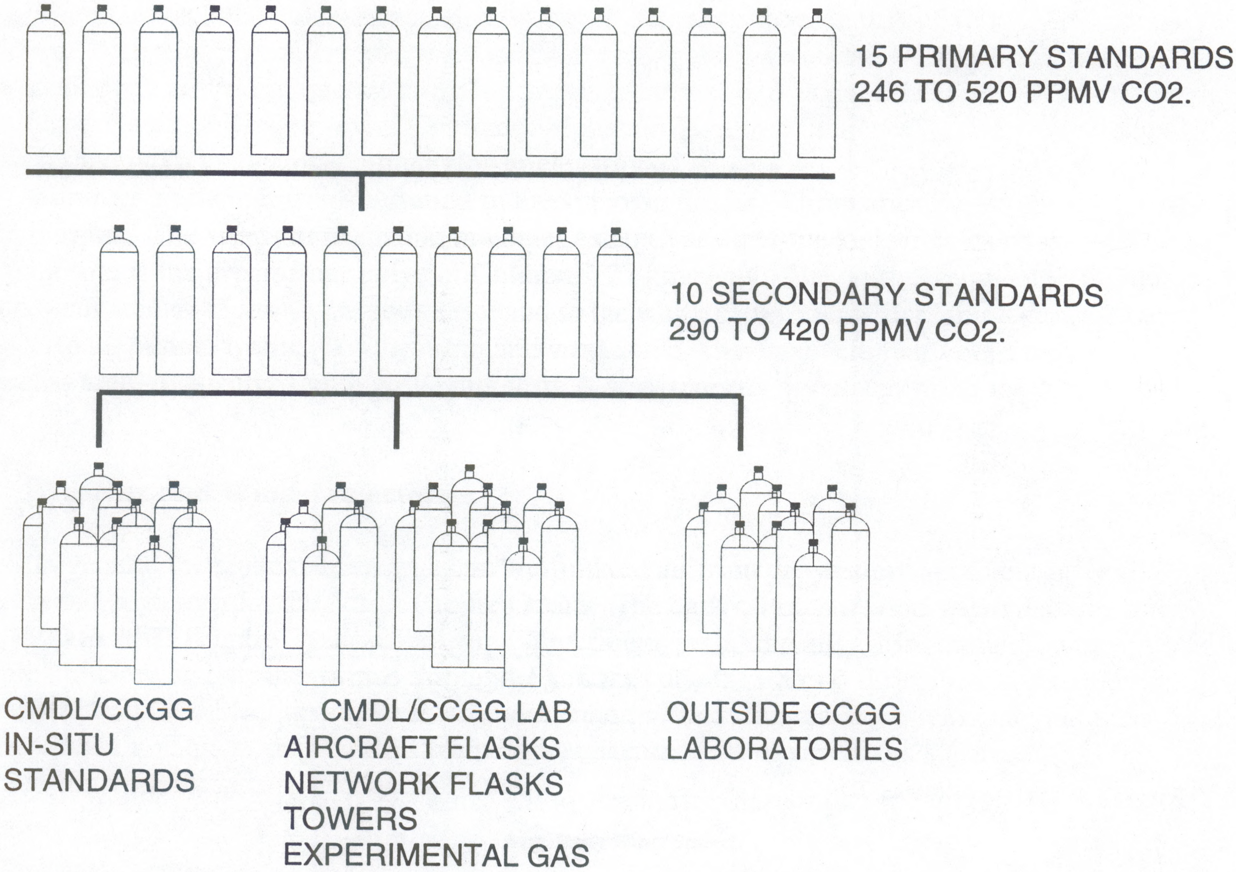


Figure 3. Wind trajectory cluster by season. Five-day back trajectories averaged from 1993 to 1997 and are grouped by the six most likely trajectories.

4. Cylinder and Pumping Facility Description

4.1. Calibrations

The hierarchy of the CCGG CO_2 standards (Figure 4) is derived from the CCGG central calibration laboratory for 15 CO_2 primary standards. The original standards ranging from 264 to 520 µmol/mol were measured three times at SIO and on the CCGG manometric system [*Zhao*, 1997]. The calibration results of these standards are currently used to provide the WMO (CO_2 in air) mole fraction scale. Currently, five new primary standards are being added at CO_2 mole



Calibration precision for CO2:
325-425 µmol/mol range; 0.014 µmol/mol [1 sd of calibrations < 6 months apart].
< 325: 0.1 approximate precision.
> 425:. 0.25 approximate precision.

Absolute Uncertainty; 0.1 µmol/mol
Internal consistency [325-425 µmol/mol]; 0.04 µmol/mol [2 sigma] [< 2 years]

Figure 4. Hierarchy of CCGG CO_2 standards. Primary standards are used to calibrate a smaller secondary set which in turn is used as a reference for all other concentrations. A subset of the secondaries is used to bracket the standards to be calibrated.

fractions of approximately 700, 1000, 1500, 2000, 2500, and 3000 µmol/mol. The ten secondaries in the range of 290 to 420 µmol/mol are calibrated using the primaries. All internal and external standards are calibrated on a single NDIR, which is referenced to these secondaries. For CO_2 stability the calibration histories of the various internal CMDL standards were checked for calibration precision and long-term drift. The mean difference of repeated measurements for CO_2 mole fractions between 325 and 425 µmol/mol is 0.002 ± 0.014 (histogram of distribution, Figure 5). This represents 381 cases since 1988 where individual cylinders were recalibrated in less than 6 months. Thus we can say that the precision of our measurement is 0.014 µmol/mol (one standard

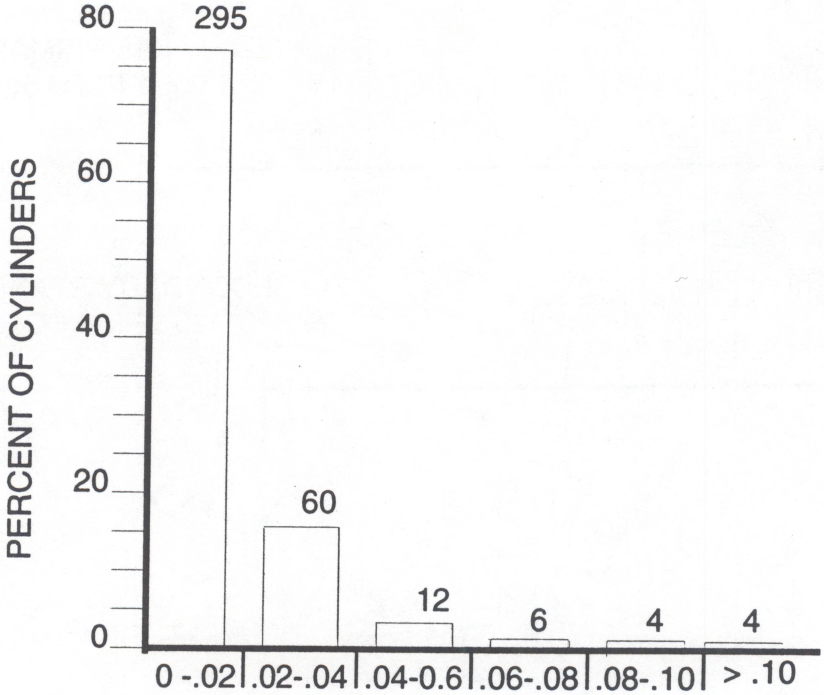


Figure 5. Histogram of calibration differences of the same 381 standards, 325-425 μmol/mol.

deviation). Outside of this range the precision was found to be 0.1 for mole fractions from 200 to 325 μmol/mol and 0.25 for mole fractions from 425 to 500 μmol/mol (histogram of distributions, Figure 6). The loss in precision of relatively low and high CO_2 mixing ratios is because of the limitations of measuring toward the end of the range of the primary standard scale and the slight degradation in measurement precision at high mole fractions. This estimate of precision takes all cylinders into account and may contain some cases of real drift and, therefore, is a worst-case scenario. The absolute accuracy stated by the CO_2 calibration laboratory is 0.1 μmol/mol. The precision and internal consistency of the standards in the range between 325 and 425 μmol/mol is 0.04 μmol/mol over a 2-year period at the 2-sigma confidence level. If a cylinder is recalibrated at the end of its useful volume, the precision of a cylinder is limited by the reproducibility of our measurements (0.028 at the two sigma level), and necessary assumptions about the history of the drift between calibrations should include this uncertainty.

4.2. Cylinders

Brass, packless taper-threaded valves are used in almost all of our cylinders with Teflon tape as the thread sealant. The Ceodeux valves have a soft seat that does not become difficult to turn or seal over years of use. Several types of cylinders and surface treatments were tested, and no evidence was found of specific coatings to improve the CO, CO_2, or CH_4 stability over bare, uncoated aluminum. Luxfer aluminum, alloy 6061, cylinders with their standard cleaning preparation are the most used cylinder in CCGG. Currently Luxfer provides a high heat

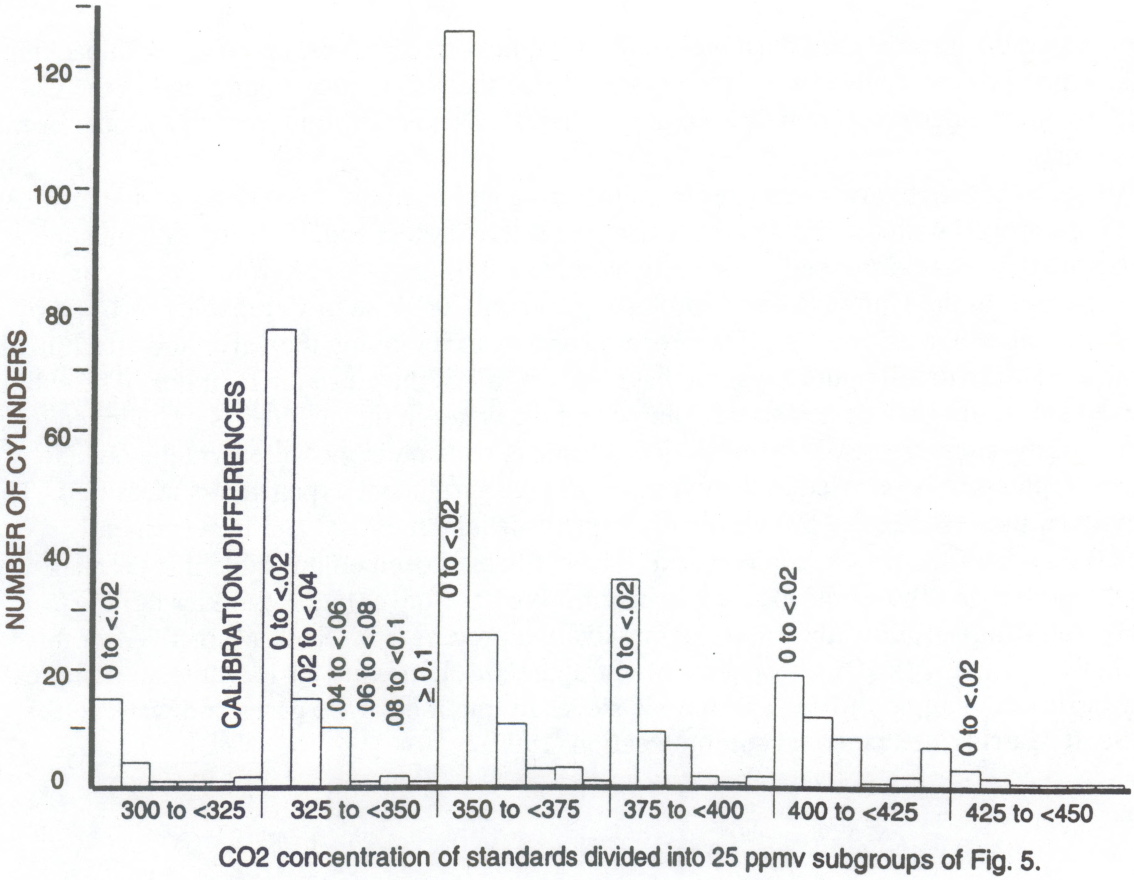


Figure 6. Histogram of calibration differences of the same standards divided into 25 μmol/mol groups. A gray shade shows that only one cylinder falls in that category.

treatment, proprietary acid wash (with no etching of the surface), steam cleaning and forced-air drying. The steel cylinders used in the past exhibited too much drift in CO_2 mixing ratios, with half of these drifts on the order of 0.05 μmol/mol CO_2 per year [*Komhyr*, 1985] could be at different rates or of a different sign in each cylinder. Aluminum cylinders have much better stability than steel for CO and CO_2. Methane seems to be stable in any type of cylinder we use, whether it is aluminum, surface treated, or steel as long as it has been air dried to a very low dew point. The same cylinders are used for stable CO_2 isotopes and have exhibited no measurable drift [*Trolier*, 1996]. There have been some cases of major drift (0.05 per mil ^{13}C per week) of the CO_2 stable isotopes, attributed to the Teflon paste used as the cylinder valve sealant and also to unknown regulator contamination. There may be some evidence for long-term drift of CO in aluminum cylinders as exhibited in smaller high-pressure cylinders [Paul Novelli, CMDL, personal communication, 1999]. This drift, however, is on the order of the measurement precision and has not yet been well quantified. A histogram of CO_2 concentration drift (Figure 7) for 125 cylinders that have a calibration history greater than 2 years, shows drift in both directions. There are some cases (8%) with evidence of drift greater than 0.045 μmol/mol per year. For this reason, it is recommend that standards be recalibrated during long use and at the end of their useful volume. The drifts, as shown in the histogram, cannot be predicted. Drift in most of our standards is often undetectable for histories of less than 2.5 years. In some documented cases the drift was attributed to H_2O mixing ratios greater than 5 μmoles $mole^{-1}$, stainless steel valves, or valves with packing materials, which preferentially absorb trace gases. There may be an increasing trend in the CO_2 with decreasing cylinder pressure below 20 atmospheres. This is different in each cylinder or may not be present at all.

All cylinders are hydrotested after manufacturing and need to be retested periodically. All cylinders are stamped with the month and year of the last hydrotest and, if out of date must be retested before they can be shipped. Currently aluminum cylinders need hyrotesting 5 years after the stamped date. In the United States hydrotesting can only be done by companies certified by the U. S. Department of Transportation. The process consists of removing the valve and attaching the cylinder to a water/hydraulic pump system that displaces all of the air in the cylinder. The cylinder is immersed in a water bath of measured volume and the water in the cylinder is pressurized to 1.67 times the working pressure of the cylinder. The elastic expansion is measured via the outside water displacement, pressure is released in the cylinder, and the permanent expansion is measured. The typical cylinder used (Size AL-150) elastically expands by about 190 cc and is permanently expanded 0-2 cc after the pressure is released. The cylinder is deemed unusable if it permanently expands by more than 10% of the elastic expansion. We have never had a cylinder fail the test.

Hydrotesting is followed by a drying/passivation process from Scott Marrin. After this process they are filled with 20 atmospheres of Ultrapure air. Ultrapure air is whole air compressed at Scott Marrin and is highly filtered with mole sieves to trap most trace gases and water. (Jack Marrin, Scott Marrin, Inc., personal communication, 1999)

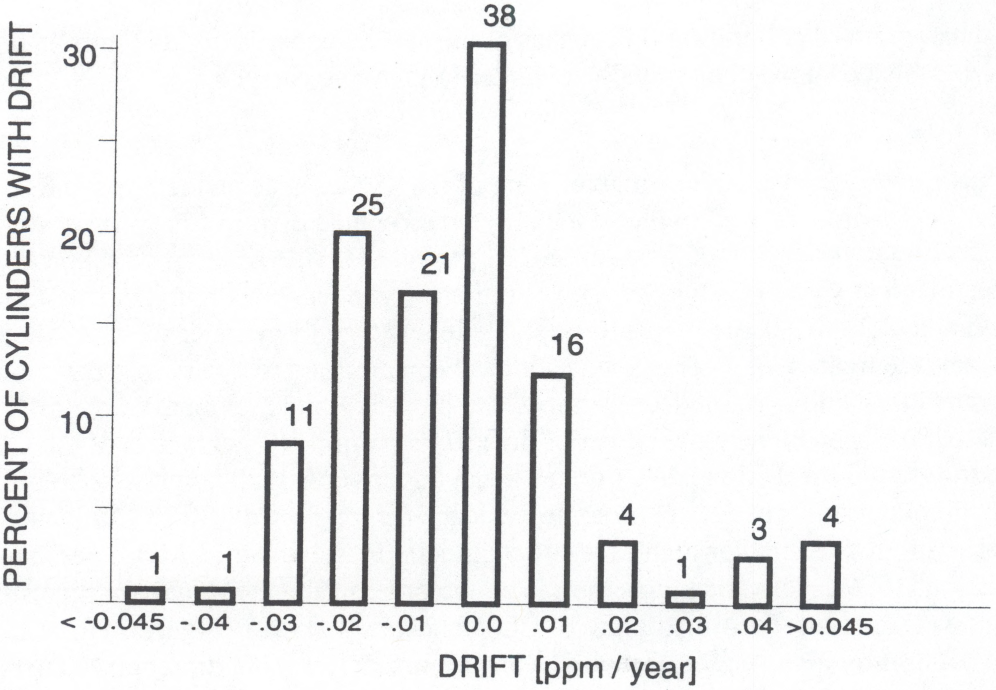


Figure 7. Distribution of drifting cylinders based on 125 cylinders that have a calibration history greater than 2 years. One standard deviation of this distribution is 0.016 μmol/mol. The number of cylinders in each subset is above the boxes.

4.3. Pump

The compressor currently in service is a RIX SA6B. It is a three-stage oilless, piston compressor commonly used for recharging scuba tanks and is used as sold with no alterations. The three stages of compression are to 6, 34, and 204 atmospheres respectively. The compression rings are made of filled PTFE plastic and require no lubrication. There are moisture separators between the second and third stage and at the output of the compressor. The third stage is designed with a 102 atmosphere back pressure regulator to maintain this minimum pressure against the piston. The flow at 3040 m altitude for this compressor is 126 L min^{-1} at ambient pressure. The temperature of the compressed air in the output-cooling coil can reach 121°C. These pumps are not airtight and some alterations of trace gases may be observed. Others have made some modifications to this pump to lower the air temperature from compression and improve its use for ambient air sampling [*Mak*, 1994]. Some of the improvements may result in some loss of pump performance however. Currently some methods to make the pump run cooler, which do not affect the air stream, are being tried.

4.4. Drying System

The stability of many trace gases is sensitive to water vapor and especially sensitive to liquid water. Therefore the drying step is important in the preparation of any gas standards. The air exiting the compressor is passed through a Balston, 1 micron coalescent filter with a manual drain. The air then passes through two stainless steel tubes of 50 cm length in series. These have a 2.5 cm cross section and are filled with Anhydrous Magnesium Perchlorate (Mg(ClO4)2) (Anhydrone®, J. T. Baker, Inc., a division of Mallinckrod & Baker, Inc.). This system reduces the water vapor in the air stream to typically less than 1 µmol/mol. After approximately 52,000 L of air have passed through the traps, the upstream trap is replaced with the downstream trap, which is replaced with a fresh one. The second moisture trap is for complete redundancy as one will dry the air stream to less than 1 µmol/mol. Water accumulated in the compressor moisture separators and the coalescent filter is blown out before and after each cylinder pressurization. Another possible desiccant is Aquasorb (Mallinckrodt). Aquasorb is phosphorus pentoxide (P2O5). However, CO_2 was found to increase by 2-5 µmol/mol with this new drying material. This problem and the safety issue of cycling phosphoric acid in a high pressure system prompted the decision to discontinue use.

4.5. Pressure Measurement and Compressor Control

The measurement, display, and control of the compressor is done with an Omega series DP205-S controller with a PX302 pressure transducer. The output solid-state relay, controlled by the alarm setting, activates a set of Crydom DC control, solid-state opto-isolated relays. These relays control the 220 V compressor power and are normally off unless turned on via the Omega controller. The setting of the control is 135 atmospheres for a full cylinder.

4.6. Complete System

The air is drawn into the system (Figure 8) through a 10-m tall, 2.5-cm diameter stainless steel intake. All high pressure flex hoses are stainless steel braided, PTFE lined with 1/4" VCR

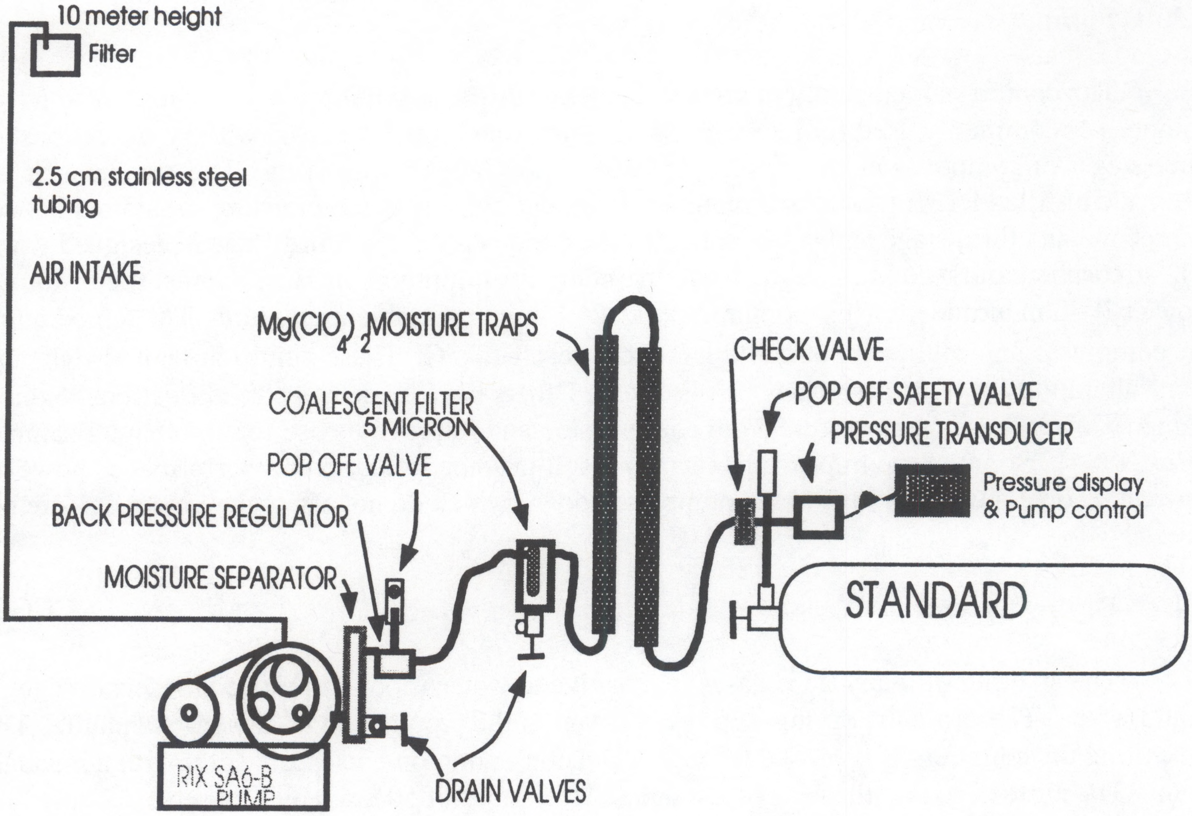


Figure 8. Pumping System. Air is drawn in through a 2.5 cm diameter, stainless steel intake approximately 10 m high. A Rix compressor pressurizes the air that is passed through 40 cm of Magnesium Perchlorate. Pressure measurements and the shut-off set point is close to the cylinder valve. Cylinders are pressurized to 135 atmospheres with dry natural air.

connections. All connections are 1/4" NPT or 1/4" VCR with silver coated nickel gaskets. A 0.5-m length between the compressor and the Balston filter allows for some extra cooling of the air and, therefore, better condensation before going through a coalescent filter. This was found to improve the performance of the filter significantly. All parts are secured to a rack for safety. The popoff valves and the check valve are for safety. Popoff valves are set to 170 atmospheres on either end in case of a trap clogging, and the check valve will prevent the cylinder from dumping all the air volume in the case of a line break. Seven micron filters are in line at the end to prevent dirt from getting to the safety valve or the pressure transducer.

4.7. Air/Cylinder Measurement System

Carbon dioxide is measured on site with a Licor NDIR, and CO is measured with a TECO NDIR. The system requires a set of six standards ranging from 300 to 450 µmol/mol CO_2 and one 200 nmol/mol CO span gas. These standards can be used to bracket ambient air measurements or test prepared standards. New standards are also tested for H_2O content with a MEECO Aquamatic that uses a P2O5 conductivity method and is set up to measure from 1 to 200 µmol/mol H_2O. The maximum allowable H_2O mixing ratio in a filled cylinder is 5 µmol/mol. Most cylinders test between 0.5 and 1.0 µmol/mol. This corresponds to dew points less than -75°C and usually less than -80°C when expanded, and less than -30°C under full pressure.

5. Air Standard Preparation

5.1. Conditioning

When a cylinder is to be refilled and contains air with the trace gases near ambient, conditioning is not usually necessary. New cylinders have Ultrapure air and cylinders with undesirable concentrations left in them must be purged of the old air to have the walls conditioned to ambient air. Drifts have persisted for months due too evacuating the cylinder down to vacuum before filling. Drifts due to spiking, discussed below, have been eliminated by filling the cylinder immediately after spiking and filling the cylinder laid down. There is no evidence to show drifting due to the filling process described below. As a result of these experiences and to remain conservative about long-term unknown effects, the following steps have been adopted by CCGG as procedure:

(1.) Blow off the residual air down to ambient pressure. This must be slow enough to avoid water condensation at the valve.

(2.) Fill to 20 atmospheres and blow down to ambient pressure two times to purge old air. This uses mass flow to flush out the original air.

(3.) Fill to 33 atmospheres and let sit for at least a week for wall equilibration.

From this flushing procedure the original air left in the cylinder is less than 0.01% of the volume at the time of spiking and less than 5E-5% after the final filling. Drifts in the stable isotopes of CO_2 have been observed, even after this procedure, and have been corrected via commercial rolling of the cylinder.

5.2. Filling

The 33 atmospheres of air is blown down to ambient pressure. The standard can now be filled with ambient air or the trace gas can be adjusted via one of the next two steps. The cylinders are rated to 153 atmospheres and are filled to 149 atmospheres in about 35 to 45 minutes. When the air cools the pressure in the tank decreases to 136 atmospheres.

5.3. Targeting Above Ambient Levels

For increased standards above ambient we use one of several cylinders with very high concentrations of the trace gas of interest. A small amount of the spiking gas is put in a 1 liter transfer volume at higher than ambient pressure. This over pressure is allowed to flow into the cylinder until pressures are equilibrated. The formula for increased trace gas values is as follows:

Trace gas increase = K × (Target Concentration - Ambient Concentration)

where K is a constant for trace gas increase/pressure of the spiking gas in the transfer volume.

The over pressures used in the transfer volume are on the order of 0.1 atm of over pressure per increased µmol/mol CO_2 in a standard 29.5-L cylinder. Because the composition of the spiking gas varies, this value varies and must be found empirically with each cylinder of spike gas. Once a few cylinders are spiked and calibrated, the constant K is the same over a wide range of increased trace gases. Examples of spike gas concentrations are 10% CO_2 in air, 1.5% CO in air, and 2.5% CH_4 in air.

5.4. Targeting Below Ambient Levels

Lowering a trace gas below ambient levels requires that some volume of air with none of the trace gas, be put in the cylinder.

$$Pf \times Vf = Pz \times Vz + Pa \times Va$$

where

Pf is the final filling pressure of the standard at room temperature
Vf is the final concentration of the trace gas
Pz is the pressure of the zero gas put in the standard first, to lower the concentration below ambient.
Vz = 0 is the concentration of the zero gas.
Pa = Pf – Pz is thethe balance pressure of ambient air necessary to fill the standard to 149 atmospheres.
Va is the ambient concentration of the trace gas.

The zero air is created with specific chemical traps for each trace gas. Carbon dioxide can be removed with sodium hydroxide, Ascarite (Thomas). Carbon monoxide is removed with Schutze reagent. The zero air from both trapping agents was tested and found to be less than 5 µmol/mol for CO_2 and immeasurable trace amounts for CO. The isotopes of CO_2 were manipulated with gases of light or heavy isotopes. The same type of trap holder is used as for the desiccant traps. Specific trace gas traps can be installed between the Mg(ClO4)2 filled tubes. The second trap will catch any residual moisture released by the trace gas traps. The zero air is put directly into the cylinder if very low final concentrations are targeted. The more precise method requires the filling of an intermediate ballast with the zero air and then transferring the partial pressure necessary to the standard cylinder. The necessary partial pressure of the zero gas is calculated from the above formula, rewritten as:

$$Pf \times Vf = [Pf - Pz] \times Va$$

$$Pf \times [Va - Vf] / Va = Pz$$

The standard cylinder is filled to the pressure P(z) from a ballast of whole air (with the specific trace gas removed) and then filled to the final pressure with dry natural air of ambient concentrations.

5.5. Adjusting Trace Gas Levels in a Cylinder

Occasionally the targeted concentration is missed by an amount that requires adjustment. If the concentration of the standard is closer to ambient than the target concentration, it is easiest to blow this off and start over. Experimenting with introducing small volumes of high pressure (high or low concentrations) into the air stream have proven very time consuming due to the time necessary for the cylinder to become evenly mixed before obtaining a usable measurement from the standard.

If, however the final concentration turns out to be farther away from ambient than the desired targeted trace gas concentration, it is possible to adjust the standard toward the desired concentration. The same partial pressure formula stated previously can be used adding a term for the gas already in the cylinder and blowing the cylinder down to the necessary partial pressure. When the cylinder is filled to the final pressure again with ambient levels of the trace gas, the concentration will be adjusted toward the targeted value fairly precisely.

In the case where the concentration in the cylinder is too low and must be increased

$$Pf \times [Va - Vf]/[Va - Vm] = Pm$$

where Vm is the concentration of the gas in the cylinder, and Pm is the pressure to lower the standard to, before refilling with ambient air. In the case where the concentration in the cylinder is too high and can be lowered

$$Pf \times [Vf - Va]/[Vm - Va] = Pm$$

5.6. Initial Calibration and Use of Trace Gases

After the standard has been filled, checked for low water content, and for targeting of the trace gas it is transported to the central calibration laboratory in Boulder. The standard is then calibrated three times with approximately 1-week intervals between each calibration. For CO_2 these measurements are done with a NDIR analyzer, comparing them to secondary CMDL standards that are closely tied to the primary WMO standards. The trace gas mixing ratio reported includes measurement repeatability as well as a check on cylinder stability. These standards are used at our base line observatories, international collaborative projects, and many national laboratories as tertiary standards. There is evidence that as the volume of pressurized air is used up, the trace gas can come off the walls in disproportionate amounts. This has sometimes been seen in cylinders with CO_2 when a standard is used at pressures below 20 atm. Thus CO_2 mole fraction may increase with pressure loss. This effect is variable and may not be measurable in all tanks. For a representative final calibration, use is discontinued when the cylinder pressure becomes lower than 20 atm.

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