Technical Report:

Infrared Analyses of NOAA Primary CO_2-in-Air

Reference Gas Standards at SIO, 1991-1999

by

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1. Introduction

Here we report on a decade-long intercalibration between the Carbon Dioxide Research Group (CDRG) at the Scripps Institution of Oceanography (SIO) and the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA). Since 1995 NOAA/CMDL has been the designated Central CO_2 Calibration Laboratory (CCL) of the World Meteorological Organization, replacing SIO/CDRG. A set of 15 natural-air primary reference gas standards, ranging in mole fraction of CO_2 from 246 to 521 parts per million (ppm) created by NOAA/CMDL, now comprises the international standard for the calibration of measurements of atmospheric CO_2. These standards have been calibrated manometrically by NOAA/CMDL using a constant volume manometer of their design [Zhao et al., 1997].

In 1999, this set of standards was sent to SIO/CDRG and analysed with a non-dispersive infrared (NDIR) gas analyzer to compare closely the calibration system of NOAA/CMDL to that of SIO/CDRG, which was the designated CCL prior to 1995. This intercomparison was the fourth, the first occurring in 1991. Also, this time 8 standards of the NOAA/CMDL set were measured manometrically on the constant volume mercury-column manometer (CMM) of SIO/CDRG, as reported to NOAA/CMDL by Guenther and Keeling [2000]. Here we report additional measurements of all 15 reference gas standards, made in 1999 on the Applied Physics Corporation (APC) NDIR analyzer of SIO/CDRG. Also we review the APC analyzer measurements for the three previous calibrations at SIO/CDRG, and the SIO/CDRG manometric analyses of 8 of these gases.

2. SIO/CDRG Infrared Analysis System

The CO_2 reference gas calibration system at SIO/CDRG interrelates the CO_2 concentrations of reference gases by means of an "index" (I) scale that is proportional to the response of the APC analyzer, expressed as a distance between traces on a chart paper record, or a digital equivalent determined directly from instrument output voltages. The I-indices are expressed in units close to parts per million in mole fraction and labeled in "ppm", although this is only an approximately correct designation. Intercomparisons of reference gases are expressed as differences in I-index ppm units, routinely calculated and tabulated using a program and data-base called "REFGAS".

SIO/CDRG maintains sets of both primary and secondary reference gas standards. The CO_2 mole fractions with respect to dry air of the primary set, determined manometrically with the CMM, represent true concentrations of CO_2-in-air. The CO_2 mole fractions of the secondary set are established by intercomparisons with the primary standards using the APC analyzer, results initially expressed in I-index units.

The instrument sensitivity, in I-index units per scale division of the instrument's recorder, is determined on each calibration day from responses of two secondary gas standards: a "principal" and a "high span" standard. These two standards are approximately 20 ppm apart in mole fraction, centered near the current mole fraction of atmospheric CO_2. REFGAS calculates and tabulates a "recorder scale factor" (RSF) which is the inverse to the instrument sensitivity and directly compares the measured scale difference between the two secondary standards to the scale difference between two original standards, defined to be 18 ppm apart in I-index at the creation of the secondary gas standard system in 1957. The RSF is thus defined as follows:

$$RSF = \frac{SD}{ID} \times 18 \tag{1}$$

where   SD = measured scale difference between the principal and high

span secondary standards

ID = assigned I-index difference between the principal and high

span secondary standards

Subsequently an "adjusted index" scale, closer to true concentration in the range of 310 to 340 ppm, was established from manometric measurements of primary standards with the CMM. This scale, called the J-index, is also proportional to the response of the APC analyzer, defined as follows

$$J = 1.2186 \times (I-311.51) + 311.51 \tag{2}$$

where   J = J-index (in ppm)

I = I-index (in ppm)

From 1974 to the present, the nonlinear response of the APC analyzer has been determined over the range of CO_2 mole fractions, from 200 to 500 ppm, with respect to natural air, dried to a water vapor concentration of about 10 ppm. The response is determined by measuring the set of SIO/CDRG primary reference gases over a sequence of days, usually five, typically spaced about a week apart. The relationship between the J-index and the manometrically determined CO_2 mole fraction for such a specific calibration period is then expressed by a cubic polynomial calibration equation. Such calibration periods have been repeated approximately every two years. For each period we designate a calibration scale, deemed to be valid for the central date of a sequence of calibrations. Cubic calibration equations for each period define the relationship of J-index to CO_2 mole fraction. Here we consider previous calibration periods as well as the most recent period. Between central calibration dates mole

fractions are calculated by interpolation. The most recent central date for any given year in the history of our program defines a "calibration scale" designated by "X" followed by 2 digits of the calendar year, e.g. "X97" for calibrations up to, and including, a central data in 1997. The scale for 1999 is further qualified by an A or B, e.g. "X99A", as discussed below. We also discuss below two special scales that apply only to 1999 calibrations: X99NA and X99NB.

In the routine operation of the APC analyzer, unknown reference gases, and gases being recalibrated, both kinds called here "unknown gases", are compared to a third secondary standard, which is close in mole fraction to the principal standard, and whose I and J indices are known from frequent comparisons with the principal and high span secondary standards. Under normal circumstances, determinations of the RSF, based on the latter two standards, are made near the beginning of each calibration day and again near the end. For especially long calibration days, additional determinations are made during the day. The REFGAS program routinely assumes that the RSF is constant on a given calibration day, using a simple average of all RSF determinations to calculate the I- and J-indices of gases of unknown current index.

3. APC Analyzer Measurements of NOAA/CMDL Primary Reference Gases in 1999

The 15 NOAA/CMDL natural-air primary reference gases, treated as unknown gases, were compared on the APC analyzer to our secondary standards on each of five days from April to July, 1999. The APC analyzer had recently been moved from the laboratory in a building where it had operated from 1957 up to the time of a major renovation of the building and conversion to almost exclusively office space. The new location of the analyzer was the instrument laboratory of SIO/CDRG, whose room temperature was significantly less stable than in the old laboratory, resulting in less consistent RSF determinations. On calibration days, when the range of CO_2 index of unknown gases was comparable to the range of the principal and high span secondary standards, this variation had only a minor affect on the determinations. The large

range in mole fraction of the set of NOAA/CMDL gases resulted, however, in large dispersions from day to day for gases with extremely high or low CO_2 index values. On the fourth and fifth calibration days (2 and 14 July), to improve calibration performance, eleven SIO/CDRG natural-air primary reference gases were added to the calibration scheme to characterize more precisely the non-linear behavior of the APC analyzer. Twenty-six gases altogether were thereby run on each of the two days, in order of increasing mole fraction CO_2. This special calibrating scheme led to the creation of two additional calibration scales, here called the "X99NA" and "X99NB", further explained, below.

To decrease the calculated day to day dispersion in calibration data for sets of gases we use a procedure called "tank concordance." This procedure adjusts the J-indices of each calibration day by means of an improved estimate of the RSF, based upon the data from all of the unknown gases, run in common on all days of the calibration (in this case, including the 15 NOAA/CMDL primary reference gas standards) rather than just the principal and high span secondary standards. The effect of the adjustment is to reduce the day to day dispersion for reference gas measurements near the low and high ends of the mole fraction range.

The tank concordance procedure in 1999, for each of the five days of calibrations, and for each of the 15 NOAA/CMDL gases, first determined the absolute difference in J-index from a midpoint value, selected to be the assigned J-index of the SIO/CDRG principal secondary standard. Daily ensemble averages of the absolute differences of these 15 gases, and a five-day set-average of the ensemble, were then calculated. The absolute difference for each gas, on each day, was then multiplied by the ratio of that set-average to the daily ensemble averages, the latter thereby made by tank concordance to be the same for all calibration days. The midpoint value was then added back to the adjusted signed differences, for each gas on each day, producing an adjusted set of J-indices for all 15 NOAA/CMDL gases for each day. The set-average

J-index for each gas is not changed by this procedure, but the calculated root mean square deviation (RMS DEV) with respect to an individual gas determination typically is almost always reduced, even after account is taken of the reduction in degrees of freedom caused by the tank concordance procedure. Before this tank concordance adjustment the RMS DEV was 0.292 ppm (J-index); after adjustment, 0.280 ppm. This unusually small improvement, as we demonstrate next, is increased when daily drift in RSF for the 1999 calibrations is corrected for.

The tank concordance procedure can reduce dispersion between the days, but cannot adjust for instability of the RSF within each day. During the five calibration days in 1999, the RSF, in fact, decreased during each day by up to 2%, a variation in RSF at least double that typically observed previously in our laboratory. Since the REF-GAS computer program does not adjust for a drifting RSF, a special RSF drift-correction procedure was instituted in which the instrument sensitivity was linearly adjusted between within-day RSF determinations before invoking the REFGAS program. The I- and J-indices for each gas were then recalculated, resulting in values designated as "indices modified to compensate for drifting RSF's".

After carrying out this RSF drift-correction procedure, the RMS DEV before tank concordance was 0.215 ppm and, after concordance, 0.106 ppm. The latter RMS DEV is comparable to that of previous calibrations [Keeling et al., 2001, page 14].

A final calibration step was then carried out in 1999, as discussed in the next section, to define the nonlinear response of the APC analyzer, determined from the data obtained for the 11 SIO/CDRG primary CO_2-in-air reference gases analyzed on the fourth and fifth days. The success of this final step rests on the hypothesis that the higher order characteristics of the APC analyzer cubic response equation, given by the quadratic and cubic coefficients, did not vary over the five calibration days even though the RSF, reflecting the linear characteristics, did vary.

4. Assignment of CO_2 Mole Fractions in Air

Manometric mole fraction values assigned to the SIO/CDRG primary standards for 1999 are those measured on the constant volume manometer in 1998, using the following manometric volume ratio

$$\frac{V_{5000\ cc}}{V_{4\ cc}} = 1322.30 \tag{3}$$

where $\qquad V_{5000\ cc} = 5015.09\ cc$

$\qquad\qquad V_{4\ cc} = 3.7927\ cc$

This volume ratio was arrived at by assuming that the gases had remained stable on average since 1985. This assumption of stability is the basis of the X99A calibrating scale reported in Keeling et al. [2001].

The following cubic relationship between CO_2 mole fraction and J-index (after modification to compensate for a drifting RSF, as discussed above) was then determined from averages of the J-indices for the 11 SIO/CDRG primary reference gases obtained on 2 and 14 July 1999:

$$X = C_o + C_1 J + C_2 J^2 + C_3 J^3 \tag{4}$$

where $\qquad$ X = mole fraction CO_2 (in ppm)

$\qquad$ J = J-index (in ppm)

$\qquad C_o = 86.40013$

$\qquad C_1 = 0.5177722$

$\qquad C_2 = 5.275435 \times 10^{-4}$

$\qquad C_3 = 5.872148 \times 10^{-7}$

This cubic equation is the basis for the "X99NA scale."

Having thus established the nonlinear characteristics of the APC analyzer on 2 and 14 July, the data for the previous three days of calibration were normalized to these two days by means of a modification of the usual tank concordance procedure, the usual version described in Section 3, above. Specifically, we adjusted the absolute J-index difference of each gas on each day to the average daily absolute difference on the 2 and 14 July calibration days, rather than to the overall set average absolute difference. Each J-index absolute difference was thus increased by a factor given by the ratio of the average for only 2 and 14 July (42.24) to the overall set average (42.12). The average J-index for the lowest mole fraction gas was decreased by 0.33 ppm using this procedure and that of the highest, increased by 0.36 ppm.

Finally, the J-indices found by the tank concordance procedure were converted to CO_2 mole fractions using equation (4). Table 1 lists the CO_2 mole fractions of each | Table 1 | primary reference gas determined on each day, along with the averages for each gas over the five days, and the standard deviations, s_i, of an individual day's determinations. The RMS DEV, taking into account the loss of degrees of freedom through the tank concordance procedure, is calculated to be 0.106 ppm in J-index. We further tested an alternative cubic relationship which determined the CO_2 mole fractions of the NOAA/CMDL gases on 2 and 14 July separately, using different cubic polynomical equations for each day. This workup yielded mole fractions that, on average, were 0.02 ppm lower on 2 July than calculated for the full 5 days of calibrations, using the X99NA scale. The average for 14 July was unchanged from the previous calculation over both days. The separate-day and X99NA-scale workups differ for individual gases by less than 0.13 ppm, except for the highest NOAA/CMDL gas, for which the difference is 0.27 ppm.

5. Summary of SIO/CDRG and NOAA/CMDL CO_2 Mole Fractions, 1991-1999

Table 2 compares SIO/CDRG data from four periods of APC analyzer calibra-
tions to NOAA/CMDL data reported in 1999. For 1999, listed in the set of columns
to the far right in Table 2, the average difference in the CO_2 mole fractions of 15
gases between SIO/CDRG (see Table 1) and NOAA/CMDL is 0.01 ppm, SIO/CDRG
lower, and the standard deviation (s_i) of an individual difference is 0.13 ppm.

Also listed in Table 2 are data based on APC analyzer calibrations at SIO/CDRG
of the NOAA/CMDL gases, made in 1991-1993 (13 to 16 days of calibrations from 22
January 1991 to 11 March 1993), in 1995-1996 (6 days of calibrations from 13
December 1995 to 26 July 1996) and in 1997 (5 days of calibrations from 28 July to
23 September, 1997). The APC analyzer data from these calibration periods were not
adjusted for within-day RSF variation, or with respect to direct use of SIO/CDRG pri-
mary gases in the calibration, as were the 1999 data. The tank concordance procedure
had no effect on the period average J-indices (see Section 3, above). The cubic cali-
bration equations for 1991 through 1997, used to convert J-indices (from the REFGAS
data base) to CO_2 mole fractions, are based on the X99A calibration scale, as reported
in Keeling et al. [2001], assuming, as noted in Section 4 above, that the manometric
mole fractions of the SIO/CDRG primary reference gases remained on average
unchanged from 1985 to 1999. Notable is the relatively large dispersion (s_i = 0.19
ppm) for the 1991-1993 results, which also exhibit the largest average difference (0.11
ppm) between SIO/CDRG and NOAA/CMDL. The 1991-1993 results are the only
evidence of possibly significant differential drift in CO_2 mole fraction between the
NOAA/CMDL and SIO/CDRG primary gases. Taking the data from all four calibra-
tion periods into account, the slope of a linear fit of the average differences to the
average dates of analysis is 0.015 ppm/year. The slope implies an upward linear drift
of 0.15 ppm in 10 years for the 15 NOAA/CMDL primary standard reference gases
relative to the SIO/CDRG gases, although most of the drift is due to the 1991-1993

data.

If the APC analyzer data for 1999 are converted to CO_2 mole fractions using the X99A scale instead of the special X99NA scale, the average difference between SIO/CDRG and NOAA/CMDL in 1999 is 0.05 ppm, SIO/CDRG higher. The s_i is 0.41 ppm, this high value due mainly to high dispersion between the five calibration days for the reference gases near the low and high ends of the concentration range.

Table 2 also shows average results for the subset of seven NOAA/CMDL gases that had been also manometrically calibrated at SIO/CDRG in 1999. The average differences and standard deviations of the subset agree closely with those of the full set, affirming that the subset well represented the full set.

Table 3 presents an alternative analysis of the data presented in Table 2, using a different calibrating scale, the X99B scale, to convert APC analyzer measurements to mole fractions [Guenther et al., Addendum, 2001]. The X99B scale posits a constant volume ratio in the CMM for 1985 to 1999, rather than constancy of the primary reference gas standards that was assumed in formulating the X99A scale [Keeling et al., 2001]. The constant volume ratio is defined by the average of 4 cc chamber volume calibrations made in 1985-1986, 1988, and 1990,

$$\frac{V_{5000\ cc}}{V_{4\ cc}} = 1321.18 \tag{5}$$

where $\qquad V_{5000\ cc} = 5015.09\ cc$

$$V_{4\ cc} = 3.7959\ cc$$

The set of cubic polynomial equations that define the X99B scale are listed in Table A4 of Guenther et al., Addendum [2001]. We additionally define a X99NB scale, analogous to the X99NA scale, with a cubic polynomial equation calculated from the manometric mole fractions of the SIO/CDRG primary air reference gas standards measured in 1998 and calculated using the CMM volume ratio given in equation (5),

Table 3

combined with the same set of J-indices used to formulate the X99A scale. The X99NB cubic polynomial equation is defined as follows:

$$X = C_o + C_1 J + C_2 J^2 + C_3 J^3 \tag{6}$$

where $\qquad$ X = mole fraction CO_2 (in ppm)

$\qquad$ J = J-index (in ppm)

$\qquad$ C_o = 86.47370

$\qquad$ C_1 = 0.5182131

$\qquad$ C_2 = 5.279927×10^{-4}

$\qquad$ C_3 = 5.877148×10^{-7}

The X99B scale, based upon a constant CMM volume ratio, causes the NOAA/CMDL primary reference gases to reflect an upward drift during the period 1991 to 1999. The slope of a linear fit of the average differences for the four periods of calibration at SIO/CDRG to the average dates of analysis is 0.051 ppm/year, or an upward linear drift of the 15 NOAA/CMDL primary reference gases of 0.51 ppm in 10 years.

6. Comparison of SIO/CDRG and NOAA/CMDL Calibration Scales

The average differences for different years between mole fractions of the NOAA/CMDL reference gases, determined by infrared analysis at SIO and manometrically by NOAA/CMDL as listed in Table 2 based on the X99A scale, indicate that the two calibration scales have not drifted differentially from 1991 to 1999 by more than 0.1 ppm, a highly satisfactory result. This conclusion results directly from the use, in this comparison, of a scale in which the volume ratio of the SIO/CDRG constant-volume mercury-column manometer (CMM) was calculated to be consistent with zero average drift in the SIO/CDRG reference gas standards after 1985. This zero drift

assumption applies to 10 primary CO_2-in-N_2 standards as well as the 11 CO_2-in-air standards used directly in the 1999 calibrations of the NOAA/CMDL gases [Keeling et al. 2001]. However, we found that there was essentially no differential drift between the sets of SIO/CDRG CO_2-in-N_2 and CO_2-in-air gases, so that the X99A scale could as well have been based only on the stability of the CO_2-in-air gases.

An additional issue to address is the degree of absolute agreement between the SIO/CDRG and NOAA/CMDL calibration scales, which is best considered for 1998 and 1999 when the most intense intercalibrations were carried out. Table 2 indicates that the X99NA scale produces mole fractions 0.01 ppm lower than NOAA/CMDL, a highly satisfactory result, but valid only if the 1998 manometric volume ratio of 1322.30 is correct for that period, and if the SIO/CDRG gases did not drift on average. Data of SIO/CDRG provide three addition estimates of the absolute calibration of mole fraction of CO_2-in-air. In all of these estimates the volume of the 5000 cc chamber of the CMM is assigned the value of 5015.09 cc, but the volume of the 4 cc chamber ($V_{4\ cc}$) is assigned different values based on a variety of evidence. The four estimates, including that of Table 2 are now listed in descending order of $V_{4\ cc}$.

1. ECM: estimate.

Measurements of archived samples of CO_2 from sea water on an Electronic Constant Volume Manometer (ECM), calibrated by transfers of aliquots of CO_2 from plenums calibrated with water, when compared with previous measurements of the same samples using the CMM, gives:

$$V_{4\ cc} = 3.7961\ cc.$$

2. Direct plenum estimate (X99B scale).

Consistent with calibrations of the 4 cc chamber of the CMM in 1985, 1988 and 1990 (based on transfers of aliquots of CO_2 from the same calibrated plenums used in the first estimate, but calibrated with mercury), the assumption is made that $V_{4\ cc}$

remained unchanged to 1999 whence:

$$V_{4\,cc} = 3.79593 \ cc.$$

3. NOAA/CMDL based estimate.

On the assumption that the NOAA/CMDL manometric calibrations of their primary reference gases are correct our manometric measurements on 7 of these gases in 1999 gives:

$$V_{4\,cc} = 3.7944 \ cc.$$

4. Stable mole fraction estimate (X99A scale).

On the assumption that our primary reference gases did not drift after 1985, and therefore that $V_{4\,cc}$ decreased after 1990 (the basis for Table 2), our manometric measurements of these gases in 1999 give, instead of estimate 2:

$$V_{4\,cc} = 3.7927 \ cc.$$

Volume estimate 1, which makes use of our ECM, however, is based on the 1999 calibration of plenum volumes using water, whereas estimates 2 and 4 are based on the plenums calibrated with mercury. (Estimate 3 makes no use of plenums). Only plenum numbers 3, 6, and 7 were employed in both the water and mercury calibrations of chamber volumes. The weight-average of data for these plenums indicates that the water-calibrated 4 cc chamber volume should be 0.00147 cc lower than as determined using the mercury-calibrated plenum volumes [Guenther et al., 2001]. If the water calibration is used in place of the mercury calibration for estimate 2, the basis of the X99B scale, we have the result:

5. Direct plenum estimate of CMM using water:

$$V_{4\,cc} = 3.79446 \ cc.$$

in very satisfactory agreement with estimate 3, based on the NOAA/CMDL manometric calibration scale. Substituting water as a calibrating medium for mercury, when applied to the X99A scale, leads, however, to a disagreement of the same magnitude in place of the good absolute agreement shown in Table 2.

The range of values, 3.7961 cc to 3.7927 cc, produces a range in calculated mole fraction of 0.32 ppm for a gas with a mole fraction of 350 ppm. The NOAA-based estimate lies approximately half way between the highest and lowest of the four estimates. Until now we have provisionally accepted the fourth estimate (associated with the X99A scale) as our preferred scale, because, in the absence of other evidence, a small differential drift between the SIO/CDML and SIO/CDRG gases should reflect little absolute drift by either set of primary standard reference gases.

We are confronted, however, with what appears to be a decisive finding that $V_{4\,cc}$ did not drift significantly from 1991 to 1999, as described in an Addendum to our main calibration report [Guenther et al., 2001]. On the basis of reanalysis of archived samples using the ECM (see the first estimate), the drift rate of the 4 cc chamber is found to be upward by 0.000103 cc/year, a value similar to the standard error of the slope of 0.000082 cc; whereas the drift implied by the X99A scale is equivalent to a downward drift of 0.00034 cc/yr ((3.7961 cc − 3.7927 cc) ÷ 10 yr), a difference in rate that is 5 times the standard error of the slope. Furthermore, the estimate of $V_{4\,cc}$ by the ECM method, (first estimate above), agrees within 0.0002 cc (equivalent to 0.02 ppm for a mole fraction of 350 ppm), with the well determined second estimate, above.

We are thus confronted by two possibilities, drifting reference gases or changing performance of CMM. The former appears to be at odds with the small differential drift found between SIO/CDRG and NOAA/CMDL gases, but the ECM data tend to rule out a drifting 4 cc chamber volume. If the gases drifted but the manometer was stable, the absolute disagreement is given by comparing the first and third, second and

third, or fifth and third estimates, a discrepancy in $V_{4\ cc}$ of about 0.0016 cc, (0.15 ppm at 350 ppm, NOAA/CMDL scale lower in 1999) or less. If the gases of both laboratories are almost free of drift, the third and fourth estimates apply, indicating a discrepancy of almost the same magnitude in the opposite direction. It is also possible within the precision of our measurements, that both the gases and the manometer drifted. Without restoration of our CMM, and with no prospect at present to replace it at SIO with another device we are unable to carry on experiments to resolve this evident dilemma. A decision on establishing a new provisional scale for reporting SIO/CDRG atmospheric CO_2 data is pending.

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Table 1. SIO/CDRG infrared measurements in 1999 of NOAA/CMDL CO_2-in-air primary reference gas standards, expressed in X99NA scale as CO_2 mole fractions in ppm.

Analysis Date	Cyl. No. 110	Cyl. No. 102	Cyl. No. 111	Cyl. No. 130	Cyl. No. 121	Cyl. No. 103	Cyl. No. 139	Cyl. No. 105	Cyl. No. 136	Cyl. No. 146	Cyl. No. 101	Cyl. No. 106	Cyl. No. 123	Cyl. No. 107	Cyl. No. 132
21-Apr-99	246.55	304.16	323.90	337.34	349.37	353.25	360.94	369.43	381.42	389.74	396.40	412.24	423.19	452.95	521.03
3-Jun-99	246.64	304.24	323.89	337.25	349.33	353.08	360.90	369.48	381.42	389.71	396.42	412.16	423.15	453.05	520.87
28-Jun-99	246.25	304.27	323.97	337.31	349.49	353.39	361.07	369.52	381.54	389.64	296.41	412.22	423.20	453.05	520.63
2-Jul-99	246.74	304.27	323.92	337.21	349.33	353.25	360.89	369.39	381.34	389.61	396.42	412.21	423.27	453.19	521.31
14-Jul-99	246.35	304.29	323.94	337.20	349.30	353.14	360.83	369.34	381.30	389.57	396.29	412.09	423.09	453.08	521.36
Average	246.50	304.24	323.93	337.26	349.36	353.22	360.93	369.43	381.40	389.65	396.39	412.18	423.18	453.06	521.04
StDev	0.20	0.05	0.03	0.06	0.08	0.12	0.09	0.07	0.09	0.07	0.06	0.06	0.06	0.08	0.31

Table 2. Comparison of NOAA/CMDL manometric and SIO/CDRG infrared analyses, from 1991 to 1999, of NOAA/CMDL primary reference gas standards, expressed in X99A and X99NA scales as CO_2 mole fractions in ppm.

Cylinder No.[b]	NOAA/CMDL[c]	SIO/CDRG Results and Differences (SIO/CDRG–NOAA/CMDL), by year[a]									
		1992[d]		1996[d]		1997[d]		1999[d]		1999[e]	
		SIO	Diff.	SIO	Diff.	SIO	Diff.	SIO	Diff.	SIO	Diff.
110*	246.59	246.71	0.12	246.56	-0.03	246.61	0.02	247.66	1.07	246.50	-0.09
102	304.39	304.44	0.05	304.35	-0.04	304.26	-0.13	304.51	0.12	304.24	-0.15
111*	323.96	324.05	0.09	324.00	0.04	323.97	0.01	323.98	0.02	323.93	-0.03
130	337.27	337.29	0.02	337.28	0.01	337.24	-0.03	337.19	-0.08	337.26	-0.01
121	349.35	349.35	0.00	349.38	0.03	349.36	0.01	349.22	-0.13	349.36	0.01
103	353.37	353.18	-0.19	353.23	-0.14	353.18	-0.19	353.06	-0.31	353.22	-0.15
139*	360.92	360.78	-0.14	360.88	-0.04	360.90	-0.02	360.73	-0.19	360.93	0.01
105*	369.35	369.31	-0.04	369.40	0.04	369.46	0.11	369.19	-0.16	369.43	0.08
136*	381.33	381.25	-0.08	381.29	-0.04	381.40	0.07	381.15	-0.18	381.40	0.07
146	389.50	389.48	-0.02	389.62	0.12	389.63	0.13	389.40	-0.10	389.65	0.15
101*	396.34	396.22	-0.13	396.26	-0.08	396.33	-0.01	396.14	-0.20	396.39	0.05
106	412.02	411.92	-0.10	412.08	0.06	412.14	0.12	411.98	-0.04	412.18	0.16
123	423.03	422.88	-0.15	423.03	0.00	423.10	0.07	423.04	0.01	423.18	0.15
107*	453.22	452.72	-0.50	453.00	-0.22	453.07	-0.15	453.18	-0.04	453.06	-0.16
132	521.30	520.77	-0.53	521.37	0.07	521.57	0.27	522.28	0.98	521.04	-0.26
Av. of 15			-0.11		-0.01		0.02		0.05		-0.01
s_i			0.19		0.09		0.12		0.41		0.13
Av. of 7[f]			-0.10		-0.05		0.00		0.05		-0.01
s_i			0.20		0.09		0.08		0.46		0.09

Notes:

[a] Years refer to periods of APC analyzer measurements at SIO/CDRG (see Section 5 of text, for inclusive dates).

[b] Subset of standards that were manometrically analyzed by SIO/CDRG in 1999, shown by stars (cylinder 103 omitted).

[c] Manometric measurements reported by NOAA/CMDL.

[d] SIO/CDRG APC analyzer measurements converted to mole fractions using X99A calibration scale.

[e] SIO/CDRG APC analyzer measurements in 1999, adjusted as described in this report, and converted to mole fractions using X99NA scale.

[f] Those with asterisks.

Table 3. Comparison of NOAA/CMDL manometric and SIO/CDRG infrared analyses, from 1991 to 1999, of NOAA/CMDL primary reference gas standards, expressed in X99B and X99NB scales as CO_2 mole fractions in ppm.

Cylinder No.[b]	NOAA/CMDL[c]	1992[d] SIO	1992[d] Diff.	1996[d] SIO	1996[d] Diff.	1997[d] SIO	1997[d] Diff.	1999[d] SIO	1999[d] Diff.	1999[e] SIO	1999[e] Diff.
		SIO/CDRG Results and Differences (SIO/CDRG–NOAA/CMDL), by year[a]									
110*	246.59	246.76	0.17	246.71	0.12	246.82	0.23	247.87	1.28	246.71	0.12
102	304.39	304.50	0.11	304.55	0.16	304.51	0.12	304.77	0.38	304.50	0.11
111*	323.96	324.12	0.16	324.21	0.25	324.24	0.28	324.25	0.29	324.20	0.24
130	337.27	337.36	0.09	337.50	0.23	337.53	0.26	337.48	0.21	337.55	0.28
121	349.35	349.42	0.07	349.61	0.26	349.65	0.30	349.52	0.17	349.66	0.31
103	353.37	353.26	-0.12	353.46	0.09	353.48	0.11	353.36	-0.01	353.52	0.15
139*	360.92	360.86	-0.06	361.12	0.20	361.20	0.28	361.03	0.11	361.23	0.31
105*	369.35	369.39	0.04	369.63	0.28	369.77	0.42	369.50	0.15	369.75	0.40
136*	381.33	381.33	0.00	381.54	0.21	381.72	0.39	381.47	0.14	381.73	0.40
146	389.50	389.56	0.06	389.88	0.38	389.96	0.46	389.72	0.22	389.99	0.49
101*	396.34	396.30	-0.04	396.52	0.18	396.66	0.32	396.48	0.14	396.73	0.39
106	412.02	412.01	-0.01	412.35	0.33	412.49	0.47	412.33	0.31	412.54	0.52
123	423.03	422.97	-0.06	423.30	0.27	423.45	0.42	423.40	0.37	423.54	0.51
107*	453.22	452.82	-0.40	453.30	0.08	453.45	0.23	453.56	0.34	453.45	0.23
132	521.30	520.89	-0.41	521.71	0.41	522.01	0.71	522.72	1.42	521.48	0.18
Av. of 15			-0.03		0.23		0.33		0.37		0.31
s_i			0.18		0.10		0.15		0.41		0.14
Av. of 7[f]			-0.02		0.19		0.31		0.35		0.30
s_i			0.19		0.07		0.07		0.42		0.11

Notes:

[a] Years refer to periods of APC analyzer measurements at SIO/CDRG (see Section 5 of text, for inclusive dates).

[b] Subset of standards that were manometrically analyzed by SIO/CDRG in 1999, shown by stars (cylinder 103 omitted).

[c] Manometric measurements reported by NOAA/CMDL.

[d] SIO/CDRG APC analyzer measurements converted to mole fractions using X99B calibration scale.

[e] SIO/CDRG APC analyzer measurements in 1999, adjusted as described in this report, and converted to mole fractions using X99NB scale.

[f] Those with asterisks.