

SCRIPPS REFERENCE GAS CALIBRATION SYSTEM
FOR CARBON DIOXIDE-IN-NITROGEN AND CARBON DIOXIDE-IN-AIR STANDARDS:
REVISION OF 1999

A Report Prepared for the Global Environmental Monitoring Program
of the World Meteorological Organization

by

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Glossary of Terms

APC Infrared Analyzer

A nondispersive infrared (NDIR) analyzer made by the Applied Physics Corporation (APC) in 1956 and used by the Carbon Dioxide Research Group (CDRG) for atmospheric CO₂ and reference gas measurements ever since.

Barometer Correction

A correction applied to the Fortin barometer reading to adjust it to the corresponding reading of the constant-volume mercury-column manometer (CMM). The correction is determined by making the CMM function as a barometer, then simultaneously reading both instruments. The barometer reading has always been higher than that of the CMM, in the range 0.1 to 0.4 mm Hg.

Calibration

Standardization, absolute or relative, of a measurement, or of a volume, or of a reference gas system.

Calibration Scale

A set of calibration equations, valid for the history of CDRG measurements, that describe the relationship between APC analyzer J-index and CO₂ mole fraction. It is designated by "X" and two digits of the calendar year of the most recent calibration event, e.g. "X97" for the calibration scale valid up to, and including, a central date in 1997.

Carbon Dioxide Research Group

Research group in the Geosciences Research Division of Scripps Institution of Oceanography, University of California, San Diego. Principal Investigator is Charles D. Keeling. Abbreviation is CDRG.

Cathetometer

In general, a device used to measure distance. Specifically, the cathetometer used to measure mercury-height levels in the CMM is a high-precision instrument made by Fred Henson and Company of Pasadena in 1956 from a design of the Chemical Engineering Department of the California Institute of Technology. A telescope with an aligning crosshair moves on a lead screw of 1-meter length and with a pitch of 1-mm. Turns of the screw are counted mechanically, with a least count of .01 mm in vertical height and a readability of .002 mm. The stated precision is .005 mm.

Central Date

The average date of an infrared calibration event, consisting (since 1985) of five marathon calibration days. The central date is the day when the cubic calibration equation of a given year applies: between central dates an interpolated calibration applies.

Chamber

A space, or volume, in the CMM defined by glass surfaces, a mercury surface, a glass pointer, and in some cases a greased stopcock. For CO₂ reference gas measurements, the important chambers are the nominally 4 cc chamber, in which the CO₂ gas fraction is measured, and the nominally 5000 cc chamber, in which the total gas fraction is measured.

Constant-Volume Mercury-Column Manometer [CMM]

The instrument used by the CDRG to measure absolutely the CO₂ mole fraction in reference gases. It has been described in Keeling et al. [1986] and in earlier reports. The abbreviation is CMM.

CO₂ Gas Fraction

The CO₂ gas removed from the total gas fraction by cryogenic extraction and transferred into the nominally 4 cc chamber of the CMM for measurement of pressure and temperature. The gas is dried by repeated sublimations at -78°C. In the case of natural-air reference gases, the CO₂ fraction also contains N₂O gas in the ratio of approximately one part in one thousand.

CO₂ Mole Fraction [X]

The concentration of CO₂ (symbol "X") calculated from the manometric measurement of primary reference gases, specifically meaning the ratio of moles of CO₂ to moles of total gas. This may also be termed a "mixing ratio" and is dimensionless.

Cubic Calibration Equation

Third degree polynomial expressing the non-linear relationship between APC analyzer response, as J-index, and manometric CO₂ mole fraction. A cubic calibration equation is determined from the measured J-indices of a set of manometrically calibrated primary reference gases run on the APC analyzer during a set of marathon calibration days.

Fortin Barometer

A standard mercury-column meteorological barometer used to measure ambient atmospheric pressure.

Imprecision

An estimate of the repeatability or reproducibility of a measurement, either from a set of replicate measurements of similar quantities, for example the mole fraction of CO₂ of a suite of primary reference gases, or from a set of repeat measurements, for example of the calibrated volume of a manometric chamber. The measure of the imprecision is the sample standard deviation, assuming a normal distribution of results.

Index Scale, I or J

A scale, linearly related to the APC infrared analyzer response, expressed in units close to CO₂ mole fraction in ppm. All data are initially recorded on the I index scale. A linear transformation converts the I index scale to the J index scale, established in 1959 on the basis of manometric calibrations.

Individual Determination

Calibration measurements of CO₂ gas in the 4 cc chamber of the CMM are routinely made in duplicate and occasionally in triplicate or more, if a measurement is suspect. Each measurement is an "individual determination." For reference gas calibrations, two measurements of the CO₂ gas fraction routinely are combined with one measurement of the total gas fraction to yield two determinations of the CO₂ mole fraction for each calibration called a "run" (qv).

Manometric Volume Ratio [VR]

The ratio of the calibrated volume of the nominally 5000 cc chamber to that of the nominally 4 cc chamber of the CMM. The mole fraction, calculated from manometric data, is inversely proportional to the volume ratio used in the calculation. May be abbreviated to Volume Ratio.

Marathon Calibration Day

A single set of measurements on the APC infrared analyzer during which all the primary reference gases, both N₂ and natural-air, are run together with the system secondary standard reference gases. Since 1985 the number of primary reference gases run each year has varied from 22 to 25.

Meniscus Correction

A correction applied to mercury height measurements in the CMM to account for differences in the diameter of the mercury columns because the mercury level is depressed in small tubes. The 4 cc chamber measurement is affected by such a difference, since the sample column diameter is smaller than that of the vacuum column. The correction is measured with a vacuum in both columns and is approximately 0.3 mm in magnitude. The diameter of the 5000 cc chamber column and its corresponding vacuum column are the same, but a meniscus correction is still measured and applied to account for a possible out-of-level swing in the telescope of the cathetometer.

Natural-Air Primary Reference Gas

One of a suite of primary reference gases with natural-air carrier gas. These were first used in 1974. Since 1981 a suite of 12 natural-air primary reference gases has been maintained. May be abbreviated to Air Primary Reference Gas.

N₂ Primary Reference Gases

One of a suite of primary reference gases with N₂ carrier gas (i.e. no O₂). These have been in use since 1959. In 1999 the suite consisted of 13 gases, three of which have been in use since 1970.

Plenum

One of a set of 7 Pyrex glass vials equipped with greased stopcocks. The contained volumes of the plenums (from 1.2 to 2.7 cc) have been determined by weighing them filled with mercury and also water. A prescribed number of moles of CO₂ is defined by filling a plenum with CO₂ gas to a known pressure at a known temperature. Measurement of the pressure and temperature of the gas after its transfer into the 4 cc chamber of the CMM yields the volume of that chamber relative to the volume of the plenum.

Primary CO₂ Reference Gas Standard

One of a number of reference gases with assigned absolute CO₂ concentrations and used to define a calibration scale for the infrared analyzer. The CO₂ concentrations have been determined by measurement in the CMM of the CDRG. May be abbreviated to Primary Reference Gas.

Primary Reference Gas System

The suite of primary reference gases, containing as carrier gas either N₂ or natural-air, and their use to calibrate measurements of CO₂ in the atmosphere by

the CDRG.

Reference Gas

A gas mixture contained in a high-pressure cylinder (to 2200 psi) and used as a standard for the measurement of atmospheric CO₂. The proportion of CO₂ gas is in the vicinity of that found in the atmosphere (300 to 380 parts per million (ppm) by volume during time of this project.) The remainder of the gas mixture, the "carrier gas", may be composed of N₂ gas, or of natural air, or of synthetic air (usually containing O₂ at close to the atmospheric proportion but no argon gas).

Run

An independent manometric analysis of a reference gas or volume calibration. For the former, a "run" is the analysis of a single aliquot of a reference gas removed from the high pressure gas cylinder. The "run result" is routinely the average of two individual determinations of the CO₂ mole fraction. Reference gas runs are always made in replicate, usually in duplicate.

Sample Standard Deviation [s_i]

Statistical quantity that estimates the dispersion, or imprecision, of a set of measurements, assuming the normal law of error. For a set of repeat measurements, the equation used to calculate s_i is as follows:

$$s_i = \left[\frac{\sum d_i^2}{(n-1)} \right]^{1/2}$$

where d_i is the difference of an individual measurement from the mean of n measurements. For a set of replicate measurements, the equation used is given in the main text (equation (3)).

Secondary Standard Reference Gases

A set of three reference gases consisting of CO₂-in-N₂ used to calibrate the APC analyzer on routine calibration days. The difference in analyzer response between two span gases is used to define the sensitivity of the analyzer for the day, expressed as an index per recorder scale division. An additional "transfer" secondary gas is directly compared to the unknowns during the day. The index values of the secondary standards are determined from those of previous secondary standards. Periodically they are directly compared with the primary reference gases during sets of marathon calibration days.

Total Gas Fraction

An aliquot of reference gas removed from a high-pressure gas cylinder, dried and measured for pressure and temperature in a nominally 5000 cc chamber of the CMM.

1. Introduction

The Carbon Dioxide Research Group (CDRG) of the Scripps Institution of Oceanography (SIO), in its role as the Central Calibrating Laboratory (CCL) of the Background Air Pollution Monitoring Network (BAPMoN) of the World Meteorological Organization (WMO) from 1975-1995, maintained primary reference gases for the measurement of the mole fraction (X) of carbon dioxide (CO_2) in the atmosphere. The CDRG has continued to maintain these gases for use by SIO and to provide further cross-calibration with other laboratories. The last formal report of calibrating activities at SIO was published in 1986 [Keeling et al., 1986]. This report summarizes the activities of the CDRG since 1985 and describes calibration scales valid for the period up to January 1, 1999, including a comprehensive new calibration completed in January, 1999.

2. Summary of Activities

Procedures adopted in 1985 for the calibration of the primary reference gas system of the CDRG [Keeling et al., 1986] have been followed closely since at intervals of one to three years, the average interval being 2 years. On each occasion a set of primary reference gases, one set using N_2 as carrier gas, and another using natural air, were analyzed on the same Applied Physic Corporation (APC) non-dispersive infrared (NDIR) gas analyzer together with three secondary gases used in routine measurements of atmospheric CO_2 . Analysis consisted of determining the instrument response of each gas, expressed as an index value, J . Each calibration, linking the CO_2 concentrations of our primary reference gases to those of secondary rank, took approximately 24 hours to complete, an effort that we call a "marathon calibration day". Five such marathon days were carried out over about 6 weeks to complete each episode of calibration. Since 1985 infrared calibrations have taken place in 1987, 1989, 1990, 1993, 1995, 1997, and 1999.

In addition primary reference gases were analyzed manometrically with a constant-volume mercury-column manometer (CMM) in 1985, 1990, 1993, 1995 and 1998. (In 1995 only natural-air standards were measured.) These manometric calibrations determined the mole fraction of CO_2 (symbol, X) in each reference gas by measuring the temperature and pressure of the original gas mixture in a 5000 cc chamber of the CMM, then stripping out the CO_2 in a cold trap, and measuring its temperature and pressure in a 4 cc chamber of the CMM.

After carrying out each set of APC gas analyzer calibrations, "cubic calibration equations" of the form $X = C_0 + C_1J + C_2J^2 + C_3J^3$ were computed relating the response of the analyzer, in J index, to the manometric concentrations of the reference gases expressed as mole fractions, X . The manometric concentrations used to formulate each cubic calibration equation were those measured nearest in time to the J index values determined in each marathon calibration, as indicated below in Table 7.1. Each cubic equation defines a calibrating scale assumed to be valid on the "central date," defined as the average date of the 5 marathon days of a particular episode of APC calibrations. The scale for a particular year is designated by X followed by the last two digits of the year, thus "X85 scale" for the scale established in 1985. Each scale comprises a set of equations which define the system's calibration for all periods of time from its inception in 1957 up to and including the designated year. The most recent scale before the completion of this report was the X97 scale. Additionally, the volume of the 4 cc chamber of the CMM was calibrated relative to a set of volume-calibrated "plenums" four times: in 1988, 1990, 1993-1994, and in 1998-1999.

Tbl 7.1

Another major activity of the CDRG has been mutual intercalibration of reference gases with other WMO programs. The Climate Modeling and Diagnostics Laboratory (CMDL) of the U.S. National Oceanic and Atmospheric Administration (NOAA, Boulder, Colorado), the CCL of the WMO since 1995, has rotated sets of reference gases between the WMO laboratories which our laboratory has analyzed against our secondary gases using the APC analyzer. Such exercises, dubbed "Round Robins," were carried out in 1991, 1996, and 2000, to be reported elsewhere. Still further calibrations of reference gases of other individual programs using the APC analyzer have also been carried out at CDRG; in particular, reference gases from Tohoku University, Sendai, Japan in 1987, the Atmospheric Environment Service of Canada (AES) in 1991 and 1995, and CMDL in 1991-1993, 1995-1996, 1997, and 1999. The latter gases were a set of primary natural-air gases from the CMDL, manometrically calibrated previously by that laboratory beginning in 1996. This last effort has provided a precise intercalibration between the past and present CCL's reported by Guenther et al. [2002].

Derivation of the cubic calibration equations is influenced by the assigned manometric volume ratio (VR, see glossary), which has been determined from precise measurements of the volumes of the 4 cc and 5000 cc chambers of the CMM. The volume ratio used to compute these equations has been adjusted from time to time. Highly precise determinations were first made in 1974 resulting in a volume ratio of 1320.61 [Guenther, 1981], which was applied retrospectively to calibration equations

for prior years.

This volume ratio was also applied to calibration equations in succeeding years. However, during the early 1980's the performance of the 4 cc chamber degraded, owing to mercury in the column slowly becoming dirty. The mercury was cleaned in 1984. A time-varying effective volume was then assigned to the chamber for the period of dirty mercury. This assignment was arrived at by assuming that our primary reference gases in use at the time on average had not drifted in concentration of CO₂ from 1974 to 1985. The volume ratio assigned for 1985 was 1321.80 [Keeling et. al, 1986]. This volume ratio was then adopted in establishing subsequent calibrating scales through X97.

The volume of the 5000 cc chamber was established precisely only once in 1974 as reported by Guenther [1981]. A slightly different, preliminary value was assigned, however, in determining both volume ratios quoted above, and the volume ratios established for the period of dirty mercury. In this report, as explained in section 6, below, the published value is adopted in determining the VR for all years of our measurements of atmospheric CO₂. In this report we have also reevaluated the volumes to be assigned to both the 4 cc and 5000 cc chambers, resulting in new cubic calibration equations for the entire period of our measurements of atmospheric CO₂ back to 1957.

3. Manometric Reference Gas Calibrations

The mole fraction ratio of CO₂ gas to total gas of each gas mixture (CO₂ plus carrier gas), is calculated from manometric data of the CMM using an equation derived from the virial equation of state, described by Guenther and Keeling [1981]:

$$\frac{n_C}{n_G} = \frac{10^6 V_C B_G}{V_G B_C} \times \frac{1 - \left[1 + \frac{4P_C B_C}{RT_C} \right]^{1/2}}{1 - \left[1 + \frac{4P_G B_G}{RT_G} \right]^{1/2}} \quad (1)$$

where:

- (1) Subscripts C and G refer to the measurement of CO₂ in the 4 cc chamber of the CMM and of the total gas in the 5000 cc chamber, respectively.
- (2) V_G/V_C is the ratio of the volume of the 5000 cc chamber to that of the 4 cc chamber (dimensionless).
- (3) The pressure P and temperature T are expressed in dynes cm⁻² and °K, respectively.
- (4) B_C and B_G are the temperature-depended second virial coefficients for CO₂ and for the total gas, respectively, in cm³/mol.
- (5) R is the gas constant, taken as 8.31436×10^7 ergs mol⁻¹ °K⁻¹.

The pressure P is calculated from the difference between two measured heights of mercury in the CMM by the equation

$$P = \Delta h \times \rho_{Hg} \times g \quad (2)$$

where:

Δh = the observed mercury height difference, in cm

ρ_{Hg} = the temperature-dependent density of mercury, in g/cm³.

g = the acceleration of gravity at 32°52'N, taken to be 979.558 cm sec⁻².

The observed mercury height differences have been adjusted by meniscus corrections to account for differing sizes of the glass tubing on the vacuum and sample columns and for non-level swing of the cathetometer telescope. The column housing the 4 cc chamber has a smaller diameter than its corresponding vacuum column, resulting in a meniscus correction of approximately -0.3 mm. The column housing the 5000 cc chamber has the same diameter as the corresponding vacuum column, thus a nominal meniscus correction of zero, but in practice a small value. Meniscus corrections for both the 4 cc and 5000 cc chambers were measured concurrent with the reference gas measurements during each episode of manometric calibrations by comparing the heights of the sample and vacuum columns of the CMM with a vacuum above each column. (See section 5, below for a description of the CMM). Meniscus corrections applied for all measurements are listed in Appendix A1.

Manometric measurements and calculations for the N₂ and natural-air primary reference gases for the five episodes from 1985 through 1999 are listed at the end of

this report, in a special section 9 devoted to data tables. In Tables 9.1a to 9.1i of this section calculations of the mole fraction (X) are listed based initially upon the manometric volume ratio of 1320.61 determined in 1974. The mole fractions are reported in parts per million (ppm) after reduction of the water vapor content of the gas mixture to about 5 ppm. The results are listed to two decimal places under the column headings "Individual Determinations" and "Run Average." The individual determinations derive from replicate measurements (usually two) of the CO₂ gas fraction in the 4 cc volume manometric column and a single measurement of the total gas fraction in the 5000 cc volume manometer.

The procedures followed for making these measurements have remained basically unchanged since they were described by Guenther and Keeling [1981] for calibrations done in 1974. Appendix A1 of this report lists all the original mercury-column data from 1969 to 1999 and the calculated mole fractions of CO₂, as copied to Table 9.1. The column headed "Run Difference" in Table 9.1 lists the difference between independent "run averages," which refer to determinations of the mole fraction of CO₂ of two separate aliquots of total gas drawn from the reference gas cylinder. In cases where there are more than two such runs, the column lists the differences between adjacent runs (1 and 2, 2 and 3, etc.). Finally, the average of all measurements, usually four individual determinations, is listed under the column heading "Overall Average". Beginning with this column, the data are tabulated to three decimal places to avoid rounding problems at the hundredth place. Under the column heading "Volume Adjusted," the averages are converted from the manometric volume ratio (VR) based on the 1974 volume calibration (1320.61) to the VR assigned in 1985 (1321.80) [Keeling et al., 1986].

The natural-air reference gases contain approximately the background atmospheric abundance of N₂O, about 1 part in 1000. This latter gas is measured manometrically as part of the extracted CO₂ gas fraction. The amount of N₂O in each reference gas, determined by gas chromatography in the laboratory of R.F. Weiss at SIO [Bacastow et al., 1983a] is listed on Tables 9.1b, 9.1d, 9.1f, 9.1g, and 9.1i and has been subtracted in the last column to produce the true CO₂ mole fraction.

The data in Table 9.1 include two sets of replicates, one replicate of individual determinations of the CO₂ gas fraction on the small manometer combined with a total gas fraction measurement, and another replicate of runs of the reference gas. Estimates of imprecision are derived from replicate data. The sample standard deviation, s_i , of an individual measurement is calculated by the expression [Laitinen, 1960, p. 548]:

$$s_i = \left(\frac{\sum d_i^2}{N_a - N_f} \right)^{1/2} \quad (3)$$

where

d_i = deviation of an individual measurement from the mean of a set

N_a = total number of measurements

N_f = number of sets of measurements

Table 3.1 lists the sample s_i 's from the sets of individual determinations, for each calibration year and type of gas mixture.

Tbl 3.1

Table 3.1. Imprecision of Manometric Data from Replicate Measurements in the 4 cc Chamber

Year	No. of Gases		<u>Replicate Determination Data</u>			
	Air	N ₂	Air		N ₂	
			No. of Det'ns	s_i (ppm)	No. of Det'ns	s_i (ppm)
1985	12	11	52	.032	48	.048
1990	12	11	50	.072	48	.046
1993	11	14	46	.073	56	.070
1995	11		42	.044		
1998	12	13	44	.066	52	.063

These sample s_i 's represent an estimate of the short-term imprecision, or repeatability, of manometric measurements, arising mostly from errors pertaining to the 4 cc chamber measurements.

A similar calculation of the s_i 's from the replicate run data, estimates the imprecision of an entire calibration on the manometer including the gas transfer and extraction of the CO₂ fraction. Table 3.2 lists these s_i 's for each calibration year and type of gas mixture.

Tbl 3.2

Table 3.2. Imprecision of Manometric Data from Replicate Run Data

Year	No. of Gases Air N ₂		Replicate Run Data					
			Air		N ₂		All Gases	
			No. of Runs	s_i (ppm)	No. of Runs	s_i (ppm)	No. of Runs	s_i (ppm)
1985	12	11	24	.067	24	.065	48	.066
1990	12	11	24	.033	25	.063	49	.050
1993	11	14	22	.050	29	.072	51	.063
1995	11		22	.057			22	.057
1998	12	13	24	.049	26	.061	50	.056

These latter s_i 's better represent reproducibility during a given calibration year than those for the short term repeatability, because runs were made over a wide range of time-intervals: from hours to months. In 1998, for example, replicate runs were purposely made well separated in time. The calculated s_i for 1998 is the second best set of results in the whole data set since 1985. The most striking characteristic, however, is that the s_i 's for each year are so similar: the range in the s_i 's for the five data sets is only .016 ppm. Appendix A2 describes the s_i calculations in more detail.

Tbl 9.2a-b

Tables 9.2a and 9.2b summarize the history of manometric calibrations of the N₂ and natural-air primary reference gas standards, respectively. The data from 1985 to 1999 are as shown in Table 9.1, calculated using the 1985 assigned manometric volume ratio (1321.80). Data for earlier years are as reported previously by Keeling et al. [1984]. From 1981 to 1999, averages are listed below the columns for the sets of mixtures that were calibrated in every year. The progression of averages shows an evident upward drift in mole fractions of the full set of primary reference gases.

4. Infrared Analyzer Calibrations

In all of the years since 1985 in which infrared calibrations were made, both the primary reference gases in N₂ and in natural-air have been run on the APC nondispersive infrared (NDIR) gas analyzer following a highly consistent scheme. The routine calibration system of the APC analyzer uses two secondary standard reference gases, a principal and a high span, to determine the recorder scale factor (RSF), that defines the sensitivity of the instrument. Comparisons of the span gases were made at the beginning and end of each marathon calibration day and twice in between. A third

secondary standard gas - the "transfer" gas - is used as the reference to which all gases are directly compared. The primary reference gases were compared to the transfer secondary standard during each marathon day in order of increasing mole fraction. Eleven natural-air primary reference gases were run during each calibration period, excluding only one with a very low mole fraction (100 ppm) because it cannot be fit properly using a cubic equation to relate infrared and manometric data. The number of N₂ primary reference gases run during each calibration period has ranged from 11 to 14. One of the N₂ gases was retired after the 1993 calibration and three new gases were added beginning with the 1993 calibration.

Infrared analyzer data are initially recorded in index units, I, proportional to the response of the APC analyzer, as explained by Bacastow et al. [1983b], and approximately equal to mole fractions of CO₂ expressed in ppm of dry air. Results for the calibrations from 1985 to 1999 are shown in Tables 9.3a to 9.3p. The tables list the average index, I, for the stated number of comparisons shown in parentheses, almost always 10. Also shown in the tables are overall averages for each reference gas expressed in I units and also converted to a second index, J, defined by the linear equation

Tbl 9.3a-p

$$J = 1.2186(I - 311.51) + 311.51 \quad (4)$$

The J-index scale was formulated after a manometric calibration in 1959 to approximate better the mole fraction of CO₂ in ambient air than the previous I-index scale. The J scale is still expressed, however, in units that are proportional to the APC instrument response.

Table 9.3 lists the standard deviations, under the column heading "Sigma J," of daily measurements relative to the mean of all the days, for each reference gas during each calibration episode consisting of 5 marathon calibration days. The greater dispersion for extreme concentrations is due to the procedure of calculating the instrument sensitivity from the difference between the principal and high span secondary reference gas standards, which only differ by about 20 ppm in mole fraction. Errors in the determination of this sensitivity are magnified for gases with CO₂ concentrations far from the concentrations of the principal and high span secondary standards, chosen to be close to that of real air, owing to greater extrapolation than for concentrations near them. These errors are minimized by calculating an overall imprecision (root mean square deviation (RMS DEV)) for each calibrating episode, after carrying out a normalization procedure. In this procedure, which we call "tank concordance," the mean of the absolute differences in J index of each gas from J of the principal span

secondary standard is forced on each "marathon" day to be the same as the mean of these differences over all days of the calibration episode. This adjustment produces a best estimate of the infrared analyzer's linear recorder scale factor (sensitivity) for each day and removes the influence of the assigned J index of the high span secondary standard from the computation. In effect, the analyzer sensitivity is based on all the gas mixtures compared during the day, reducing the scatter for reference gases near the low and high ends of the concentration range [Bacastow et al., 1983b, p. 54]. The mean J index over all the calibration days remains, however, unchanged. The degrees of freedom used in computing the RMS DEV's summarized in Table 4.1 take into account the tank concordance adjustment.

Tbl 4.1

Table 4.1. Root Mean Square Deviations (RMS DEV) of Infrared Measurements*

Year	N ₂ Gases				Air Gases				Combined RMS DEV
	No. of gases	No. of Analyses	Degrees of Freedom	RMS DEV	No. of gases	No. of Analyses	Degrees of Freedom	RMS DEV	
1985	11	55	40	0.154	11	55	40	0.142	0.148
1987	11	55	40	0.135	11	55	40	0.132	0.134
1989	11	55	40	0.077	11	55	40	0.081	0.079
1990	11	55	40	0.069	11	55	40	0.064	0.067
1993	14	70	52	0.148	11	55	40	0.152	0.150
1995	13	65	48	0.195	11	55	40	0.166	0.182
1997	13	65	48	0.168	11	55	40	0.164	0.166
1999	13	65	48	0.123	11	55	40	0.113	0.118

* Expressed in J index units approximately the same as mole fraction of CO₂ in ppm.

5. Manometric Volume Calibrations

The CMM consists of two separate devices, a Large Volume Manometer and a Small Volume Manometer. Calibration of the CMM requires the determination of the volume ratio between a nominally 5000 cc chamber in the Large Volume Manometer, where the total gas fraction is measured, and a nominally 4 cc chamber in the Small Volume Manometer, where the CO₂ gas fraction is measured. As discussed in the 1986 WMO report [Keeling et al., 1986], the overall calibration, in practice, has consisted of separate absolute determinations of these volumes. The 4 cc chamber volume has been calibrated with respect to plenums directly calibrated for their volumes by weighing them filled with mercury or water, as discussed below. The 5000 cc chamber volume has been calibrated with respect to the volume of a 4000 cc flask in the CMM which had been weighed filled with water.

The Addendum to the WMO Report of 1986 [Keeling et al., 1986, p. 3-4] describes calibrations of the volumes of the 4 cc and 5000 cc chambers in 1974 and 1985. A laboratory report [Guenther, 1981] of the 1974 calibrations presented more details of procedure. Description of procedures will not be repeated here, except when procedures have changed or results are affected.

Large Manometer Volume Calibrations. The Large Volume Manometer contains three sample columns ("chambers"), each of approximately 5000 cc volume, connected to one vacuum column. Large Manometer chamber No. 1 was used for reference gas calibrations. The nominally 4000 cc volume in Large Manometer chamber No. 2, consisting of a glass flask with stopcock, was removed from the cabinet and weighed filled with water in 1974 to determine its volume for the first time. The volume of Large Manometer chamber No. 1 was determined relative to the volume of the calibrated flask by measuring the pressure and temperature of the same CO₂ gas aliquot in both Large Manometer chambers Nos. 1 and 2. Large Manometer chamber No. 3 has not been used. The calibration of the Large Manometer in 1974 was described by Guenther [1981].

Three calibrations of the 5000 cc chamber were made in 1974, all with reference to the calibrated 4000 cc flask volume of 3947 cc. The average of the three calibrations was 5015.09 cc. However, as discussed in Keeling et al. [1986], a preliminary value of 5014.9 cc was used, along with the 1974 average for the 4 cc volume, 3.7974 cc, to formulate a volume ratio (VR) of 1320.61, used from 1974 until 1983. This small correction, however, was still not applied in 1985, and the VR used from 1985 until this report, 1321.80, was still referenced to the preliminary volume of 5014.9 cc.

In 1980 two additional determinations of the volume of the 5000 cc chamber were made with reference to the volume of the 4000 cc flask of chamber No. 2. The volumes found were 5015.15 cc and 5015.20 cc. These agreed so closely with the average volume of 5015.09 cc found in 1974, that the latter value was accepted for use, instead of the overall average of 5015.12 cc ($s_i = 0.13$ cc) for the total of five determinations.

Small Manometer Volume Calibrations. The volume of the nominally 4 cc chamber of the Small Volume Manometer has been calibrated by the measurement of a known amount of CO₂ gas transferred into it. The known amount is established by filling glass vials ("plenums") with purified CO₂ gas to ambient atmospheric pressure, precisely measured on a Fortin barometer attached nearby on a wall, at a measured temperature.

The correct determination of the 4 cc chamber volume is critical to the relative stability of the manometric calibration. In 1983 and 1985, an apparent drift seen in the manometric measurements of the primary reference gas standards was attributed to an operational change in the effective volume of the 4 cc chamber, caused by progressive fouling of the mercury, that affected the meniscus shape and the contact of the mercury with the volume-defining glass pointer. The manometer was disassembled, cleaned, and reassembled with clean mercury in 1984.

Since the measurements reported in Keeling et al. [1986], additional volume calibrations of the 4 cc chamber were made with plenums in 1988, 1990, 1993-1994, and in 1998-1999. The 4 cc chamber volumes resulting from these calibrations, along with the previously reported 1985-86 data, are listed in Tables 9.4a to 9.4e. All listed volumes are referenced to the plenum volumes determined in 1974 by weighing them filled with mercury.

Tbl 9.4a-e

Two corrections have been applied to the mercury column measurements of the CMM and Fortin barometer. One type is the meniscus correction for the CMM mercury column readings at the pointer demarking the 4 cc chamber, accounting for differences caused by the smaller diameter of the sample column relative to that of the vacuum column. The meniscus correction is determined by comparing the mercury heights of the two columns with a vacuum above each. The measured correction was approximately 0.3 mm, the mercury being depressed in the smaller diameter tubing. The correction is thus subtracted from the "raw" mercury column height differences. Measurement and application of the meniscus correction has been described in detail [Guenther and Keeling, 1981, p. 16]. The meniscus corrections applied to the volume calibration measurements are listed in Appendix A3, along with the manometric mercury column data for all calibrations of the volume of the 4 cc chamber since 1974.

A second type of correction applies to the atmospheric pressure measurements made on the Fortin barometer. These barometer corrections account for differences between its readings and those made on the CMM. The corrections were determined by first making the CMM function as a barometer, i.e. with atmospheric pressure bearing on the sample column, and then making nearly simultaneous readings of the atmospheric pressure in the laboratory on the barometer and on the CMM. The temperature of the barometer was read on a thermometer attached to its mercury column and the temperature of the CMM on its thermometer, as during routine measurements. The readings of the two instruments were adjusted to the same temperature using the density of mercury. The difference between the measurements, in mm of mercury height, was designated as the "barometer correction" to be applied to the barometer

readings to normalize them to the CMM. The corrections were applied by subtracting the listed corrections from the "raw" barometer readings. As with the meniscus corrections, the barometer corrections were measured near the dates of each set of calibrations. They are listed with the mercury column data in Appendix A3.

Tbl 5.1

Table 5.1 lists the average 4 cc chamber volumes found for each set of volume calibrations, from Tables 9.4a - 9.4e, along with the meniscus and barometer corrections for each set.

Table 5.1. CMM 4 cc Chamber Volume Determinations, by Year

Year	Months	Meniscus Correction (mm)	Barometer Correction (mm)	Overall average		
				Volume (cc)	No. of Det'ns	s_i (cc)
1985-86	Oct-Jan	-0.340	-0.2	3.7955	15	.00070
1988	Feb-Mar	-0.294	-0.2	3.7961	15	.00082
1990	Feb,Oct	-0.313	-0.1	3.7962	21	.00128
1993-94	Oct-Feb	-0.288	-0.4	3.7939	14	.00185
1998-99	Dec-Jan	-0.208	-0.3	3.7953	22	.00220

Each 0.1 mm of barometer correction lowers the calculated 4 cc chamber volume by 0.0005 cc. Application of the corrections significantly increases the set-to-set variability of the volume calibrations. Table 5.2 compares the 4 cc chamber volumes obtained by applying the corrections listed in Table 5.1 with those obtained by setting the barometer correction to zero for all years.

Table 5.2. Effect of Barometer Corrections on 4 cc Chamber Volume Calibrations

Year	Average Volume, cc	
	With correction ^a	Without correction ^b
1974	3.7974	3.7974
1985-1986	3.7955	3.7965
1988	3.7961	3.7971
1990	3.7962	3.7967
1993-1994	3.7939	3.7959
1998-1999	3.7953	3.7968
Average(1974-1999)(s_i)	3.7957 (0.0012)	3.7967 (0.0005)
Average(1985-1999)(s_i)	3.7954 (0.0009)	3.7966 (0.0005)

^a Barometer corrections listed in Table 5.1 (no correction in 1974)

^b Barometer correction of 0.0

The overall average of the measured 4 cc chamber volume is lowered by 0.0010 cc by applying the measured barometer corrections. Further, the standard deviation calculated from either the set of all six average volumes (including the 1974 volume), or of the set of five since 1985, is approximately doubled by application of the barometer corrections. In addition to this increase in variability, it is also noteworthy that application of the measured barometer corrections increases the disagreement between the 1974 data and the post-1985 data. We elect to apply the measured barometer corrections (as well as meniscus corrections) to the data reported and discussed here because of the probability that the CMM measurements have a lesser absolute bias.

Discussion of Sets of Small Manometer Volume Calibrations, 1988-1999.

Two measurements using plenums P-4 and P-5 were rejected in 1988 because they appeared to be significantly biased from the results using the other plenums, a circumstance also found during the 1985-1986 calibrations. See Tables 9.4a and 9.4b. These two plenums have not been used in any subsequent calibrations reported here.

In 1988 the sample standard deviation of an individual volume measurement, irrespective of plenum (s_i), was calculated to be 0.00082 cc, comparable to the standard deviations calculated from the data of the 1974 and 1985-1986 calibrations. The average 4 cc volume found was 3.7961 cc, or 0.0006 (1 part in 6300) higher than the result of 1985-1986.

The calibration of the 4 cc chamber in 1990 had an almost identical average result, 3.7962 cc, but the s_i was significantly larger, approximately 1 in 3000. The 1985, 1988 and 1990 calibrations viewed together indicate that the volume of the 4 cc chamber remained stable to within approximately 1 part in 5000 after the cleaning of 1984. There was thus no sign of progressive change such as that previously found in 1983 and ascribed to fouling of the mercury.

The volume calibrations of 1993-1994, however, indicated a significantly lower apparent volume of the 4 cc chamber, determined to be 3.7939 cc. The change toward a lower volume is in the opposite direction from the change previously ascribed to mercury fouling. Furthermore, the s_i (for 14 measurements) increased again, to approximately 1 part in 2000.

The volume of the 4 cc chamber was calibrated again with plenums in December, 1998 and January, 1999, soon after primary reference gases had been measured manometrically. As shown in Table 5.1, the imprecision of the measurements was again still larger, but the average 4 cc chamber volume agreed more closely with the 1985-1990 data than did the 1993-1994 volume.

Prior to the 1998-1999 volume calibrations, the plenums were cleaned by ashing at 510°C in a glass-annealing oven and were freshly regreased. However, some replicate second and even a few third fillings of the plenums with CO₂ gas were made before the plenum stopcocks were again regreased. The volume calibrations made without regreasing the plenum stopcocks tend to produce larger volumes for the 4 cc chamber, especially for those plenums holding the CO₂ gas for a longer time. This effect could be due to CO₂ gas leaking out of the plenums through the stopcocks. There was no evidence that any non-condensable gases (i.e. from room air) had leaked into the plenums, however. For the last two sets of calibrations in 1998-1999, the plenums were regreased each time before refilling with CO₂ gas. If all of the runs made without regreasing the plenum stopcocks are removed from the data set (Nos. 3, 7 to 12), then 15 of 22 determinations remain. The average 4 cc chamber volume found for these 15 reduces by 0.0008 cc to 3.7945 cc and the s_i reduces to 1 in 2500 from 1 in 1700. Possible effects of the regreasing were subsequently checked for in the volume calibration sets of previous years. In 1993-1994, 9 of the 14 determinations were made without regreasing the plenum stopcocks. The remaining five had a resultant volume reduced by 0.0011 to 3.7928 cc, but there are too few data remaining to judge the significance of the difference between regreasing or not doing it. Table 5.3 summarizes the average calibration results for the volume of the 4 cc chamber, both for the overall data sets, after rejection of outliers, and for only those calibrations made immediately after regreasing the plenum stopcocks. For the data sets of previous years, 1985-1986, 1988, and 1990, a regreasing effect can not be detected. In 1988, all calibrations were made with freshly regreased plenums.

Table 5.3. CMM 4 cc Chamber Volume Determinations: Effect of Regreasing

Year	Overall average			Average retaining only measurements after regreasing		
	Volume (cc)	No. of Det'ns	s_i (cc)	Volume (cc)	No. of Det'ns	s_i (cc)
1985-86	3.7955	15	.00070	3.7955	13	.00057
1988	3.7961	15	.00082	3.7961	15	.00082
1990	3.7962	21	.00128	3.7961	17	.00134
1993-94	3.7939	14	.00185	3.7928	5	.00153
1998-99	3.7953	22	.00220	3.7945	15	.00148

Recent Recalibrations of Plenum Volumes. In July of 1999, Guy Emanuele of the CDRG recalibrated the volumes of the seven plenums by weighing them filled with water. Five of the plenums were calibrated four times each, and the remaining two, twice each. The imprecisions are satisfactory (s_i 's between 1 in 6000 and 1 in 15000), although they are somewhat larger than the imprecisions obtained in 1974 by weighing them filled with mercury (average of 1 in 15000). All of the resultant plenum volumes are smaller than those determined in 1974, although for plenums P-1, P-2, P-3, P-6, and P-7 the average difference is only 1 in 3000. The new determinations of volumes for Plenums P-4 and P-5 are smaller than the 1974 volumes by more than 1 in 1000. If the new plenum volumes are used to recalculate previous calibrations of the 4 cc chamber, calibrations using plenums P-4 and P-5 in 1985-1986 and 1988 then agree well with those using the remaining plenums. Since the volumes found using plenums P-4 and P-5 agreed with those using the other plenums in 1974, it seems that the effective volumes of plenums P-4 and P-5 significantly changed between 1974 and 1985, perhaps due to overheating in the oven. See Addendum to this report for more details.

6. Reevaluation of Calibrations of Primary Standard Reference Gases since 1985

Manometric measurements of primary reference gases since 1985 have hitherto been calculated assuming the CMM volume ratio assigned in 1985 be valid for calculating the mole fractions of the gases for all succeeding years, as noted in section 3 above (also see Table 9.2). The resulting mole fractions for these gases, together with APC infrared analyzer measurements (Table 9.3), were used to formulate cubic calibration equations for each year in which these measurements were made as explained in section 2, above. As discussed in section 5, calibrations of the volume of the 4 cc chamber indicated near constancy of the manometric volume ratio (VR) through 1990 but a possible decrease in VR thereafter.

The mole fractions of almost all of the primary reference gases calculated on the assumption of a constant manometric volume ratio showed evidence of drift at the time of the 1993 and 1995 manometric calibrations. A greater drift (one part in 1200) became evident at the time of the 1998 calibrations. This drift is seen in plots of the yearly average departures of manometric mole fractions from the 1985 value, for N_2 and air primary reference gases, in Figures 1a and 1b, respectively. (The data are from Tables 9.2a and 9.2b.) A progressively smaller effective volume of the 4 cc might explain the apparent upward drift for the reference gases. It is unlikely that the fault lies with the 5000 cc chamber, since a cumulative apparent drift of one part in

Fig 1a

Fig 1b

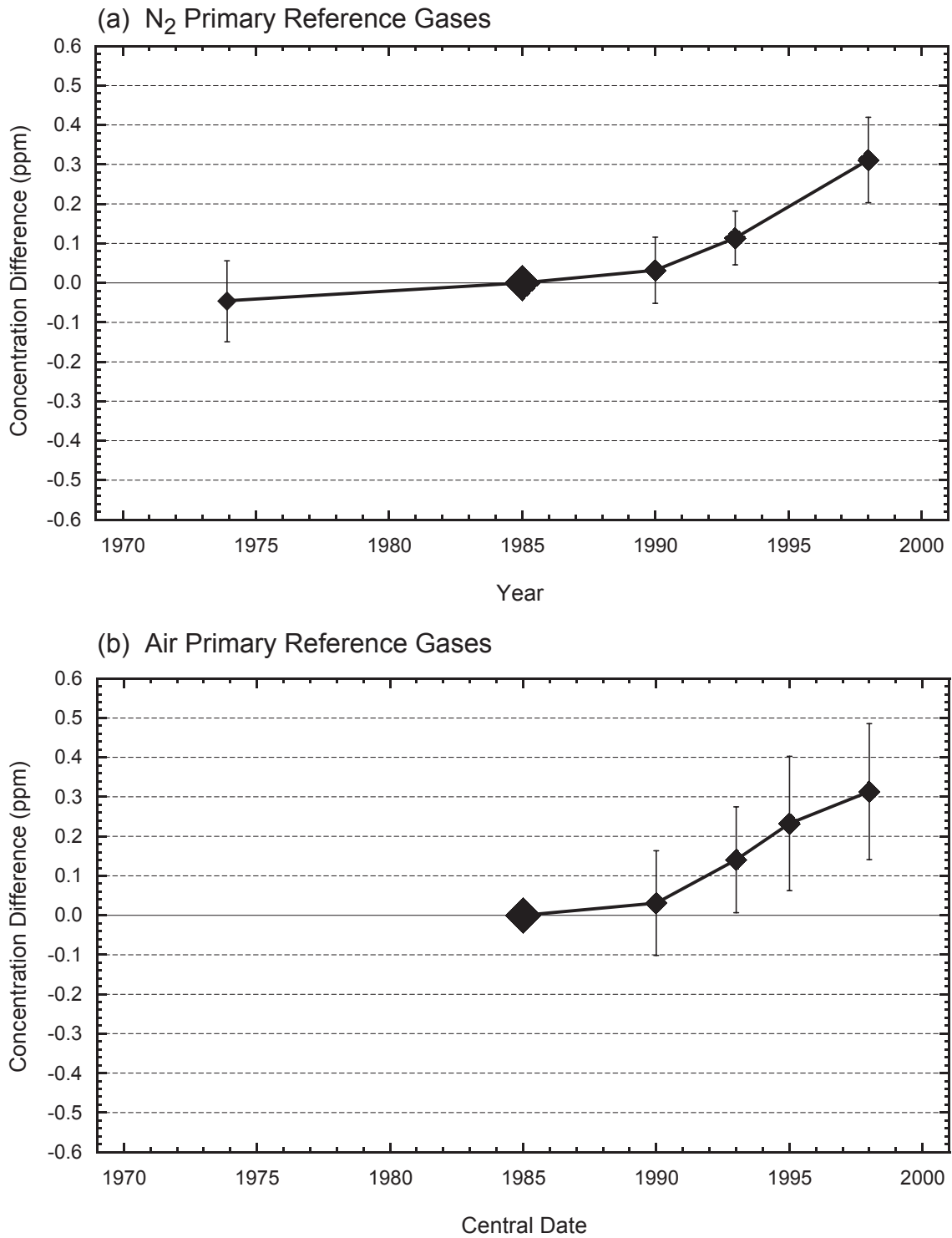


Figure 1. Average differences from the 1985 value of manometric measurements of a) N₂ and b) air primary reference gases, in mole fraction of CO₂, by year. Volume ratio of constant-volume mercury-column manometer is held constant, at 1321.80. Plotted averages are for a) 10 N₂ gases and b) 11 air gases analyzed in all years. Error bars represent +/- one standard deviation of an individual difference.

1200 from 1985 to 1998 would require a large, highly unlikely change of 4.3 cc in the effective volume of the large manometer chamber. Although an upward drift in the mole fractions of the gases could be real, we deem this possibility unlikely, given the similar behavior on average for N₂ and air primary reference gases and the drift rate being closely proportional to mole fraction (relative drifts nearly the same for all gases).

As reported in section 5 above, the volume calibrations made in 1993 indicated that the effective volume of the 4 cc chamber was significantly lower than previous results indicated. However, the volume determined in 1998-1999 was again close to the previous values, as shown in Figure 2.

Fig 2

In 1983, manometric calibrations of the N₂ and natural-air primary reference gases showed a small shift toward lower manometric mole fractions, proportional to the mole fraction with respect to previous years [Keeling et al., 1984]. We assumed that the shift between 1980-81 and 1983 was caused by a change in the effective volume of the 4 cc chamber and used a procedure to infer its volume in 1983, assuming that the primary reference gases on average had remained constant. In 1985-1986 the method of assuming constancy in the reference gases was extended back to infer a history of the effective volume of the 4 cc chamber from 1970 to 1985 [Keeling et al., 1986].

We now apply this method of assuming constancy in the reference gases also to the post-1985 results. In so doing we create a new calibrating scale which we call the X99A scale to be distinguished from an X99B scale that would assume an invariant 4 cc chamber volume. The X99B scale is described in an addendum to this report [Guenther et al., 2001].

The justification for this new X99A scale is demonstrated in Figures 3a to 3d which show plots of changes in mole fraction proportional to the mole fraction, i.e. changes increasing as the mole fraction increases for each of the years 1990, 1993, 1995, and 1998. The plotted data are from Tables 9.2a and 9.2b and are all referenced to the volume ratio 1321.80 assigned for 1985. Two reference gases, which displayed anomalous drift behavior, were not included in the linear least square fits of the data. Dashed lines represent fits with the y-intercepts determined; solid lines represent fits forced through the origin. The fits using determined and forced intercepts agree with each other each year within the scatter of the data and support the assumption of a change in effective volume of the 4 cc chamber, producing a proportional concentration-dependent effect.

Fig 3a-d

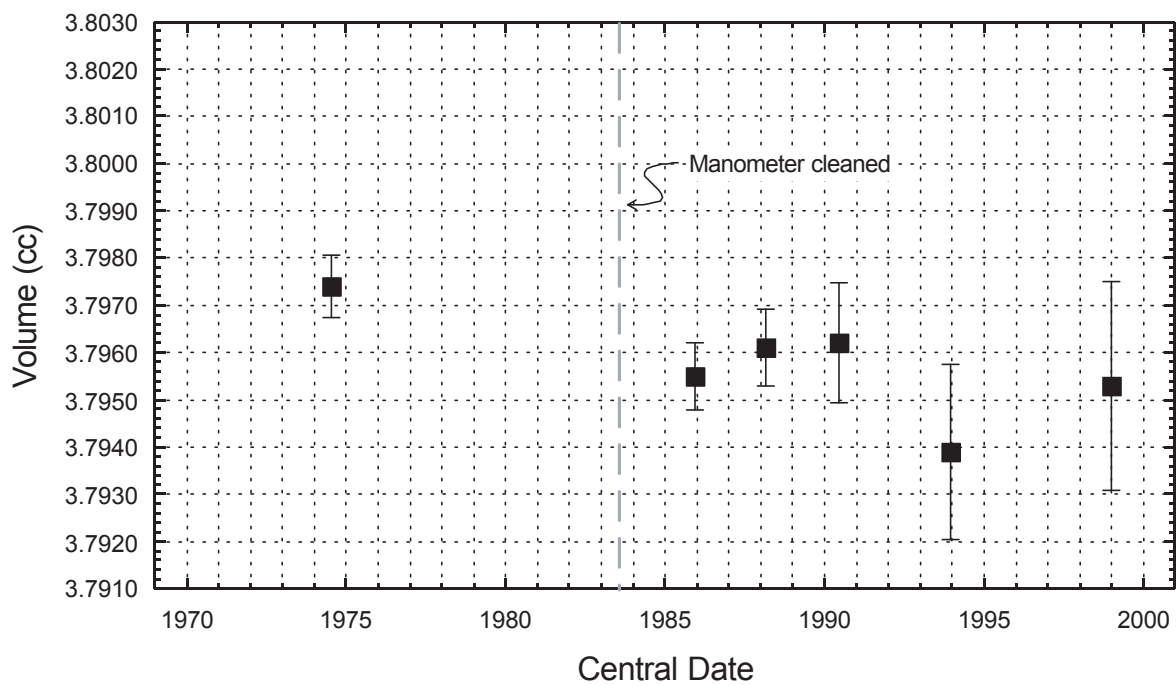


Figure 2. History of calibrations of the volume of the 4cc chamber in the constant-volume mercury-column manometer, with reference to the volumes of a set of plenums calibrated in 1974 by weighing them filled with mercury. Averages are plotted for each year: error bars represent +/- one standard deviation of an individual calibration.

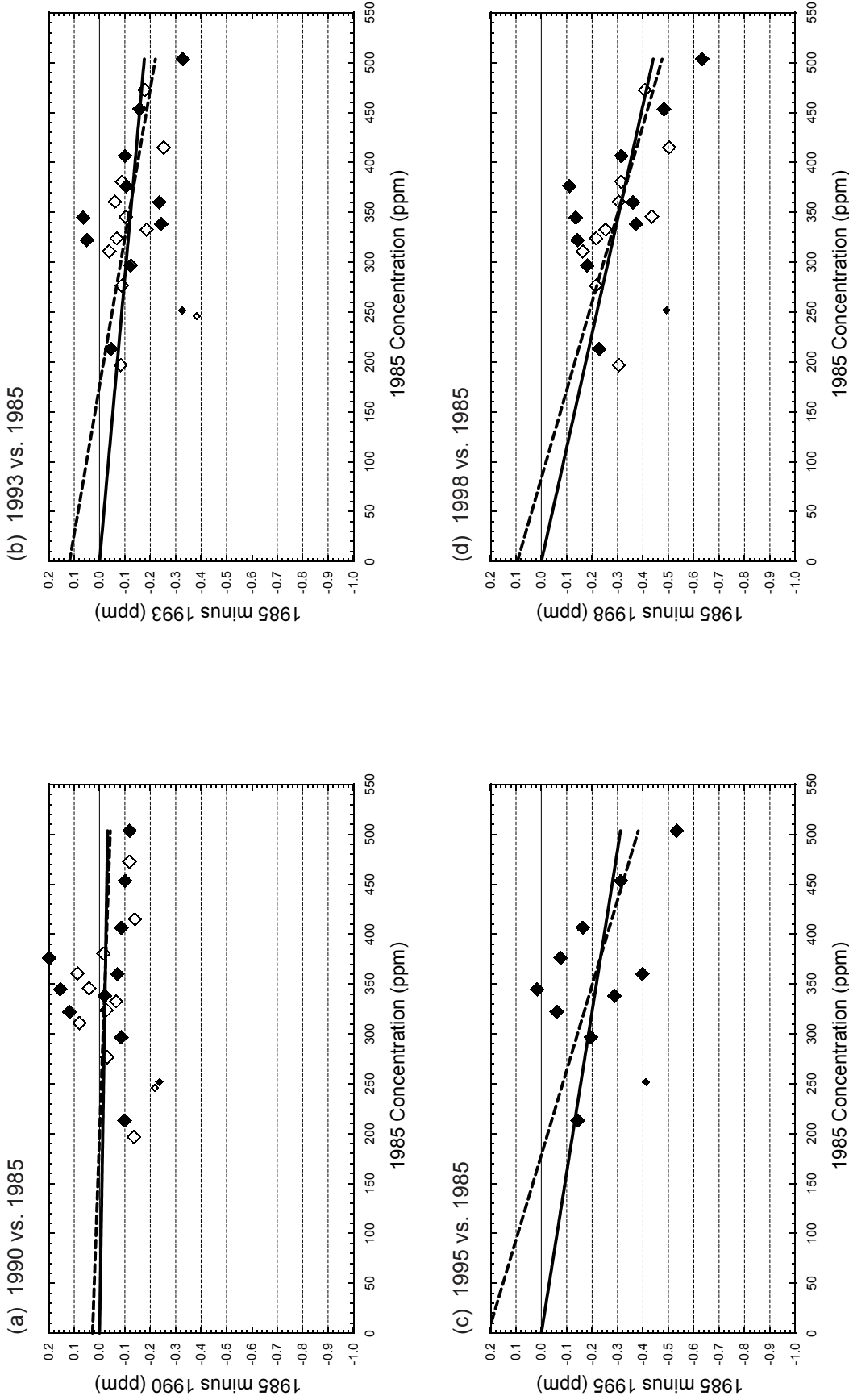


Figure 3. Inference plots for manometric measurements of primary reference gases in a) 1990, b) 1993, c) 1995, and d) 1998. Differences from the 1985 results are plotted versus the 1985 results, in mole fraction of CO₂. The sense of these plots is identical to that of similar plots in Keeling et al. [1986]. The downward slopes imply that the mole fractions of reference gases have increased with time when they are calculated using a constant manometric volume ratio (1321.80). Open symbols denote CO₂-in-N₂ gases and closed symbols, CO₂-in-air gases. Small symbols denote gases rejected from the fits. Dashed lines represent linear fits with the y-intercepts determined from the fits. Solid lines represent linear fits with y-intercepts of zero.

Relative changes in inferred volumes of the 4 cc chamber for the four years of measurements were established from the linear fits through the origin, assuming that the effective volume of the 5000 cc chamber of the manometer remained constant. The slopes "a" are used to calculate the inferred volumes, V_{inf} relative to the volume of 1985, V_{85} , according to the formula:

$$V_{inf} = V_{85} / (1 - a) \tag{5}$$

Table 6.1 lists the inferred volumes, V_{inf} , and also the measured volumes, V_{ple} , based on plenum calibrations (section 5 of this report).

Tbl 6.1

Table 6.1. Inferred 4 cc Volumes for 1985 through 1998

Year	1 - a	Std. Error of Fit	V_{inf} (cc)	V_{ple} (cc)
1985	1.000000	---	3.79400	3.7955
1988	---	---	---	3.7961
1990	1.000068	0.100972	3.79376	3.7962
1993	1.000350	0.087583	3.79267	3.7938
1995	1.000620	0.145957	3.79165	---
1998	1.000875	0.110325	3.79068	3.7953

Since both V_{inf} and V_{ple} are essentially constant for the period 1985 to 1990, in creating a new X99A calibration scale for this report we have based the absolute calibration of the volume of the 4 cc chamber on data obtained for that period.

The volume of the 4 cc chamber for this period was calculated to be 3.79593cc, as the unweighted average of V_{ple} values listed in Table 6.1 for 1985-1986, 1988 and 1990. Next, the unweighted average of the V_{inf} for the same period (1985 and 1990 values listed in Table 6.1) was calculated. A factor was then found to bring the average inferred volume, 3.79388 cc, into agreement with the measured average,

$$3.79593 / 3.79388 = 1.000541 \tag{6}$$

The inferred volumes of the 4 cc chamber from 1985 to 1998, V_{inf} , were then multiplied by this factor to normalize them to the average of the actual measurements of the volume made in 1985-1986, 1988, and 1990, consistent with an assumption of constancy in the mole fractions of the primary reference gases. These normalized volumes, listed in Table 6.2 as V_{adj} , are thus the basis for reporting primary reference gas mole fractions in this report on the X99A scale. They are to be considered

Tbl 6.2

provisional pending further manometric measurements and volume calibrations.

Table 6.2. Adjusted Inferred 4 cc Volumes for 1985 through 1998

Year	V_{inf} (cc)	Factor	V_{adj} (cc)
1985	3.79400	1.000541	3.7961
1990	3.79376	1.000541	3.7958
1993	3.79267	1.000541	3.7947
1995	3.79165	1.000541	3.7937
1998	3.79068	1.000541	3.7927

Changing the apparent volume of the 4 cc chamber assigned for 1985 necessarily changes the pre-1985 calibration scale. The volume used for all calibrations prior to 1983, as previously reported, was 3.7974 cc, based on measurements made in 1974. The mole fractions obtained from the manometric measurements of 1983, when referenced to this volume, were systematically low, and in creating the X85 scale the assumption was made that the apparent volume of the 4 cc chamber had increased in and near the year 1983 to cause apparent changes in the mole fractions of the primary reference gases prior to 1985. In particular, the average of all pre-1983 manometric determinations for each gas was assigned as the value in 1983 [Keeling et al., 1984]. The apparent volume of the 4 cc chamber required to produce this result in 1983 was 3.8003 cc. Then, after the manometer had been cleaned in 1984 but before new volume calibrations could be made, measurements of the primary reference gases were again made in 1985. The volume of the 4 cc chamber was assigned then to be consistent with the volume that had been assigned in 1983, assuming overall stability of the primary reference gases [Keeling et al., 1986]. On average the measured 1983 and 1985 mole fractions of the primary reference gases were made identical. This method resulted in an assigned 4 cc chamber volume of 3.7940 cc for 1985.

In order that the pre-1985 variable assigned volumes of the 4 cc chamber be consistent with the X99A scale, the previously assigned volumes are here multiplied by the factor 1.000541. Table 6.3 summarizes the assigned volumes for the X99A scale, this scale based on the assumption that the primary reference gases were stable, on average, when referenced to the volume ratio of the CMM determined from the 4 cc chamber volume calibrations of 1985, 1988, and 1990. The inference ratios (1-a) for 1970 to 1984 are reproduced from Table 12 of Keeling et al. [1986]. Note however

Tbl 6.3

that the inferred volume in column 3 of Table 6.3 is based upon an assigned volume of 3.7940 cc in 1985, while in Table 12 of Keeling et al. [1986] the "computed volume" is based upon the 1985 measured volume of 3.7955 cc.

Table 6.3. Measured and Inferred 4 cc Chamber Volumes, 1970-1998

Year	Inference ratio (1 - a)	3.7940-based inferred volume (cc)	Adjustment factor	Assigned volume for X99A scale (cc)	Measured volume (cc)
1970	0.999428	3.7962	1.000541	3.7982	---
1974	0.999374	3.7964	1.000541	3.7984	3.7974
1980	0.999163	3.7972	1.000541	3.7992	---
1981	0.998973	3.7979	1.000541	3.8000	---
1982	0.998825	3.7985	1.000541	3.8005	---
1983	0.998340	3.8003	1.000541	3.8024	---
1984	0.998323	3.8004	1.000541	3.8024	---
1985	1.000000	3.79400	1.000541	3.7961	3.7955
1988	---	---	---	---	3.7961
1990	1.000063	3.79376	1.000541	3.7958	3.7962
1993	1.000350	3.79267	1.000541	3.7947	3.7939
1995	1.000620	3.79165	1.000541	3.7937	---
1998	1.000875	3.79068	1.000541	3.7927	3.7953

Figure 4 shows the adjusted inferred volumes of the 4 cc chamber during the history of calibrations since 1970. The calibration line (dashed line for pre-1985, solid line for post-1985) represents the change in the apparent volume of the 4 cc chamber assuming the primary reference gases remained on average stable over the entire period. The change in volume between calibrations is assumed to be linear, shown by connecting the points with straight lines. For the purpose of calibrating the APC analyzer, however, only the discrete calibrations are used. In order to apply strictly the inferred volumes for the pre-1985 period, cubic calibration curves for each pre-1985 calibration period would have to have been redetermined. We choose instead as a very close approximation to this procedure, to multiply the coefficients of the cubic equations by the constant factor (1.000541) for all pre-1985 calibrations. Since 3.7974 cc was used prior to 1983 and 3.80036 for 1983-1984 as the apparent volume of the 4 cc chamber, this adjustment has the effect of producing a new "step function" for the volume. This is shown in Figure 4 as the solid line before 1985. It is evident that in 1970 and 1974 the calibration based on the 1974 measured volume (adjusted by the factor) is about 0.1 ppm higher than the inferred volume. This small adjustment could be made in the future if it is deemed desirable to do so, but we assert that the change is not important for the interpretation of atmospheric CO₂ data.

Fig 4

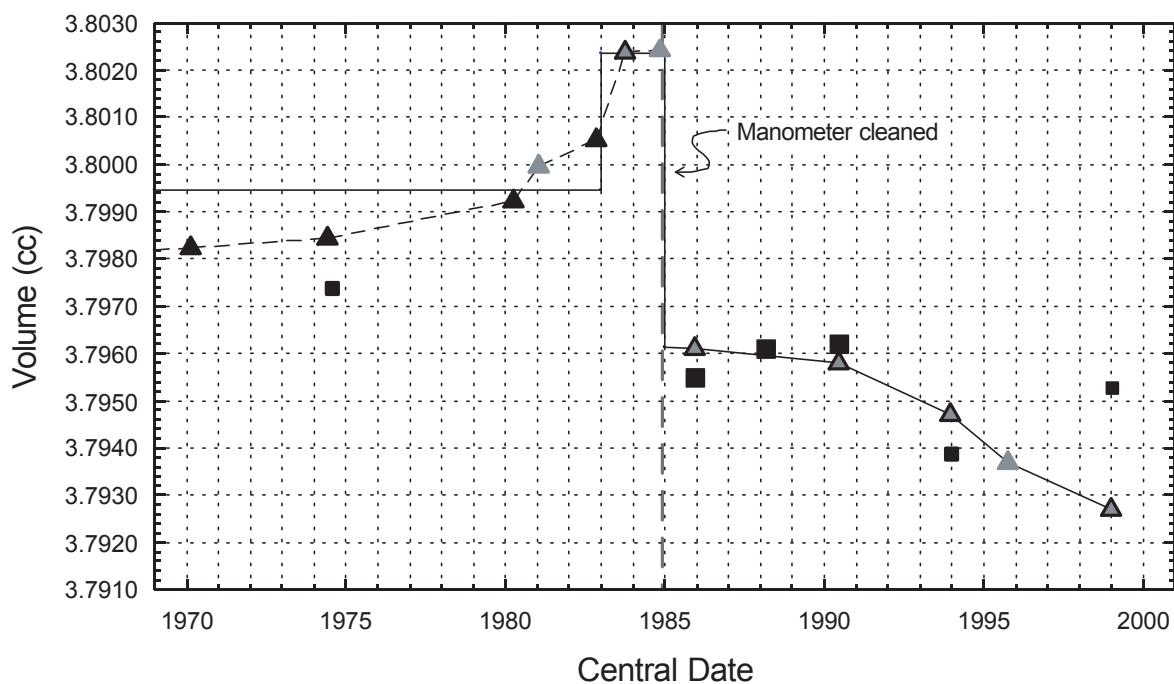


Figure 4. History of the volume of the 4cc chamber in the constant-volume mercury-column manometer, as inferred from measurements of primary reference gases, assuming that those gases have remained stable on average. Solid black triangles represent calibrations of N₂ primary reference gases; gray triangles, calibrations of air primary reference gases; and black-bordered gray triangles, calibrations of both N₂ and air primary reference gases. Squares represent calibrations of the volume of the 4cc chamber using plenums (as in Figure 2). Smaller squares designate calibrations that have not been used for the provisional calibration reported here. The solid line connects the 4cc volumes used for manometric reference gas calibrations for the years indicated. The dotted line prior to 1985 connects the 4cc volumes inferred for that period, assuming stability of the primary reference gases.

The only serious discrepancy between measured and inferred volumes is for the 1998-1999 period. It is possible that the apparent volume of the 4 cc chamber had changed between the times of the manometric measurements during mid-1998 (see data in Table 9.1, from which the volume was inferred) and the times of the volume calibrations of the 4 cc chamber in December 1998 and January 1999.

A second, very small correction of 1 part in 26000 has been applied to produce the manometric mole fractions for this report to provide consistency with previously reported data. The manometric volume ratio of 1321.80, assigned for the X85 scale, is the ratio of an assigned value of the 5000 cc chamber volume, 5014.9 cc, to that of the 4 cc volume, 3.7940. As discussed in Keeling et al. [1986], the volume of the 5000 cc chamber was later assigned a value of 5015.09 cc for 1974. The volume ratios for each year from 1985 to 1999 are redefined in Table 6.4 as the ratio of 5015.09 cc to the volume of the 4 cc chamber listed in Table 6.3.

Tbl 6.4

Table 6.4. Adjusted Volume Ratios, 1985-1998 for the X99A Scale

Year	V _{4cc} (cc)	Vol. Ratio
1985	3.7961	1321.116
1990	3.7958	1321.221
1993	3.7947	1321.604
1995	3.7937	1321.952
1998	3.7927	1322.301

The manometric mole fractions listed in Table 9.2, for 1985 and later years, have been adjusted using the volume ratios listed in Table 6.4 to establish the adjusted mole fractions listed in Tables 9.5a and 9.5b, for N₂ and air primary reference gas standards, respectively. These adjusted mole fractions have then been used together with the infrared analyzer data for each year of infrared calibrations (Table 9.3) to determine cubic calibration equations.

Tbl 9.5a-b

For calibrations prior to 1985, as noted above, apply a constant factor to adjust the previous calibration scale to the X99A scale. This correction factor is:

$$\begin{aligned}
 X_{\text{cub,final}} &= X_{\text{cub,orig}} \left[\frac{3.79593}{3.79388} \right] \left[\frac{5014.90}{5015.09} \right] \quad (7) \\
 &= X_{\text{cub,orig}} (1.000503)
 \end{aligned}$$

Departures of the average results in Table 9.5 for each calibration year from 1985 to 1998 are plotted in Figures 5a and 5b for N₂ and natural-air primary reference gases, respectively. By comparing these plots to those in Figures 1a and 1b it is clear that the apparent upward drift in reference gas mole fractions after 1985, that would have appeared in a constant volume ratio scale, has been removed in the X99A scale.

Fig 5a

Fig 5b

The 1970-1983 data plotted in Figure 5 are the averages from Table 9.2 multiplied by the factor 1.000503. The 1970 and 1974 calibrations are systematically high by approximately 0.1 ppm, as shown also in Figure 4. We did not adjust the pre-1983 calibrations to reduce year to year variations in computed mole fractions when using the previous calibration scales, X85 to X97.

7. Equations to Convert Index Values to Mole Fractions

The relationships of APC analyzer index values to mole fractions of CO₂ during calibration periods on the X99A scale, are now formulated using the absolute calibration of manometric results established above. We follow procedures adopted in 1985 and described by Keeling et al., [1986]. From 1985 to 1999 there were a total of eight infrared calibration periods (specified by their calendar year of determination). The infrared data (J Index values) are summarized in Table 9.3. For each calibration year, cubic polynomial calibration equations were found by fitting the J index values in Table 9.3 with the manometric mole fraction values in Table 9.5. For those years without manometric measurements, the set nearest in time to the infrared data was chosen. Table 7.1 lists the cubic coefficients for all of the calibration equations, as well as the standard error of the fit residuals and identification of the data sets used. The listed central dates are defined as the average dates of the sets of marathon calibration days on the infrared analyzer. Appendix A4 contains plots of the calibration curves and residuals of the data.

Tbl 7.1

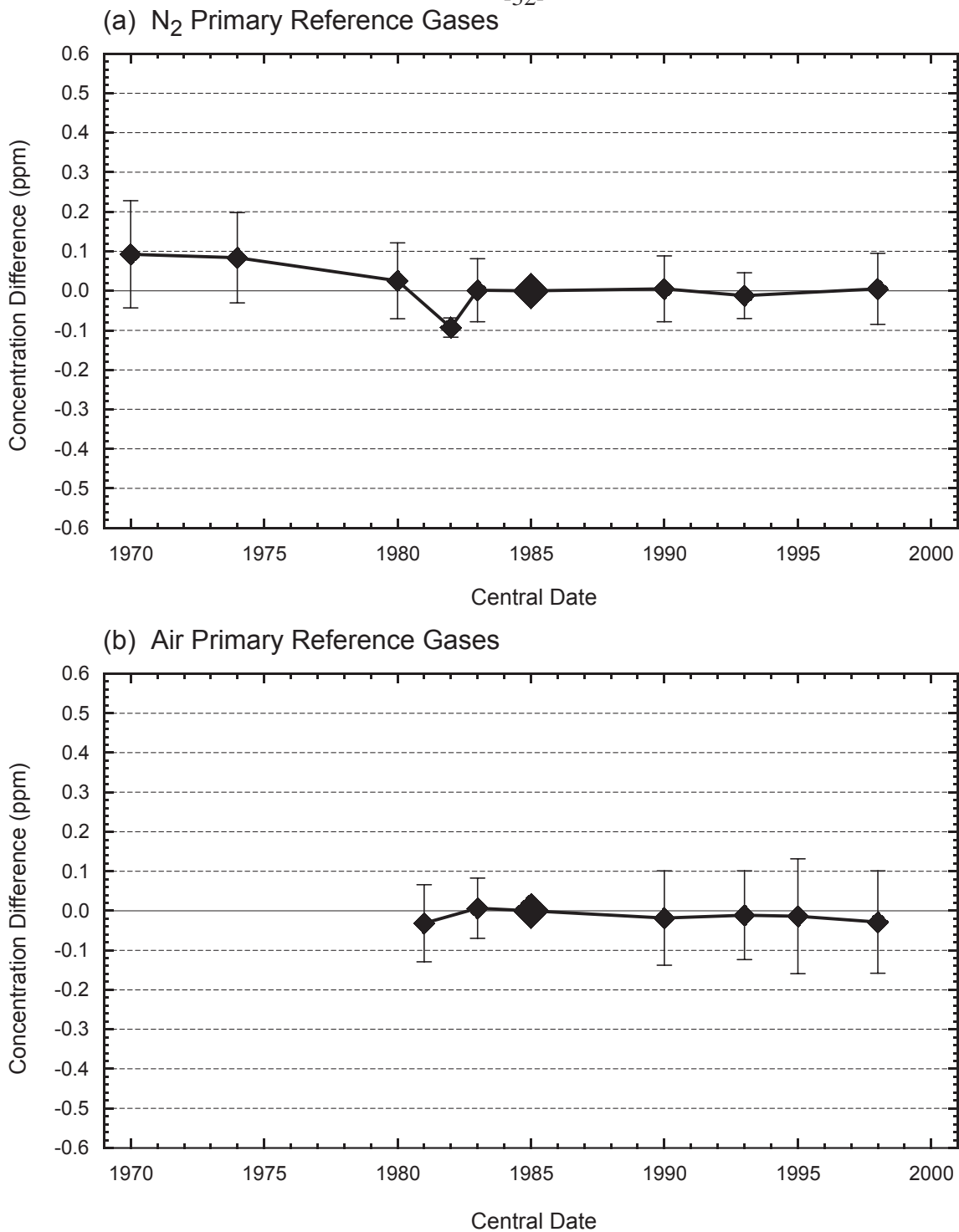


Figure 5. Average differences from the 1985 value of manometric measurements of a) N₂ and b) air primary reference gases, in mole fraction of CO₂, by year. Volume ratios of constant-volume mercury-column manometer for 1985 and later are different for each year, as determined by inference, assuming that the primary reference gases remained stable, on average. Volume ratios for the period before 1985 are the historical ratios divided by the factor 1.000503. Plotted averages for the N₂ primary reference gases in a) are for three gases in 1970, eight in 1974 and 1980, three in 1982, and ten for 1983 to 1998. Plotted averages for the air primary reference gases in b) are for ten gases in all years (one gas deleted as in Figure 3). Error bars represent +/- one standard deviation of an individual difference.

Table 7.1. Coefficients of Infrared Analyzer Calibration Equations, X99A Scale

Year	Central Date	Input Data		No. of Data Pairs	C ₀	C ₁	C ₂ x 10 ⁴	C ₃ x 10 ⁷	STD error of Fit Residuals (ppm)
		J(Index)	X(mole fraction)						
1985 N ₂	29 Jul 85	J _{N₂} 85	X _{N₂} 85	11	87.5132	.532444	4.01685	6.72004	0.062
1985 Air	29 Jul 85	J _{Air} 85	X _{Air} 85	11	87.4192	.540829	4.04859	6.97240	0.090
1987 N ₂	6 Dec 87	J _{N₂} 87	X _{N₂} 85	11	89.3581	.516401	4.44805	6.41311	0.076
1987 Air	6 Dec 87	J _{Air} 87	X _{Air} 85	11	88.5029	.532263	4.25404	6.87557	0.109
1989 N ₂	3 Mar 89	J _{N₂} 89	X _{N₂} 90	11	86.3029	.547548	3.41802	7.52766	0.048
1989 Air	3 Mar 89	J _{Air} 89	X _{Air} 90	11	85.5430	.562631	3.26679	7.90715	0.049
1990 N ₂	22 May 90	J _{N₂} 90	X _{N₂} 90	11	87.1374	.533709	3.87607	7.17569	0.045
1990 Air	22 May 90	J _{Air} 90	X _{Air} 90	11	86.8145	.544559	3.85617	7.42175	0.061
1993 N ₂	20 May 93	J _{N₂} 93	X _{N₂} 93	14	81.6951	.565859	3.08776	8.16209	0.060
1993 Air	20 May 93	J _{Air} 93	X _{Air} 93	11	78.3201	.606319	2.15415	9.33424	0.085
1995 N ₂	9 Jul 95	J _{N₂} 95	X _{N₂} 93	13	86.0513	.539767	3.57859	7.91844	0.078
1995 Air	9 Jul 95	J _{Air} 95	X _{Air} 95	11	83.3810	.575679	2.71623	9.07824	0.074
1997 N ₂	19 Aug 97	J _{N₂} 97	X _{N₂} 98	13	89.1481	.519170	4.09851	7.44049	0.088
1997 Air	19 Aug 97	J _{Air} 97	X _{Air} 98	11	89.9872	.519429	4.37303	7.44874	0.038
1999 N ₂	1 Jan 99	J _{N₂} 99	X _{N₂} 98	13	87.2317	.537682	3.43132	8.27005	0.089
1999 Air	1 Jan 99	J _{Air} 99	X _{Air} 98	11	87.0885	.548176	3.37978	8.60155	0.070

Note: Calibration equations are cubic polynomials, of the form: $X = C_0 + C_1 J + C_2 J^2 + C_3 J^3$ Application of these equations is described in Appendix A5.

Cubic formulations for pre-1985 calibrations have not been changed for the X99A scale. Instead, mole fractions for that period are calculated from the previously established formulations [Keeling et al., 1986] and then multiplied by the constant factor 1.000503, from equation (7).

To convert infrared data from dates intermediate between the central dates of calibration periods, we interpolate linearly between the appropriate equations, either for CO₂-in-N₂ or CO₂-in-air mixtures. By convention, the most recent calibration remains constant for preliminary use after its central date, until a future calibration is done. A copy of a FORTRAN program, CONVERT99A, used to calculate mole fractions of CO₂ from APC analyzer index values, is included in Appendix A5.

Tables 9.6a and 9.6b list all the cubic equation coefficients, for CO₂-in-nitrogen and CO₂-in-air respectively, that were used in previous provisional calibration scales of the CDRG from X85 to X97, and also include the coefficients for the X99A scale. (See Table 7.1 of this report). The vertical columns list the cubic equation coefficients for each scale and the ditto marks represent horizontal repetition of the coefficients to the left. Conceptually, each new scale is formulated by simply adding a new cubic calibration equation to the set of equations in the immediately preceding scale. In

practice, however, previous preliminary data were finalized and corrected, so that most scales also included changes in the cubic equations for prior calibration years. In the case of the X99A scale, of course, all of the cubic equations change from the X97 scale due to assumed changes in the manometric volume ratios described in this report.

8. Comparison of New Calibration with Previous Formulation

Tbl 9.6a-b

Tables 9.7a and 9.7b list the differences, for January 1 of each year and for every 10 ppm from 170 to 450 ppm of J Index, between the new X99A calibration scale and the previous calibration scale (X97) that assumed the assigned manometric volume ratio of 1985 (1321.80) had remained constant through the central date of the 1997 calibration. As described in section 6, the X99A scale applies a constant-factor adjustment of 1.000503 to data prior to 1985. Tables 9.7a and 9.7b show that in the concentration range of ambient air the X97 scale calibration for the pre-1985 period has been increased by approximately 0.2 ppm.

In summary, the assigned calibration relating data from the CDRG APC infrared analyzer to mole fraction CO₂ has been revised from the beginning of the project in 1957 to the present, with new cubic calibration equations based on reassessed volume ratios of the constant-volume mercury-column manometer. Data prior to 1985 were adjusted by a constant factor to maintain as much of the previous calibration as possible. The results in this report are provisional because of unresolved ambiguity in the recent manometric calibrations.

References

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Table 9.1a. Manometric analyses of CO₂-in-nitrogen primary reference gases during 1985 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume* Adjusted
2408	1	3Sep85	196.97	196.97	196.97			
	2	3Sep85	196.98	196.91	196.94	-0.03	196.958	196.781
3753	1	20Sep85	246.20	246.32	246.26			
	2	21Sep85	246.32	246.31	246.32	0.06	246.288	246.066
7366	1	12Sep85	276.89	276.84	276.86			
	2	13Sep85	276.82	276.81	276.82	-0.04	276.840	276.591
6078	1	10Jul85	311.18	311.16	311.17			
	2	10Jul85	311.17	311.17	311.17	0.00	311.170	310.890
2399	1	12Jul85	324.33	324.34	324.34			
	2	29Jul85	324.17	324.11	324.14	-0.20	324.238	323.946
39239	1	19Jun85	332.89	332.92	332.90			
	2	31Jul85	333.08	333.05	333.06	0.16		
39256	3	19Sep85	333.05	333.03	333.04	-0.02		
	4	6Sep85	333.00	332.98	332.99	-0.05	333.000	332.700
39272	1	25Jun85	346.02	345.91	345.96			
	2	25Jun85	346.02	346.04	346.03	0.07	345.998	345.687
1540	1	19Jun85	360.83	360.93	360.88			
	2	20Jun85	360.90	361.02	360.96	0.08	360.920	360.595
35299	1	6Aug85	380.87	380.93	380.90			
	2	6Aug85	380.98	380.93	380.96	0.06	380.928	380.585
35316	1	14Aug85	415.24	415.34	415.29			
	2	14Aug85	415.28	415.29	415.28	-0.01	415.288	414.914
	1	27Aug85	473.22	473.19	473.20			
	2	28Aug85	473.14	472.98	473.06	-0.14	473.133	472.707

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/N_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

Table 9.1b. Manometric analyses of CO₂-in-air primary reference gases during 1985 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume [*]		N ₂ O	
								Adjusted	Adjusted ^{††}	N ₂ O	Adjusted ^{††}
66556	1	5Sep85	101.37	101.36	101.36						
	2	5Sep85	101.33	101.33	101.33	-0.03	101.348	101.256	.370	100.886	
71251	1	28Aug85	213.68	213.67	213.68						
	2	29Aug85	213.58	213.59	213.58	-0.10	213.630	213.438	.340	213.098	
34819	1	20Aug85	252.30	252.32	252.31						
	2	20Aug85	252.17	252.11	252.14	-0.17	252.225	251.998	.240	251.758	
71286	1	7Aug85	297.24	297.19	297.22						
	2	7Aug85	297.21	297.21	297.21	-0.01	297.213	296.945	.320	296.625	
71341	1	26Jun85	322.71	322.70	322.70						
	2	26Jun85	322.76	322.77	322.76	0.06	322.735	322.444	.310	322.134	
66638	1	26Jun85	338.92	338.88	338.90						
	2	9Jul85	338.91	338.83	338.87	-0.03	338.885	338.580	.310	338.270	
66625	1	11Jul85	345.27	345.27	345.27						
	2	11Jul85	345.27	345.27	345.27	0.00	345.270	344.959	.290	344.669	
66696	1	31Jul85	360.63	360.56	360.60						
	2	1Aug85	360.71	360.72	360.72	0.12	360.655	360.330	.310	360.020	
71308	1	5Aug85	376.29 ^{††}	376.30 ^{††}	376.30 ^{††}						
	2	5Aug85	376.83	376.81	376.82						
3	12Aug85	376.53 ^{††}	376.62 ^{††}	376.58 ^{††}							
	4	19Aug85	376.89	376.90	376.90	0.08	376.858	376.518	.320	376.198	
71370	1	13Aug85	407.06	407.07	407.06						
	2	13Aug85	407.12	407.10	407.11	0.05	407.088	406.721	.310	406.411	
71479	1	26Aug85	454.14	454.05	454.10						
	2	27Aug85	453.95	454.01	453.98	-0.12	454.038	453.629	.300	453.329	
67615	1	4Sep85	504.25	504.36	504.30						
	2	4Sep85	504.45	504.46	504.46	0.16	504.380	503.926	.300	503.626	

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}N_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns. N₂O is included in the mole fraction.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Volume adjusted minus N₂O

^{††} Rejected

Table 9.1c. Manometric analyses of CO₂-in-nitrogen primary reference gases during 1990 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations	Run Average	Run Difference	Overall [†] Average	Volume* Adjusted
2408	1	10Jul90	197.09	197.09			
	2	11Jul90	197.10	197.10	0.01	197.093	196.916
3753	1	2Jul90	246.52	246.48			
	2	2Jul90	246.53	246.49	0.01	246.505	246.283
7366	1	23May90	276.89	276.85			
	2	24May90	276.89	276.85	0.00	276.870	276.621
6078	1	10Apr90	311.09	311.10			
	2	10Apr90	311.09	311.08	-0.02	311.090	310.810
2399	1	18Apr90	324.31	324.26			
	2	18Apr90	324.17	324.32	-0.04	324.265	323.973
39239	1	21Mar90	333.02	333.06			
	2	19Apr90	333.00	333.01	-0.04		
	3	13Jun90	332.88	333.05	-0.04		
	4	12Jul90	333.18	333.20	0.23		
39256	5	29Aug90	333.13	333.12	-0.07	333.065	332.765
	1	27Mar90	345.93	345.99			
39272	2	27Mar90	345.99	345.91	-0.01	345.955	345.644
	1	22Mar90	360.62 [†]	360.84			
1540	2	22Mar90	360.83	360.83	-0.01	360.833	360.508
	1	11May90	380.80	380.92			
35299	2	21May90	381.07	380.98	0.16	380.943	380.600
	1	12Jun90	415.40	415.41			
35316	2	12Jun90	415.48	415.42	0.05	415.428	415.054
	1	5Jul90	473.31	473.30			
	2	9Jul90	473.18	473.21	-0.10	473.250	472.824

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/N_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Rejected

Table 9.1d. Manometric analyses of CO₂-in-air primary reference gases during 1990 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume* Adjusted	N ₂ O	N ₂ O Adjusted [†]
66556	1	20Aug90	101.50	101.51	101.50					
	2	21Aug90	101.46	101.45	101.46	-0.04	101.480	101.389	0.370	101.019
71251	1	9Jul90	213.71	213.73	213.72					
	2	10Jul90	213.74	213.73	213.74	0.02	213.728	213.536	0.340	213.196
34819	1	14Jun90	252.39	252.49	252.44					
	2	19Jun90	252.48	252.48	252.48	0.04	252.460	252.233	0.240	251.993
71286	1	22May90	297.34	297.24	297.29					
	2	23May90	297.34	297.27	297.30	0.01	297.298	297.030	0.320	296.710
71341	1	28Mar90	322.58	322.62	322.60					
	2	28Mar90	322.59	322.67	322.63	0.03	322.615	322.325	0.310	322.015
66638	1	9Apr90	338.85	338.90	338.88					
	2	9Apr90	338.90	338.97	338.94	0.06	338.905	338.600	0.310	338.290
66625	1	16Apr90	345.03	345.17	345.10					
	2	17Apr90	345.14	345.12	345.13	0.03	345.115	344.804	0.290	344.514
66696	1	9May90	360.79	360.75	360.77					
	2	10May90	360.30 ^{††}	360.55 ^{††}	360.42 ^{††}					
71308	3	21May90	360.77	360.59	360.68	-0.09	360.725	360.400	0.310	360.090
	1	10May90	376.66	376.62	376.64					
71370	2	11May90	376.59	376.76	376.68	0.04	376.658	376.319	0.320	375.999
	1	11Jun90	407.11	407.24	407.18					
71479	2	11Jun90	407.16	407.18	407.17	-0.01	407.173	406.806	0.310	406.496
	1	3Jul90	454.13	454.06	454.10					
67615	2	5Jul90	454.17	454.19	454.18	0.08	454.138	453.729	0.300	453.429
	1	12Jul90	504.45	504.59	504.52					
	2	12Jul90	504.39	504.56	504.48	-0.04	504.498	504.044	0.300	503.744

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}N_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns. N₂O is included in the mole fraction.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Volume adjusted minus N₂O

^{††} Rejected

Table 9.1e. Manometric analyses of CO₂-in-nitrogen primary reference gases during 1993 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume* Adjusted
			Determinations	Average				
2408	1	13Jul93	196.95	196.99	196.97			
	2	13Jul93	197.05	197.17	197.11	0.14	197.040	196.863
4274	1	14May93	243.53	243.52	243.52			
	2	20May93	243.37	243.42	243.40	-0.12	243.460	243.241
3753	1	16Jun93	246.65	246.64	246.64			
	2	17Jun93	246.68	246.71	246.70	0.06	246.670	246.448
7366	1	14Jul93	276.92	277.01	276.96			
	2	14Jul93	276.83	276.95	276.89	-0.07	276.928	276.679
6071	1	20May93	310.43	310.35	310.39			
	2	20May93	310.48	310.53	310.50	0.11	310.448	310.169
6078	1	17Jun93	311.27	311.27	311.27			
	2	23Jun93	311.09	311.20	311.14	-0.13	311.208	310.928
4296	1	26May93	320.69	320.80	320.74			
	2	26May93	320.77	320.84	320.80	0.06	320.775	320.486
2399	1	23Jun93	324.33	324.32	324.32			
	2	24Jun93	324.19	324.38	324.28	-0.04	324.305	324.013
39239	1	23Feb93	333.24	333.24	333.24			
	2	23Feb93	333.19	333.18	333.18	-0.06	333.185	332.885
39256	3	3Jun93	333.14	333.12	333.13	-0.05		
	1	26May93	346.10	346.11	346.10			
39272	2	27May93	346.09	346.10	346.10	0.00	346.100	345.788
	1	23Feb93	360.90	361.09	361.00	-0.04	360.980	360.655
1540	2	24Feb93	360.87	361.06	360.96			
	1	7Jul93	380.91	381.09	381.00			
35299	2	8Jul93	381.03	381.03	381.03	0.03	381.015	380.672
	1	16Jun93	415.22 [†]	415.66	415.66			
35316	2	16Jun93	415.43	415.53	415.48	-0.18	415.540	415.166
	1	24Jun93	473.36	473.43	473.40			
	2	30Jun93	473.13	473.32	473.22	-0.18	473.310	472.884

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/V_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Rejected

Table 9.1f. Manometric analyses of CO₂-in-air primary reference gases during 1993 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume [*]		N ₂ O Adjusted [†]
								Adjusted	N ₂ O	
71251	1	13May93	213.61	213.60	213.60		213.675	213.483	.340	213.143
	2	14May93	213.73	213.76	213.74	0.14				
34819	1	10Jun93	252.54	252.59	252.56					
	2	10Jun93	252.49	252.58	252.54	-0.02	252.550	252.323	.240	252.083
71286	1	1Jul93	297.39	297.31	297.35					
	2	2Jul93	297.31	297.33	297.32	-0.03	297.335	297.067	.320	296.747
71341	1	4Jun93	322.75	322.76	322.76					
	2	9Jun93	322.59	322.64	322.62	-0.14	322.685	322.394	.310	322.084
66638	1	26Apr93	339.04	339.17	339.10					
	2	26Apr93	339.17	339.13	339.15	0.05	339.128	338.823	.310	338.513
66625	1	2Jun93	345.15	345.32	345.24					
	2	2Jun93	345.61 ^{††}	345.69 ^{††}	345.65 ^{††}					
	3	9Jun93	345.20	345.15	345.18	-0.06	345.205	344.894	.290	344.604
66696	1	27Apr93	360.82	360.93	360.88					
	2	27Apr93	360.92	360.89	360.90	0.02	360.890	360.565	.310	360.255
71308	1	7Jul93	376.91	377.02	376.96					
	2	7Jul93	376.98	376.94	376.96	0.00	376.963	376.624	.320	376.304
71370	1	10Jun93	407.14	407.17	407.16					
	2	11Jun93	407.17	407.27	407.22	0.06	407.188	406.821	.310	406.511
71479	1	5May93	454.07	454.28	454.18					
	2	6May93	454.16	454.27	454.22	0.04	454.195	453.786	.300	453.486
67615	1	30Jun93	504.63	504.73	504.68					
	2	1Jul93	504.61	504.86	504.74	0.06	504.708	504.254	.300	503.954

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/V_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns. N₂O is included in the mole fraction.

^{*} "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Volume adjusted minus N₂O

^{††} Rejected

Table 9.1g. Manometric analyses of CO₂-in-air primary reference gases during 1995 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume*		N ₂ O Adjusted [‡]
								Adjusted	N ₂ O	
71251	1	27Sep95	213.72	213.83	213.78		213.773	213.581	0.340	213.241
	2	27Sep95	213.76	213.78	213.77	-0.01				
34819	1	12Oct95	252.56	252.62	252.59					
	2	17Oct95	252.90 ^{††}	252.89 ^{††}	252.90 ^{††}					
71286	3	2Apr96	252.69	252.67	252.68	0.09	252.635	252.408	0.240	252.168
	1	10Oct95	297.37	297.37	297.37					
71341	2	10Oct95	297.43	297.46	297.44	0.07	297.408	297.140	0.320	296.820
	1	4Oct95	322.78	322.86	322.82					
66638	2	4Oct95	322.70	322.84	322.77	-0.05	322.795	322.504	0.310	322.194
	1	21Sep95	339.14	339.14	339.14					
66625	2	26Sep95	339.24	339.17	339.20	0.06	339.173	338.868	0.310	338.558
	1	21Sep95	345.22	345.31	345.26					
66696	2	21Sep95	345.25	345.23	345.24	-0.02	345.253	344.942	0.290	344.652
	1	26Sep95	361.05	361.06	361.06					
71308	2	27Sep95	361.07	361.03	361.05	-0.01	361.053	360.728	0.310	360.418
	1	5Oct95	376.82	376.96	376.89					
71370	2	5Oct95	376.96	376.99	376.98	0.09	376.933	376.594	0.320	376.274
	1	11Oct95	407.31	407.34	407.32					
71479	2	11Oct95	407.15	407.20	407.18	-0.14	407.250	406.883	0.310	406.573
	1	17Oct95	454.37	454.37	454.37					
67615	2	18Oct95	454.04 ^{††}	454.31	454.31	-0.06	454.350	453.941	0.300	453.641
	1	28Sep95	504.64 ^{††}	504.82	504.82					
	2	28Sep95	504.97	504.95	504.96	0.14	504.913	504.458	0.300	504.158

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/V_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns. N₂O is included in the mole fraction.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Volume adjusted minus N₂O

^{††} Rejected

Table 9.1h. Manometric analyses of CO₂-in-nitrogen primary reference gases during 1998 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume* Adjusted
2408	1	06May98	197.27	197.22	197.24			
	2	13Aug98	197.28	197.28	197.28	0.04	197.263	197.085
4274	1	08May98	243.67	243.71	243.69			
	2	20Aug98	243.81	243.89	243.85	0.16	243.770	243.551
7366	1	08Jul98	276.94	277.08	277.01			
	2	09Sep98	277.06	277.14	277.10	0.09	277.055	276.806
6071	1	12Aug98	310.95	310.99	310.97			
	2	21Oct98	310.95	311.06	311.00	0.03	310.988	310.708
6078	1	19Aug98	311.27	311.30	311.28			
	2	22Oct98	311.42	311.34	311.38	0.10	311.333	311.052
4296	1	08Sep98	320.98	321.07	321.02			
	2	05Nov98	320.98	321.14	321.06	0.04	321.043	320.753
2399	1	20Oct98	324.38	324.55	324.46			
	2	06Nov98	324.46	324.42	324.44	-0.02	324.453	324.160
39239	1	20Oct98	333.35	333.31	333.33			
	2	06Nov98	333.12	333.23	333.18	-0.15	333.253	332.952
39256	1	09Sep98	346.44	346.47	346.46			
	2	05Nov98	346.45	346.37	346.41	-0.05	346.433	346.121
39272	1	20Aug98	361.30	361.20	361.25			
	2	21Oct98	361.22	361.18	361.20	-0.05	361.225	360.900
1540	1	12Aug98	381.22	381.25	381.24			
	2	10Sep98	381.23	381.27	381.25	0.01	381.243	380.899
35299	1	07Jul98	415.66	415.80	415.73			
	2	21Aug98	415.93	415.77	415.85	0.12	415.790	415.416
35316	1	06May98	473.49	473.51	473.50			
	2	13Aug98	473.60	473.56	473.58	0.08	473.540	473.114

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/V_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns.

* "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

Table 9.1i. Manometric analyses of CO₂-in-air primary reference gases during 1998-1999 (mole fraction of CO₂ in ppm)

Cylinder	Run No.	Date	Individual Determinations		Run Average	Run Difference	Overall [†] Average	Volume [*] Adjusted		N ₂ O Adjusted [†]
								N ₂ O	N ₂ O	
66556	1	02Mar99	101.49	101.46	101.48					
	2	02Mar99	101.49	101.43	101.46	-0.02	101.468	101.377	.370	101.007
71251	1	11Mar98	213.85	213.87	213.86					
	2	19Mar98	213.87	213.84	213.86	0.00	213.858	213.665	.340	213.325
34819	1	12Mar98	252.62	252.70	252.66					
	2	03Apr98	252.78	252.77	252.78	0.12	252.718	252.490	.240	252.250
71286	1	18Mar98	297.30	297.42	297.36					
	2	15Apr98	297.42	297.43	297.42	0.06	297.393	297.125	.320	296.805
71341	1	01Apr98	322.55 ^{††}	322.90	322.90					
	2	09Jul98	322.77	322.96	322.86	-0.04	322.877	322.586	.310	322.276
66638	1	14Apr98	339.21	339.29	339.25					
	2	07May98	339.24	339.29	339.26	0.01	339.258	338.952	.310	338.642
66625	1	14Apr98	345.25	345.43	345.34					
	2	09Jul98	345.43	345.51	345.47	0.13	345.405	345.094	.290	344.804
66696	1	11Mar98	360.95	361.11	361.03					
	2	19Mar98	360.96	361.04	361.00	-0.03	361.015	360.690	.310	360.380
71308	1	02Apr98	376.99	376.95	376.97					
	2	07May98	376.93	377.00	376.96	-0.01	376.968	376.628	.320	376.308
71370	1	18Mar98	407.28	407.40	407.34					
	2	15Apr98	407.48	407.45	407.46	0.12	407.403	407.036	.310	406.726
71479	1	12Mar98	454.54	454.48	454.51					
	2	02Apr98	455.02 ^{††}	455.25 ^{††}	455.14 ^{††}					
67615	3	10Jul98	454.52	454.54	454.53					
	1	10Mar98	504.64 ^{††}	504.97	504.97	0.02	454.520	454.111	.300	453.811
	2	13Mar98	504.96	505.11	505.04	0.07	505.013	504.559	.300	504.259

[†] Using $V_{4cc} = 3.7974cc$ ($V_{500cc}/V_{4cc} = 1320.61$) as determined in 1974 (see text p. 11), as in the previous 4 columns. N₂O is included in the mole fraction.

^{*} "Overall average" multiplied by 1320.61/1321.80, to be as assigned in 1985 (see text p. 11).

[†] Volume adjusted minus N₂O

^{††} Rejected

Table 9.2a. Summary of manometric measurements (mole fraction of CO₂ in ppm), by year. Averages for each reference gas are weighted by the number of runs (shown in parentheses)

CO₂-IN-NITROGEN GASES

Cyl No	1970	1974	1980	1982	1983	1985	1990	1993	1998	Wt. Average
2408		196.895 (2)	196.800 (2)		196.831 (3)	196.781 (2)	196.916 (2)	196.863 (2)	197.085 (2)	196.878 (15)
4274								243.241 (2)	243.551 (2)	243.396 (4)
3753		246.018 (2)	245.993 (2)		246.074 (2)	246.066 (2)	246.283 (2)	246.448 (2)		246.147 (12)
7366	276.570 (3)	276.798 (2)	276.673 (2)		276.536 (2)	276.591 (2)	276.621 (2)	276.679 (2)	276.806 (2)	276.654 (17)
6071								310.169 (2)	310.708 (2)	310.438 (4)
6078	310.947 (7)	310.820 (3)	310.963 (2)		310.753 (2)	310.890 (2)	310.810 (2)	310.928 (2)	311.052 (2)	310.904 (22)
4296								320.486 (2)	320.753 (2)	320.620 (4)
2399	324.188 (8)	324.030 (4)	324.150 (2)		324.005 (2)	323.946 (2)	323.973 (2)	324.013 (2)	324.160 (2)	324.088 (24)
39239		332.780 (2)	332.728 (2)		332.713 (5)	332.700 (4)	332.765 (5)	332.885 (3)	332.952 (2)	332.761 (25)
39256				332.635 (2)	345.573 (3)	345.687 (2)	345.644 (2)	345.788 (2)	346.121 (2)	345.750 (13)
10069	355.640 (4)	355.595 (2)	355.820 (2)							355.674 (8)
39272				360.495 (3)						360.614 (13)
1540		380.565 (2)	380.448 (2)		380.453 (2)	380.585 (2)	380.600 (2)	380.672 (2)	380.899 (2)	380.603 (14)
35299		415.055 (2)	414.935 (2)		415.012 (2)	414.914 (2)	415.054 (2)	415.166 (2)	415.416 (2)	415.079 (14)
35316		472.973 (2)	472.718 (4)		472.733 (2)	472.707 (2)	472.824 (2)	472.884 (2)	473.114 (2)	472.834 (16)
Av. of 10*					341.540	341.539	341.571	341.653	341.851	341.617

Source of data:

1970-1983: Table 1c of Keeling et al. [1984]

1985-1998: Final column of Tables 9.1a, 9.1c, 9.1e, 9.1h of this report

* Unweighted average of reference gases (10 gases, excluding 4274, 3753, 6071, 4296, 10069, see text p. 13).

Table 9.2b. Summary of manometric measurements (mole fraction of CO₂ in ppm), by year. Averages for each reference gas are weighted by the number of runs (shown in parentheses)

CO ₂ -IN-AIR GASES										
Cyl no	1981	1983	1985	1990	1993	1995	1998	Wt. Av.		
66556	100.990 (2)	100.987 (2)	100.886 (2)	101.019 (2)			101.007 (2)	100.978 (10)		
71251	213.148 (2)	213.164 (2)	213.098 (2)	213.196 (2)	213.143 (2)	213.241 (2)	213.325 (2)	213.188 (14)		
34819	251.723 (2)	251.803 (2)	251.758 (2)	251.993 (2)	252.083 (2)	252.168 (2)	252.250 (2)	251.968 (14)		
71286	296.560 (2)	296.672 (2)	296.625 (2)	296.710 (2)	296.747 (2)	296.820 (2)	296.805 (2)	296.706 (14)		
71341	322.455 (2)	322.227 (2)	322.134 (2)	322.015 (2)	322.084 (2)	322.194 (2)	322.276 (2)	322.198 (14)		
66638	338.078 (2)	338.209 (2)	338.270 (2)	338.290 (2)	338.513 (2)	338.558 (2)	338.642 (2)	338.366 (14)		
66625	344.620 (2)	344.522 (4)	344.669 (2)	344.514 (2)	344.604 (2)	344.652 (2)	344.804 (2)	344.613 (16)		
66696	359.873 (2)	359.923 (2)	360.020 (2)	360.090 (2)	360.255 (2)	360.418 (2)	360.380 (2)	360.137 (14)		
71308	376.480 (2)	376.200 (2)	376.198 (2)	375.999 (2)	376.304 (2)	376.274 (2)	376.308 (2)	376.252 (14)		
71370	406.390 (2)	406.408 (2)	406.411 (2)	406.496 (2)	406.511 (2)	406.573 (2)	406.726 (2)	406.502 (14)		
71479	453.400 (2)	453.369 (2)	453.329 (2)	453.429 (2)	453.486 (2)	453.641 (2)	453.811 (2)	453.495 (14)		
67615	503.205 (2)	503.624 (2)	503.626 (2)	503.744 (2)	503.954 (2)	504.158 (2)	504.259 (2)	503.796 (14)		
Av of 11*	351.448	351.466	351.467	351.498	351.608	351.700	351.781	351.566		

Source of data:

1981-1983: Table 1d of Keeling et al. [1984]

1985-1998: Final column of Tables 9.1b, 9.1d, 9.1f, 9.1g, 9.1i, of this report

* Unweighted average of reference gases (11 gases, excluding 66556, see text p. 13).

Table 9.3a. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1985 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	Jun 19	Jul 9	Jul 30	Aug 20	Sep 4	Average I	Average J	Average J + .110*	Sigma J
2408	199.75 (10)	199.83 (18)	199.88 (10)	199.77 (10)	199.26 (10)	199.698	175.256	175.366	0.305
3753	251.40 (14)	251.37 (10)	251.42 (10)	251.26 (10)	251.01 (10)	251.292	238.128	238.238	0.206
7366	280.19 (12)	280.12 (10)	280.11 (10)	280.04 (10)	279.83 (10)	280.058	273.183	273.293	0.168
6078	310.11 (10)	310.05 (10)	310.04 (10)	309.93 (12)	309.82 (10)	309.990	309.658	309.768	0.140
2399	321.07 (10)	321.05 (10)	320.95 (10)	320.82 (10)	320.78 (10)	320.934	322.994	323.104	0.160
39239	328.11 (10)	328.09 (10)	328.00 (12)	327.92 (10)	327.87 (10)	327.998	331.602	331.712	0.127
39256	338.40 (10)	338.44 (10)	338.32 (10)	338.27 (10)	338.24 (10)	338.334	344.198	344.308	0.103
39272	349.83 (20)	349.91 (10)	349.75 (10)	349.72 (10)	349.68 (10)	349.778	358.143	358.253	0.112
1540	364.84 (12)	364.82 (10)	364.77 (10)	364.69 (10)	364.63 (10)	364.750	376.388	376.498	0.108
35299	389.27 (10)	389.28 (10)	389.21 (10)	389.16 (10)	389.09 (10)	389.202	406.185	406.295	0.096
35316	427.06 (10)	427.12 (10)	427.14 (10)	427.12 (10)	427.03 (12)	427.094	452.361	452.471	0.057

See text, p. 14.

* Adjustment for drift in secondary standard <34850>, see Keeling et al. [1986], p. 4.

Table 9.3b. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1985 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	Jun 19	Jul 9	Jul 30	Aug 20	Sep 4	Average I	Average J	Average J + .110*	Sigma J
71251	215.62 (10)	215.62 (12)	215.63 (10)	215.51 (10)	215.13 (12)	215.502	194.515	194.625	0.260
34819	254.61 (10)	254.58 (10)	254.58 (10)	254.48 (10)	254.22 (10)	254.494	242.030	242.140	0.196
71286	295.17 (10)	295.11 (10)	295.10 (10)	295.01 (10)	294.85 (10)	295.048	291.449	291.559	0.152
71341	316.43 (10)	316.38 (10)	316.34 (10)	316.29 (10)	316.15 (10)	316.318	317.369	317.479	0.131
66638	329.36 (10)	329.37 (10)	329.24 (10)	329.20 (10)	329.13 (10)	329.260	333.140	333.250	0.126
66625	334.29 (10)	334.26 (10)	334.21 (12)	334.16 (10)	334.11 (10)	334.206	339.167	339.277	0.089
66696	346.13 (12)	346.15 (10)	346.07 (12)	345.99 (10)	345.95 (10)	346.058	353.610	353.720	0.106
71308	358.13 (10)	358.13 (10)	358.10 (10)	358.05 (10)	357.92 (12)	358.066	368.243	368.353	0.107
71370	379.56 (10)	379.67 (10)	379.55 (10)	379.45 (10)	379.45 (10)	379.536	394.406	394.516	0.112
71479	410.87 (10)	410.86 (12)	410.88 (10)	410.89 (10)	410.75 (10)	410.850	432.566	432.676	0.069
67615	441.66 (10)	441.71 (10)	441.79 (10)	441.70 (10)	441.68 (10)	441.708	470.169	470.279	0.061

See text, p. 14.

* Adjustment for drift in secondary standard <34850>, see Keeling et al. [1986], p. 4.

Table 9.3c. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1987 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	Nov 15	Dec 1	Dec 8	Dec 15	Dec 22	Average I	Average J	Sigma J
2408	199.82 (10)	199.66 (12)	199.52 (10)	199.20 (10)	199.66 (10)	199.572	175.102	0.285
3753	251.41 (10)	251.35 (10)	251.40 (12)	251.19 (10)	251.33 (10)	251.336	238.182	0.107
7366	280.10 (10)	280.12 (10)	280.10 (10)	279.99 (10)	280.11 (10)	280.084	273.214	0.065
6078	310.02 (10)	310.01 (10)	309.98 (10)	309.99 (10)	309.97 (10)	309.994	309.663	0.025
2399	320.96 (10)	320.95 (10)	320.94 (10)	320.94 (10)	320.91 (10)	320.940	323.001	0.023
39239	327.97 (10)	327.99 (10)	328.00 (10)	327.94 (10)	327.96 (10)	327.972	331.571	0.029
39256	338.30 (10)	338.30 (10)	338.31 (10)	338.27 (10)	338.26 (10)	338.288	344.142	0.026
39272	349.69 (10)	349.67 (10)	349.70 (10)	349.68 (10)	349.70 (10)	349.688	358.034	0.016
1540	364.63 (10)	364.64 (10)	364.62 (10)	364.52 (10)	364.67 (10)	364.616	376.225	0.069
35299	389.09 (10)	389.08 (10)	389.03 (10)	388.86 (10)	389.17 (10)	389.046	405.995	0.141
35316	426.97 (10)	426.88 (10)	426.80 (10)	426.50 (10)	426.97 (10)	426.824	452.032	0.237

See text, p. 14.

Table 9.3d. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1987 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	Nov 15	Dec 1	Dec 8	Dec 15	Dec 22	Average I	Average J	Sigma J
71251	215.62 (10)	215.53 (10)	215.47 (10)	215.17 (10)	215.46 (10)	215.450	194.451	0.206
34819	254.57 (10)	254.57 (10)	254.56 (10)	254.44 (10)	254.56 (10)	254.540	242.086	0.068
71286	295.05 (10)	295.08 (10)	295.05 (10)	295.04 (10)	295.06 (10)	295.056	291.459	0.018
71341	316.27 (10)	316.24 (10)	316.26 (10)	316.31 (10)	316.25 (10)	316.266	317.306	0.033
66638	329.25 (10)	329.28 (10)	329.27 (10)	329.25 (12)	329.26 (10)	329.262	333.143	0.016
66625	334.19 (10)	334.16 (10)	334.19 (10)	334.11 (10)	334.17 (10)	334.164	339.116	0.040
66696	346.03 (10)	346.02 (10)	346.01 (10)	346.02 (10)	346.02 (10)	346.020	353.564	0.009
71308	357.94 (10)	357.94 (10)	357.94 (10)	357.86 (10)	357.93 (10)	357.922	368.068	0.043
71370	379.53 (10)	379.47 (10)	379.49 (10)	379.31 (10)	379.54 (10)	379.468	394.324	0.113
71479	410.72 (10)	410.71 (10)	410.65 (10)	410.37 (10)	410.80 (12)	410.650	432.322	0.202
67615	441.65 (10)	441.50 (10)	441.45 (10)	440.99 (10)	441.64 (10)	441.446	469.850	0.328

See text, p. 14.

Table 9.3e. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1989 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	Feb 13	Feb 21	Mar 1	Mar 16	Mar 23	Average I	Average J	Sigma J
2408	199.80 (10)	199.85 (10)	199.85 (10)	200.03 (10)	200.01 (10)	199.908	175.512	0.127
3753	251.46 (10)	251.43 (10)	251.36 (10)	251.43 (10)	251.46 (10)	251.428	238.294	0.050
7366	280.14 (10)	280.07 (10)	280.05 (10)	280.09 (10)	280.07 (10)	280.084	273.214	0.042
6078	309.99 (10)	310.01 (10)	309.97 (10)	309.90 (10)	309.91 (10)	309.956	309.616	0.059
2399	320.87 (10)	320.98 (10)	320.90 (10)	320.88 (10)	320.89 (10)	320.904	322.958	0.054
39239	327.97 (10)	327.87 (10)	327.95 (10)	327.92 (10)	327.94 (10)	327.930	331.519	0.046
39256	338.25 (10)	338.30 (10)	338.31 (10)	338.23 (10)	338.23 (10)	338.264	344.112	0.047
39272	349.68 (10)	349.67 (10)	349.61 (10)	349.64 (10)	349.63 (10)	349.646	357.983	0.035
1540	364.62 (10)	364.63 (10)	364.53 (10)	364.63 (10)	364.60 (10)	364.602	376.208	0.051
35299	389.05 (10)	389.04 (10)	388.87 (10)	388.94 (10)	389.06 (10)	388.992	405.930	0.102
35316	426.80 (10)	426.70 (10)	426.52 (10)	426.81 (10)	426.81 (10)	426.728	451.915	0.153

See text, p. 14.

Table 9.3f. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1989 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	Feb 13	Feb 21	Mar 1	Mar 16	Mar 23	Average I	Average J	Sigma J
71251	215.60 (10)	215.58 (10)	215.51 (10)	215.74 (10)	215.70 (10)	215.626	194.666	0.114
34819	254.62 (10)	254.55 (10)	254.52 (10)	254.55 (10)	254.60 (10)	254.568	242.120	0.050
71286	295.05 (10)	294.97 (10)	294.96 (10)	294.98 (10)	295.03 (10)	294.998	291.388	0.048
71341	316.22 (10)	316.18 (10)	316.19 (10)	316.18 (10)	316.16 (10)	316.186	317.208	0.027
66638	329.27 (10)	329.28 (10)	329.21 (10)	329.24 (10)	329.25 (10)	329.250	333.128	0.033
66625	334.17 (10)	334.11 (10)	334.13 (10)	334.11 (10)	334.13 (10)	334.130	339.075	0.030
66696	346.01 (10)	346.01 (10)	345.97 (10)	345.99 (10)	346.00 (10)	345.996	353.535	0.020
71308	357.89 (10)	357.92 (10)	357.80 (10)	357.89 (10)	357.85 (10)	357.870	368.004	0.057
71370	379.49 (10)	379.44 (10)	379.33 (10)	379.42 (10)	379.46 (10)	379.428	394.275	0.074
71479	410.66 (11)	410.58 (10)	410.37 (10)	410.64 (10)	410.65 (10)	410.580	432.237	0.148
67615	441.58 (10)	441.33 (10)	441.19 (10)	441.49 (10)	441.47 (10)	441.412	469.809	0.186

See text, p. 14.

Table 9.3g. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1990 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	May 3	May 14	May 21	Jun 1	Jun 11	Average I	Average J	Sigma J
2408	200.47 (10)	200.36 (10)	200.33 (10)	200.27 (10)	200.20 (10)	200.326	176.021	0.123
3753	251.83 (10)	251.75 (10)	251.81 (10)	251.78 (10)	251.67 (10)	251.768	238.708	0.076
7366	280.36 (8)	280.29 (10)	280.29 (10)	280.19 (10)	280.25 (10)	280.276	273.448	0.076
6078	310.06 (10)	310.05 (10)	310.04 (10)	310.04 (10)	310.00 (10)	310.038	309.716	0.028
2399	320.96 (10)	320.98 (10)	320.96 (10)	320.96 (10)	320.94 (10)	320.960	323.026	0.017
39239	327.96 (10)	327.97 (10)	327.93 (10)	327.97 (10)	327.94 (10)	327.954	331.549	0.022
39256	338.18 (10)	338.24 (10)	338.23 (10)	338.21 (10)	338.22 (10)	338.216	344.054	0.028
39272	349.48 (10)	349.59 (10)	349.61 (10)	349.53 (10)	349.49 (10)	349.540	357.853	0.071
1540	364.39 (10)	364.42 (10)	364.49 (10)	364.42 (10)	364.35 (10)	364.414	375.979	0.062
35299	388.65 (10)	388.73 (10)	388.80 (10)	388.74 (10)	388.63 (10)	388.710	405.586	0.085
35316	426.37 (10)	426.29 (10)	426.35 (10)	426.38 (10)	426.14 (10)	426.306	451.400	0.121

See text, p. 14.

Table 9.3h. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1990 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	May 3	May 14	May 21	Jun 1	Jun 11	Average I	Average J	Sigma J
71251	216.11 (10)	216.04 (10)	216.07 (10)	215.99 (10)	215.90 (10)	216.022	195.148	0.099
34819	254.90 (10)	254.89 (10)	254.90 (10)	254.86 (10)	254.88 (10)	254.886	242.508	0.020
71286	295.16 (10)	295.11 (10)	295.16 (10)	295.10 (10)	295.15 (10)	295.136	291.557	0.035
71341	316.23 (10)	316.29 (10)	316.25 (10)	316.26 (10)	316.25 (10)	316.256	317.293	0.027
66638	329.22 (10)	329.26 (10)	329.23 (10)	329.29 (10)	329.23 (10)	329.246	333.123	0.035
66625	334.10 (10)	334.12 (10)	334.16 (10)	334.13 (10)	334.19 (10)	334.140	339.087	0.043
66696	345.89 (10)	345.95 (10)	345.97 (10)	345.95 (10)	345.94 (10)	345.940	353.466	0.037
71308	357.66 (10)	357.77 (10)	357.80 (10)	357.72 (10)	357.68 (10)	357.726	367.829	0.072
71370	379.09 (12)	379.18 (12)	379.25 (10)	379.20 (10)	379.17 (10)	379.178	393.970	0.071
71479	410.24 (10)	410.25 (10)	410.29 (10)	410.22 (10)	410.15 (10)	410.230	431.810	0.063
67615	441.07 (10)	440.97 (10)	440.98 (10)	441.00 (10)	440.84 (10)	440.972	469.272	0.102

See text, p. 14.

Table 9.3i. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1993 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	May 6	May 13	May 20	May 27	Jun 3	Average I	Average J	Sigma J
2408	201.73 (10)	202.22 (10)	201.99 (10)	201.77 (10)	202.48 (10)	202.038	178.107	0.384
4274	249.47 (10)	249.81 (10)	249.70 (10)	249.72 (10)	249.88 (10)	249.716	236.208	0.189
3753	252.52 (10)	252.69 (10)	252.73 (10)	252.72 (10)	252.84 (10)	252.700	239.844	0.141
7366	280.57 (10)	280.73 (10)	280.87 (10)	280.75 (10)	280.73 (10)	280.730	274.001	0.130
6071	309.51 (10)	309.55 (10)	309.61 (10)	309.61 (10)	309.57 (10)	309.570	309.146	0.052
6078	310.13 (10)	310.15 (10)	310.14 (10)	310.15 (10)	310.16 (10)	310.146	309.848	0.014
4296	317.95 (10)	317.97 (10)	318.02 (10)	317.96 (10)	317.97 (10)	317.974	319.387	0.033
2399	320.90 (10)	320.90 (10)	320.92 (10)	320.88 (10)	320.88 (10)	320.896	322.948	0.020
39239	327.81 (10)	327.81 (10)	327.83 (10)	327.82 (10)	327.78 (10)	327.810	331.373	0.023
39256	338.00 (10)	338.04 (10)	338.01 (10)	337.97 (10)	338.02 (10)	338.008	343.800	0.032
39272	349.17 (10)	349.20 (10)	349.22 (10)	349.12 (10)	349.23 (10)	349.188	357.424	0.054
1540	363.88 (10)	363.86 (10)	363.97 (10)	363.78 (10)	363.96 (10)	363.890	375.340	0.095
35299	387.82 (10)	387.92 (10)	388.12 (10)	387.70 (10)	387.97 (10)	387.906	404.606	0.193
35316	424.84 (10)	424.90 (10)	425.32 (10)	424.73 (10)	425.09 (10)	424.976	449.780	0.283

See text, p. 14.

Table 9.3j. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1993 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	May 6	May 13	May 20	May 27	Jun 3	Average I	Average J	Sigma J
71251	217.10 (10)	217.63 (10)	217.38 (10)	217.37 (10)	217.73 (10)	217.442	196.879	0.301
34819	255.35 (10)	255.72 (10)	255.73 (10)	255.71 (10)	255.62 (10)	255.626	243.410	0.195
71286	295.24 (10)	295.36 (10)	295.46 (10)	295.42 (10)	295.36 (12)	295.368	291.839	0.101
71341	316.19 (10)	316.18 (10)	316.26 (10)	316.25 (10)	316.21 (12)	316.218	317.247	0.043
66638	329.05 (10)	329.11 (10)	329.11 (10)	329.09 (10)	329.05 (10)	329.082	332.923	0.037
66625	333.88 (10)	333.89 (10)	333.91 (10)	333.84 (10)	333.86 (10)	333.876	338.765	0.033
66696	345.56 (10)	345.61 (10)	345.62 (10)	345.54 (10)	345.65 (10)	345.596	353.047	0.055
71308	357.16 (10)	357.20 (10)	357.20 (10)	357.13 (10)	357.26 (10)	357.190	367.176	0.060
71370	378.42 (10)	378.47 (10)	378.59 (10)	378.30 (10)	378.56 (10)	378.468	393.105	0.141
71479	408.92 (10)	409.09 (10)	409.38 (10)	408.83 (10)	409.15 (10)	409.074	430.401	0.261
67615	439.27 (10)	439.27 (10)	439.80 (10)	439.15 (10)	439.43 (10)	439.384	467.337	0.308

See text, p. 14.

Table 9.3k. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1995 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	May 30	Jun 7	Jun 27	Aug 17	Aug 24	Average I	Average J	Sigma J
2408	201.51 (10)	201.24 (10)	200.43 (10)	200.44 (10)	200.31 (10)	200.786	176.582	0.668
4274	249.29 (10)	249.24 (10)	249.07 (10)	248.91 (10)	249.05 (10)	249.112	235.472	0.187
7366	280.32 (10)	280.36 (10)	280.25 (10)	280.28 (10)	280.32 (10)	280.306	273.485	0.051
6071	309.37 (10)	309.41 (10)	309.42 (10)	309.41 (10)	309.29 (10)	309.380	308.914	0.066
6078	309.87 (10)	309.90 (12)	309.95 (10)	309.97 (10)	309.86 (10)	309.910	309.560	0.059
4296	317.77 (10)	317.77 (12)	317.86 (10)	317.87 (10)	317.70 (10)	317.794	319.168	0.086
2399	320.72 (10)	320.66 (10)	320.71 (10)	320.74 (10)	320.77 (10)	320.720	322.733	0.049
39239	327.64 (10)	327.65 (10)	327.63 (10)	327.69 (10)	327.66 (10)	327.654	331.183	0.028
39256	337.87 (10)	337.86 (10)	337.88 (10)	337.92 (10)	337.94 (10)	337.894	343.662	0.042
39272	349.09 (10)	349.04 (10)	349.07 (10)	349.01 (10)	348.91 (10)	349.024	357.225	0.086
1540	363.78 (10)	363.74 (10)	363.73 (10)	363.69 (10)	363.78 (12)	363.744	375.162	0.046
35299	387.84 (10)	387.77 (10)	387.74 (12)	387.57 (10)	387.81 (12)	387.746	404.411	0.129
35316	424.87 (10)	424.90 (10)	424.88 (10)	424.48 (14)	424.76 (10)	424.778	449.538	0.214

See text, p. 14.

Table 9.31. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1995 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	May 30	Jun 7	Jun 27	Aug 17	Aug 24	Average I	Average J	Sigma J
71251	216.82 (10)	216.76 (10)	216.20 (10)	216.17 (12)	216.17 (12)	216.424	195.638	0.408
34819	255.20 (10)	255.24 (10)	254.99 (12)	255.07 (10)	255.22 (10)	255.144	242.822	0.133
71286	295.11 (10)	295.11 (10)	295.09 (10)	295.04 (10)	295.13 (10)	295.096	291.508	0.042
71341	316.04 (10)	316.00 (10)	316.05 (12)	316.00 (10)	316.05 (10)	316.028	317.016	0.032
66638	329.03 (10)	328.98 (10)	328.98 (10)	328.97 (10)	329.02 (10)	328.996	332.818	0.033
66625	333.75 (10)	333.80 (10)	333.74 (10)	333.74 (10)	333.86 (10)	333.778	338.646	0.064
66696	345.50 (10)	345.52 (10)	345.46 (10)	345.51 (10)	345.58 (12)	345.514	352.947	0.053
71308	357.19 (10)	357.08 (10)	357.04 (10)	357.03 (12)	356.98 (14)	357.064	367.022	0.096
71370	378.42 (10)	378.35 (10)	378.29 (12)	378.24 (12)	378.19 (14)	378.298	392.898	0.110
71479	409.06 (10)	409.05 (10)	408.92 (10)	408.71 (12)	408.98 (12)	408.944	430.243	0.174
67615	439.24 (10)	439.42 (10)	439.31 (12)	438.83 (12)	439.17 (10)	439.194	467.106	0.272

See text, p. 14.

Table 9.3m. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1997 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	Jul 15	Aug 4	Aug 26	Sep 4	Sep 18	Average I	Average J	Sigma J
2408	200.55 (12)	199.81 (10)	199.72 (10)	199.96 (10)	200.15 (10)	200.038	175.670	0.401
4274	248.74 (10)	248.48 (10)	248.46 (10)	248.91 (10)	248.76 (10)	248.670	234.933	0.237
7366	280.05 (10)	279.98 (10)	279.96 (10)	280.18 (10)	280.02 (10)	280.038	273.158	0.106
6071	309.31 (10)	309.28 (10)	309.26 (10)	309.30 (10)	309.27 (10)	309.284	308.797	0.025
6078	309.66 (10)	309.79 (10)	309.73 (10)	309.74 (10)	309.74 (10)	309.732	309.343	0.057
4296	317.73 (10)	317.77 (10)	317.78 (10)	317.64 (10)	317.69 (10)	317.722	319.080	0.071
2399	320.53 (10)	320.59 (10)	320.58 (10)	320.47 (10)	320.53 (10)	320.540	322.514	0.058
39239	327.47 (10)	327.50 (10)	327.50 (10)	327.55 (12)	327.47 (10)	327.498	330.993	0.040
39256	337.81 (10)	337.72 (10)	337.72 (10)	337.68 (10)	337.73 (10)	337.732	343.464	0.058
39272	348.89 (10)	348.90 (10)	348.88 (10)	348.91 (10)	348.91 (10)	348.898	357.071	0.016
1540	363.63 (10)	363.56 (10)	363.60 (10)	363.70 (10)	363.56 (10)	363.610	374.999	0.071
35299	387.77 (10)	387.58 (10)	387.64 (10)	387.92 (10)	387.57 (10)	387.696	404.350	0.181
35316	424.92 (10)	424.60 (10)	424.66 (10)	425.17 (10)	424.52 (10)	424.774	449.534	0.326

See text, p. 14.

Table 9.3n. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1997 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	Jul 15	Aug 4	Aug 26	Sep 4	Sep 18	Average I	Average J	Sigma J
71251	215.94 (10)	215.54 (10)	215.51 (10)	215.80 (10)	215.76 (10)	215.710	194.768	0.222
34819	254.76 (10)	254.65 (10)	254.56 (10)	254.97 (10)	254.80 (10)	254.748	242.340	0.190
71286	294.74 (10)	294.84 (10)	294.85 (10)	294.91 (20)	294.77 (10)	294.822	291.174	0.082
71341	315.78 (10)	315.96 (10)	315.90 (10)	315.85 (10)	315.81 (10)	315.860	316.811	0.087
66638	328.82 (10)	328.84 (10)	328.85 (10)	328.67 (10)	328.80 (10)	328.796	332.575	0.089
66625	333.56 (10)	333.59 (10)	333.55 (10)	333.50 (10)	333.55 (10)	333.550	338.368	0.039
66696	345.34 (10)	345.38 (10)	345.39 (10)	345.29 (10)	345.30 (10)	345.340	352.735	0.055
71308	356.94 (10)	356.88 (10)	356.89 (10)	356.92 (10)	356.88 (10)	356.902	366.825	0.033
71370	378.33 (10)	378.14 (10)	378.15 (10)	378.27 (10)	378.08 (10)	378.194	392.771	0.125
71479	408.96 (10)	408.73 (10)	408.81 (10)	409.11 (10)	408.63 (10)	408.848	430.126	0.231
67615	439.36 (10)	439.11 (10)	439.15 (10)	439.77 (10)	438.99 (10)	439.276	467.206	0.374

See text, p. 14.

Table 9.3o. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1998-1999 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-NITROGEN

Cyl No.	Dec 14	Dec 22	Dec 29	Jan 13	Jan 20	Average I	Average J	Sigma J
2408	200.38 (10)	199.66 (10)	200.68 (10)	200.74 (10)	200.27 (10)	200.346	176.046	0.526
4274	248.89 (10)	248.55 (10)	249.04 (10)	249.03 (10)	248.73 (10)	248.848	235.150	0.255
7366	280.20 (10)	279.92 (10)	280.27 (10)	280.25 (10)	280.00 (10)	280.128	273.268	0.193
6071	309.47 (10)	309.32 (10)	309.47 (10)	309.47 (10)	309.33 (10)	309.412	308.953	0.097
6078	309.86 (10)	309.76 (10)	309.88 (10)	309.82 (10)	309.76 (10)	309.816	309.446	0.068
4296	317.89 (10)	317.75 (10)	317.93 (10)	317.84 (10)	317.74 (10)	317.830	319.212	0.102
2399	320.63 (10)	320.63 (10)	320.68 (10)	320.68 (10)	320.59 (10)	320.642	322.638	0.047
39239	327.58 (10)	327.51 (10)	327.64 (10)	327.58 (10)	327.46 (10)	327.554	331.061	0.085
39256	337.78 (10)	337.79 (10)	337.84 (10)	337.81 (10)	337.76 (10)	337.796	343.542	0.037
39272	348.95 (10)	348.88 (10)	348.94 (10)	348.92 (10)	348.90 (10)	348.918	357.095	0.035
1540	363.59 (10)	363.59 (10)	363.58 (10)	363.63 (10)	363.60 (10)	363.598	374.984	0.023
35299	387.59 (10)	387.55 (10)	387.53 (10)	387.64 (10)	387.59 (10)	387.580	404.209	0.052
35316	424.45 (10)	424.41 (10)	424.35 (10)	424.67 (10)	424.63 (10)	424.502	449.202	0.171

See text, p. 14.

Table 9.3p. Applied Physics analyzer results in index units, I, for manometrically analyzed standards during 1998-1999 calibration. Averages, not weighted, are also expressed in Adjusted Index units, J.

CO₂-IN-AIR

Cyl No.	Dec 14	Dec 22	Dec 29	Jan 13	Jan 20	Average I	Average J	Sigma J
71251	215.99 (10)	215.47 (10)	216.26 (10)	216.18 (10)	215.89 (10)	215.958	195.070	0.378
34819	254.88 (10)	254.59 (10)	254.98 (10)	254.96 (10)	254.68 (10)	254.818	242.425	0.212
71286	295.05 (10)	294.85 (10)	295.02 (10)	294.97 (10)	294.84 (10)	294.946	291.325	0.118
71341	315.97 (10)	315.86 (10)	-	315.91 (10)	315.84 (10)	315.895	316.854	0.071
66638	328.89 (10)	328.88 (10)	328.91 (10)	328.91 (10)	328.84 (10)	328.886	332.684	0.035
66625	333.61 (10)	333.61 (10)	333.67 (10)	333.64 (10)	333.59 (10)	333.624	338.458	0.038
66696	345.42 (10)	345.39 (10)	345.41 (10)	345.40 (10)	345.38 (10)	345.400	352.808	0.019
71308	356.92 (10)	356.91 (10)	356.89 (10)	356.92 (10)	356.93 (10)	356.914	366.839	0.018
71370	378.14 (10)	378.19 (10)	378.12 (10)	378.16 (10)	378.17 (10)	378.156	392.725	0.033
71479	408.61 (10)	408.62 (10)	408.53 (10)	408.81 (10)	408.71 (10)	408.656	429.892	0.131
67615	438.83 (10)	438.88 (10)	438.80 (10)	439.16 (10)	439.03 (10)	438.940	466.796	0.185

See text, p. 14.

Table 9.4a. Volume calibration of 4 cc manometric chamber in 1985-1986

Experiment No.	Date of Plenum Fillings	Plenum No.	Computed 4cc Chamber Volume (cc)
1	24 Oct 85	P-1	3.7954
2	24 Oct 85	P-7	3.7959
3	24 Oct 85	P-1	3.7939
4	24 Oct 85	P-7	3.7962
5	30 Oct 85	P-1	3.7952
6	30 Oct 85	P-3	3.7954
7	30 Oct 85	P-4	3.7978 #
8	30 Oct 85	P-5	3.7986 #
9	30 Oct 85	P-7	3.7958
10	21 Jan 86	P-1	3.7953
11	21 Jan 86	P-2	3.7947
12	21 Jan 86	P-3	3.7961
13	21 Jan 86	P-6	3.7961
14	21 Jan 86	P-7	3.7953
15	23 Jan 86	P-1	3.7944
16	23 Jan 86	P-3	3.7963
17	23 Jan 86	P-5	3.7989 #
18	23 Jan 86	P-7	3.7961
19	23 Jan 86	P-4	3.8001 #

Mean of 15 = 3.7955
 σ_{in} = 0.00071
 σ_m = 0.00018

Deleted: Plenum numbers P-4 and P-5 disagree with others, see text p. 19.

Table 9.4b. Volume calibration of 4 cc manometric chamber in 1988

Experiment No.	Date of Plenum Fillings	Plenum No.	Computed 4cc Chamber Volume (cc)
1	19 Feb 88	P-1	3.7955
2	19 Feb 88	P-7	3.7954
3	23 Feb 88	P-1	3.7949
4	23 Feb 88	P-2	3.7952
5	23 Feb 88	P-3	3.7973
6	23 Feb 88	P-6	3.7966
7	23 Feb 88	P-7	3.7961
8	25 Feb 88	P-7	3.7960
9	25 Feb 88	P-6	3.7977 *
10	25 Feb 88	P-3	3.7967
11	25 Feb 88	P-2	3.7966
12	25 Feb 88	P-1	3.7964
13	2 Mar 88	P-1	3.7950
14	2 Mar 88	P-2	3.7957
15	2 Mar 88	P-4	3.7994 #
16	2 Mar 88	P-5	3.8008 #
17	2 Mar 88	P-7	3.7961

Mean of 15 = 3.7961
 σ_{in} = 0.00082
 σ_m = 0.00021

* Singlet (One measurement of two rejected)

Deleted: Plenum numbers P-4 and P-5 disagree with others,
see text p. 19.

Table 9.4c. Volume calibration of 4 cc manometric chamber in 1990

Experiment No.	Date of Plenum Fillings	Plenum No.	Computed 4cc Chamber Volume (cc)
1	8 Feb 90	P-1	3.7938
2	8 Feb 90	P-7	3.7952
4	12 Feb 90	P-1	3.7975*
5	12 Feb 90	P-7	3.7972
7	14 Feb 90	P-1	3.7956
8	14 Feb 90	P-7	3.7962
9	14 Feb 90	P-2	3.7964
10	14 Feb 90	P-3	3.7975
11	14 Feb 90	P-6	3.7975
13	4 Oct 90	P-1	3.7937
14	4 Oct 90	P-7	3.7948
15	4 Oct 90	P-2	3.7952
16	4 Oct 90	P-3	3.7979
17	4 Oct 90	P-6	3.7962
18	5 Oct 90	P-7	3.7954
19	5 Oct 90	P-1	3.7968
20	8 Oct 90	P-3	3.7965
21	8 Oct 90	P-1	3.7956
22	8 Oct 90	P-7	3.7973
23	8 Oct 90	P-2	3.7957
24	8 Oct 90	P-6	3.7983

Mean of 21 = 3.7962
 σ_{in} = 0.00128
 σ_m = 0.00028

*Singlet (One measurement of two rejected)

Note: Experiment Numbers 3, 6 and 12 with large plenum number P-8 for 64cc chamber calibration, not reported here.

Table 9.4d. Volume calibration of 4 cc manometric chamber in 1993-1994

Experiment No.	Date of Plenum Fillings	Plenum No.	Computed 4cc Chamber Volume (cc)
1	12 Oct 93	P-1	3.7907
2	12 Oct 93	P-7	3.7920
4	31 Jan 94	P-1	3.7937
5	31 Jan 94	P-7	3.7962
6	31 Jan 94	P-2	3.7927
7	31 Jan 94	P-3	3.7940
8	31 Jan 94	P-6	3.7945*
9	2 Feb 94	P-1	3.7915
10	2 Feb 94	P-7	3.7945
12	7 Feb 94	P-1	3.7931
13	7 Feb 94	P-7	3.7944
14	7 Feb 94	P-2	3.7958
15	7 Feb 94	P-3	3.7936
16	7 Feb 94	P-6	3.7975

Mean of 14 = 3.7939
 σ_{in} = 0.00185
 σ_m = 0.00049

*Singlet (One measurement of two rejected)

Note: Experiment Numbers 3, 11 and 17 with large plenum number P-8 for 64cc chamber calibration, not reported here.

Table 9.4e. Volume calibration of 4 cc manometric chamber in 1998-1999

Experiment No.	Date of Plenum Fillings	Plenum No.	Computed 4cc Chamber Volume (cc)
1	10 Dec 98	P-1	3.7924
2	10 Dec 98	P-7	3.7947
3	14 Dec 98	P-1	3.7927
4	14 Dec 98	P-2	3.7948
5	14 Dec 98	P-3	3.7955
6	14 Dec 98	P-6	3.7967
7	14 Dec 98	P-7	3.7982*
8	06 Jan 99	P-2	3.7942
9	06 Jan 99	P-7	3.7981
10	06 Jan 99	P-1	3.7966
11	06 Jan 99	P-6	3.7991
12	06 Jan 99	P-3	3.7999
13	13 Jan 99	P-1	3.7938
14	13 Jan 99	P-7	3.7946
15	13 Jan 99	P-2	3.7935
16	13 Jan 99	P-6	3.7953
17	13 Jan 99	P-3	3.7958
18	21 Jan 99	P-1	3.7913
19	21 Jan 99	P-7	3.7944
20	21 Jan 99	P-2	3.7931
21	21 Jan 99	P-6	3.7960
22	21 Jan 99	P-3	3.7959

Mean of 22 = 3.7953
 σ_{in} = 0.00220
 σ_m = 0.00047

* Doublet (One of three measurements rejected)

Table 9.5a. Summary of manometric measurements (mole fraction of CO₂ in ppm), by year, since 1985. Averages for each reference gas are weighted by the number of runs (shown in parentheses)

CO ₂ -IN-NITROGEN GASES						
Cyl No	1985	1990	1993	1998	Wt. Average	
2408	196.881 (2)	197.001 (2)	196.892 (2)	197.010 (2)	196.946 (8)	
4274			243.277 (2)	243.458 (2)	243.368 (4)	
3753	246.193 (2)	246.391 (2)	246.484 (2)		246.356 (6)	
7366	276.734 (2)	276.742 (2)	276.719 (2)	276.701 (2)	276.724 (8)	
6071			310.213 (2)	310.590 (2)	310.402 (4)	
6078	311.050 (2)	310.946 (2)	310.973 (2)	310.934 (2)	310.976 (8)	
4296			320.533 (2)	320.631 (2)	320.582 (4)	
2399	324.113 (2)	324.114 (2)	324.061 (2)	324.037 (2)	324.081 (8)	
39239	332.872 (2)	332.910 (5)	332.934 (3)	332.825 (2)	332.896 (12)	
39256	345.864 (2)	345.795 (2)	345.839 (2)	345.989 (2)	345.872 (8)	
39272	360.781 (2)	360.665 (2)	360.708 (2)	360.763 (2)	360.729 (8)	
1540	380.781 (2)	380.766 (2)	380.728 (2)	380.754 (2)	380.757 (8)	
35299	415.128 (2)	415.234 (2)	415.227 (2)	415.258 (2)	415.212 (8)	
35316	472.951 (2)	473.030 (2)	472.953 (2)	472.934 (2)	472.967 (8)	
Av. of 10*	341.716	341.720	341.703	341.721	341.716	

Source of data:

1985: Table 2a of this report multiplied by (1321.798/1321.116)

1990: Table 2a of this report multiplied by (1321.798/1321.221)

1993: Table 2a of this report multiplied by (1321.798/1321.604)

1998: Table 2a of this report multiplied by (1321.798/1322.301)

* Unweighted average of reference gases (10 gases, excluding 4274, 3753, 6071, 4296)

Table 9.5b. Summary of manometric measurements (mole fraction of CO₂ in ppm), by year, since 1985. The number of runs is shown in parentheses.

CO ₂ -IN-AIR GASES						
Cyl no	1985	1990	1993	1995	1998	Av.
66556	100.938 (2)	101.063 (2)			100.969 (2)	100.990 (6)
71251	213.208 (2)	213.289 (2)	213.174 (2)	213.216 (2)	213.244 (2)	213.226 (10)
34819	251.888 (2)	252.103 (2)	252.120 (2)	252.139 (2)	252.154 (2)	252.081 (10)
71286	296.778 (2)	296.840 (2)	296.791 (2)	296.785 (2)	296.692 (2)	296.777 (10)
71341	322.300 (2)	322.156 (2)	322.131 (2)	322.156 (2)	322.153 (2)	322.179 (10)
66638	338.444 (2)	338.438 (2)	338.563 (2)	338.518 (2)	338.513 (2)	338.495 (10)
66625	344.847 (2)	344.664 (2)	344.655 (2)	344.612 (2)	344.673 (2)	344.690 (10)
66696	360.206 (2)	360.247 (2)	360.308 (2)	360.376 (2)	360.243 (2)	360.276 (10)
71308	376.392 (2)	376.163 (2)	376.359 (2)	376.230 (2)	376.165 (2)	376.262 (10)
71370	406.621 (2)	406.673 (2)	406.571 (2)	406.525 (2)	406.571 (2)	406.592 (10)
71479	453.563 (2)	453.627 (2)	453.552 (2)	453.588 (2)	453.638 (2)	453.594 (10)
67615	503.886 (2)	503.964 (2)	504.028 (2)	504.099 (2)	504.067 (2)	504.009 (10)
Av of 11*	351.648	351.651	351.659	351.659	351.647	351.653

Source of data:

- 1985: Table 2b of this report multiplied by (1321.798/1321.116)
 - 1990: Table 2b of this report multiplied by (1321.798/1321.221)
 - 1993: Table 2b of this report multiplied by (1321.798/1321.604)
 - 1995: Table 2b of this report multiplied by (1321.798/1321.952)
 - 1998: Table 2b of this report multiplied by (1321.798/1322.301)
- * Unweighted average of reference gases (11 gases, excluding 66556)

Table 9.6a. Coefficients of 1985-1999 cubic calibration equations in 1985-1999 CO₂-in-N₂ calibration scales*

Designated Cubic	Cubic Coefficient ^a	X85 Scale	X87 Scale	X90 Scale	X93 Scale	X95 Scale	X97 Scale	X99A Scale
CUB85	C ₀	87.592 ^b	ditto ^c	ditto	ditto	ditto	ditto	87.51316 ^o
	C ₁	0.530735 ^b	ditto	ditto	ditto	ditto	ditto	.5324440 ^o
	C ₂ (X10 ⁴)	4.0661 ^b	ditto	ditto	ditto	ditto	ditto	4.016849 ^o
	C ₃ (X10 ⁷)	6.6595 ^b	ditto	ditto	ditto	ditto	ditto	6.720037 ^o
CUB87	C ₀		89.519 ^d	ditto	89.37936 ^f	89.26957 ⁱ	ditto	89.35812 ^o
	C ₁		0.5141841 ^d	ditto	0.5153639 ^f	0.5165722 ⁱ	ditto	.5164008 ^o
	C ₂ (X10 ⁴)		4.5126 ^d	ditto	4.474744 ^f	4.432576 ⁱ	ditto	4.448049 ^o
	C ₃ (X10 ⁷)		6.3390 ^d	ditto	6.375607 ^f	6.422056 ⁱ	ditto	6.413108 ^o
CUB89	C ₀			(not used)	86.11240 ^g	86.10552 ^j	ditto	86.30291 ^o
	C ₁				0.5487304 ^g	0.5491640 ^j	ditto	.5475480 ^o
	C ₂ (X10 ⁴)				3.363977 ^g	3.349575 ^j	ditto	3.418023 ^o
	C ₃ (X10 ⁷)				7.583929 ^g	7.599323 ^j	ditto	7.527658 ^o
CUB90	C ₀			87.03689 ^e	ditto	86.93749 ^k	ditto	87.13737 ^o
	C ₁			0.5338652 ^e	ditto	0.5353530 ^k	ditto	.5337088 ^o
	C ₂ (X10 ⁴)			3.857944 ^e	ditto	3.806676 ^k	ditto	3.876065 ^o
	C ₃ (X10 ⁷)			7.192074 ^e	ditto	7.248319 ^k	ditto	7.175689 ^o
CUB93	C ₀				81.58785 ^h	81.33812 ^l	ditto	81.69511 ^o
	C ₁				0.5664659 ^h	0.5693753 ^l	ditto	.5658587 ^o
	C ₂ (X10 ⁴)				3.070776 ^h	2.970689 ^l	ditto	3.087755 ^o
	C ₃ (X10 ⁷)				8.176814 ^h	8.278050 ^l	ditto	8.162087 ^o
CUB95	C ₀					87.17948 ^m	ditto	86.05133 ^o
	C ₁					0.5273961 ^m	ditto	.5397667 ^o
	C ₂ (X10 ⁴)					3.982520 ^m	ditto	3.578591 ^o
	C ₃ (X10 ⁷)					7.496791 ^m	ditto	7.918435 ^o
CUB97	C ₀						91.01927 ⁿ	89.14810 ^o
	C ₁						0.4971282 ⁿ	.5191699 ^o
	C ₂ (X10 ⁴)						4.831165 ⁿ	4.098514 ^o
	C ₃ (X10 ⁷)						6.689967 ⁿ	7.440487 ^o
CUB99	C ₀							87.23173 ^o
	C ₁							.5376818 ^o
	C ₂ (X10 ⁴)							3.431323 ^o
	C ₃ (X10 ⁷)							8.270052 ^o

* Footnotes on next page in alphabetical order from left to right in table.

Table 9.6a. Notes

- (a) Coefficients of cubic relationship between X (mole fraction) and J (Index):
 $X = C_0 + C_1J + C_2J^2 + C_3J^3$.
- (b) The 1985 N₂ cubic data set for the X85 through X97 scales consists of J values measured in 1985 (Table 9.3a) and X values measured in 1985 (Table 9.2a). Data are expressed to 2 decimal places and are exactly the same as reported in Keeling et al. [1986]. J values have all been increased by 0.11 ppm to account for secondary standard drift during the 1985 marathon calibrations.
- (c) Denotes repetition of coefficient to the left.
- (d) The 1987 N₂ cubic data set for the X87 and X90 scales consists of preliminary J values measured in 1987 (0.03 to 0.04 ppm lower than Table 9.3c) and X values measured in 1985 (see note b). Data are expressed to 2 decimal places.
- (e) The 1990 N₂ cubic data set for the X90 and X93 scales consists of J values measured in 1990 (Table 9.3g) and preliminary X values measured in 1990 (using preliminary meniscus corrections of -0.340 mm for 4 cc chamber and 0.000 mm for 5000 cc chamber measurements and using all data for No. 39272 (see Table 9.1c)). Data are expressed to 2 decimal places.
- (f) The 1987 N₂ cubic data set for the X93 scale consists of J values measured in 1987 (Table 9.3c) and X values measured in 1985 (see note b). Data are expressed to 2 decimal places.
- (g) The 1989 N₂ cubic data set for the X93 scale consists of J values measured in 1989 (Table 9.3e) and X values measured in 1990 (see note d). Data are expressed to 2 decimal places.
- (h) The 1993 N₂ cubic data set for the X93 scale consists of J values measured in 1993 (Table 9.3i) and preliminary X values measured in 1993 (using preliminary meniscus corrections of -0.340 mm for 4 cc chamber and 0.000 mm for 5000 cc chamber). Data are expressed to 2 decimal places.
- (i) The 1987 N₂ cubic data set for the X95 and X97 scales consists of J values measured in 1987 (Table 9.3c, except 309.641 ppm for No. 6078 for unknown reason) and X values measured in 1985 (Table 9.2a, except 332.695 for No. 39239 for unknown reason). Data are expressed to 3 decimal places.
- (j) The 1989 N₂ cubic data set for the X95 and X97 scales consists of J values measured in 1989 (Table 9.3e) and X values measured in 1990 (Table 9.2a, except the average of all data was used for No. 39272 (see Table 9.1c)). Data are expressed to 3 decimal places.
- (k) The 1990 N₂ cubic data set for the X95 and X97 scales consists of J values measured in 1990 (Table 9.3g) and X values measured in 1990 (see note i). Data are expressed to 3 decimal places.
- (l) The 1993 N₂ cubic data set for the X95 and X97 scales consists of J values measured in 1993 (Table 9.3i) and X values measured in 1993 (Table 9.2a, except the average of all data was used for No. 35299 (see Table 9.1e)). Data are expressed to 3 decimal places.

- (m) The 1995 N₂ cubic data set for the X95 and X97 scales consists of J values measured in 1995 (Table 9.3k) and X values measured in 1993 (Table 9.2a, except for No. 35299 (see note k) and No. 7366 - 276.448 ppm due to typo). Data are expressed to 3 decimal places.
- (n) The 1997 N₂ cubic data set for the X97 scale consists of preliminary J values measured in 1997 (8 of 12 are 0.001 to 0.003 different than Table 9.3m) and X values measured in 1993 (Table 9.2a, except for No. 7366 (see note l) and data for No. 35299 are omitted). Data are expressed to 3 decimal places.
- (o) This report (Table 7.1: cubic calibration equation coefficients derived from X values in Table 9.5a and J values in Tables 9.3a, 9.3c, 9.3e, 9.3g, 9.3i, 9.3k, 9.3m, 9.3o).

Table 9.6b. Coefficients of 1985-1999 cubic calibration equations in 1985-1999 natural-air calibration scales*

Designated Cubic	Cubic Coefficient ^a	X85 Scale	X87 Scale	X90 Scale	X93 Scale	X95 Scale	X97 Scale	X99A Scale
ACUB85	C ₀	87.437 ^b	ditto ^c	ditto	ditto	ditto	ditto	87.41915 ^o
	C ₁	0.539971 ^b	ditto	ditto	ditto	ditto	ditto	.5408285 ^o
	C ₂ (X10 ⁴)	4.0632 ^b	ditto	ditto	ditto	ditto	ditto	4.048589 ^o
	C ₃ (X10 ⁷)	6.9533 ^b	ditto	ditto	ditto	ditto	ditto	6.972401 ^o
ACUB87	C ₀		88.472 ^d	ditto	88.41010 ^f	88.45327 ⁱ	ditto	88.50291 ^o
	C ₁		0.5318281 ^d	ditto	0.5322826 ^f	0.5320256 ⁱ	ditto	.5322630 ^o
	C ₂ (X10 ⁴)		4.2659 ^d	ditto	4.248717 ^f	4.250774 ⁱ	ditto	4.254044 ^o
	C ₃ (X10 ⁷)		6.8519 ^d	ditto	6.870007 ^f	6.873000 ⁱ	ditto	6.875569 ^o
ACUB89	C ₀			(not used)	85.34976 ^g	85.51778 ^j	ditto	85.54302 ^o
	C ₁				0.5636964 ^g	0.5622643 ^j	ditto	.5626305 ^o
	C ₂ (X10 ⁴)				3.218512 ^g	3.269152 ^j	ditto	3.266791 ^o
	C ₃ (X10 ⁷)				7.955842 ^g	7.899927 ^j	ditto	7.907150 ^o
ACUB90	C ₀			86.53137 ^e	ditto	86.78888 ^k	ditto	86.81452 ^o
	C ₁			0.5466209 ^e	ditto	0.5441992 ^k	ditto	.5445588 ^o
	C ₂ (X10 ⁴)			3.773212 ^e	ditto	3.858314 ^k	ditto	3.856169 ^o
	C ₃ (X10 ⁷)			7.508333 ^e	ditto	7.414694 ^k	ditto	7.421745 ^o
ACUB93	C ₀				77.77432 ^h	78.31770 ^l	ditto	78.32011 ^o
	C ₁				0.6114029 ^h	0.6061471 ^l	ditto	.6063189 ^o
	C ₂ (X10 ⁴)				1.992009 ^h	2.156214 ^l	ditto	2.154148 ^o
	C ₃ (X10 ⁷)				9.499736 ^h	9.330685 ^l	ditto	9.334236 ^o
ACUB95	C ₀					82.54768 ^m	ditto	83.38100 ^o
	C ₁					0.5844231 ^m	ditto	.5756788 ^o
	C ₂ (X10 ⁴)					2.449161 ^m	ditto	2.716229 ^o
	C ₃ (X10 ⁷)					9.330916 ^m	ditto	9.078236 ^o
ACUB97	C ₀						87.91449 ⁿ	89.98723 ^o
	C ₁						0.5397380 ⁿ	.5194290 ^o
	C ₂ (X10 ⁴)						3.765930 ⁿ	4.373030 ^o
	C ₃ (X10 ⁷)						8.021745 ⁿ	7.448742 ^o
ACUB99	C ₀							87.08846 ^o
	C ₁							.5481764 ^o
	C ₂ (X10 ⁴)							3.379783 ^o
	C ₃ (X10 ⁷)							8.601554 ^o

* Footnotes on next page in alphabetical order from left to right in table.

Table 9.6b. Notes

- (a) Coefficients of cubic relationship between X (mole fraction) and J (Index):
 $X = C_0 + C_1J + C_2J^2 + C_3J^3$.
- (b) The 1985 Air cubic data set for the X85 through X97 scales consists of J values measured in 1985 (Table 9.3b) and X values measured in 1985 (Table 9.2b). Data are expressed to 2 decimal places and are exactly the same as reported in Keeling et al. [1986]. J values have all been increased by 0.11 ppm to account for secondary standard drift during the 1985 marathon calibrations.
- (c) Denotes repetition of coefficient to the left.
- (d) The 1987 Air cubic data set for the X87 and X90 scales consists of preliminary J values measured in 1987 (0.03 to 0.04 ppm lower than Table 9.3d) and X values measured in 1985 (see note b). Data are expressed to 2 decimal places.
- (e) The 1990 Air cubic data set for the X90 and X93 scales consists of J values measured in 1990 (Table 9.3h) and preliminary X values measured in 1990 (using preliminary meniscus corrections of -0.340 mm for 4 cc chamber and 0.000 mm for 5000 cc chamber measurements and using all data for No. 66696 (see Table 9.1d)). Data are expressed to 2 decimal places.
- (f) The 1987 Air cubic data set for the X93 scale consists of J values measured in 1987 (Table 9.3d except for No. 71341, where a typo in the data summary caused a value of 317.26 ppm instead of 317.31 ppm) and X values measured in 1985 (see note b). Data are expressed to 2 decimal places.
- (g) The 1989 Air cubic data set for the X93 scale consists of J values measured in 1989 (Table 9.3f) and X values measured in 1990 (see note d). Data are expressed to 2 decimal places.
- (h) The 1993 Air cubic data set for the X93 scale consists of J values measured in 1993 (Table 9.3j) and preliminary X values measured in 1993 (using preliminary meniscus corrections of -0.340 mm for 4 cc chamber and 0.000 mm for 5000 cc chamber, and for Nos. 71286 and 67615, preliminary manometric values, later corrected (.03 and .02 different, respectively). Data are expressed to 2 decimal places.
- (i) The 1987 Air cubic data set for the X95 and X97 scales consists of J values measured in 1987 (Table 9.3d) and X values measured in 1985 (Table 9.2b). Data are expressed to 3 decimal places.
- (j) The 1989 Air cubic data set for the X95 and X97 scales consists of J values measured in 1989 (Table 9.3f) and X values measured in 1990 (Table 9.2b). Data are expressed to 3 decimal places.
- (k) The 1990 Air cubic data set for the X95 and X97 scales consists of J values measured in 1990 (Table 9.3h) and X values measured in 1990 (Table 9.2b). Data are expressed to 3 decimal places.
- (l) The 1993 Air cubic data set for the X95 and X97 scales consists of J values measured in 1993 (Table 9.3j) and X values measured in 1993 (Table 9.2b). Data are expressed to 3 decimal places.

- (m) The 1995 Air cubic data set for the X95 and X97 scales consists of J values measured in 1995 (Table 9.3l) and X values measured in 1995. The X values are as reported in Table 9.2b except for three gases: for No. 34819, the average of Run Nos. 1 and 2 was used - later Run No. 3 was made and Run No. 2 rejected; for No. 71479, the average of all 4 determinations was used - later one determination was rejected; for No. 67615, the average of all 4 determinations was used (504.099 instead of 504.090 - typo?) - later one determination was rejected (see Table 9.1g). Data are expressed to 3 decimal places.
- (n) The 1997 Air cubic data set for the X97 scale uses J values measured in 1997, but preliminary values differing from Table 9.3n by 0.001 or 0.002 ppm for seven of the gases and by 0.014 ppm for No. 71286, because the J values were weighted by the number of jogs. The X values used are the same as described in note l. Data are expressed to 3 decimal places.
- (o) This report (Table 7.1: cubic calibration equation coefficients derived from X values in Table 9.5b and J values in Tables 9.3b, 9.3d, 9.3f, 9.3h, 9.3j, 9.3l, 9.3n, 9.3p).

Table 9.7a Comparison of XN2 computed with the X99A calibration scale and with the X97 scale, from 1970 to 1999.

X99A – X97 (IN HUNDREDTHS OF A PPM)

YEAR	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	
J	170	10	10	10	10	9	9	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	8	6	5	3	2	4	9	5-16	
	180	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	8	6	4	4	4	6	12	9-10	
	190	10	10	10	10	10	10	10	10	10	10	10	10	10	11	11	11	11	10	9	9	8	6	4	4	5	8	15	12	-5	
	200	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	9	9	8	6	4	4	6	10	17	15	-1	
	210	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	12	12	12	11	10	9	8	6	4	4	7	11	18	17	2
	220	11	11	11	11	11	11	12	12	12	12	12	12	12	12	12	12	12	12	10	10	8	6	4	4	7	12	19	18	4	
	230	12	12	12	12	12	12	12	12	12	12	12	12	12	12	13	13	12	12	10	10	9	6	4	5	8	13	19	19	6	
	240	12	12	12	12	12	12	12	12	12	12	12	12	12	13	13	13	13	12	11	10	9	6	4	5	8	13	19	19	7	
	250	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	11	11	9	7	4	5	8	13	19	19	7	
	260	13	13	13	13	13	13	13	13	13	13	13	13	13	14	14	14	14	14	13	12	11	10	7	4	5	8	13	19	18	7
	270	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	12	12	10	7	4	5	8	12	18	18	7
	280	14	14	14	14	14	14	14	14	14	14	14	14	14	14	15	15	15	14	14	13	12	11	8	5	5	8	12	17	17	6
	290	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	13	13	11	8	5	5	8	11	16	15	5
	300	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	14	14	12	9	5	6	8	11	15	14	5	
	310	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	14	14	12	9	6	6	7	10	13	13	4
	320	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	15	15	13	9	6	6	7	9	12	11	3
	330	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	15	15	13	10	7	6	7	8	11	10	3
	340	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	16	16	14	10	7	6	6	7	9	8	3	
	350	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	17	16	14	11	8	6	6	7	8	7	3	
	360	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	17	17	15	11	8	6	6	6	7	6	4	
	370	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	18	17	15	12	8	7	6	6	6	6	6	
	380	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	20	18	16	12	9	7	6	5	5	5	5	8	
	390	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	19	18	16	13	9	7	6	5	4	5	11	
	400	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	19	19	17	13	9	7	6	5	4	6	15	
	410	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	22	20	17	13	10	8	7	5	3	7	20	
	420	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	20	17	14	10	8	7	6	4	9	26	
	430	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	23	20	18	14	10	8	6	6	4	11	33	
	440	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	21	20	18	14	10	9	8	5	14	41	
	450	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	21	20	18	14	10	9	10	9	7	18	51

**Table 9.7b Comparison of XAIR computed with the X99A calibration scale
and with the X97 scale, from 1970 to 1999.**

X99A – X97 (IN HUNDREDTHS OF A PPM)

YEAR	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	
J																															
170	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	8	7	5	3	2	0	2	6	1	-22
180	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	8	6	4	1	-1	3	-2	-22	
190	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	9	9	8	6	4	1	-2	-3	0	-5	-22
200	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	10	9	8	6	4	1	-3	-4	-3	-7	-22	
210	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	10	10	8	6	4	1	-4	-6	-5	-9	-22	
220	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	10	10	9	7	4	0	-4	-7	-7	-11	-22	
230	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	11	11	9	7	4	0	-5	-8	-8	-12	-22		
240	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	11	11	9	7	5	0	-5	-8	-9	-13	-22		
250	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	12	11	10	7	5	0	-5	-8	-10	-14	-22		
260	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	12	10	8	5	1	-5	-9	-10	-14	-22			
270	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	12	10	8	5	1	-5	-9	-10	-14	-22			
280	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	12	10	8	5	1	-5	-8	-10	-14	-22			
290	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	13	11	8	5	1	-4	-8	-10	-14	-21			
300	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	13	11	8	5	1	-4	-8	-9	-13	-20			
310	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	14	12	9	6	1	-4	-7	-9	-12	-19			
320	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	14	12	9	6	1	-4	-7	-9	-12	-19			
330	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	14	12	9	6	2	-3	-6	-8	-11	-18			
340	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	14	12	9	6	2	-3	-6	-7	-10	-16			
350	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	15	13	10	6	2	-2	-5	-6	-9	-14			
360	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	15	13	10	7	3	-2	-4	-5	-7	-12			
370	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	16	14	10	7	3	-1	-3	-4	-6	-9			
380	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	17	14	11	7	3	-1	-3	-3	-4	-5			
390	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	17	15	11	7	4	0	-2	-2	-2	-2	-1		
400	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	18	15	11	7	4	0	-1	-1	0	3			
410	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	21	18	16	12	8	4	1	-1	-1	2	8			
420	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	19	16	12	8	4	1	0	0	4	14			
430	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	20	17	12	8	5	2	0	0	6	20			
440	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23	20	17	13	8	5	2	0	1	8	27			
450	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	21	18	13	9	5	2	1	1	10	35			
	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	21	18	13	9	5	2	0	1	12	44			