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SCRIPPS REFERENCE GAS CALIBRATION SYSTEM
FOR CARBON DIOXIDE-IN-AIR STANDARDS: REVISION OF 1985

by

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1. *Introduction*

The Carbon Dioxide Program of the Scripps Institution of Oceanography, under Contract with the United States Bureau of Standards (NBS), maintains primary reference gases as part of the world-wide Background Air Pollution Monitoring Network (BAPMoN) of the World Meteorological Organization (WMO). This report is a summary of activities carried out in connection with the BAPMoN program and was made available to a meeting of experts convened in November, 1985 by WMO. The new calibration of primary standards, discussed below, was adopted at this meeting as the WMO manometric scale of 1985, to be used in reporting carbon dioxide data in the BAPMoN program.

The report is submitted as a final report of activities carried out under NBS contract NB83-SBCA-2971, as well as a formal report to WMO.

2. *Summary of activities*

An extensive calibration of 23 primary standard reference gas mixtures was carried out at the Scripps Central CO₂ Laboratory of WMO from June to September, 1985. The calibration was a repetition of a similar exercise carried out in 1983 and reported by Keeling et al. [1984]. Eleven CO₂-in-nitrogen and twelve CO₂-in-air gas mixtures were measured. All mixtures were analyzed manometrically using a constant volume manometer described by Keeling et al. [1984], and were compared with each other and with secondary CO₂-in-nitrogen standards by infrared analysis using the same nondispersive infrared gas analyzer (manufactured by the Applied Physics Corporation) as during 1983 and in previous work. In addition, nine CO₂-in-air mixtures prepared by NBS were analyzed manometrically.

After the calibration of 1983 the Scripps Carbon Dioxide Program planned to adopt CO₂-in-air mixtures exclusively as both primary and secondary standards for the BAPMoN program, superseding CO₂-in-nitrogen standards used previously. Nevertheless, owing to interference from contaminated mercury in the manometer during the 1983 calibration and the consequent need for further manometric calibrations after cleaning the manometer, this change was postponed. Instead the system of CO₂-in-nitrogen secondary standards was continued in day-to-day calibration of the Scripps program, and both sets of primary standards were preserved.

In April, 1984, as an interim check pending further manometric calibrations, these secondary CO₂-in-nitrogen standards were compared by infrared analysis with the set of primary CO₂-in-nitrogen standards. The results, which agreed closely but not identically with the 1983 infrared comparison data, were used to establish a provisional calibrating scale for 1984.

In November, 1984 the Scripps manometer was disassembled, cleaned, and annealed. The mercury, which in 1983 had developed a considerable amount of oxidation products especially in the reservoir column, was replaced. The manometer was reassembled and used to analyze CO₂ from seawater beginning almost immediately after cleaning, but was not used for reference gas measurements until June, 1985. At this time the small shift in calibration, noted between 1981 and 1983 [Keeling et al., 1984, p. 6], appears to have been replaced by a somewhat larger shift in the other direction, as expected if some contamination had already been present in 1981 and the first observed shift had been due to further contamination of the mercury between 1981 and 1983. The volume of the 4 cc chamber of the manometer has not yet been redetermined. This is planned for the near future. Pending this recalibration, the manometric volume has been adjusted on the basis of a comparison of the 1983 and 1985 calibrations, so as to cancel out the average observed shift between 1983 and 1985.

The present report describes the 1984 and 1985 calibrating results. The terminology and mathematical development follows closely the previous report of Keeling et al., [1984] and three earlier reports [Bacastow et al., 1983a,b and Keeling et al., 1983] to which the reader is referred for background information. By way of summary, some of the tables of data recapitulate tables appearing in earlier reports. A few small adjustments in tabular entries of the report

of Keeling et al. [1984], owing to updated information, are also shown but are too small to justify any recomputation of the calibrating curves for 1983 and earlier.

The manometrically determined concentration of CO₂ in gas mixtures is expressed as a mole fraction in parts per million (ppm). The concentration, when determined by infrared analyzer, is expressed as an index which is proportional to analyzer response and approximately equal to concentration. The system of CO₂-in-nitrogen secondary standards used routinely in the Scripps laboratory have produced index values which tend to drift slowly downward in time relative to manometric mole fraction concentrations.

From 1980 to 1983 this system showed a faster rate of drift in index than in earlier years, as noted by Keeling et al. [1984, p. 10]. The 1984 calibration came too soon after the 1983 calibration to establish clearly whether this increased rate continued after 1983. The 1985 infrared data, however, indicate conclusively that no net measurable system drift has occurred after 1983. This result suggests the effectiveness of technical reforms carried out in 1982 and 1983: especially the use of new low-volume pressure regulators and the purging of the connecting gas lines during installation of a gas cylinder on line.

At present, it has not been decided when to terminate the use of CO₂-in-nitrogen standards. The very close concordance of the 1983 and 1985 calibrations for both CO₂-in-nitrogen and CO₂-in-air primary standards indicates no immediate problem in continuing the use of CO₂-in-nitrogen mixtures as secondary standards. This requires, however, the maintenance of two sets of primary standards, and the effort to do so is too great to be continued indefinitely.

Because the Scripps laboratory has experienced increasing difficulty with stability of secondary gas mixtures prepared in steel cylinders, of both CO₂-in-nitrogen and CO₂-in-air mixtures, and as yet has only a short experience with gas mixtures stored in aluminum cylinders, it seems advisable to continue the double system for at least another two years.

3. *Manometric calibrations*

The 23 primary standard gas mixtures employed in the 1985 calibration were analyzed manometrically between 19 June and 6 September. All mixtures had been analyzed in 1983. Most of the CO₂-in-nitrogen mixtures in the set had also been analyzed in 1974 and 1980, and all of the CO₂-in-air mixtures in 1981. Three of the CO₂-in-nitrogen cylinders dated from a calibration in 1970.

The manometric data of 1985 for these primary standards are listed in Tables 1a and 1b. These data are expressed using the manometric volume ratio determined in 1974 and employed for all manometric data before 1983. In Tables 1c and 1d are shown the 1983 manometric data similarly expressed. These latter data differ from the corresponding data in Tables 1a and 1b of Keeling et al. [1984] because of a volume ratio change applied by Keeling et al. [1984] and because of changes of up to 0.02 ppm resulting from the use now of final meniscus corrections to the mercury heights. To indicate directly the changes owing to revised meniscus corrections, the 1983 data are also shown, in Tables 1e and 1f, with the volume ratio used by Keeling et al. [1984], but with final meniscus corrections. In Table 1g are further listed data for nine gas mixtures supplied by the National Bureau of Standards (NBS, see Section 9, below) analyzed manometrically in 1984 and 1985. All measurements in Tables 1a to 1g are reported as mole fractions in parts per million by volume (ppm) after reduction of the water vapor content to about 5 ppm.

The CO₂-in-air mixtures contain approximately the normal atmospheric abundance of N₂O. This gas is measured manometrically along with the extracted CO₂, as reported in Tables 1a to 1g. The amount, determined by gas chromatography [see Keeling et al., 1984, p. 6], and shown in Table 1h, has been subtracted to produce summaries of the manometric data for the primary standards in Table 1j.

The 1985 manometric data are based on preliminary meniscus corrections, which, however, are in such good agreement with meniscus corrections made after the calibrations were completed that they are regarded as final corrections. As explained below, the volume assigned to the 4 cc manometric chamber in these tables has been adjusted for measurements made in

both 1983 and 1985 to allow for changes attending renovation of the manometer in November, 1984.

The volume ratio for the 5000 cc chamber relative to the 4 cc chamber of the manometer was determined in 1974 to be 1320.61. In 1983 employing this ratio produced systematically lower manometric concentrations than hitherto for the 23 mixtures analyzed. This suggests a change in performance of the small volume chamber that year. Keeling et al. [1984 p.7] attributed the change to contaminated mercury. On the assumption that the 23 gas mixtures on average did not drift in concentrations from 1981 to 1983, a new volume ratio of 1319.61 was computed and used to establish the 1983 calibration [Keeling et al., 1984, p. 6], retaining the former ratio for the calibrating data of 1970, 1974, 1980, 1981, and 1982. After the manometer was cleaned and the mercury replaced in November, 1984, the manometric concentrations for the same 23 gas mixtures all showed increases from 1983 when the ratio of 1319.61 was used to compute the new 1985 manometric mole fraction. Assuming again that the gas mixtures on average did not change concentration, we obtain a ratio for 1985 of 1321.80. The statistical fit of the 1983 and 1985 data to obtain this new volume ratio yields a standard error of 1 part in 20,000 in the shift in ratio. The volume ratios cited above for 1970 to 1982, 1983, and 1985 are used to compute manometric data shown in Tables 1i and 1j and employed subsequently in the report. After a recalibration of the 4 cc chamber is carried out, the volume ratio, as a function of time, will be recomputed on the basis of both this calibration and the volume calibration of 1974 and with regard to the manometric calibrations of gas mixtures performed between 1970 and 1985. Afterwards, rather than carrying out a recomputation of the manometric data as they appear in Tables 1i and 1j, the Scripps mole fraction scale connecting infrared and manometric data will be adjusted, if necessary, to reflect the recalibration of the 4 cc chamber.

The manometer performed well in 1985, although the data are not quite as reproducible as in 1983. The standard deviation of replicate analyses of CO₂-in-nitrogen and CO₂-in-air combined was 0.066 ppm, compared to 0.041 ppm in 1983. The average values, as listed in Tables 1i and 1j differ statistically from those in 1985 with a standard error of 0.076 ppm, only slightly greater than predicted by the root mean square of the sum of standard deviations for 1983 and 1985 based on pairs of replicate analyses: $((0.066^2 + 0.041^2)/2)^{1/2} = 0.055$ ppm.

4. Infrared Analyzer Calibrations

As in 1983, all but one of the 23 gas mixtures of the 1985 manometric calibration were compared with three gas mixtures of the Scripps CO₂-in-nitrogen standard system during five special test periods, each lasting approximately 22 hours. (The lowest concentration CO₂-in-air mixture was omitted because it can't be properly fit using a cubic equation to link infrared and manometric data.) The same Applied Physics Corporation (APC) nondispersive infrared gas analyzer was used as in the previous calibrations. No significant alteration in the optical system of the analyzer was made since the 1983 calibration.

The infrared data are expressed in index units, I, proportional to the response of the APC analyzer, as explained by Bacastow et al., [1983a]. The results for 1985 are shown in Tables 2a and 2b. Also shown are averages converted to an adjusted index, J, in ppm defined by the formula:

$$J = 1.2186 (I - 311.51) + 311.51 \quad (1)$$

The J scale approximates the mole fraction of CO₂ in dry air for concentration of mixtures close to the concentration in air (about 340 ppm), but is still expressed in units proportional to APC instrument response.

During the five calibrations of 1985, as is normal procedure, a secondary gas was mutually compared with a principal and high span gas and with the 22 manometric standards. It was found that this gas showed a short term drift in index, I, with respect to the principal and high span mixtures during the calibration runs. Normally, i.e. in the absence of such a drift, all available data for the secondary gas would be used to determine a mean index value for that

gas, including comparisons on other calibrating days in addition to the special ones. In this case, however, to allow for drift, the secondary gas data have been treated simply as a transfer of index level between the span gases and the manometric primary standards, as discussed next.

To preserve the format of previous data, the results in Tables 2a and 2b are expressed using the mean index for the secondary (cylinder no. 34850) over its entire use period, but the index values of the compared gas mixtures are then corrected for the drift in the secondary gas as shown in Table 3 by establishing the departures (in J units) for each special calibration data, and averaging the results for the five special days. During these days, the adjusted index, J, of the secondary is on average 0.11 ppm higher than its mean over the entire use period. This difference was added to the J value for each manometric mixture to obtain the results listed in Table 4a and 4b. Also shown are the results for the earlier calibration periods of 1970, 1974, 1980, 1981, and 1983. For CO₂-in-nitrogen gas mixtures the data are as given previously in Table 4 of Keeling et al., [1984]. For CO₂-in-air the data are from Tables 2f and 2h of Keeling et al. [1984] for 1981 and 1983, respectively. The adjusted index differences between successive periods since 1974 are also tabulated in Tables 4a and 4b. It can be seen that the drift in J values between 1983 and 1985 is negligible for both CO₂-in-nitrogen and CO₂-in-air gas mixtures. The average drift for CO₂-in-nitrogen mixtures is 0.003 ppm yr⁻¹ upward with a standard deviation for an individual difference of 0.027 ppm yr⁻¹. For CO₂-in-air it is 0.014 ppm yr⁻¹ upward with a deviation of 0.028 ppm yr⁻¹.

A remarkable feature of the comparison of the 1983 and 1985 calibrations is the good agreement in adjusted index for the extremely high and low concentration mixtures. This is the first instance in which all of the data for two successive calibrations were obtained by computer processing of the digitized APC analyzer output signal voltage; the infrared data before 1983 had been obtained by lining out pen traces by hand. Evidently, the machine processed data are considerably more precise.

In April and May of 1984 a special comparison was carried out of the 11 CO₂-in-nitrogen primary standards versus the Scripps system of span gases. The results are listed in Table 5 and summarized along with a comparison with 1983 and 1985 special calibration data in Table 6. For mixtures with concentrations near air, the J values tend to be about 0.10 ppm lower in 1984 than in 1983. The index values of the lowest concentration mixtures deviate considerably between 1983 and 1984 as was often the case between earlier calibrations. This is explained by the technique used of obtaining the index, I, and adjusted index J, in which I values are initially assigned to the principal and high span gases from previous data and the I (and hence J) values of the compared mixtures obtained by interpolation or extrapolation. Since the two span gases typically vary by only about 30 ppm, large extrapolations occur in computing index values at the highest and lowest concentrations of the compared primary standards. In 1984 the computer for the APC analyzer was not operational, and the data were lined out by hand from pen traces. This circumstance probably explains why, as previous to 1983, large departures occur in I (and J) for the extreme concentrations of primary standards. This does not compromise the calibration exercise because afterwards the adjusted index, J of the primary standards is fit to the manometric data, and then the computation turned around to determine manometric values for the span gases of the Scripps system. Nevertheless it leads to changes in I and J values from year to year for the high and lower concentration mixtures which appear to be systematic but actually reflect mainly random reading errors.

The differences in J values in 1984 from values in 1983 and 1985, as shown in Table 6, are hardly greater than expected from random errors in the manually worked-up data of 1984. Since there is no evidence of drift in J between 1983 and 1985, the 1984 calibration will not be used in establishing a long term calibration scale. Instead it will be assumed that the only changes in index are as given by the essentially negligible shifts between 1983 and 1985. Thus the 1984 data appear here only as background information.

5. System Drift

Because the 1983 and 1985 calibrations are in close agreement, no preliminary procedures are invoked in this report to allow for drift in the system of secondary gas mixtures used during routine calibrating at the Scripps laboratory after the central date of the 1983 calibration. Drift before the date of that calibration is handled by the computer subroutines described by Keeling et al. [1984], unchanged from past procedures.

6. Equations and Computer Program to Convert Index Values to Mole Fraction

The special calibrations of 1983 and 1985 present us with two sets of almost equally precise calibrating data. The essentially insignificant changes in calibration for both CO₂-in-nitrogen and CO₂-in-air gas mixtures between the central dates of the two calibrations are therefore prorated in this report as linear functions of time. These changes in calibration would not be considered in the computer program at all, except that they provide consistent bases for future calibrations. The next future calibration will be better linked logically to the 1985 calibration than to any earlier calibration or combination of calibrations.

Because of different carrier gas response for CO₂-in-nitrogen and CO₂-in-air gas mixtures, the sets of data for each gas type are separately fit to the infrared and manometric data for 1983 and 1985. The 1983 data have already been fit by Keeling et al. [1984, pp. 13-17] resulting in the cubic equation:

$$X_{83} = CUB10 (J83) \quad (2)$$

for CO₂-in-nitrogen gas mixtures and:

$$X_{83} = ACUB13 (J83) \quad (3)$$

for CO₂-in-air mixtures.

Here X₈₃ denotes to the averages for 1970 through 1983 of the manometric data listed for each mixture in Tables 1c and 1d of Keeling et al. [1984], and J₈₃ denotes the average adjusted index values for 1983 listed in Tables 4a and 4b of this report. The fits, by least squares, result in the coefficients listed in Table 7 for the specified functions.

Similarly, the 1985 calibration data, as listed in Tables 1i, 1j, 4a, and 4b of this report, result in the cubic equation:

$$X_{85} = CUB14 (J85) \quad (4)$$

for CO₂-in-nitrogen and

$$X_{85} = ACUB15 (J85) \quad (5)$$

for CO₂-in-air.

The functions are labeled by consecutive numbers, consistent with the scheme used by Keeling et al. [1984].

We carry out the computation for any given CO₂-in-nitrogen mixture by computing:

$$X_{10} = CUB10 (J) \quad (6)$$

$$X_{14} = CUB14 (J) \quad (7)$$

$$X_{N2} = \left(\frac{CD85 - D}{CD85 - CD83} \right) X_{10} + \left(\frac{D - CD83}{CD85 - CD83} \right) X_{14} \quad (8)$$

where J refers to the adjusted index on any day, D, between the two central dates (i.e. the average dates) of the respective infrared calibrations:

$$CD83 = 17 \text{ September, } 1983$$

$$CD85 = 29 \text{ July, } 1985$$

The final sought for mole fraction for a given CO₂-in-nitrogen gas mixture is denoted by XN2. Unlike previous computations by Keeling et al. [1984], there are no preliminary computations to correct J values for drift (with resulting quantities denoted by JA, JB, JC and JF). In the computer program which is appended to this report, J (called "Y59" in the program) is, however, set equal to JF ("FJ" in the program) with all drift adjustments set equal to zero, as a convenience in programming.

For CO₂-in-air mixtures the corresponding equations are:

$$X13 = ACUB13 (J) \quad (9)$$

$$X15 = ACUB15 (J) \quad (10)$$

$$XAIR = \left(\frac{CD85 - D}{CD85 - CD83} \right) X13 + \left(\frac{D - CD83}{CD85 - CD83} \right) X15 \quad (11)$$

For computations of infrared analyses before central date CD83 the formulation of Keeling et al. [1984] is used, and should be consulted for an explanation of the sequence of equations involved. The coefficients of all of the equations required to compute XN2 and XAIR since the beginning of the Scripps Carbon Dioxide Program are listed in Table 7.

The results of using the above formulation to calculate mole fractions for the special calibrations of 1983 and 1985 are shown in Tables 8a and 8b, corresponding to Tables 7a to 7c of Keeling et al. [1984]. The FORTRAN computer program to carry out these computations, and conversions from adjusted index J to mole fractions XN2 and XAIR, in general, is listed below after the tables.

7. Test of the Validity of the Formulation

Throughout the Scripps CO₂ program, as noted above, CO₂-in-nitrogen standard gas mixtures have been used in the direct calibration of the Scripps APC infrared analyzer. CO₂-in-air mixtures have been used only to determine a carrier gas correction to the index values obtained using CO₂-in-nitrogen mixtures.

Before the central date of the 1983 calibration (CD83), the carrier gas correction was assumed by Keeling et al. [1984] to be given, for a given value of J, by the difference in mole fraction for gas type as determined by cubic functions CUB10(J) and ACUB13(J). These functions were derived from weighted averages of all of the manometric data, from 1970 through 1983 for CO₂-in-nitrogen mixtures, and from 1981 through 1983 for CO₂-in-air mixtures. The use of long term averages was justified because of the lack of evidence for significant change in the manometric values through 1981, and because the concentration-proportional change from 1981 to 1983 was attributed to a change in manometer performance. Thus a time invariant carrier gas correction, varying with concentration, was applied by Keeling et al. [1984] to all data before CD83. This procedure is continued in this report. For computations between central dates CD83 and CD85, however, the assumption is now made that the slight observed changes in calibration for CO₂-in-nitrogen and CO₂-in-air gas mixtures both took place as linear functions of time, and hence the carrier gas correction also changed linearly with time. This procedure is a logical basis for future recalibrations. Even though the shift in calibration is essentially negligible from 1983 to 1985, it may not be in the future. It seems prudent to link future calibrations directly to the 1985 calibration, as this procedure permits.

As a test of the performance of the present calibration procedure, mole fractions, XAIR, have been computed from infrared data for a set of surveillance CO₂-in-air standards analyzed since 1973 and called "red stripe cylinders". (Correspondingly, the primary standards are called "white stripe" cylinders. Both designations refer to the color coding of the cylinders themselves). Annual average values of XAIR for the red stripe cylinder gas mixtures are compared with manometric long term averaged data for the same mixtures, the latter data assumed to be time invariant. The computations are as explained by Keeling et al. [1984, pp. 18-20]. The results are summarized in Table 9.

It can be seen that annual average departures in XAIR from the manometric mole fractions are negligible (i.e. less than 0.10 ppm) for all years from 1973 to 1985. This suggests that both the analyzer optical system and the gas mixtures themselves have remained stable over this long time period.

8. *Comparison with Previous Calibrations*

The results of computing XN2 and XAIR from J by the formulism of section 5, above, are compared in Table 10a and 10b, respectively, with a similar computation based on the 1983 calibration as reported by Keeling et al. [1983]. For prescribed values of J, in increments of 10 ppm for 170 to 450 ppm, XAIR was computed both ways. The differences (1985 calibration minus 1983 calibration) are listed in Table 10a and 10b for 1 January and 1 July of each year from 1980 through 1985. In the range of CO₂ concentration in normal air, they are between 0.00 and 0.03 ppm. The shift of 0.01 ppm which appears for CO₂-in-air computations before 1983 is owing to two small errors found in the FORTRAN computer version of ACUB13 in Keeling et al. [1984] and corrected in the new version. This shift applies to all data before 1980 as well.

9. *Comparison with NBS Standards*

During 1982 Dr. Ernest Hughes of the U.S. National Bureau of Standards supplied us with six gas mixtures of CO₂-in-air which had been analyzed with an infrared gas analyzer against a suite of primary gravimetric standards which he had synthesized. During 1985 Dr. Hughes returned three of these gas mixtures to Scripps together with six new mixtures. Manometric measurements on all 9 mixtures were made as listed in Table 1h. Infrared analyses were also carried out. A discussion of both sets of data and their comparison with gravimetric data of NBS will be postponed to a later report describing the pending recalibration of the Scripps manometer.

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Table 1a. Manometric analyses of CO₂-in-nitrogen standards during 1985⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
2408	1	3 SEP 85	196.97	196.97	196.96	2
	2	3 SEP 85	196.98			
3753	1	20 AUG 85	246.20	246.26	246.29	2
	2	21 AUG 85	246.32			
7366	1	12 AUG 85	276.89	276.86	276.84	2
	2	13 AUG 85	276.82			
6078	1	10 JUL 85	311.18	311.17	311.17	2
	2	10 JUL 85	311.17			
2399	1	12 JUL 85	324.33	324.34	324.24	2
	2	29 JUL 85	324.17			
39239	1	19 JUN 85	332.89	332.90	333.00	4
	2	31 JUL 85	333.08			
	3	19 AUG 85	333.05			
	4	6 SEP 85	333.00			
39256	1	25 JUN 85	346.02	345.96	346.00	2
	2	25 JUN 85	346.03			
39272	1	19 JUN 85	360.83	360.88	360.92	2
	2	20 JUN 85	360.90			
1540	1	6 AUG 85	380.87	380.90	380.93	2
	2	6 AUG 85	380.98			
35299	1	14 AUG 85	415.24	415.29	415.29	2
	2	14 AUG 85	415.28			
35316	1	27 AUG 85	473.22	473.20	473.13	2
	2	28 AUG 85	473.14			

⁺Using V_{4cc} = 3.7974cc (V_{5000cc}/V_{4cc} = 1320.61) and final meniscus corrections.

Table 1b. Manometric analyses of CO₂-in-air standards during 1985⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
66556	1	5 SEP 85	101.37 101.36	101.36	101.35	2
	2	5 SEP 85	101.33 101.33	101.33		
71251	1	28 AUG 85	213.68 213.67	213.68	213.63	2
	2	29 AUG 85	213.58 213.59	213.58		
34819	1	20 AUG 85	252.30 252.32	252.31	252.22	2
	2	20 AUG 85	252.17 252.11	252.14		
71286	1	7 AUG 85	297.24 297.19	297.22	297.21	2
	2	7 AUG 85	297.21 297.21	297.21		
71341	1	26 JUN 85	322.71 322.70	322.70	322.74	2
	2	26 JUN 85	322.76 322.77	322.76		
66638	1	26 JUN 85	338.92 338.88	338.90	338.88	2
	2	9 JUL 85	338.91 338.83	338.87		
66625	1	11 JUL 85	345.27 345.27	345.27	345.27	2
	2	11 JUL 85	345.27 345.27	345.27		
66696	1	31 JUL 85	360.63 360.56	360.60	360.66	2
	2	1 AUG 85	360.71 360.72	360.72		
71308	1	5 AUG 85	376.29* 376.30*	376.30*	376.86	2
	2	5 AUG 85	376.83 376.81	376.82		
	3	12 AUG 85	376.53* 376.62*	376.58*		
	4	19 AUG 85	376.89 376.90	376.90		
71370	1	13 AUG 85	407.06 407.07	407.06	407.09	2
	2	13 AUG 85	407.12 407.10	407.11		
71479	1	26 AUG 85	454.14 454.05	454.10	454.04	2
	2	27 AUG 85	453.95 454.01	453.98		
67615	1	4 SEP 85	504.25 504.36	504.30	504.38	2
	2	4 SEP 85	504.45 504.46	504.46		

*Run Nos. 1 and 3 deleted for cause

⁺Using V_{4cc} = 3.7974cc (V_{5000cc}/V_{4cc} = 1320.61) and final meniscus corrections.

Table 1c. Manometric analyses of CO₂-in-nitrogen standards during 1983⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
2408	1	25 OCT 83	196.71 196.73	196.72	196.68	3
	2	25 OCT 83	196.61 196.68			
	3	27 OCT 83	196.69 196.67	196.68		
3753	1	6 OCT 83	245.83 245.95	245.89	245.89	2
	2	6 OCT 83	245.89 245.88			
7366	1	30 SEP 83	276.37	276.30	276.33	2
	2	30 SEP 83	276.29 276.32			
6078	1	29 AUG 83	310.58 310.48	310.53	310.52	2
	2	30 AUG 83	310.51 310.50			
2399	1	20 SEP 83	323.75 323.82	323.78	323.76	2
	2	20 SEP 83	323.70 323.77			
39239	1	16 AUG 83	332.50 332.52	332.51	332.46	5
	2	26 SEP 83	332.49 332.46			
	3	27 OCT 83	332.44 332.48	332.46		
	4	8 NOV 83	332.43 332.47	332.45		
	5	8 NOV 83	332.41 332.41	332.41		
39256	1	22 AUG 83	345.62 345.55 345.56	345.58	345.51	2
	2	22 AUG 83	345.70* 345.39 345.44			
39272	1	17 AUG 83	360.33 360.32	360.32	360.32	2
	2	17 AUG 83	360.39 360.24			
1540	1	28 SEP 83	380.19 380.19	380.19	380.16	2
	2	28 SEP 83	380.14 380.14			
35299	1	4 OCT 83	414.71 414.67	414.69	414.70	2
	2	5 OCT 83	414.80 414.61			
35316	1	20 OCT 83	472.44 472.31	472.38	472.38	2
	2	21 OCT 83	472.41 472.34			

*Omit - instrumental problem

+Using $V_{4cc} = 3.7974cc$ (V_{5000cc}/V_{4cc} ratio of 1320.61) and Final Meniscus Corrections.

Table 1d. Manometric analyses of CO₂-in-air standards during 1983⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
66556	1	31 OCT 83	101.31 101.32	101.32	101.28	2
	2	31 OCT 83	101.27 101.22	101.24		
71251	1	21 OCT 83	213.33 213.37	213.35	213.34	2
	2	25 OCT 83	213.30 213.37	213.34		
34819	1	5 OCT 83	251.85 251.83	251.84	251.85	2
	2	5 OCT 83	251.88 251.85	251.86		
71286	1	29 SEP 83	296.79 296.70	296.74	296.77	2
	2	29 SEP 83	296.78 296.80	296.79		
71341	1	23 AUG 83	322.32 322.31	322.32	322.29	2
	2	23 AUG 83	322.29 322.25	322.27		
66638	1	24 AUG 83	338.27 338.25	338.26	338.26	2
	2	29 AUG 83	338.26 338.27	338.26		
66625	1	30 AUG 83	344.50 344.48	344.49	344.55	4
	2	31 AUG 83	344.52 344.52	344.52		
	3	9 NOV 83	344.62 344.55	344.58		
	4	9 NOV 83	344.63 344.59	344.61		
66696	1	21 SEP 83	359.90 359.94	359.92	359.96	2
	2	21 SEP 83	360.04 359.96	360.00		
71308	1	26 SEP 83	376.24 376.25	376.24	376.24	2
	2	26 SEP 83	376.24 376.21	376.22		
71370	1	3 OCT 83	406.45 406.37	406.41	406.41	2
	2	4 OCT 83	406.41 406.41	406.41		
71479	1	7 OCT 83	453.24 453.25	453.24	453.32	2
	2	20 OCT 83	453.39 453.42	453.40		
67615	1	26 OCT 83	503.57 503.56	503.56	503.54	2
	2	26 OCT 83	503.57 503.47	503.52		

⁺Using $V_{4cc} = 3.7974cc$ (V_{5000cc}/V_{4cc} ratio of 1320.61) and Final Meniscus Corrections.

Table 1e. Manometric analyses of CO₂-in-nitrogen standards during 1983⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
2408	1	25 OCT 83	196.86 196.88	196.87	196.83	3
	2	25 OCT 83	196.76 196.83	196.80		
	3	27 OCT 83	196.84 196.82	196.83		
3753	1	6 OCT 83	246.02 246.14	246.08	246.08	2
	2	6 OCT 83	246.07 246.07	246.07		
7366	1	30 SEP 83	276.58	276.58	276.54	2
	2	30 SEP 83	276.50 276.53	276.52		
6078	1	29 AUG 83	310.81 310.72	310.76	310.75	2
	2	30 AUG 83	310.75 310.73	310.74		
2399	1	20 SEP 83	324.00 324.06	324.03	324.01	2
	2	20 SEP 83	323.95 324.02	323.98		
39239	1	16 AUG 83	332.75 332.77	332.76	332.71	5
	2	26 SEP 83	332.74 332.72	332.73		
	3	27 OCT 83	332.69 332.73	332.71		
	4	8 NOV 83	332.69 332.72	332.70		
	5	8 NOV 83	332.66 332.66	332.66		
39256	1	22 AUG 83	345.88 345.81 345.83	345.84	345.78	2
	2	22 AUG 83	345.97* 345.65 345.71	345.68		
39272	1	17 AUG 83	360.60 360.60	360.60	360.59	2
	2	17 AUG 83	360.66 360.51	360.58		
1540	1	28 SEP 83	380.48 380.48	380.48	380.46	2
	2	28 SEP 83	380.43 380.43	380.43		
35299	1	4 OCT 83	415.03 414.99	415.01	415.02	2
	2	5 OCT 83	415.12 414.92	415.02		
35316	1	20 OCT 83	472.80 472.67	472.74	472.74	2
	2	21 OCT 83	472.77 472.70	472.74		

*Omit - instrumental problem

+Using $V_{4cc} = 3.8003cc$ (V_{5000cc}/V_{4cc} ratio of 1319.61) and Final Meniscus Corrections.

Table 1f. Manometric analyses of CO₂-in-air standards during 1983⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
66556	1	31 OCT 83	101.39 101.40	101.40	101.36	2
	2	31 OCT 83	101.35 101.30	101.32		
71251	1	21 OCT 83	213.49 213.53	213.51	213.50	2
	2	25 OCT 83	213.47 213.53	213.50		
34819	1	5 OCT 83	252.04 252.03	252.04	252.05	2
	2	5 OCT 83	252.07 252.04	252.06		
71286	1	29 SEP 83	297.01 296.93	296.97	296.99	2
	2	29 SEP 83	297.00 297.03	297.02		
71341	1	23 AUG 83	322.57 322.56	322.56	322.54	2
	2	23 AUG 83	322.54 322.50	322.52		
66638	1	24 AUG 83	338.53 338.51	338.52	338.52	2
	2	29 AUG 83	338.52 338.53	338.52		
66625	1	30 AUG 83	344.76 344.75	344.76	344.82	4
	2	31 AUG 83	344.78 344.78	344.78		
	3	9 NOV 83	344.89 344.81	344.85		
	4	9 NOV 83	344.89 344.86	344.88		
66696	1	21 SEP 83	360.17 360.22	360.20	360.23	2
	2	21 SEP 83	360.31 360.23	360.27		
71308	1	26 SEP 83	376.53 376.53	376.53	376.52	2
	2	26 SEP 83	376.53 376.50	376.52		
71370	1	3 OCT 83	406.76 406.68	406.72	406.72	2
	2	4 OCT 83	406.72 406.72	406.72		
71479	1	7 OCT 83	453.59 453.59	453.59	453.67	2
	2	20 OCT 83	453.74 453.76	453.75		
67615	1	26 OCT 83	503.95 503.94	503.94	503.92	2
	2	26 OCT 83	503.95 503.85	503.90		

⁺Using $V_{4cc} = 3.8003cc$ (V_{5000cc}/V_{4cc} ratio of 1319.61) and Final Meniscus Corrections.

Table 1g. Manometric Analyses during 1984 and 1985 of CO₂-in-air secondary standards obtained from NBS⁺

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
11835	1	30 OCT 84	303.99 303.93	303.96	303.96	1
11429	1	30 OCT 84	341.55 341.51	341.53	341.53	1
11062	1	30 OCT 84	375.17 375.12	375.14	375.14	1
11835	1	12 JUN 85	304.32 304.32	304.32	304.32	1*
11429	1	12 JUN 85	341.99 341.91	341.95	341.95	1*
11062	1	12 JUN 85	375.70 375.64	375.67	375.67	1*
11835	2	26 SEP 85	304.49 304.37	304.43	304.43	1
8699	1	14 JUN 85	304.54 304.63	304.58	304.58	1
18027	1	29 JUL 85	336.34 336.30	336.32	336.32	1
11429	2	26 SEP 85	342.08 342.00	342.04	342.04	1
8386	1	14 JUN 85	342.13 342.18	342.16	342.16	1
18067	1	30 JUL 85	342.95 342.90	342.92	342.92	1
16417	1	30 JUL 85	351.51 351.51	351.51	351.51	1
8433	1	17 JUN 85	375.40 375.40	375.40	375.40	1
11062	2	27 SEP 85	375.87 375.84	375.86	375.86	1

*Measurement in 4cc manometric chamber made on 30 OCT '84 CO₂ extraction (which had been saved in flame off tube) combined with OCT '84 measurement in 5000cc chamber.

⁺Using $V_{4cc} = 3.7974cc$ ($V_{5000cc} / V_{4cc} = 1320.61$) and preliminary meniscus corrections.

Table 1h. N₂O corrected concentrations of CO₂-in-air standards
manometrically analyzed during 1984 and 1985

Cylinder No.	Manometric Average* (ppm)	N ₂ O Concentration (ppm)	Corrected Concentration [†] (ppm)
White Stripe Cylinders ¹⁾			
66556	101.35	0.37	100.98
71251	213.63	0.34	213.29
34819	252.22	0.24	251.98
71286	297.21	0.32	296.89
71341	322.74	0.31	322.43
66638	338.88	0.31	338.57
66625	345.27	0.29	344.98
66696	360.66	0.31	360.35
71308	376.86	0.32	376.54
71370	407.09	0.31	406.78
71479	454.04	0.30	453.74
67615	504.38	0.30	504.08
NBS Cylinders ²⁾			
11835	303.96	0.27	303.69 (1984)
	304.43	"	304.16 (1985)
	304.32	"	304.05 (1985-stored)
11429	341.53	0.30	341.23 (1984)
	342.04	"	341.74 (1985)
	341.95	"	341.65 (1985-stored)
11062	375.14	0.33	374.81 (1984)
	375.86	"	375.53 (1985)
	375.67	"	375.34 (1985-stored)
18027	336.32	0.06	336.26 (1985)
18067	342.92	0.08	342.84 (1985)
16417	351.51	0.03	351.48 (1985)
8699	304.58	0.27	304.31 (1985)
8386	342.16	0.30	341.86 (1985)
8433	375.40	0.33	375.07 (1985)

1) [N₂O] determined by SIO in 1981

2) [N₂O] determined by NBS

* see Tables 1b and 1g

† For NBS standards the year of analysis is shown in parentheses.

Table 1i. Summary of manometric measurements (in ppm), by year. The number of determinations are shown in parentheses. Averages are weighted by the number of determinations carried out that year.

CO2-IN-NITROGEN GASES							
CYL.NO.	1970	1974	1980	1982	1983	1985	AVERAGE
2408		196.90 (2)	196.80 (2)		196.84 (3)	196.78 (2)	196.83 (9)
3753		246.02 (2)	245.99 (2)		246.08 (2)	246.07 (2)	246.04 (8)
7368	276.57 (3)	276.80 (2)	276.67 (2)		276.55 (2)	276.59 (2)	276.63 (11)
6078	310.95 (7)	310.82 (3)	310.96 (2)		310.75 (2)	310.89 (2)	310.89 (16)
2399	324.19 (8)	324.05 (4)	324.15 (2)		324.00 (2)	323.95 (2)	324.11 (18)
39239		332.78 (2)	332.72 (2)	332.64 (2)	332.71 (5)	332.70 (4)	332.71 (15)
39256				345.57 (3)	345.80 (2)	345.69 (2)	345.67 (7)
10069	355.64 (4)	355.60 (2)	355.82 (2)				355.68 (8)
39272				360.49 (3)	360.59 (2)	360.60 (2)	360.55 (7)
1540		380.56 (2)	380.45 (2)		380.44 (2)	380.59 (2)	380.51 (8)
35299		415.06 (2)	414.94 (2)		415.01 (2)	414.92 (2)	414.98 (8)
35316		472.97 (2)	472.72 (4)		472.72 (2)	472.70 (2)	472.77 (10)

Source of data:

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

1985: Table 1a of this report times factor (1320.61/1321.80)

Table 1j. Summary of manometric measurements (in ppm), by year. The number of determinations are shown in parentheses. Averages are weighted by the number of determinations carried out that year.

CO2-IN-AIR GASES (WHITE STRIPES)				
CYL.NO.	1981	1983	1985	AVERAGE
66556	101.00 (2)	101.00 (2)	100.89 (2)	100.96 (6)
71251	213.15 (2)	213.16 (2)	213.10 (2)	213.14 (6)
34819	251.72 (2)	251.81 (2)	251.75 (2)	251.76 (6)
71286	296.56 (2)	296.67 (2)	296.62 (2)	296.62 (6)
71341	322.45 (2)	322.23 (2)	322.14 (2)	322.27 (6)
66638	338.08 (2)	338.21 (2)	338.27 (2)	338.19 (6)
68625	344.62 (2)	344.53 (4)	344.67 (2)	344.59 (8)
66696	359.87 (2)	359.92 (2)	360.03 (2)	360.94 (6)
71308	376.48 (2)	376.20 (2)	376.20 (2)	376.29 (6)
71370	406.39 (2)	406.41 (2)	406.41 (2)	406.40 (6)
71479	453.40 (2)	453.36 (2)	453.33 (2)	453.36 (6)
67615	503.20 (2)	503.62 (2)	503.63 (2)	503.48 (6)

Source of data:

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

1985: Table 1b of this report times factor (1320.61/1321.80)

TABLE 2a. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1985 calibration. The number of comparisons is shown in parentheses. Averages, not weighted, are expressed in Index units, I, and Adjusted Index units, J.

CO2-IN-NITROGEN GASES								
CYL.NO.	19 JUN	09 JUL	30 JUL	20 AUG	04 SEP	AVG. I	AVG. J	
2408	199.75 (10)	199.83 (18)	199.88 (10)	199.77 (10)	199.28 (10)	199.70	175.26	
3753	251.40 (14)	251.37 (10)	251.42 (10)	251.26 (10)	251.01 (10)	251.29	238.13	
7366	280.19 (12)	280.12 (10)	280.11 (10)	280.04 (10)	279.83 (10)	280.06	273.19	
6078	310.11 (10)	310.05 (10)	310.04 (10)	309.93 (12)	309.82 (10)	309.99	309.66	
2399	321.07 (10)	321.05 (10)	320.95 (10)	320.82 (10)	320.78 (10)	320.93	322.99	
39239	328.11 (10)	328.09 (10)	328.00 (12)	327.92 (10)	327.87 (10)	328.00	331.60	
39256	338.40 (10)	338.44 (10)	338.32 (10)	338.27 (10)	338.24 (10)	338.33	344.19	
39272	349.83 (20)	349.91 (10)	349.75 (10)	349.72 (10)	349.68 (10)	349.78	358.15	
1540	364.84 (12)	364.82 (10)	364.77 (10)	364.69 (10)	364.63 (10)	364.75	376.39	
35299	389.27 (10)	389.28 (10)	389.21 (10)	389.16 (10)	389.09 (10)	389.20	406.18	
35316	427.06 (10)	427.12 (10)	427.14 (10)	427.12 (10)	427.03 (12)	427.09	452.36	
AVERAGE:	323.64	323.64	323.60	323.52	323.39			

Summary of Adjusted Index averages (J) for the 1985 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	175.26	0.30	5
3753	238.13	0.21	5
7366	273.19	0.17	5
6078	309.66	0.16	5
2399	322.99	0.16	5
39239	331.60	0.12	5
39256	344.19	0.10	5
39272	358.15	0.11	5
1540	376.39	0.11	5
35299	406.18	0.10	5
35316	452.36	0.06	5

TABLE 2b. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during the 1985 calibration. The number of comparisons is shown in parentheses. Averages, not weighted, are expressed in Index units, I, and Adjusted Index units, J.

CO2-IN-AIR GASES (WHITE STRIPES)								
CYL.NO.	19 JUN	09 JUL	30 JUL	20 AUG	04 SEP	AVG. I	AVG. J	
71251	215.62 (10)	215.62 (12)	215.63 (10)	215.51 (10)	215.13 (12)	215.50	194.51	
34819	254.61 (10)	254.58 (10)	254.58 (10)	254.48 (10)	254.22 (10)	254.49	242.03	
71286	295.17 (10)	295.11 (10)	295.10 (10)	295.01 (10)	294.85 (10)	295.05	291.45	
71341	316.43 (10)	316.38 (10)	316.34 (10)	316.29 (10)	316.15 (10)	316.32	317.37	
66638	329.36 (10)	329.37 (10)	329.24 (10)	329.20 (10)	329.13 (10)	329.26	333.14	
66625	334.29 (10)	334.26 (10)	334.21 (12)	334.16 (10)	334.11 (10)	334.21	339.17	
66696	346.13 (12)	346.15 (10)	346.07 (12)	345.99 (10)	345.95 (10)	346.06	353.61	
71308	358.13 (10)	358.13 (10)	358.10 (10)	358.05 (10)	357.92 (12)	358.07	368.25	
71370	379.56 (10)	379.67 (10)	379.55 (10)	379.45 (10)	379.45 (10)	379.54	394.41	
71479	410.87 (10)	410.86 (12)	410.88 (10)	410.89 (10)	410.75 (10)	410.85	432.57	
67616	441.66 (10)	441.71 (10)	441.79 (10)	441.70 (10)	441.68 (10)	441.71	470.17	
AVERAGE:	334.71	334.71	334.68	334.61	334.49			

Summary of Adjusted Index averages (J) for the 1985 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
71251	194.51	0.28	5
34819	242.03	0.19	5
71286	291.45	0.15	5
71341	317.37	0.13	5
66638	333.14	0.12	5
66625	339.17	0.09	5
66696	353.61	0.11	5
71308	368.25	0.11	5
71370	394.41	0.11	5
71479	432.57	0.07	5
67616	470.17	0.06	5

Table 3. Summary of Calibrations of Secondary Cylinder <34850>
During Manometric Infrared Calibrations of 1985

<u>Calibration Date (1985)</u>	<u>Index I*</u> (ppm)	<u>Average</u>
		<u>Adjusted Index, J</u> (ppm)
June 19	322.89 (2)	325.38
July 9	322.92 (2)	325.41
July 30	322.97 (2)	325.48
Aug 20	328.04 (2)	325.56
Sept 4	323.18 (3)	325.73
<hr/>		
Average	323.00	325.51
Average During Entire Calibration History	322.91	325.40
Difference	.09	0.11

*Number of comparison sets per day is shown in parentheses.

Table 4a. Summary of Infrared Analyses during Special Calibration Periods and Inferred System Drift*

Cylinder No.	(X83) Manometric Concentration (ppm)	Adjusted Index, J (ppm)					Drift in J (ppm)		
		1970 (J70)	1974 (J74)	1980 (J80)	1983 (J83)	1985 (J85)	(J80-J74)/6	(J83-J80)/3	(J85-J83)/2
CO ₂ -IN-NITROGEN CYLINDERS									
2408	196.85		180.83	176.96	175.39	175.37	-0.65	-0.52	-0.01
3753	246.03		241.32	238.93	238.16	238.24	-0.40	-0.26	0.04
7366	276.64	275.88	275.55	273.84	273.27	273.30	-0.29	-0.19	0.02
6078	310.90	311.49	311.17	310.23	309.73	309.77	-0.16	-0.17	0.02
2399	324.13	324.56	324.23	323.53	323.07	323.10	-0.12	-0.15	0.02
39239	332.71		332.82	332.23	331.70	331.71	-0.10	-0.18	0.00
39256	345.66			344.73	344.29	344.30		-0.15	0.00
10069	355.68	354.38	354.47	354.36			-0.02		
39272	360.53			358.71	358.23	358.26		-0.16	0.02
1540	380.48		377.02	377.07	376.49	376.50	0.01	-0.19	0.00
35299	415.00		406.55	407.19	406.33	406.29	0.11	-0.29	-0.02
35316	472.78		452.55	453.98	452.59	452.47	0.24	-0.46	-0.06

*Data for 1970 to 1983 are as they appear in Table 4 of Keeling et al. [1984]. The 1985 data are as they appear in Table 2a, above, except that all values are raised by 0.11 ppm, as discussed in the text on page 4.

Table 4b. Summary of Infrared Analyses during Special Calibration Periods and Inferred System Drift*

Cylinder No.	(X83) Manometric Concentration (ppm)	Adjusted Index, J (ppm)			Drift in J (ppm)	
		1981 (J81)	1983 (J83)	1985 (J85)	(J83-J81)/2	(J85-J83)/2
CO ₂ -IN-AIR GASES						
71251	213.00	195.89	194.61	194.62	-0.68	0.00
34819	251.61	242.85	241.98	242.14	-0.44	0.08
71286	296.45	291.98	291.50	291.56	-0.25	0.03
71341	321.98	318.11	317.52	317.48	-0.30	-0.02
66638	337.95	333.51	333.20	333.25	-0.16	0.02
66625	344.26	339.64	339.27	339.28	-0.19	0.00
66696	359.65	353.91	353.64	353.72	-0.14	0.04
71308	375.92	368.83	368.35	368.36	-0.24	0.00
71370	406.10	394.87	394.53	394.52	-0.17	0.00
71479	453.02	433.35	432.70	432.68	-0.33	-0.01
67615	503.24	470.94	470.31	470.28	-0.37	-0.02

*The source of the data for 1981 and 1983 are as indicated in the text on page 11. The 1985 data have been adjusted as in the case of Table 4a, i.e., Table 2b values are raised by 0.11 ppm.

TABLE 5. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1984 calibration. The number of comparisons is shown in parentheses. Averages, not weighted, are expressed in Index units, I, and Adjusted Index units, J.

CO2-IN-NITROGEN GASES						
CYL.NO.	18 APR	25 APR	09 MAY	AVG. I	AVG. J	
2408	200.14 (10)	200.34 (10)	200.99 (10)	200.49	176.22	
3753	251.39 (10)	251.78 (10)	252.01 (10)	251.73	238.68	
7368	280.24 (10)	280.33 (10)	280.52 (10)	280.30	273.55	
6078	310.09 (10)	310.07 (11)	310.18 (10)	310.11	309.80	
2399	320.99 (10)	321.05 (10)	320.93 (10)	320.99	323.06	
39239	328.21 (10)	328.08 (10)	328.01 (10)	328.10	331.73	
39258	338.29 (10)	338.39 (10)	338.37 (10)	338.35	344.22	
39272	349.83 (10)	349.78 (10)	349.63 (10)	349.75	358.11	
1540	364.99 (10)	364.78 (10)	364.56 (10)	364.78	376.42	
35299	389.51 (10)	389.21 (10)	388.95 (9)	389.22	406.21	
35316	427.75 (10)	427.15 (10)	426.89 (10)	427.26	452.56	
AVERAGE:	323.77	323.72	323.73			

Summary of Adjusted Index averages (J) for the 1984 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	176.22	0.54	3
3753	238.68	0.38	3
7368	273.55	0.17	3
6078	309.80	0.07	3
2399	323.06	0.07	3
39239	331.73	0.12	3
39258	344.22	0.06	3
39272	358.11	0.12	3
1540	376.42	0.27	3
35299	406.21	0.34	3
35316	452.56	0.54	3

Table 6. Summary of Infrared Analyses during Special Calibration of 1984 Compared with 1983 and 1985*

Cylinder No.	(X83) Manometric Concentration (ppm)	Adjusted Index, J (ppm)			Drift in J (ppm) (J84-J83)
		1983 (J83)	1984 (J84)	1985 (J85)	
CO ₂ -IN-NITROGEN					
2408	196.85	175.39	176.22	175.37	0.83
3753	246.03	238.16	238.66	238.24	0.50
7366	276.64	273.27	273.55	273.30	0.28
6078	310.90	309.73	309.80	309.77	0.07
2399	324.13	323.07	323.06	323.10	-0.01
39239	332.71	331.70	331.73	331.71	0.03
39256	345.66	344.29	344.22	344.30	-0.07
39272	360.53	358.23	358.11	358.26	-0.12
1540	380.48	376.49	376.42	376.50	-0.07
35299	415.00	406.33	406.21	406.29	-0.12
35316	472.78	452.59	452.56	452.47	-0.03

*1983 and 1985 data are quoted from Table 4a.
1984 data are quoted from Table 5.

Table 7. Coefficients used in computing mole fractions from infrared data

<u>Year</u>	<u>Central Date</u>	<u>Y_{out}</u>	<u>Y_{in}</u>	<u>Name</u>	<u>C₀</u>	<u>C₁</u>	<u>C₂</u> <u>x 10⁴</u>	<u>C₃</u> <u>x 10⁷</u>	<u>Limits of Validity of J</u>	
1960	1 JUL 60	J74-J60	J60	LIN3	0.576	-0.005011			285	350
1974	15 AUG 74	XN2	J74	CUB1	77.455	0.573302	3.5735	6.7618	181	453
1980	19 SEP 80	XN2	J80	CUB2	84.370	0.542223	4.2284	5.8862	177	454
1980	19 SEP 80	XN2	J80	CUB9	84.776	0.537732	4.3849	5.7171	177	454
1983	17 SEP 83	XN2	J83	CUB10	86.946	0.537883	3.8471	6.8562	175	453
1983	17 SEP 83	XAIR	J83	ACUB13	88.579	0.529183	4.4239	6.5448	195	470
1985	29 JUL 85	XN2	J85	CUB14	87.592	0.530735	4.0661	6.6595	175	453
1985	29 JUL 85	XAIR	J85	ACUB15	87.437	0.539971	4.0632	6.9533	195	470
1962	1 JUL 62	JC-JB	JB	LIN7	-1.736	0.005661			289	348
1966	1 JUL 66	JC-JB	JB	LIN8	3.059	-0.009219			289	348
1970	1 JUL 70	JB-JA	JA	QUAD4	7.036	-0.051734	0.93176		239	354
1972	28 SEP 72	JB-JA	JA	QUAD5	6.566	-0.051026	0.93967		239	354
1978	18 FEB 78	JB-JA	JA	QUAD6	-0.444	0.005385	-0.12695		177	455
1981	7 SEP 81	JB-JA	JA	QUAD11	0.110	-0.003606	0.09029		176	452
1982	18 NOV 82	JB-JA	JA	QUAD12	-4.202	0.021108	-0.26370		274	452

Note: The equations are all of the form

$$Y_{out} = C_0 + C_1 Y_{in} + C_2 (Y_{in})^2 + C_3 (Y_{in})^3$$

where Y_{out} and Y_{in} are listed in the third and fourth columns, respectively. Blank entries indicate zero values for the coefficients. Parameters in columns headed Y_{out} and Y_{in} are in ppm.

Table 8a. Comparison of Manometric and Infrared calibrating data for Scripps CO2 Project gas standards during the 1985 calibration. Quoted values are differences in ppm.

CO2-IN-NITROGEN GASES

CYLINDER NO.	J	JA	(JA-J)	JF	(JF-JA)	XCALC	XMANO	(XCALC-XMANO)
2408	175.37	175.37	0.00	175.37	0.00	196.76	196.76	-0.02
3753	238.24	238.24	0.00	238.24	0.00	246.12	246.07	0.05
7366	273.30	273.30	0.00	273.30	0.00	276.61	276.59	0.02
6078	309.77	309.77	0.00	309.77	0.00	310.81	310.89	-0.08
2399	323.10	323.10	0.00	323.10	0.00	323.98	323.95	0.03
39239	331.71	331.71	0.00	331.71	0.00	332.69	332.70	-0.01
39256	344.30	344.30	0.00	344.30	0.00	345.70	345.69	0.01
39272	358.28	358.28	0.00	358.28	0.00	360.54	360.60	-0.06
1540	376.50	376.50	0.00	376.50	0.00	380.59	380.59	0.00
35299	406.29	406.29	0.00	406.29	0.00	415.01	414.92	0.09
35316	452.47	452.47	0.00	452.47	0.00	472.67	472.70	-0.03

Table 8b. Comparison of Manometric and Infrared calibrating data for Scripps CO2 Project gas standards during the 1985 calibration. Quoted values are differences in ppm.

CO2-IN-AIR GASES (WHITE STRIPES)

CYLINDER NO.	J	JA	(JA-J)	JF	(JF-JA)	XN2	XAIR	XAIR-XN2	XMANO	XAIR-XMANO
71251	194.62	194.62	0.00	194.62	0.00	211.19	213.04	1.85	213.10	-0.06
34819	242.14	242.14	0.00	242.14	0.00	249.40	251.88	2.48	251.75	0.13
71286	291.56	291.56	0.00	291.56	0.00	293.40	296.64	3.24	296.62	0.02
71341	317.48	317.48	0.00	317.48	0.00	318.38	322.07	3.69	322.14	-0.07
66638	333.25	333.25	0.00	333.25	0.00	334.26	338.24	3.98	338.27	-0.03
66625	339.28	339.28	0.00	339.28	0.00	340.47	344.57	4.09	344.67	-0.10
66696	353.72	353.72	0.00	353.72	0.00	355.67	360.05	4.38	360.03	0.02
71308	368.36	368.36	0.00	368.36	0.00	371.55	376.23	4.68	376.20	0.03
71370	394.52	394.52	0.00	394.52	0.00	401.16	406.41	5.25	406.41	0.00
71479	432.68	432.68	0.00	432.68	0.00	447.30	453.46	6.17	453.33	0.13
67615	470.28	470.28	0.00	470.28	0.00	496.38	503.56	7.18	503.63	-0.07

Table 9. Annual averages of XAIR-XMANO (in ppm) of gas mixtures containing oxygen

Cyl. No: %O ₂	CO ₂ -IN-AIR			CO ₂ -IN-N ₂ + O ₂			Av. Departure	Av. Departure	HIGH O ₂ MIXTURES				Av. Departure	
	35405	34770	35401	35452	35434	35389			35442	35441	35442	35441		Reduced Departures from Average [†]
XMANO (ppm)	336.98	338.48	352.82	323.76	323.86	335.42			326.92	331.97				
1973	-0.03	0.01	0.28	0.65	0.72	-0.18	0.24	0.04	-7.07	-3.31	0.01	0.03	0.02	
1974	-0.23	-0.03	0.02	0.60	0.57	-0.15	0.13	-0.07	-7.33	-3.58	-0.09	-0.11	-0.10	
1975	0.00	0.00	0.17	0.61	0.58	-0.09	0.21	0.01	-7.19	-3.51	-0.04	-0.08	-0.06	
1976	-0.18	-0.06	-0.09	0.60	0.51	-0.06	0.12	-0.08	-7.26	-3.50	-0.06	-0.07	-0.06	
1977	-0.19	-0.02	-0.04	0.63	0.62	0.05	0.18	-0.02	-7.18	-3.40	-0.03	-0.02	-0.02	
1978	-0.07*	0.04	-0.11	0.62	0.68	0.05	0.20	0.00	-7.07	-3.42	0.01	-0.03	-0.01	
1979	-0.02	0.04	-0.01	0.70	0.70	0.13	0.26	0.06	-7.00	-3.26	0.03	0.06	0.04	
1980	-0.06	0.03	0.02	0.67	0.62	0.03	0.22	0.02	-7.06	-3.34	0.01	0.02	0.02	
1981	-0.05	0.04	-0.01	0.62*	0.80	-0.03*	0.23	0.03	-6.85	-3.23	0.09	0.07	0.08	
1982	-0.11	0.01	0.00	0.59	0.60	0.04	0.19	-0.01	-7.02	-3.32	0.03	0.03	0.03	
1983	-0.04	0.02	0.07	0.60	0.62	0.11	0.23	0.03	-6.97	-3.26	0.04	0.06	0.05	
1984	-0.06	0.05	0.00	0.60	0.69	0.15	0.24	0.04	-6.94	-3.25	0.05	0.06	0.06	
1985	0.03	0.12	0.13	0.62	0.68	0.19	0.30	0.10	-6.91	-3.17	0.06	0.10	0.08	
Wt. Av.	-0.07	0.01	0.06	0.62	0.62	-0.03	0.20	0.00	-7.09	-3.37	-	-	0.00	

[†] Departures from Average divided by percent O₂ times 20.9.

* No data. Wt'd. Av. substituted.

Table 10a. Comparison of XN2 computed in 1983 and 1985 (1985 minus 1983), in hundredths of a ppm.

NEWXN2 - OLDXN2 (IN HUNDREDTHS OF A PPM)												
YEAR	80	80	81	81	82	82	83	83	84	84	85	85
J												
170	0	0	0	0	0	0	0	0	-1	-1	-2	-3
180	0	0	0	0	0	0	0	0	-1	-2	-3	-4
190	0	0	0	0	0	0	0	0	-1	-2	-4	-5
200	0	0	0	0	0	0	0	0	-1	-3	-5	-6
210	0	0	0	0	0	0	0	0	-1	-3	-5	-7
220	0	0	0	0	0	0	0	0	-1	-3	-5	-7
230	0	0	0	0	0	0	0	0	-1	-3	-5	-8
240	0	0	0	0	0	0	0	0	-1	-3	-6	-8
250	0	0	0	0	0	0	0	0	-1	-3	-6	-8
260	0	0	0	0	0	0	0	0	-1	-3	-5	-7
270	0	0	0	0	0	0	0	0	-1	-3	-5	-7
280	0	0	0	0	0	0	0	0	-1	-3	-5	-7
290	0	0	0	0	0	0	0	0	-1	-3	-4	-6
300	0	0	0	0	0	0	0	0	-1	-2	-4	-6
310	0	0	0	0	0	0	0	0	-1	-2	-4	-5
320	0	0	0	0	0	0	0	0	-1	-2	-3	-4
330	0	0	0	0	0	0	0	0	-1	-1	-2	-3
340	0	0	0	0	0	0	0	0	0	-1	-2	-2
350	0	0	0	0	0	0	0	0	0	-1	-1	-2
360	0	0	0	0	0	0	0	0	0	0	0	-1
370	0	0	0	0	0	0	0	0	0	0	0	0
380	0	0	0	0	0	0	0	0	0	1	1	1
390	0	0	0	0	0	0	0	0	0	1	2	2
400	0	0	0	0	0	0	0	0	0	1	2	3
410	0	0	0	0	0	0	0	0	1	2	3	4
420	0	0	0	0	0	0	0	0	1	2	3	5
430	0	0	0	0	0	0	0	0	1	2	4	6
440	0	0	0	0	0	0	0	0	1	3	5	6
450	0	0	0	0	0	0	0	0	1	3	5	7

Table 10b. Comparison of XAIR computed in 1983 and 1985 (1985 minus 1983), in hundredths of a ppm.

NEWXAIR - OLDXAIR (IN HUNDREDTHS OF A PPM)												
YEAR	80	80	81	81	82	82	83	83	84	84	85	85
J												
170	1	1	1	1	1	1	1	1	-2	-6	-10	-14
180	1	1	1	1	1	1	1	1	-2	-5	-9	-12
190	1	1	1	1	1	1	1	1	-1	-4	-7	-10
200	1	1	1	1	1	1	1	1	-1	-4	-6	-9
210	1	1	1	1	1	1	1	1	-1	-3	-6	-8
220	1	1	1	1	1	1	1	1	-1	-3	-5	-7
230	1	1	1	1	1	1	1	1	-1	-3	-4	-6
240	1	1	1	1	1	1	1	1	-1	-2	-4	-6
250	1	1	1	1	1	1	1	1	0	-2	-4	-5
260	1	1	1	1	1	1	1	1	0	-2	-3	-5
270	1	1	1	1	1	1	1	1	0	-2	-3	-5
280	1	1	1	1	1	1	1	1	0	-2	-3	-5
290	1	1	1	1	1	1	1	1	0	-2	-3	-4
300	1	1	1	1	1	1	1	1	0	-2	-3	-4
310	1	1	1	1	1	1	1	1	0	-1	-3	-4
320	1	1	1	1	1	1	1	1	0	-1	-3	-4
330	1	1	1	1	1	1	1	1	0	-1	-2	-3
340	1	1	1	1	1	1	1	1	0	-1	-2	-3
350	1	1	1	1	1	1	1	1	0	-1	-2	-3
360	1	1	1	1	1	1	1	1	0	-1	-1	-2
370	1	1	1	1	1	1	1	1	0	0	-1	-1
380	1	1	1	1	1	1	1	1	0	0	0	0
390	1	1	1	1	1	1	1	1	1	1	1	1
400	1	1	1	1	1	1	1	1	1	1	2	2
410	1	1	1	1	1	1	1	1	1	2	3	4
420	1	1	1	1	1	1	1	1	1	3	4	6
430	1	1	1	1	1	1	1	1	2	4	6	8
440	1	1	1	1	1	1	1	1	2	5	8	10
450	1	1	1	1	1	1	1	1	3	6	10	13

FORTRAN PROGRAM

C*****

C SCRIPPS INSTITUTION OF OCEANOGRAPHY: CO2 PROGRAM

C SUBROUTINES TO COMPUTE MOLE FRACTION FOR CO2-IN-N2 AND
C CO2-IN-AIR BASED ON THE 1985 CALIBRATION.
C A SINGLE CALL TO CALDAY IS NECESSARY BEFORE CALLING
C CAL85. (PROGRAM WRITTEN THIS WAY SO THAT CALDAY IS
C CALLED ONLY ONCE WHEN MULTIPLE CALCULATIONS OF MOLE
C FRACTION ARE INVOLVED.) CAL85 CAN THEN BE CALLED
C AS MANY TIMES AS DESIRED.

C INPUTS TO CAL85 ARE:

C ID: DATE (ARRAY OF 3 2-DIGIT INTEGERS)
C GAS: GAS TYPE (CHARACTER) "A" OR "N"
C Y59: "J" VALUE (REAL)

C OUTPUTS OF CAL85:

C DAYN: DAY NUMBER (REAL) DAYS SINCE 1 JAN. 1955.
C FJ: DRIFT CORRECTED "J" VALUE (REAL)
C X: MOLE FRACTION VALUE (REAL)

C Manometric revision by S. Lowe 11 October 1985

C CORR4 and CORR5 revised to correct illogical error in DAYN which
C formerly was set to CD85 if DAYN exceeded CD85. Now DAYN is not
C reset under any circumstances.

C.....TABLE OF VARIABLES, ARRAYS, AND FUNCTIONS:

NAME (DATA TYPE)	DESCRIPTION IN 1983 CALIBRATION REPORT
ACUB83 (REAL FUNCTION)	"ACUB13".
ACUB85 (REAL FUNCTION)	"ACUB15".
AJ (REAL)	"JA"="J" AFTER FIRST LEVEL DRIFT CORRECTION.
BJ (REAL)	"JB"="J" AFTER SECOND LEVEL DRIFT CORRECTION.
CDyy (REAL)	CENTRAL DATE FOR CALIBRATION OR CORRECTION OF YEAR 19yy EXPRESSED AS NUMBER OF DAYS SINCE 1/1/55.
CDSB (REAL)	END DATE FOR SOURCE BLOCK CORRECTION, EXPRESSED AS THE NUMBER OF DAYS SINCE 1/1/55.
CDSB0 (REAL)	START DATE FOR SOURCE BLOCK CORRECTION, EXPRESSED AS THE NUMBER OF DAYS SINCE 1/1/55.
CJ (REAL)	"JC"="J" AFTER THIRD LEVEL DRIFT CORRECTION.
CUB60 (REAL FUNCTION)	"CUB1(J+LIN3(J))".
CUB74 (REAL FUNCTION)	"CUB1".
CUB80 (REAL FUNCTION)	"CUB2".
CUB83 (REAL FUNCTION)	"CUB10".
CUB85 (REAL FUNCTION)	"CUB14".
CUB83I (REAL FUNCTION)	INVERSE OF "CUB10".
CUBQ80 (REAL)	"CUB9".

```

C      FUNCTION)
C      CUB80I (REAL)      INVERSE OF "CUB9".
C      FUNCTION)
C      DJ      (REAL)      "DELTA J".
C      DJyy   (REAL)      IN GENERAL: DJyy=QUADyy(AJ) OR DJyy=STLNyy(BJ).
C      DJ82   (REAL)      "DELTA J82".
C      DJ88   (REAL)      "DELTA J88".
C      DJ70   (REAL)      "DELTA J70".
C      DJ72   (REAL)      "DELTA J72".
C      DJ78   (REAL)      "DELTA J78".
C      DJ81   (REAL)      "DELTA J81".
C      DJ82   (REAL)      "DELTA J82".
C      DAYN   (REAL)      DATE OF ANALYSIS, EXPRESSED AS NUMBER OF DAYS
C                               SINCE 1/1/55.
C      FJ      (REAL)      "JF"="J" FULLY DRIFT CORRECTED.
C      GAS     (CHARACTER) INDICATES GAS TYPE: "A"=CO2-IN-AIR, "N"=CO2-IN-N2.
C      ID      (INTEGER    DATE OF ANALYSIS, EXPRESSED AS YY,MM,DD.
C              ARRAY)
C      QUAD70  (REAL)      "QUAD4".
C      FUNCTION)
C      QUAD72  (REAL)      "QUAD5".
C      FUNCTION)
C      QUAD78  (REAL)      "QUAD6".
C      FUNCTION)
C      QUAD81  (REAL)      "QUAD11" (OF 1983 REPORT ONLY).
C      FUNCTION)
C      QUAD82  (REAL)      "QUAD12".
C      FUNCTION)
C      STLN82  (REAL)      "LIN7".
C      FUNCTION)
C      STLN88  (REAL)      "LIN8".
C      FUNCTION)
C      X      (REAL)      MOLE FRACTION VALUE RETURNED BY ROUTINE.
C      Xyy    (REAL)      IN GENERAL: Xyy = CUByy(Y59).
C      X80    (REAL)      "X3".
C      X74    (REAL)      "X1".
C      X80    (REAL)      "X9".
C      X83    (REAL)      "X10".
C      XAIR   (REAL)      MOLE FRACTION VALUE FOR A CO2-IN-AIR GAS.
C      XN2    (REAL)      MOLE FRACTION VALUE FOR A CO2-IN-N2 GAS.
C      XX     (REAL)      "XINTERP".
C      XXX    (REAL)      "XSHIFT".
C      Y59    (REAL)      "J".

```

```

SUBROUTINE CAL85(ID,GAS,Y59,DAYN,FJ,X)
COMMON/CAL/CD60,CD62,CD68,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
CD85,DAY74,CDSB0,CDSB

```

```

DIMENSION ID(3)
CHARACTER*1 GAS,AIR,GN2
DATA AIR,GN2/'A','N'/

```

```

C
DAYN=DAYNO(ID(1),ID(2),ID(3))
CALL CORR1(DAYN,Y59,AJ)
CALL CORR2(DAYN,AJ,BJ)
CALL CORR3(DAYN,BJ,CJ)
CALL CORR4(DAYN,CJ,XN2,FJ)
IF (GAS.EQ.'A' .or. gas.eq.'a') THEN
  CALL CORR5(DAYN,FJ,XAIR)
  X=XAIR
ELSE

```

```
X=XN2  
END IF  
RETURN  
END
```

C
C

```
SUBROUTINE CALDAY  
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,  
* CD85,DAY74,CDSB0,CDSB  
CD60=DAYNO(60,7,1)  
CD62=DAYNO(62,7,1)  
CD66=DAYNO(66,7,1)  
CD70=DAYNO(70,7,1)  
CD72=DAYNO(72,9,28)  
CD74=DAYNO(74,8,15)  
CD78=DAYNO(78,2,18)  
CD80=DAYNO(80,9,19)  
CD81=DAYNO(81,9,7)  
CD82=DAYNO(82,11,18)  
CD83=DAYNO(83,09,17)  
CD85=DAYNO(85,07,29)  
CDSB0=DAYNO(72,06,19)  
CDSB=DAYNO(80,10,30)  
RETURN  
END
```

C
C

```
FUNCTION DAYNO(MYEAR,MONTH,MDAY)  
C THIS SUBROUTINE CALCULATES THE NO. OF DAYS FROM JAN 1,1955  
C DIMENSION MONTHR(12),IDATE(3)  
C DATA MONTHR/31,28,31,30,31,31,30,31,31,30,31,31/  
C
```

```
NDAYS=0  
LYEAR=MYEAR-1  
IF(LYEAR.LT.55)GO TO 102  
DO 101 I=55,LYEAR  
NDAYS=NDAYS+365  
J=MOD(I,4)  
IF(J.EQ.0) NDAYS=NDAYS+1  
101 CONTINUE  
102 CONTINUE  
IF(MONTH.EQ.1)GO TO 105  
LMONTH=MONTH-1  
J=MOD(MYEAR,4)  
DO 103 I=1,LMONTH  
NDAYS=NDAYS+MONTHR(I)  
IF(I.EQ.2.AND.J.EQ.0) NDAYS=NDAYS+1  
103 CONTINUE  
105 NDAYS=NDAYS+MDAY  
DAYNO=NDAYS  
RETURN  
END
```

C
C

```
SUBROUTINE CORR1(DAYN,Y59,AJ)  
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,  
* CD85,DAY74,CDSB0,CDSB
```

```
C  
C.....THIS PROCEDURE EXTRAPOLATES PRIOR TO CD60.  
IF(DAYN.GT.CD74)GO TO 20
```

X80=CUB60(Y59)
X74=CUB74(Y59)
XX=(X74*(DAYN-CD60)+X80*(CD74-DAYN))/(CD74-CD60)
AJ=CUB80I(XX)
GO TO 50

C

20 CONTINUE
IF (DAYN.GT.CD80) GO TO 30
X74=CUB74(Y59)
X80=CUB80(Y59)
XX=(X80*(DAYN-CD74)+X74*(CD80-DAYN))/(CD80-CD74)
AJ=CUB80I(XX)
GO TO 50

C

30 CONTINUE
IF (DAYN.GT.CD83) GO TO 40
X80=CUB80(Y59)
X83=CUB83(Y59)
XX=(X83*(DAYN-CD80)+X80*(CD83-DAYN))/(CD83-CD80)
AJ=CUB83I(XX)
GO TO 50

C

40 CONTINUE
AJ=Y59

C

50 CONTINUE
RETURN
END

C

C

SUBROUTINE CORR2(DAYN,AJ,BJ)
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
CD85,DAY74,CDS80,CDSB

QUAD70(AJ) = 7.036 + AJ*(-0.051734 + 0.93176E-4*AJ)
QUAD72(AJ) = 6.566 + AJ*(-0.051028 + 0.93987E-4*AJ)
QUAD78(AJ) = -0.444 + AJ*(0.005385 - 0.12695E-4*AJ)
QUAD81(AJ) = 0.110 + AJ*(-0.003806 + 0.09029E-4*AJ)
QUAD82(AJ) = -4.202 + AJ*(0.021108 - 0.26370E-4*AJ)

C

DJ=0.

C

IF (DAYN.GT.CD70) GO TO 10
IF (DAYN.LT.CD60) GO TO 100
DJ70=QUAD70(AJ)
DJ=(DAYN-CD60)/(CD70-CD60)*DJ70
GO TO 100

C

10 IF (DAYN.GT.CD72) GO TO 20
DJ70=QUAD70(AJ)
DJ72=QUAD72(AJ)
DJ=(DJ72*(DAYN-CD70)+DJ70*(CD72-DAYN))/(CD72-CD70)
GO TO 100

C

20 IF (DAYN.GT.CD74) GO TO 30
DJ72=QUAD72(AJ)
DJ=(CD74-DAYN)/(CD74-CD72)*DJ72
GO TO 100

C

30 IF (DAYN.GT.CD78) GO TO 40
DJ78=QUAD78(AJ)

```
DJ=(DAYN-CD74)/(CD78-CD74)*DJ78
GO TO 100
C
40 CONTINUE
IF(DAYN.GT.CD80)GO TO 50
DJ78=QUAD78(AJ)
DJ=(CD80-DAYN)/(CD80-CD78)*DJ78
GO TO 100
C
50 CONTINUE
IF(DAYN.GT.CD81)GO TO 60
DJ81=QUAD81(AJ)
DJ=DJ81*(DAYN-CD80)/(CD81-CD80)
GO TO 100
C
60 CONTINUE
IF(DAYN.GT.CD82)GO TO 70
DJ81=QUAD81(AJ)
DJ82=QUAD82(AJ)
DJ=(DJ82*(DAYN-CD81)+DJ81*(CD82-DAYN))/(CD82-CD81)
GO TO 100
C
70 CONTINUE
IF(DAYN.GT.CD83)GO TO 100
DJ82=QUAD82(AJ)
DJ=DJ82*(CD83-DAYN)/(CD83-CD82)
GO TO 100
C
100 BJ=AJ+DJ
RETURN
END
C
C
SUBROUTINE CORR3(DAYN,BJ,CJ)
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
CD85,DAY74,CDSB0,CDSB
STLN62(BJ) = -1.736 + 0.005661*BJ
STLN66(BJ) = 3.059 - 0.009219*BJ
C
DJ=0.
C
IF(DAYN.GT.CD62)GO TO 10
IF(DAYN.LT.CD60)GO TO 50
DJ62=STLN62(BJ)
DJ=(DAYN-CD60)/(CD62-CD60)*DJ62
GO TO 50
C
10 IF(DAYN.GT.CD66)GO TO 20
DJ62=STLN62(BJ)
DJ66=STLN66(BJ)
DJ=(DJ66*(DAYN-CD62)+DJ62*(CD66-DAYN))/(CD66-CD62)
GO TO 50
C
20 CONTINUE
IF(DAYN.GT.CD70)GO TO 50
DJ66=STLN66(BJ)
DJ=(CD70-DAYN)/(CD70-CD66)*DJ66
C
50 CJ=BJ+DJ
RETURN
```

```
END
C
C SUBROUTINE CORR4 (DAYN,CJ,XN2,FJ)
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
& CD85,DAY74,CDSB0,CDSB
C IF (DAYN.GT.CD80) GO TO 10
XXX=CUBQ80(CJ)
XN2=XXX
FJ=CUB83I(XXX)
GO TO 40
C 10 IF (DAYN.GT.CD83) GO TO 20
FJ=CJ
XN2=CUB83(FJ)
GO TO 40
C 20 IF (DAYN.GT.CD85) GO TO 30
FJ=CJ
X83=CUB83(FJ)
X85=CUB85(FJ)
XN2=(X85*(DAYN-CD83)+X83*(CD85-DAYN))/(CD85-CD83)
GO TO 40
C 30 FJ=CJ
XN2=CUB85(FJ)
C 40 CONTINUE
RETURN
END
C
C THE FOLLOWING SUBROUTINE IS USED ONLY FOR CO2-IN-AIR GAS MIXTURES
C
C SUBROUTINE CORR5 (DAYN,FJ,XAIR)
COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
& CD85,DAY74,CDSB0,CDSB
C .....ASCARITE TRAP CLEANED ON CDSB0, CONTAMINATED AND NOT CLEANED
C AGAIN UNTIL CDSB.
C IF (DAYN.GT.CD83) GO TO 10
IF ((DAYN.LT.CDSB) .AND. (DAYN.GE.CDSB0))
&FJ=FJ+0.00033*FJ
XAIR=ACUB83(FJ)
GO TO 30
C 10 IF (DAYN.GT.CD85) GO TO 20
X83=ACUB83(FJ)
X85=ACUB85(FJ)
XAIR=(X85*(DAYN-CD83)+X83*(CD85-DAYN))/(CD85-CD83)
GO TO 30
C 20 XAIR=ACUB85(FJ)
C 30 CONTINUE
RETURN
END
C
C
```

C CUBIC FUNCTIONS FOR C02-IN-N2

C
FUNCTION CUB80(A80)
DJ=0.576-0.005011*A80
A74 = A80 + DJ
CUB80=CUB74(A74)
RETURN
END

C
FUNCTION CUB74(A74)
CUB74=77.455+A74*(0.573302+A74*(3.5735E-4+6.7618E-7*A74))
RETURN
END

C
FUNCTION CUB80(A80)
CUB80=84.370+A80*(0.542223+A80*(4.2284E-4+5.8862E-7*A80))
RETURN
END

C
FUNCTION CUBQ80(A80)
C.....THIS FIT INCLUDES QUARTERLY RUNS ON THE NEW N2 MANOS AROUND 1980
CUBQ80=84.776+A80*(0.537732+A80*(4.3849E-4+5.7171E-7*A80))
RETURN
END

C
FUNCTION CUB80I(X)
AJ=X
DO 10 I=1,100
XX=CUB80(AJ)
IF (ABS(XX-X) .LT..001) GO TO 20
AJ=AJ-XX+X
10 CONTINUE
WRITE(6,101)X
101 FORMAT(' INVERSE OF 1980 CUBIC DID NOT CONVERGE, X = ',E14.6)
20 CUB80I=AJ
RETURN
END

C
FUNCTION CUB83(A83)
CUB83=86.946+A83*(0.537883+A83*(3.8471E-4+6.8562E-7*A83))
RETURN
END

C
FUNCTION CUB83I(X)
AJ=X
DO 10 I=1,100
XX=CUB83(AJ)
IF (ABS(XX-X) .LT..001) GO TO 20
AJ=AJ-XX+X
10 CONTINUE
WRITE(6,101)X
101 FORMAT(' INVERSE OF 1983 CUBIC DID NOT CONVERGE, X = ',E14.6)
20 CUB83I=AJ
RETURN

```
END
C
C
FUNCTION CUB85(A85)
CUB85=87.592+A85*(0.530735+A85*(4.0661E-4+8.6595E-7*A85))
RETURN
END
C
C
CUBIC FUNCTIONS FOR CO2-IN-AIR
C
FUNCTION ACUB83(C83)
ACUB83=88.579 + C83*(0.529183+C83*(4.4239E-4+8.5448E-7*C83))
RETURN
END
C
C
FUNCTION ACUB85(C85)
ACUB85=87.437 + C85*(0.539971+C85*(4.0632E-4+6.9533E-7*C85))
RETURN
END
C
C
END OF X85 SUBROUTINES
C*****
```

ADDENDUM

SCRIPPS REFERENCE GAS CALIBRATION SYSTEM
FOR CARBON DIOXIDE-IN-NITROGEN AND CARBON DIOXIDE-IN-AIR STANDARDS:
RESULTS OF THE MANOMETRIC VOLUME REANALYSIS OF 1986

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1. Introductory summary

The Carbon Dioxide Program of the Scripps Institution of Oceanography (SIO), under Contract with the United States National Bureau of Standards (NBS), has maintained primary standard reference gases as part of the world-wide Background Air Pollution Monitoring Network (BAPMoN) of the World Meteorological Organization (WMO). This report describes a redetermination of the volume of a chamber in a mercury manometer used at Scripps to establish the number of moles of CO₂ gas extracted from samples of standard reference gases. These data contribute to the calibrations of primary standards maintained by the Scripps Institution of Oceanography. This document is an addendum to the report of Keeling et al. [1985], and is submitted as part of the final report of activities carried out under NBS contract NB83-SBCA-2971.

The data reported here establish that a change in volume of the small-volume chamber occurred, relative to a previous determination in 1974, when the manometer was cleaned in 1985. This change corresponds closely to an apparent shift in mole fraction of primary standards measured in 1974 and again in 1985. At a meeting of experts, convened by WMO in November, 1985 to discuss future plans for measuring atmospheric carbon dioxide, we postulated a drift in the concentrations of the set of primary standards, on the assumption that the small volume chamber had not changed in volume between 1974 and 1985. The new results do not support this hypothesis, but indicate, instead, that almost no net drift in concentration occurred in the primary standards during the past 11 years.

The Scripps primary standards, eleven mixtures each of CO₂-in-air and CO₂-in-nitrogen, have been repeatedly compared against secondary gas mixtures using a non-dispersive infrared gas analyzer. A calibrating curve for each type of gas mixture has been derived and used to relate data by infrared analysis to the concentration scale established by the manometric data. The curve fits of the manometric and infrared data appear to follow closely normal Gaussian statistics. The over-all standard error of fit, based on calibrations carried out in 1983 and 1985, is 0.057 parts of CO₂ per million parts of dry air (ppm) in the range 100 to 500 ppm. The standard deviation of the mean of the manometric analyses is 0.027 ppm and of the infrared analyses 0.045 ppm. This implies that an ideal calibrating curve would fit the data with a standard error only 9% less than observed.

The new volume determination of the small-volume manometer induces us to reevaluate measurements carried out between 1982 and 1985 on standard reference gas mixtures supplied to Scripps by the National Bureau of Standards. The mole fractions of CO₂ in these mixtures were determined at NBS by a gravimetric method. For nine mixtures measured at Scripps in 1984 and 1985 by both manometric and infrared gas analysis, we find that the NBS determinations are 0.08 ± 0.08 ppm lower than the manometric analyses at SIO after excluding two mixtures which are more than 0.50 ppm higher. Thus, the two laboratories agree in the mean within one standard deviation in the mean of the differences. The standard deviation of individual NBS mixtures, again excluding the two probable outliers, is 0.22 ppm, approximately eight times less precise than the means of manometric analyses of individual Scripps primary standards. The Scripps infrared analyses of the NBS mixtures produce almost the same results: the NBS determinations are 0.05 ± 0.08 ppm lower than those of Scripps; the standard deviation of the NBS mixtures is computed to be 0.19 ppm.

We have also carried out infrared analyses of four gas mixtures prepared by gravimetry in France. The French determinations on average are 0.06 ± 0.09 ppm higher than our measurements with a standard deviation of 0.17 ppm for an individual mixture.

In addition we have reassessed manometric and infrared analyses carried out at Scripps on five gas mixtures employed by the National Oceanic and Atmospheric Administration (NOAA) as primary standards in their atmospheric CO₂ program based in Boulder, Colorado. The data

exhibit statistics similar to those of our primary standards except that the mixtures appear to have drifted upward in concentration by 0.33 ppm between 1978 and 1985.

The results of intercomparisons with NBS and French reference gas mixtures indicate that the gravimetric method at present is significantly less precise than the manometric method. It would appear premature to discontinue the manometric method in the near future as the basis for establishing standard gases for the BAPMoN program of WMO. The results of our analyses of NOAA primary standards indicate a need to recalibrate reference gases in use by the national programs of the BAPMoN program every year or two since reference gas mixtures stored under high pressure in cylinders may drift in concentration.

2. Description of the Manometer

The 4 cc chamber whose volume recalibration is described here, is part of a constant volume manometric system built in 1959 and permanently installed in Room 2317 of Ritter Hall of the Scripps Institution of Oceanography. The chamber is part of an assembly of three Pyrex glass columns (Figure 1) which attaches to a vacuum system and permits a column of mercury to be brought to near-contact with a series of glass pointers which define a set of volumes ranging from approximately 1 cc to 324 cc. The mercury level in the column which confines the sample is controlled by varying the pressure on a mercury reservoir (left column in Figure 1) after subliming the CO₂ sample into the sample column (right column in Figure 1) via a sample gas inlet from a remote location.

Applying pressure to the reservoir causes mercury to rise in the sample column. The rising mercury first cuts off the inlet so as to confine the gas sample and then compresses it to a constant volume above a selected pointer. Simultaneously the mercury also rises in an evacuated column (middle column in Figure 1). This column is maintained at a vacuum so that the pressure exerted on the sample is expressed by the height difference in mercury between the vacuum and sample columns when the mercury is held just below the chosen pointer in the sample column.

Before and after a series of measurements the mercury is also brought to the same pointer without a sample being present. The mercury height difference, determined without a sample, is applied as a meniscus correction to the measured pressure of the sample. (Guenther, 1978a,b)

The present calibration involved only the chamber with a nominal volume of 4 cc. This chamber is one of five chambers with volumes ranging from 1 to 324 cc (Figure 1). The entire three column apparatus is called the "small volume manometer". The Scripps manometric system also contains a "large volume manometer": a set of columns which includes three large sample chambers nominally of 1000 cc and 5000 cc capacity (Figure 2). Both manometers are housed in the same insulated wooded case. A second small volume manometer housed in the same case is not used for calibrations. In the determination of the mole fraction of CO₂ in a gas standard, the 5000 cc chamber of the large volume manometer is first filled with the test gas mixture to a pressure of about 600 mm of mercury. The pressure is read on a vacuum column in the same manner as with the small volume manometer, and the temperature is determined from a set of mercury thermometers. The amount of the total gas sample, previously dried to remove water vapor, is computed in moles, using the virial equation of Guenther [1981, p. 26]. Virial coefficients for air are interpolated from the table of Sengers et al. [1971].

After the moles of air have thus been determined, the air sample is slowly pumped through a concentric spherical trap to a diffusion pump exhaust. The trap is held at liquid nitrogen temperature to remove the CO₂ quantitatively. The noncondensable gases are pumped away, and the trap is then warmed and the evolved CO₂ transferred to the sample chamber of the small volume manometer by freezing it down with liquid nitrogen poured into a cup surrounding a portion of the chamber. On the way it is sublimed at dry ice temperature three or four times to remove any traces of water. After the mercury height difference has been measured, the moles of CO₂ are determined using the same virial equation cited above, with appropriate coefficients for CO₂ gas instead of air, and with the temperature again determined

from the same set of thermometers read previously. The ratio of moles of CO₂ to moles of air is the sought after mole fraction. It is expressed in parts per million (ppm). For samples of real air (as opposed to synthetic air), the mole fractions include small contributions from N₂O which are corrected for as discussed by Keeling et al. [1984, p. 6].

3. Initial calibration of the 4 cc chamber

In 1974 a series of 7 plenums were constructed of Pyrex glass. Each plenum consisted of a cylindrical tube cut off with a 2 mm hollow plug stopcock, except that for one plenum a 4 mm bore was used. The plenum volumes, ranging from 1.3 to 2.3 cc were calibrated five times each with mercury as described by Adams [1977]. The results are shown in Table 1.

To calibrate the 4 cc manometric chamber, instrument grade-4 CO₂ gas from a storage cylinder was expanded into a set of these plenums, mounted together on a gas manifold emersed in a constant temperature water bath and then evacuated (Figure 3). After bringing the CO₂ pressure to slightly above ambient pressure, the manifold was opened to the room to equalize the CO₂ pressure in the plenums with the air pressure of the room, and the latter was measured with a wall-mounted barometer. From the temperature of the water bath and the pressure of the room at time of filling of the plenums, the number of moles of CO₂ in each plenum was computed by the virial equation cited above. The gas samples were then successively transferred to the 4 cc chamber of the small volume manometer by sublimation with liquid nitrogen. From the measured temperature and pressure of the 4 cc chamber and the moles of CO₂ calculated for each plenum, the volume of the chamber was determined 16 times. The results are shown in Table 2.

Two chamber calibrations (experiment numbers 3 and 6) appear statistically as outliers. When these are omitted, the mean volume of the 4 cc chamber, based on 14 determinations, is found to be 3.7974 cc with a standard deviation of an individual measurement, σ_{in} of 0.00067 cc, and a standard deviation of the mean, σ_m , of 0.00018 cc, where

$$\sigma_{in} = \left[\frac{\sum_{i=1}^{N_a} d_i^2}{N_a - 1} \right]^{1/2} \quad (3.1)$$

and

$$\sigma_m = \left[\frac{\sigma_{in}^2}{N_a} \right]^{1/2} \quad (3.2)$$

In these equations d_i denotes the departure of the single volume determination from the mean found for the measurements, irrespective of the plenum used, and N_a denotes the number of determinations. The volumes for the plenums, according to replicate weighings, readings, and fillings during the mercury calibrations of 1974, are imprecise to 0.00006 cc [Adams, 1977, Table 5]. Since the plenum volumes are approximately half the volume of the 4 cc chamber, the error in determining the latter which arises from uncertainty in individual plenum volumes should be approximately 0.00012 cc. Since most of the 4 cc chamber calibrations in 1975 were made with only two plenums, this number cannot be verified from the consistency of these calibrations, but the 4 cc chamber calibrations during 1985 suggest that the plenum volumes, which are subject to variation each time the stopcocks are greased, are probably more uncertain than 0.00012 cc.

In 1974, on the basis of provisional calibrations of the 5000 cc chamber of the large chamber manometer, the ratio of the 5000 cc to the 4 cc chamber was assigned a value of 1320.61. This ratio was the basis for the WMO manometric scale of 1974 [WMO, 1975]. After the completion of final calibrations the 5000 cc chamber volume was established to be 5015.09 cc with a standard deviation of the mean of 0.09 cc [Guenther, 1981, p. 37]. Based on the 4 cc chamber volume of 3.7974 cc, the volume ratio for 1974 is thus computed to be 1320.66. Because this value differs only slightly from the provisional value of 1320.61, the

latter was retained in computing mole fractions at Scripps through 1981 to avoid recomputation of CO₂ concentration data carried out using the WMO scale already adopted for use in 1974. When the volume ratio was adjusted in 1983 by Keeling et al. [1984] and again in 1985 by Keeling et al. (1985), these adjustments were also derived from the provisional value of 1320.61. Thus the mole fraction scale of 1985, adopted at the November, 1985 WMO meeting of experts, is based on a provisional volume of the 5000 cc chamber, as well as on a provisional value of the 4 cc chamber. Later in this report when the new results of the 4 cc chamber calibration are put to use, the final volume determination of the 5000 cc chamber is also adopted.

4. Repeat calibration of 1985

After the 1974 calibration exercise, the plenums were stored in a special wooden box which protected them from accidental abuse. In 1985 they were cleaned, heated to 525° C., and, after cooling, lubricated with a minimum amount of Apiezon-N stopcock grease. Even though Mr. Adams and the first author, who carried out the 1974 and 1985 plenum preparations, respectively, were both experienced in greasing stopcocks and handling gas systems, it is difficult to be sure that the greasing was done exactly the same way as in 1975, owing to the 10 year time span and different persons involved.

The plenums were not recalibrated with mercury but used immediately to redetermine the volume of the 4 cc chamber. The results are shown in Table 3. Nineteen runs were made using all seven plenums at least once. The statistical deviation of a single calibration of an individual plenum, σ_{rep} , is 0.00067 cc, where:

$$\sigma_{rep} = \left[\frac{\sum_{i=1}^{N_d} d_i^2}{N_a - N_d} \right]^{1/2} \quad (4.1)$$

In equation (4.1) d_i denotes the departure of a single volume determination from the mean for that plenum, N_a denotes the number of determinations, and N_d the number of plenums. A similar value for σ_{rep} , 0.00077 cc was found in 1974 (when runs 3 and 6 are omitted). When the volume means for the individual plenums are examined, some evidence of discrepancies is found during 1985. Plenum number 5, which was equipped with a 4 mm bore stopcock, shows a mean volume for the 4 cc chamber which is 0.0026 cc higher than the overall mean of 3.7962 cc for all plenums. This difference is over three times the standard error of a single volume determination of 0.00067 cc. The discrepancy is possibly owing to a problem with stopcock grease applied to the larger stopcock. Plenum number 4, however, also shows a similar discrepancy, of 0.00028 cc in the same direction, and in this case there is no obvious explanation. If the four runs involving these two plenums are deleted from further consideration, the mean of the remaining 15 runs is 3.7955 cc with a standard deviation of individual measurement irrespective of plenum, σ_{in} , equal to 0.00071 cc, thus a standard deviation of the mean of 0.00018 cc. That σ_{in} is in this case nearly the same as σ_{rep} suggests that the remaining five plenums give the same mean volume for the 4 cc chamber within statistics of the gas fillings. We therefore adopt the value of 3.7955 cc as the most likely estimate of the volume of the 4 cc chamber in 1985, pending a recalibration of the plenum volumes with mercury.

The 1985 recalibration suggests a decrease in volume of the 4 cc chamber of 0.0019 cc \pm .00025 cc since 1974. Since the choice of plenums used in 1985 was different from that in 1974, a more logical approach to finding the change in chamber size is to compute the change indicated for each plenum used both years, and then to combine the results weighted according to the number of runs for each plenum. The decrease computed in this way is 0.0019 cc, identical to four decimal places with the previous estimate.

5. Performance of the manometer

The reproducibility of analyses using the constant volume manometric system over the past 15 years can be determined from replicate measurements of the mole fraction of reference gas mixtures. Our normal practice is to measure each mixture manometrically at least twice on every occasion that a suite of mixtures is calibrated. The standard deviation of repeat

measurement is defined by the formula:

$$\sigma_{anal} = \left[\frac{\sum_{i=1}^{N_a} d_i^2}{N_a - N_f} \right]^{1/2} \quad (5.1)$$

where d_i denotes the departure of the mole fraction of a single analysis from the mean found for the gas mixture, N_a denotes the number of analyses, and N_f the number of mixtures analyzed. Table 4 lists these computed deviations for each calibration exercise from 1969 to 1985. The original data are found in the tables of previous reports as noted in the table. The deviations vary from year to year but are generally in the vicinity of 0.06 ppm since 1974. The deviations are particularly well established in 1983 and 1985 when 23 gas mixtures were each measured two or more times. For the data of these two years combined, σ_{anal} is 0.054 ppm. There are no statistically significant differences between σ_{anal} for CO₂-in-nitrogen and CO₂-in-air mixtures. Since the relative errors in the determination of the moles of air in the 5000 cc chamber are of the order of 1 part in 10000, σ_{anal} reflects mainly the deviations in the 4 cc chamber measurements. The relative deviation for analyses from 1980 to 1985 with respect to the average concentration of the gas mixtures analyzed (332 ppm) is 0.019%, almost the same as found for repeat determinations of the volume of the 4 cc chamber (0.018%).

6. Performance of the infrared gas analyzer

All of the reference gas mixtures which contribute to the manometric data of Table 4 were mutually compared using an Applied Physics Corporation (APC) non-dispersive infrared gas analyzer several times during each major calibration exercise. The individual readings of the analyzer were first combined into averages of approximately 10 comparisons each, and from these differences the instrument response was determined for each gas. The response based on a single set of 10 comparisons was expressed by an index as described by Keeling et al. [1976]. The index for convenience was normalized to approximate numerically the CO₂ concentration of air in ppm.

The standard deviations of repeat determinations of this index, using equation (5.1) are listed in Table 5. The deviations are smaller after 1981 when manual scaling of strip charts was replaced with digital processing of the analyzer output. The standard deviation for the mean of index values of each gas mixture for the extensive calibrations of 1983 and 1985 combined (10 sets of comparisons per mixture) is 0.045 ppm.

7. Comparison of infrared and manometric calibrations of primary standard reference gases

The performance of the manometer has been further tested by comparing the results of manometric measurements with analyses of CO₂ concentration by infrared analysis using the APC analyzer, as described above. The response of this instrument to gas mixtures containing CO₂ was studied theoretically by Griffith et al. [1982] using a numerical model to compute the radiative energy absorbed in the detector of the analyzer. The absorbed energy was computed from the known CO₂ spectrum and the optical properties of the analyzer. The contributions of the numerous lines of the CO₂ spectrum were integrated using a Cray computer. It is possible to show that the theoretical model response, over the range of our reference gases excepting the lowest concentration, can be represented by a cubic power series. Specifically, if the infrared responses to the various gases are expressed by the index discussed above, then the mole fraction X is expressed by the formula:

$$X = A_0 + A_1J + A_2J^2 + A_3J^3 \quad (7.1)$$

where the A_i are coefficients found by fitting the infrared index, J, to the mole fraction, X.

In Tables 6 to 9 are summarized the infrared and manometric analyzer data from our calibration exercises for CO₂-in-nitrogen and CO₂-in-air gas mixtures beginning in 1970. In Table 10 standard errors of the corresponding curve fits are listed for years where 10 or more gas mixtures were calibrated. The calculations are shown in detail for the combined 1983 and 1985

data in Table 11. Curves for these combined data are also plotted in figures 4 and 5 for CO₂-in-nitrogen and CO₂-in-air gas mixtures, respectively.

The standard errors were computed by the formula:

$$\sigma_{fit} = \left[\frac{\sum_{i=1}^N d_i^2}{N - 4} \right]^{1/2} \quad (7.2)$$

where d_i denotes the departures of the observed manometric mole fractions from those calculated via equation (7.1) on the basis of the infrared index values, J . N denotes the number of points, and $N - 4$ represents the number of degrees of freedom of the fit, taking into account that the fit determines four coefficients, A_j . The standard errors of the fits are in the same range as the standard deviations predicted from repetitive manometric and infrared analyses. This agreement is illustrated by comparing results for the extensive calibrations of 1983 and 1985, each involving 22 gas mixtures, combined statistically as though they represent a single calibration exercise. On the basis that four manometric analyses contribute to the estimated manometrically determined concentration of each mixture, the manometric analysis error is computed to be $1/\sqrt{4}$ of σ_{anal} in Table 4, thus 0.0272 ppm. With ten determinations of index contributing to the infrared analysis of each mixture the corresponding analysis error is $1/\sqrt{10}$ of σ_{anal} in Table 5, thus 0.0451 ppm. The combined root mean square deviation is thus 0.0527 ppm. For the CO₂-in-nitrogen mixtures σ_{fit} is equal to 0.0468 ppm, for CO₂-in-air it is 0.0660 ppm (see Table 10). The root mean square of these two values is 0.0572 ppm, 1.09 times the error expected from the dispersions of the replicate manometric and infrared measurements.

There are no obvious outliers to the fits. Equation (7.1) represents the data equally well throughout the range of measurements as shown in Table 11 for combined calibrations of 1983 and 1985.

8. Evidence of change in volume of the 4 cc chamber

The manometric data of 1983 and 1985 differ slightly but systematically, as shown by plotting their differences, DEL(85-83), versus mole fraction in figure 6. Within the statistics of the data, DEL(85-83) is proportional to concentration. A similar proportionality was seen by Keeling et al. [1984] when comparing the 1981 and 1983 manometric data, but the differences were in the opposite direction. We attribute these shifts to a change in the performance of the small chamber manometer possibly resulting from fouling of the mercury which might have affected the level of the mercury column when brought close to the glass pointer. The reversed change between 1983 and 1985 transgresses the period when the manometer was cleaned and is thus consistent with this hypothesis. Although no obvious explanation has been found for a change in chamber volume from mercury fouling, we suggest that surface tension or an electrostatic effect may have been involved. In any case, we postulate that progressive fouling caused the apparent volume of the 4 cc chamber gradually to become larger until it was cleaned. After that it might be expected to have returned to nearly the condition of 1969, a time when the manometer had just been cleaned and the old mercury replaced with clean mercury.

To establish a more detailed history of apparent volume changes, the manometric data have been compared for all of the calibration exercises beginning in 1970. The comparisons are made in terms of the differences, DEL(85-yy), where yy denotes the year of a calibration being compared to the 1985 calibration. The quantity DEL(85-yy) is fit to the equation:

$$DEL(85-yy) = a X \quad (7.3)$$

where X denotes the mole fractions found in 1985 corresponding to each difference in mole fraction and a is a proportionality constant.

The results of fits to equation (7.3) are listed in Table 12 and plotted in Figures 7 to 12. Also listed are standard errors, σ_{fit} , of individual determinations of DEL(85-yy). These errors are near the values expected from the statistics of the individual measurements, taking into account that the variances add when computing errors for the differences. For example, for

1983 and 1985 combined the standard deviation of an individual measurement is 0.0544 ppm (see Table 4), hence of the mean of the pairs for one year (see equation 3.2) is 0.0385 ppm. Thus, we expect an error of fit (see Parratt, 1961, p. 116) of

$$0.0385 \sqrt{2} = 0.0544 \text{ ppm}$$

whereas the observed standard error of DEL(85-83) is 0.0757 ppm. Table 12 also lists the factors (1-a), their standard errors, and the results of a computation of the 4 cc chamber volume, assuming the volume in 1985 to be as directly measured, and that the volume in previous years has varied from this value by the factor, 1/(1-a). In the last two columns of the table are listed the volume ratios based on the computed 4 cc chamber volume and as employed to establish the calibration scales reported in previous reports. Of particular interest is that the computed volume in 1974 based on the 1985 calibration and the manometric differences, DEL(85-74), is 3.7979 cc. This value indicates a decrease of 0.0024 cc from 1974 to 1985 whereas the observed decrease, discussed in section 4, above, is 0.0019 cc. If the observed decrease is correct, the discrepancy of 0.0005 cc is equivalent to an upward drift in concentration of the primary standards of 0.013%, e.g. of 0.04 ppm for a standard gas with the CO₂ concentration of present day air. Such a drift in concentration in 11 years could not be detected directly and is not of scientific significance in terms of establishing secular changes in atmospheric CO₂. Moreover, the errors in determining the manometric chamber volume are of the same order as the discrepancy so that the computed drift cannot be regarded as statistically significant.

Given this good agreement for the 1974 calibration versus that of 1985, we feel justified in using the data of Table 12 to reconstruct the history of the 4 cc chamber volume since 1970. Calibrations in 1980 and 1981, based on nine gas mixtures, produce estimates of the proportionality factor, a, with relative errors below 1 part in 10,000. In 1982, calibrations of three standards provide a less certain estimate. For 1984 no Scripps standards were measured manometrically, but we estimated the factor, (1-a), from a set of three gas mixtures supplied to us by NBS in 1984 and calibrated before and after the manometer cleaning. We include an uncertain but seemingly quite reasonable estimate of the volume for 1970 as well. A plot of the computed volume of the 4 cc chamber versus time (figure 13) suggests a progressive increase in volume from 1970 to the time of cleaning, then a shift to a volume even lower than in 1970 just after the manometer had been cleaned previously. During the 1985 cleaning, as in 1969, the manometric glass parts were disassembled and annealed. It is possible that a small change in volume occurred. It seems to us more likely, however, that the mercury put into the manometer in 1969 was less clean than in 1985 and that the apparent difference in volume between 1970 and 1985 reflects cleaner mercury in 1985.

9. Evidence of stability of the primary standards

Because the operational volume of the 4 cc chamber of the manometer evidently did not remain constant over the past 15 years, it is not possible to use the manometric analyses to prove that the individual primary standard reference gas mixtures maintained a constant concentration of CO₂ except between 1974 and 1985 when the volume was independently calibrated with a set of plenums. The quite steady shift in volume inferred from the manometric data as shown in Figure 13, is, however, consistent with the hypothesis that the mercury became steadily more fouled, and that the primary standards did not drift erratically between 1970 and 1985.

A further check on stability of the primary standards is afforded by extensive infrared analyses of a series of six CO₂-in-air surveillance gas mixtures summarized in Table 9 of the manometric report of Keeling et al. [1985]. When mole fractions are computed for these gases on the assumption that the primary standards were stable, they show no significant departures in the annual average concentration from the long term mean between 1973 and 1985 (Figure 14, circles).

A series of four gas mixtures of CO₂-in-air, prepared more recently as reserve primary standards, also show stability in their concentrations, as shown in Table 13. Here the mole fractions computed from infrared gas analyses over the past five years are expressed as

differences from manometric data obtained in 1982. The infrared data are adjusted to agree with the new 4 cc chamber calibration by multiplying the mole fractions calculated according to the 1985 calibration scale of Keeling et al. [1985] by the factor 1321.80/1321.33 (equal to 1.000356) derived from data of Table 12. The manometric data are recomputed from the values of Table 1b of Keeling et al. [1983] by multiplying by the factor 1320.61/1319.78. In addition to a lack of evidence of drift in these mixtures, it is noteworthy that the mean difference between infrared and manometric computations of the mole fractions for all mixtures is negligible (0.005 ± 0.021 ppm). This result is evidence that the shift in manometric ratio from 1982 to 1985, computed from independent manometric data for three CO₂-in-nitrogen primary standards is nearly correct. The mean differences are plotted in Figure 14 (as plus marks).

All of the Scripps gas mixtures discussed in this report were stored in chrome-molybdenum steel cylinders.

10. Comparisons with NOAA reference gases

In 1978 Dr. Walter Komhyr of the GMCC laboratory of the United States National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado, supplied our laboratory with five reference gas mixtures of CO₂-in-air prepared in molybdenum steel cylinders similar to our cylinders. The air had been pumped from a mountain site near Boulder. These gases were compared with Scripps secondary gases by infrared analysis using the normal procedures for gas mixtures supplied to Scripps by participants in the WMO CO₂ program. In 1982, after use in the GMCC laboratory, the gases were returned to the Scripps laboratory and received manometric analyses as well as additional infrared comparisons. The manometric data are reported by Keeling et al. [1983, Table 1c] using a 5000 cc to 4 cc volume ratio of 1320.61 (see Table 12). The infrared data for 1982 are listed in Table 3b of the same report. In 1985, after further use of the gas mixtures in Boulder, Colorado, they were again sent to the Scripps laboratory and received a third set of infrared comparisons. In Table 14 these data are summarized, where again, as in Table 13, the manometric and infrared data are adjusted to be consistent with the new calibration of the 4 cc chamber volume. The manometric analyses were carried out at the same time as those of the four Scripps reserve primary CO₂-in-air mixtures cited in Table 13. The agreement between manometric and infrared data for the NOAA mixtures in 1982 is additional confirmation that the shift in 4 cc chamber volume from 1982 and 1985, as expressed by the data of Table 12, is nearly correct. For 1978 and 1985 the infrared data do not agree as closely with the manometric data as in 1982. As seen in Figure 14 (squares) the computed NOAA mole fractions have drifted significantly upward.

11. Comparisons with NBS reference gases

In 1980, Dr. Ernest Hughes of the United States National Bureau of Standards (NBS) supplied our laboratory at the Scripps Institution of Oceanography (SIO) with three reference gas mixtures of CO₂-in-air prepared in small aluminum cylinders each with a capacity of about 850 standard liters. Mole fractions had previously also been determined by Dr. Hughes at NBS from infrared comparisons versus a suite of gravimetric standards. The gravimetric standards had been prepared using a 100 g balance for the CO₂ and a 10 kg balance for the final mixture and were stored in cylinders with a capacity of about 500 standard liters each.

At Scripps each mixture was analyzed manometrically twice. Manometric mole fractions were computed using the original 5000 cc/4 cc volume ratio of 1320.61 (see Table 12). The agreement between laboratories was good. On average the mole fractions of the mixtures as determined by NBS were 0.09 ppm higher than the SIO determinations, with a standard deviation in the mean of the differences of 0.047 ppm, as noted by Bacastow et al. [1983, p. 30]. In Table 15 these data are listed after recomputation in which the mole fractions measured at SIO are adjusted to be consistent with the revised 4 cc chamber volume listed in Table 12 for 1980. The agreement between laboratories is improved. The mole fractions agree within 0.01 ppm with the same standard deviation as before.

In 1982 Dr. Hughes supplied our laboratory with six additional reference gas mixtures of CO₂-in-air prepared in small aluminum cylinders. The contents were aliquots of three gas mixtures originally prepared at NBS in large batches for use as standard reference materials (SRM's). Two aliquots were supplied as representatives of each batch. Each mixture was analyzed manometrically once. Manometric mole fractions were again computed using the original 5000 cc/4 cc volume ratio of 1320.61. The agreement was excellent. On average the mole fractions of the six mixtures agreed between laboratories to 0.00 ppm with a standard deviation in the mean of the differences of 0.015 ppm as noted by Keeling et al. (1983b, p. 12). On the basis of this good agreement, NBS prepared certificates which directly cited the Scripps analyses of the first author.

In Table 16 these data are listed after recomputation in which the mole fractions measured at the Scripps Institution of Oceanography (SIO) are adjusted to be consistent with the revised 4 cc chamber volume listed in Table 12 for 1982. The agreement between laboratories is no longer entirely satisfactory. The NBS values are all lower than the SIO values, on average by 0.21 ppm. The standard deviation of the mean of the differences is 0.015 ppm, unchanged from the earlier calculation of Keeling et al. [1983].

In 1985 three of these six gas mixtures were returned to Scripps and additional manometric analyses carried out. Infrared analyses were also performed. (Infrared analyses were not carried out in 1982 owing to the small amount of gas in each cylinder. In 1985 it was deemed important to obtain infrared analyses to confirm the manometric results in spite of this using up additional gas.)

As shown by the first three entries in Table 17 and in Figure 15 (by triangles), the infrared and manometric data obtained at SIO during 1985 for the NBS gas mixtures are concordant. The infrared results are expressed using the 1985 calibration scale of Keeling et al. [1985] multiplied again by the factor 1.000356 to be consistent with the 4 cc chamber volume of 3.7955 cc found directly from calibrations with plenums. The manometric data are also expressed consistent with this volume. In Table 18 and Figure 16 the manometric data are similarly compared with the mole fractions determined by Dr. Hughes at NBS in 1985 from infrared comparisons versus a suite of gravimetric standards. The NBS values are lower than the SIO values for all three gas mixtures. The average difference based on manometric data (first three entries of Table 18), is 0.28 ppm with a standard deviation of the mean difference of 0.08 ppm. The NBS values are lower than the SIO infrared analyses by 0.23 ppm with a standard deviation of the mean difference of 0.09 ppm.

There is no evidence of systematic instability in the three NBS gas mixtures as was seen in the NOAA gas mixtures (see section 10). The SIO manometric measurements in 1985 on average are 0.09 ppm higher than the 1982 measurements. The gravimetric data from NBS similarly indicate a negligible increase of 0.05 ppm from 1982 to 1985. The results for the individual gas mixtures, however, are not so concordant between the laboratories. The NBS gravimetric data indicate that all three mixtures had negligible differences from 1982 to 1985, but the SIO measurements indicate that the concentration of cylinder 18027 increased significantly. The manometric data indicate an increase of 0.25 ± 0.08 ppm; the 1982 manometric and 1985 infrared data indicate an increase of 0.37 ± 0.10 ppm. Both methods of measurement indicate an increase more than three times the expected standard deviation of the difference. In contrast the NBS gravimetric data indicate an increase of only 0.04 ppm. As noted above, all six of the NBS mixtures analyzed in 1982 showed good precision between laboratories. The standard deviation of an individual difference is only 0.04 ppm (see Table 13). As discussed below the comparisons between laboratories for six new mixtures in 1985 is about 5 times greater than 0.04 ppm. Thus, it appears likely to us that the concentration in cylinder 18027 in 1985 is not well established by gravimetry.

In 1984 Dr. Hughes supplied our laboratory with six additional gas mixtures prepared from three new batches of CO₂-in-air for use as standard reference materials by NBS. At the time of their arrival at Scripps, there was evidence that the manometric 4 cc chamber volume was uncertain. The main examination of these gases therefore, was postponed until after the

manometer had been cleaned. At the request of NBS, three of the six mixtures were, however, analyzed manometrically soon after arrival. These were in large aluminum cylinders with a capacity of 4250 liters, while the other three were in small aluminum cylinders similar to those used in the 1982 study. Also, soon after arrival, all six were compared with Scripps standards by infrared analysis.

In 1985 after the manometer had been cleaned, all six mixtures were analyzed manometrically. The 1985 manometric and 1984 infrared data are in good agreement as shown in Table 17. As in the case of the three gas mixtures prepared in 1982, the differences between manometric and infrared analyses never exceed 0.10 ppm. The average difference, for all nine mixtures, is 0.04 ± 0.05 ppm (infrared data being lower). The 1984 manometric data are not independent data in this comparison, because the 4 cc chamber volume cannot be established that year except by comparing manometric results of these same cylinders for 1984 and 1985, as was done in the preparation of Table 12. The manometric data are listed in Table 17 using the 4 cc chamber volume of 3.7955 cc found directly in 1985 and the computed volume for 1984, listed in Table 12. Since the 1984 data had been used to determine the 4 cc chamber volume that year, they are, in essence, forced to agree on average with the 1985 analyses. Nevertheless the dispersion of the individual values contributes additional information, and the data are therefore listed in Table 17 and averages computed for the combined manometric data of both years. In Table 18 mole fractions determined from infrared comparisons versus gravimetric standards by Dr. Hughes are compared with the manometric data of Table 17. The pair of gas mixtures with concentrations near 304 ppm are clearly in poor agreement between laboratories. The NBS gravimetric values are 0.67 and 0.82 ppm higher than the SIO manometric values. The other four mixtures, based on manometric analyses, are on average 0.06 ppm higher with a standard deviation of the mean of 0.07 ppm; based on infrared analyses they are 0.09 ppm higher with a deviation of 0.06 ppm. Thus, within statistics, the two laboratories agree for these four gas mixtures, but the results scatter considerably.

With respect to the three mixtures prepared in 1982 and reanalyzed in 1985, there is no established basis for treating them in 1985 in any way differently than the new mixtures. If these three are considered together with the four mixtures for 1985, excluding again as outliers the two of lowest concentration, the NBS values are lower on average by 0.08 ppm with a standard deviation of the mean difference of 0.085 ppm, thus indicating no difference between laboratories within statistics. For the seven mixtures, the standard deviation of the differences is 0.223 ppm. Given that the standard deviation of an individual SIO manometric analysis for 1983 and 1985 measurements combined is 0.0635 ppm (see Table 4), the computed standard deviation of a NBS analysis is 0.214 ppm, assuming that the squares of the NBS and SIO standard deviations are additive in determining the standard deviation of the differences.

The infrared analyses carried out at Scripps yield a similar result. For the seven mixtures, the NBS values are lower on average by 0.05 ppm with a standard deviation of the mean difference of 0.080 ppm, again indicating no difference between laboratories within statistics. The standard deviation of the differences is 0.211 ppm. Given that the standard deviation per set of ten SIO infrared analyzer comparisons for the 1983 and 1985 measurements combined is 0.142 ppm (see Table 5), and that each gas mixture received three sets of comparisons, the computed standard deviation of an NBS analysis is 0.194 ppm.

12. Comparisons with French reference gases

In 1985 Dr. André Gaudry of the Centre des Faibles Radioactivites (CNRS/CEA), Gif/Yvette, France, supplied our laboratory with four CO₂-in-air gas mixtures of approximately 6000 liters capacity. These were compared by infrared analysis with Scripps standards. The original supplier, Air Liquide of Paris, had prepared the mixtures for Dr. Gaudry in 1982 by direct gravimetry using a 160 g balance for the CO₂ and a 100 kg balance for the final mixtures. Mole fraction values quoted for each cylinder by Air Liquide are compared with the SIO infrared data in Table 19 and Figure 17. The SIO data, originally computed using the 1985 calibration scale of Keeling et al. (1985) have been multiplied by the quotient 1321.80/1321.33 in order to be consistent with the observed volume of the 4 cc chamber in 1985.

The Air Liquide gravimetric analyses of the four mixtures are on average 0.06 ppm higher in concentration than the SIO infrared analyses with a standard deviation of the mean of 0.087 ppm. Thus, as with the NBS mixtures the results of the two laboratories agree within statistics. The standard deviation of the difference is 0.175 ppm. Based on a standard deviation of 0.142 ppm per set of ten SIO infrared analyzer comparisons (see Table 5) and 10 sets of comparisons made for each gas mixture, the computed error of a replicate Air Liquide analysis is 0.169 ppm.

13. *Need for further statistical analysis.*

In preparing this report there was not sufficient time to carry out an entirely satisfactory statistical analysis of our measurements. In particular, equation (7.1), which links the manometric and infrared data, is fit by the conventional method of least squares in which the sum of squares of the deviations in a single variable, X, was minimized. This was done in spite of clear evidence that the two variables had equivalent standard errors. In the absence of a correlation between variables, the probability density function for a straight line function connecting two variables, say x and y, is the same as for the case where all of the error resides in one variable, say y, except for a normalization factor and substitution of the $\sqrt{\sigma_x^2 + \sigma_y^2}$ for σ_y^2 [Acton, 1957, p. 132]. When we compare the standard error in our curve fit to the root mean square of the standard deviations in both variables, our data very nearly fulfill this relation, as discussed in section 7, above, but we haven't investigated the appropriate probability density function and fitting procedure for a power series function with both variables having assigned errors. Furthermore, there is evidence in our data, not discussed above, that the errors, in ppm, are smaller for gas mixtures near the lower end of concentration, near 100 ppm than at the high end near 500 ppm. We have not yet carried out an analysis to allow for this. Thus, some additional statistical analysis is needed to complete the reporting of our measurements of standard reference gas mixtures.

14. Conclusions

Our recalibration of the 4 cc chamber of the small volume manometer, used to calibrate standard reference gas mixtures for the atmospheric CO₂ measuring program of WMO, leads to a reinterpretation of our previously reported data. We restate our principal finding here and several additional conclusions.

1. We cannot rely upon the 4 cc chamber to maintain its calibration over several years of service because of its sensitivity to impurities in the mercury which can gradually be introduced during use. The chamber volume, which is sensitive to mercury fouling, should be recalibrated with external plenums each time that a major calibration exercise is carried out, i.e. approximately every two years.

2. The volumes of the plenums, determined in 1974, should themselves be recalibrated, as well as the volume of the 5000 cc chamber.

3. The manometric method, in use at the Scripps Institution of Oceanography, has been shown to produce highly precise analyses of gas mixtures during a period of more than ten years. By employing as many as 22 primary standards, each measured repetitively, the precision of the calibrating curve of the infrared gas analyser used to verify the consistency of the manometric data has become more and more precise as the manometric method continues in use. At present each primary standard at Scripps has received at least four manometric determinations, with a precision in the mean of 0.032 ppm. If calibrations similar to those of 1983 and 1985 are repeated every two years, the manometric imprecision is likely to fall below 0.020 ppm within four more years. This precision is probably adequate for calibrating a new generation of more precise infrared gas analysers which may soon become available.

4. Because the manometric method produces consistently low imprecisions, the imprecision of the gravimetric method can be determined for gas mixtures supplied to Scripps by other laboratories by subtracting the variance of the manometric analyses from the variance of the differences between the two methods. We thus find a standard deviation of 0.21 ppm for NBS gravimetric measurements. If we carry out the same computations based on Scripps infrared

analyses, we find a standard deviation of 0.19 ppm for the NBS measurements. These imprecisions are 8 times and 7 times, respectively, greater than the manometric imprecision. For similar computation for Air Liquide gravimetric measurements compared to SIO infrared measurements, we find a standard deviation of 0.17 ppm, 6 times greater than the manometric imprecision. The comparisons, however, are based on only a few samples, and in the case of NBS involved the rejection of two gas mixtures with differences greater than 0.50 ppm out of the nine compared. It would clearly be worthwhile to carry out comparisons on additional gas mixtures to obtain more reliable statistics.

5. Our manometric and infrared measurements of the CO₂ concentration of gas mixtures supplied by the National Bureau of Standards and Air Liquide in France agree in their means with the gravimetric data of these laboratories with the statistics established for the different methods used.

6. Goodness of fit tests of calibrating curves require at least six degrees of freedom to be reliable, i.e. six more measured points than are needed to determine the parameters of the curve being fit (Parratt, 1961, p. 187). Since the response of the Scripps infrared gas analyzer to CO₂ gas mixtures requires four parameters to achieve a demonstratively good fit over the range of standard gases needed for atmospheric CO₂ studies, a minimum of ten primary gas mixtures is required.

7. Statisticians often preach the value of repetitive measurements to establish the reliability of data. The combination of manometric and infrared measurements on chemically well-defined gas mixtures permits the fulfillment of this need for statistics, because both methods permit numerous repetitions to be made on exactly the same original materials. Even cross correlation parameters could be established, if this were necessary. It is thus possible to establish all of the probability functions required to establish the goodness-of-fit of the calibrating curve connecting the two methods. In contrast the needed statistics cannot all be derived when the gravimetric method is substituted for manometry, because this method is a synthesis and, of necessity, produces a single concentration measurement for each gas mixture.

8. The direct gravimetric method of Air Liquide, employing a 100 kg balance and large capacity storage cylinders, would appear to have advantages over the NBS method in which gravimetric standards are first prepared in small storage cylinders using a 10 kg balance, and these primary standards are then used to prepare secondary standards with an infrared analyzer.

9. From a scientific point of view, the study of variations in the abundance of atmospheric CO₂ in time and space demands high precision, but only moderate accuracy. Especially important is that the secondary and tertiary standard reference gas mixtures used by the national laboratories of the WMO program and in the field be precisely and repeatedly compared directly or indirectly against a set of well determined primary standards. The maintenance of such standards is the principle function of the WMO Central CO₂ laboratory presently at the Scripps Institution of Oceanography. The demonstrably reliable way to maintain these standards is to check their CO₂ concentrations periodically by an analytical technique which directly produces highly precise data. The manometric method clearly is capable of carrying out this function. The gravimetric method is not. The maintenance of a set of primary standards by gravimetry, even if the direct technique of Air Liquide were adopted, would require that a secondary method such as infrared analysis be employed to establish the precision of the gravimetric method and the long term stability of the primary standards. This secondary method would introduce additional and to some degree unknown errors into the determination of the gravimetric precision. Furthermore, according to the information available to us, the gravimetric method is considerably less precise than the manometric method. We therefore recommend continued reliance on manometric analyses to maintain the primary standard reference gas mixtures of the WMO central CO₂ laboratory.

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Table 1. Plenum volume determinations of February and March 1974 (in cc)

<u>Plenum no:</u>	<u>P-1</u>	<u>P-2</u>	<u>P-3</u>	<u>P-4</u>	<u>P-5</u>	<u>P-6</u>	<u>P-7</u>
1.2976	1.4619	1.6359	1.7457	1.8357	2.0368	2.2733	
1.2977	1.4619	1.6362	1.7456	1.8360	2.0365	2.2732	
1.2978	1.4619	1.6359	1.7456	1.8361	2.0367	2.2732	
1.2978	1.4619	1.6358	1.7458	1.8359	2.0367	2.2732	
1.2981	1.4618	1.6360	1.7459	1.8360	2.0367	2.2734	
Mean	1.2978	1.4619	1.6360	1.7457	1.8359	2.0367	2.2733
Standard deviation of the mean	0.00008	0.00002	0.00007	0.00006	0.00007	0.00005	0.00004

Table 2. Calibration of 4 cc chamber volume in 1974

<u>Experiment No.†</u>	<u>Date of Plenum Filling</u>	<u>Plenum No.</u>	<u>Computed 4cc Chamber Volume (cc)</u>
1	20 JUN 74	P-7	3.7982
2	20 JUN 74	P-1	3.7959
3	26 JUN 74	P-1	3.7927
4	26 JUN 74	P-7	3.7980
6	9 JUL 74	P-7	3.8106
7	9 JUL 74	P-1	3.7971
8	29 JUL 74	P-7	3.7965
9	29 JUL 74	P-1	3.7975
10	30 JUL 74	P-1	3.7979
11	30 JUL 74	P-7	3.7968
12	1 AUG 74	P-7	3.7974
13	1 AUG 74	P-1	3.7982
14	7 AUG 74	P-3	3.7971
15	7 AUG 74	P-5	3.7975
16	7 AUG 74	P-4	3.7979
17	7 AUG 74	P-1	3.7973

Mean of 16* = 3.7973 cc

σ_{in} = 0.00159cc

Mean of 14** = 3.7974 cc

σ_{in} = 0.00067cc

σ_m = 0.00018cc

†Experiment No. 5 was not a volume calibration

* All measurements; σ_{in} denotes standard deviation of individual measurement

** Measurements of experiments 3 and 6 omitted; σ_m denotes standard deviation of the mean

Table 3. Calibration of 4 cc chamber volume in 1985

<u>Experiment No.</u>	<u>Date of Plenum Filling</u>	<u>Plenum No.</u>	<u>Computed 4cc Chamber Volume (cc)</u>
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 19* = 3.7962 cc

σ_{in} = 0.00159cc

Mean of 15** = 3.7955 cc

σ_{in} = 0.00071cc

σ_m = 0.00018cc

* All measurements

** Measurements with P-4 and P-5 omitted

σ_{in} and σ_m have same meaning as in Table 2

Table 4. Standard deviations of individual manometric analyses

<u>Year</u>	<u>No. of Samples</u>	<u>No. of Analyses</u>	<u>σ_{anal} (ppm)</u>	<u>Type of Gas Mixture</u>	<u>Source of Data</u>
1959-61	3	6	0.088	CO ₂ -in-N ₂	Bacastow et al. (1983a) p. 20
1969-70	4	22	0.176	"	Bacastow et al. (1983a) p. 21
1972	3	7	0.167	"	Guenther (1978) p. 27
1974	23	50	0.083	"	Bacastow et al. (1983a) p. 22-23 and (1983b) p. 13-14
1980	24	51	0.058	"	Bacastow et al. (1983a) p. 24-25 and (1983b) p. 15-16
1981	12	24	0.071	CO ₂ -in-air	Bacastow et al. (1983b) p. 14-15*
1982	12	26	0.048	combined	Keeling et al. (1983) p. 15-17
1983	23	52	0.041	combined	Keeling et al. (1984) p. 28-31
1985	23	48	0.066	combined	Keeling et al. (1985) p. 22-25
Separated by type of mixture:					
1983	11	26	0.032	CO ₂ -in-N ₂	
	12	26	0.048	CO ₂ -in-air	
1985	11	24	0.065	CO ₂ -in-N ₂	
	12	24	0.067	CO ₂ -in-air	
1983/1985 combined:					
	11	50	0.0506	CO ₂ -in-N ₂	
	11	50	0.0579	CO ₂ -in-air	
	46	100	0.0544	combined	

*1980 runs combined with 1981 runs on p. 14.

Table 5. Standard deviations of daily averaged infrared analyses

<u>Year</u>	<u>No. of Samples</u>	<u>No. of Analyses</u>	<u>No. of Degrees of Freedom</u>	<u>σ_{anal} (ppm)</u>	<u>Type of Gas Mixture</u>	<u>Source of Data</u>
1974	10	128	91	0.177	CO ₂ -in-N ₂	Keeling et al. (1984) p. 35
1980	10	80	63	0.164	"	Keeling et al. (1984) p. 36
1981	15	100	68	0.163	combined	Keeling et al. (1984) p. 37, 40
1982	15	60	36	0.041	"	Keeling et al. (1984) p. 38, 41
1983	22	110	84	0.136	"	Keeling et al. (1984) p. 39, 42
1984	11	33	20	0.095	CO ₂ -in-N ₂	Keeling et al. (1984) p. 43
1985	22	110	84	0.149	"	Keeling et al. (1985) p. 38-39
Separated by type of mixture:						
1983	11	55	42	0.141	CO ₂ -in-N ₂	
	11	55	42	0.131	CO ₂ -in-air	
1985	11	55	42	0.155	CO ₂ -in-N ₂	
	11	55	42	0.143	CO ₂ -in-air	
1983/1985 combined:						
	11	110	84	0.1479	CO ₂ -in-N ₂	
	11	110	84	0.1369	CO ₂ -in-air	
	22	220	168	0.1425	combined	

Note: The original index values, as listed in the references in the last column, were computed from assigned values of a pair of gas mixtures, called "principle" and "high span" standards. In computing standard deviations these data were first adjusted so that the sum of differences in index from the principle standard on each day on a series of calibrations was made to be the same as the mean of all days of the series. This adjustment had the effect of producing a best estimate of the infrared recorder's linear scaling factor for each day and removed the influence of the assigned index of the high span standard from the computation. As shown by Bacastow et al. [1983, p. 54] the effect of this adjustment was to reduce scatter for gas mixtures near the low and high end of the concentration range. The degrees of freedom used in computing the standard deviations take this adjustment into account.

Table 6. Summary of infrared analyses during periods of special manometric calibrations. The numbers of days with calibrations are shown in parentheses.

CO2-IN-NITROGEN GASES						
CYL.NO.	1970	1974	1980	1981	1983	1985
2408		180.83 (16)	176.96 (8)	176.68 (5)	175.39 (5)	175.37 (5)
3753		241.32 (8)	238.93 (8)		238.16 (5)	238.24 (5)
7368	275.88 (8)	275.55 (8)	273.84 (8)	273.89 (5)	273.27 (5)	273.30 (5)
8078	311.49 (8)	311.17 (16)	310.23 (8)		309.73 (5)	309.77 (5)
2399	324.56 (8)	324.23 (16)	323.53 (8)		323.07 (5)	323.10 (5)
39239		332.82 (8)	332.23 (8)	332.07 (5)	331.70 (5)	331.71 (5)
39256					344.29 (5)	344.30 (5)
10089	354.38 (7)	354.47 (16)	354.36 (8)			
39272					358.23 (5)	358.26 (5)
1540		377.02 (8)	377.07 (8)		376.49 (5)	376.50 (5)
35299		406.55 (16)	407.19 (8)		406.33 (5)	406.29 (5)
35316		452.55 (16)	453.98 (8)	453.20 (5)	452.59 (5)	452.47 (5)

Source of adjusted index data:
 1970, 1974, 1980, and 1983:
 Table 4 of Keeling et al. (1984)
 1981: Table 2c of Keeling et al. (1984)
 1985: Table 4a of Keeling et al. (1985)

Table 7. Summary of infrared analyses during periods of special manometric calibrations. The numbers of days with calibrations are shown in parentheses.

CO2-IN-AIR GASES (WHITE STRIPES)			
CYL.NO.	1981	1983	1985
71251	195.89 (10)	194.61 (5)	194.62 (5)
34819	242.85 (5)	241.98 (5)	242.14 (5)
71286	291.98 (10)	291.50 (5)	291.56 (5)
71341	318.11 (5)	317.52 (5)	317.48 (5)
66638	333.51 (10)	333.20 (5)	333.25 (5)
66625	339.64 (5)	339.27 (5)	339.28 (5)
66696	353.91 (5)	353.64 (5)	353.72 (5)
71308	368.83 (5)	368.35 (5)	368.36 (5)
71370	394.84 (10)	394.53 (5)	394.52 (5)
71479	433.35 (5)	432.70 (5)	432.68 (5)
67615	470.94 (10)	470.31 (5)	470.28 (5)

Source of data:
 1981: Table 2f of Keeling et al. (1984)
 1983, 1985: Table 4b of Keeling et al. (1985)

Table 8. Summary of manometric measurements (in ppm), by year expressed with respect to a 5000cc to 4cc chamber volume ratio of 1320.61. The number of determinations are shown in parentheses.

CO2-IN-NITROGEN GASES						
CYL.NO.	1970	1974	1980	1982	1983	1985
2408		196.90 (2)	196.80 (2)		196.68 (3)	196.96 (2)
3753		246.02 (2)	245.99 (2)		245.89 (2)	246.29 (2)
7366	276.57 (3)	276.80 (2)	276.87 (2)		276.33 (2)	276.84 (2)
6078	310.95 (7)	310.82 (3)	310.96 (2)		310.52 (2)	311.17 (2)
2399	324.19 (8)	324.05 (4)	324.15 (2)		323.76 (2)	324.24 (2)
39239		332.78 (2)	332.72 (2)	332.64 (2)	332.46 (5)	333.00 (4)
39256				345.57 (3)	345.51 (2)	346.00 (2)
10069	355.64 (4)	355.60 (2)	355.82 (2)			
39272				360.49 (3)	360.32 (2)	360.92 (2)
1540		380.56 (2)	380.45 (2)		380.16 (2)	380.93 (2)
35299		415.06 (2)	414.94 (2)		414.70 (2)	415.29 (2)
35316		472.97 (2)	472.72 (4)		472.38 (2)	473.13 (2)

Source of data:
 1970-1982: Table 1i of Keeling et al. (1985)
 1983: Table 1a of Keeling et al. (1985)
 1985: Table 1c of Keeling et al. (1985)

Table 9. Summary of manometric measurements (in ppm), by year expressed with respect to a 5000cc to 4cc chamber volume ratio of 1320.61. The number of determinations are shown in parentheses.

CO2-IN-AIR GASES (WHITE STRIPES)			
CYL.NO.	1981	1983	1985
66556	101.00 (2)	100.91 (2)	100.98 (2)
71251	213.15 (2)	213.00 (2)	213.29 (2)
34819	251.72 (2)	251.61 (2)	251.98 (2)
71286	296.56 (2)	296.45 (2)	296.89 (2)
71341	322.45 (2)	321.98 (2)	322.43 (2)
66638	338.08 (2)	337.95 (2)	338.57 (2)
66625	344.62 (2)	344.26 (4)	344.98 (2)
66696	359.87 (2)	359.65 (2)	360.35 (2)
71308	376.48 (2)	375.92 (2)	376.54 (2)
71370	406.39 (2)	406.10 (2)	406.78 (2)
71479	453.40 (2)	453.02 (2)	453.74 (2)
67615	503.20 (2)	503.24 (2)	504.08 (2)

Source of data:
 1981: Table 1j of Keeling et al. (1985)
 1983: Table 1d of Keeling et al. (1985) (except that N2O concentrations listed in Table 1h of Keeling et al. (1985) are subtracted)
 1985: Table 1h of Keeling et al. (1985)

Table 10. Standard errors of estimate of X in cubic equation (7.1)

<u>Year</u>	<u>Samples</u>	<u>Standard Error (ppm)</u>	<u>Type of Gas Mixture</u>
1974	10	0.093	CO ₂ -in-N ₂
1980	10	0.091	CO ₂ -in-N ₂
1981	11	0.098	CO ₂ -in-Air
1983	11	0.069	CO ₂ -in-N ₂
1983	11	0.054	CO ₂ -in-Air
1985	11	0.058	CO ₂ -in-N ₂
1985	11	0.092	CO ₂ -in-Air
1983/1985 combined:			
	11	0.0468	CO ₂ -in-N ₂
	11	0.0660	CO ₂ -in-Air
	22	0.0572	combined

Table 11. Fit of manometric analyses to infrared analyses via equation (7.1) for 1983 and 1985 data combined (in ppm)

<u>Observation No.</u>	<u>Observed J</u>	<u>Observed X</u>	<u>Fit to X</u>	<u>Residuals</u>
CO ₂ -in-nitrogen gas mixtures				
1	175.380	196.820	196.809	0.011
2	238.200	346.090	246.110	-0.020
3	273.285	276.585	276.621	-0.036
4	309.750	310.845	310.820	0.025
5	323.085	324.000	323.997	0.003
6	331.705	332.730	332.713	0.017
7	344.295	345.755	345.729	0.026
8	358.245	360.620	360.556	0.064
9	376.495	380.545	380.612	-0.067
10	406.310	414.995	415.046	-0.051
11	452.530	472.755	472.730	0.026
	σ_{fit}			0.0468
Coefficients:				
	A ₀ = 87.8899			
	A ₁ = 0.527790			
	A ₂ = 4.17145 x 10 ⁻⁴			
	A ₃ = 6.53703 x 10 ⁻⁷			
CO ₂ -in-air gas mixtures				
1	194.615	213.145	213.105	0.040
2	242.060	251.795	251.889	-0.094
3	291.530	296.670	296.674	-0.004
4	317.500	322.205	322.135	0.070
5	333.225	338.260	338.247	0.013
6	339.275	344.620	344.590	0.030
7	353.680	360.000	360.023	-0.023
8	368.355	376.230	376.235	-0.005
9	394.525	406.440	406.415	0.025
10	432.690	453.380	453.481	-0.101
11	470.295	503.660	503.610	0.050
	σ_{fit}			0.0660
Coefficients:				
	A ₀ = 86.8076			
	A ₁ = 0.547493			
	A ₂ = 3.80939 x 10 ⁻⁴			
	A ₃ = 7.21640 x 10 ⁻⁷			

Table 12. Implied volume of 4 cc chamber based on fits of manometric analyses to equation (7.3)

Year	Samples	1-a	Standard Error of 1-a	σ_{fit} (ppm)	Computed Volume (cc)	Standard Error of Computed Volume (cc)	Computed Volume Ratio [†]	Previously used Volume Ratios
1970	3	0.999428	0.000242	0.128	3.7977	0.0009	1320.57	-
1974	9	0.999374	0.000108	0.110	3.7979	0.0004	1320.50	1320.61 ^a
1980	9	0.999163	0.000095	0.096	3.7987	0.0004	1320.22	1320.61 ^a
1981	9	0.998973	0.000097	0.094	3.7994	0.0004	1319.97	1320.61 ^a
1982	3	0.998825	0.000047	0.028	3.8000	0.0002	1319.78	1320.61 ^a
1983	23	0.998340	0.000046	0.076	3.8018	0.0002	1319.14	1319.61 ^b
1984	3	0.998323	0.000140	0.083	3.8019	0.0005	1319.11	-
1985					3.7955*		1321.33	1321.80 ^c

* Direct Determination

† Ratio of 5000 cc chamber to 4 cc chamber where volume of 5000 cc chamber is 5015.09 cc

^a for manometric scales of 1974, 1980 and 1981

^b for manometric scale of 1983

^c for manometric scale of 1985

Table 13. Comparison of manometric and infrared analyses of SIO secondary gas mixtures of CO₂-in-air

Cylinder No.	Manometric Concentration (ppm)	Difference (ppm)*					
		1981	1982	1983	1984	1985	Mean
34891	298.11	0.07	-0.03	-0.04	0.13	0.07	0.04
62807	338.57	-0.02	-0.06	-0.02	0.03	0.08	0.00
62817	365.58	0.00	-0.01	-0.02	-0.08	0.04	-0.01
62814	425.19	-0.09	-0.06	0.29	-0.16	-0.03	-0.01
Mean difference		-0.010	-0.040	0.052	-0.020	0.040	
Mean difference for all years							0.005
Standard deviation of individual differences for all years							0.095
Standard deviation of mean difference for all years							0.021

* Manometric minus infrared derived concentrations

Table 14. Comparison of manometric and infrared analyses of NOAA gas mixtures of CO₂-in-air

Cylinder No.	Manometric Concentration (ppm)	Differences (ppm)*		
		1978	1982	1985
3082	316.52	-0.20	-0.11	0.05
3074	329.29	-0.29	-0.12	0.05
3091	341.83	-0.33	-0.12	0.11
3071	352.62	-0.29	-0.07	0.11
3092	366.86	-0.06	0.02	0.15
Mean difference		-0.234	-0.080	0.094
Standard deviations of individual annual differences for one year		0.108	0.060	0.043
Root mean square standard deviation of individual annual differences for all years (in ppm)				0.076

* Infrared derived concentrations minus manometric

Table 15. Comparison of manometric and gravimetric analyses of NBS reference gas mixtures in small cylinders analyzed in 1980

Cylinder No.	SIO Individual Manometric Analysis (ppm)	NBS Gravimetric Concentration (ppm)	Difference (NBS-SIO) (ppm)	
			Individual Analysis	Cylinder Average
62206	333.34	333.34	0.00	
"	333.27	"	0.07	0.035
61130	340.04	340.05	0.01	
"	339.97	"	0.08	0.045
243988	346.77	346.68	-0.09	
"	346.79	"	-0.11	-0.100
Mean difference				-0.007
Standard deviation of individual difference				0.081
Standard deviation of mean difference				0.046

Table 16. Comparison of manometric and gravimetric analyses of NBS reference gas mixtures in small cylinders analyzed in 1982

<u>Cylinder No.</u>	<u>SIO Manometric Concentration (ppm)</u>	<u>NBS Gravimetric Concentration (ppm)</u>	<u>Difference (NBS-SIO) (ppm)</u>
18027	335.82	335.61	-0.21
18040	335.67	335.49	-0.18
18067	342.58	342.31	-0.27
16410	342.86	342.65	-0.21
18042	351.25	351.08	-0.17
16417	351.35	351.11	-0.24
Mean difference			-0.213
Standard deviation of individual difference			0.037
Standard deviation of mean difference			0.015

Table 17. Comparison of manometric and infrared analyses of NBS reference gas mixtures carried out at SIO in 1984 and 1985

<u>Cylinder No.</u>	<u>Manometric Concentration</u>	<u>Infrared Derived Concentration* (ppm)</u>	<u>Difference (Infrared-Manometric)</u>
Small cylinders - prepared in 1982			
18027	336.08	336.02	-0.06
18067	342.65	342.66	0.01
16417	351.29	351.21	-0.08
Small cylinders - prepared in 1984			
8699	304.14	304.10	-0.04
8386	341.67	341.68	0.01
8432	374.87	374.93	0.06
Large cylinders - prepared in 1984**			
11835	304.02	303.96	-0.06
11429	341.58	341.49	-0.09
11062	375.28	375.19	-0.09
Mean difference			-0.038
Standard deviation of individual difference			0.053
Standard deviation of mean difference			0.018

*Averages of 3 sets of 10 comparisons for each mixture.

**Manometric data are averages of 1984 and 1985 analyses. (All other manometric data in this table from 1985 analyses only).

Table 18. Comparison of manometric and gravimetric analyses of NBS reference gas mixtures analyzed in 1984 and 1985

Cylinder No.	SIO Manometric Concentration		Av.	NBS Gravimetric Concentration (ppm)	Difference (NBS-SIO) (ppm)
	1984	1985			
Small cylinders-prepared in 1982					
18027		336.08		335.65	-0.43
18067		342.65		342.39	-0.26
16417		351.29		351.15	-0.14
Small cylinders-prepared in 1984					
8699		304.14		304.96	0.82*
8386		341.67		341.75	0.08
8433		374.87		375.05	0.18
Large cylinders-prepared in 1984					
11835	304.04	303.99	304.02	304.69	0.67*
11429	341.62	341.55	341.58	341.44	-0.14
11062	375.24	375.33	375.28	375.41	0.13
Mean difference					-0.083
Standard deviation of individual difference					0.223
Standard deviation of mean difference					0.084
* Excluded from mean					

Table 19. Comparison of infrared and gravimetric analyses of Air-Liquide reference gas mixtures analyzed in 1984

Cylinder No.	SIO Infrared Derived Concentration* (ppm)	Air-Liquid Gravimetric Concentration (ppm)	Difference (Air Liquid-SIO) (ppm)
166017	332.59	332.86	0.27
165962	335.93	335.94	0.01
166119	340.88	340.97	0.09
276103	354.00	353.85	-0.15
Mean difference			0.055
Standard deviation of individual difference			0.175
Standard deviation of mean difference			0.087

* Averages of 10 sets of 10 comparisons for each mixture

CONSTANT VOLUME MANOMETER

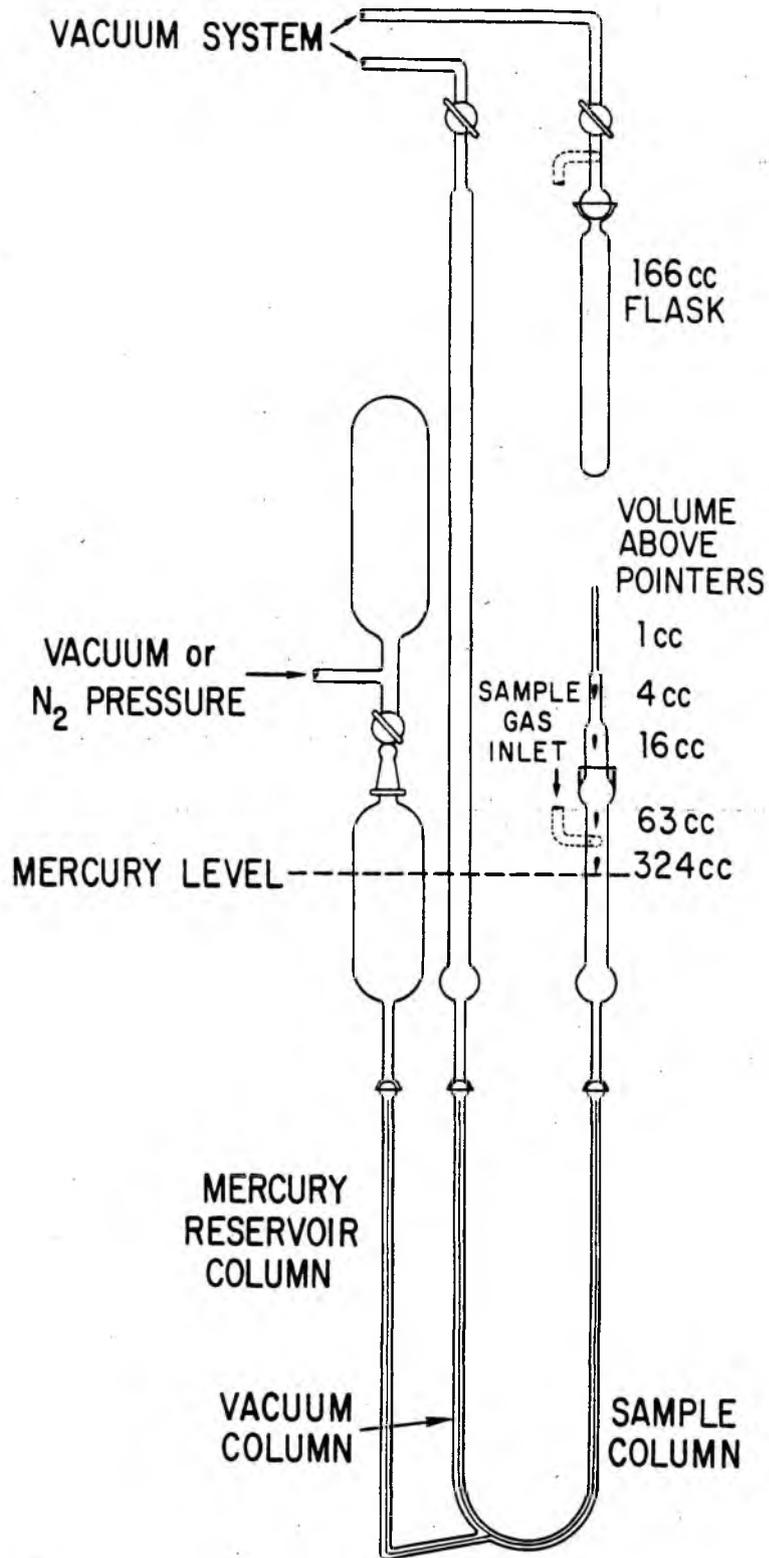
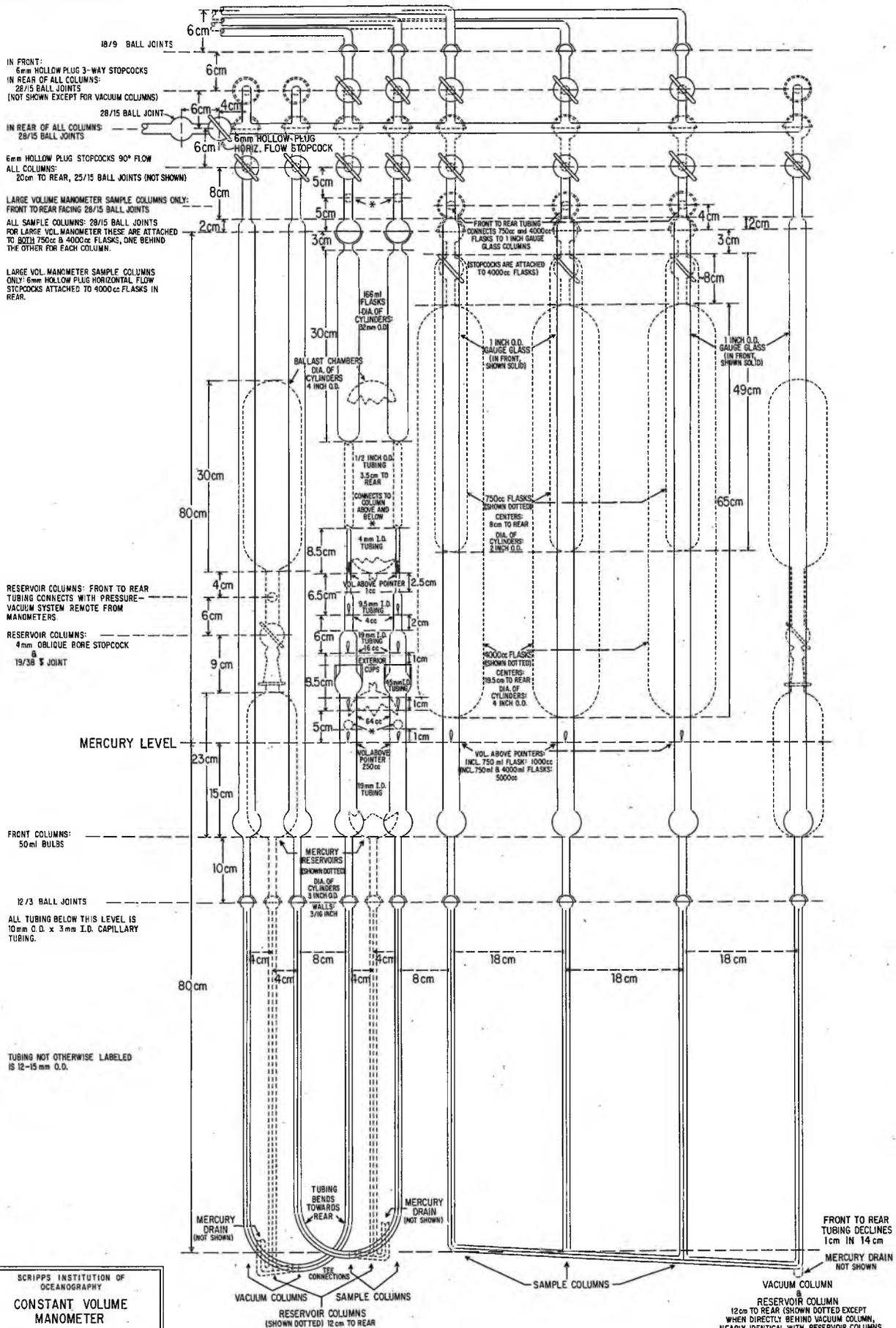


Figure 1. Schematic of small volume manometer used to calibrate gas mixtures containing carbon dioxide.

Figure 2. Detailed drawing of the system of constant volume manometers. One large and one small volume manometer are used to calibrate gas mixtures containing carbon dioxide. The other small volume manometer is not in use.

Column Numbers: 1 2 3 4 5 6 7 8



18/9 BALL JOINTS
 IN FRONT:
 6mm HOLLOW PLUG 3-WAY STOPCOCKS
 IN REAR OF ALL COLUMNS:
 28/15 BALL JOINTS
 (NOT SHOWN EXCEPT FOR VACUUM COLUMNS)
 IN REAR OF ALL COLUMNS:
 28/15 BALL JOINTS
 6mm HOLLOW PLUG STOPCOCKS 90° FLOW
 ALL COLUMNS:
 20cm TO REAR, 25/15 BALL JOINTS (NOT SHOWN)
 LARGE VOLUME MANOMETER SAMPLE COLUMNS ONLY:
 FRONT TO REAR FACING 28/15 BALL JOINTS
 ALL SAMPLE COLUMNS: 28/15 BALL JOINTS
 FOR LARGE VOL. MANOMETER THESE ARE ATTACHED
 TO BOTH 750cc & 4000cc FLASKS, ONE BEHIND
 THE OTHER FOR EACH COLUMN.
 LARGE VOL. MANOMETER SAMPLE COLUMNS
 ONLY: 6mm HOLLOW PLUG HORIZONTAL FLOW
 STOPCOCKS ATTACHED TO 4000cc FLASKS IN
 REAR.

RESERVOIR COLUMNS: FRONT TO REAR
 TUBING CONNECTS WITH PRESSURE-
 VACUUM SYSTEM REMOTE FROM
 MANOMETERS
 RESERVOIR COLUMNS:
 4mm OBLIQUE BORE STOPCOCK
 19/38 BALL JOINT
 MERCURY LEVEL

FRONT COLUMNS:
 50ml BULBS
 12/3 BALL JOINTS
 ALL TUBING BELOW THIS LEVEL IS
 10mm O.D. x 3mm I.D. CAPILLARY
 TUBING.

TUBING NOT OTHERWISE LABELED
 IS 12-15mm O.D.

SCRIPPS INSTITUTION OF
 OCEANOGRAPHY
**CONSTANT VOLUME
 MANOMETER**
 TO DETERMINE THE CONCENTRATION
 OF CARBON DIOXIDE IN AIR
 SCALE: 1/2
 DATE: JULY 2, 1957

SMALL VOLUME MANOMETERS

LARGE VOLUME MANOMETER

CO₂ SAMPLE PREPARATION VACUUM LINE

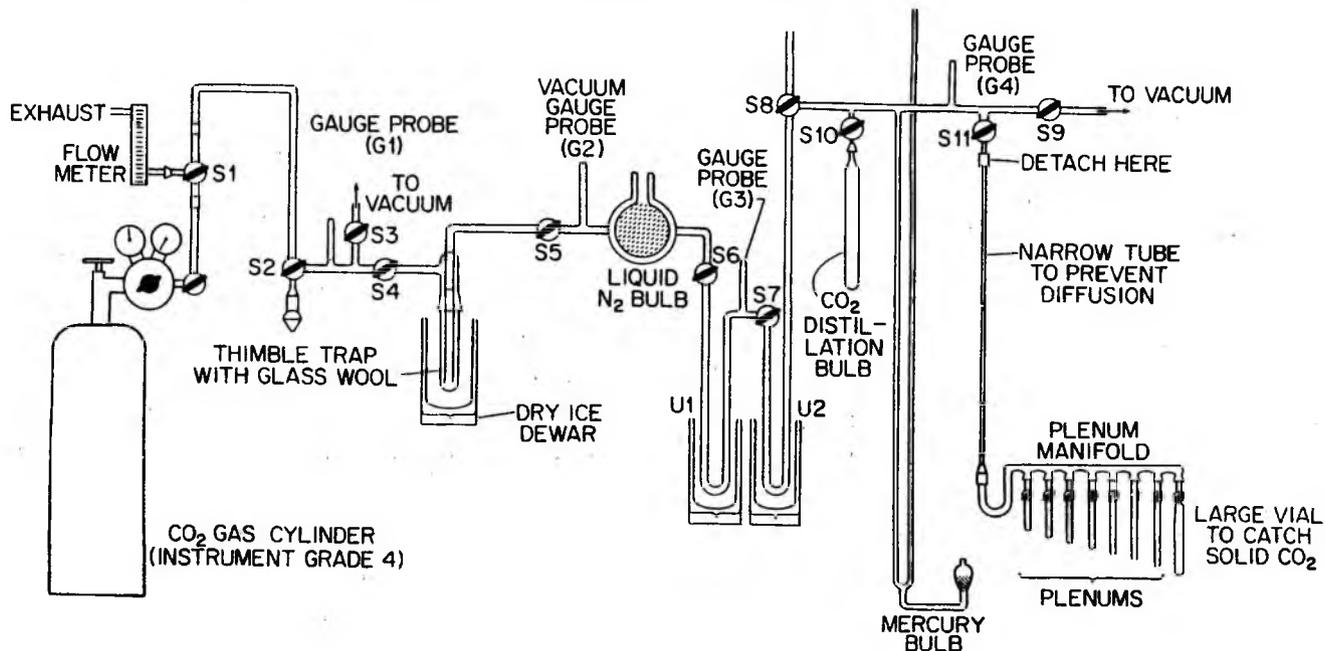


Figure 3. Schematic of vacuum line used to prepare aliquots of carbon dioxide in glass plenums for calibrating the small volume manometer.

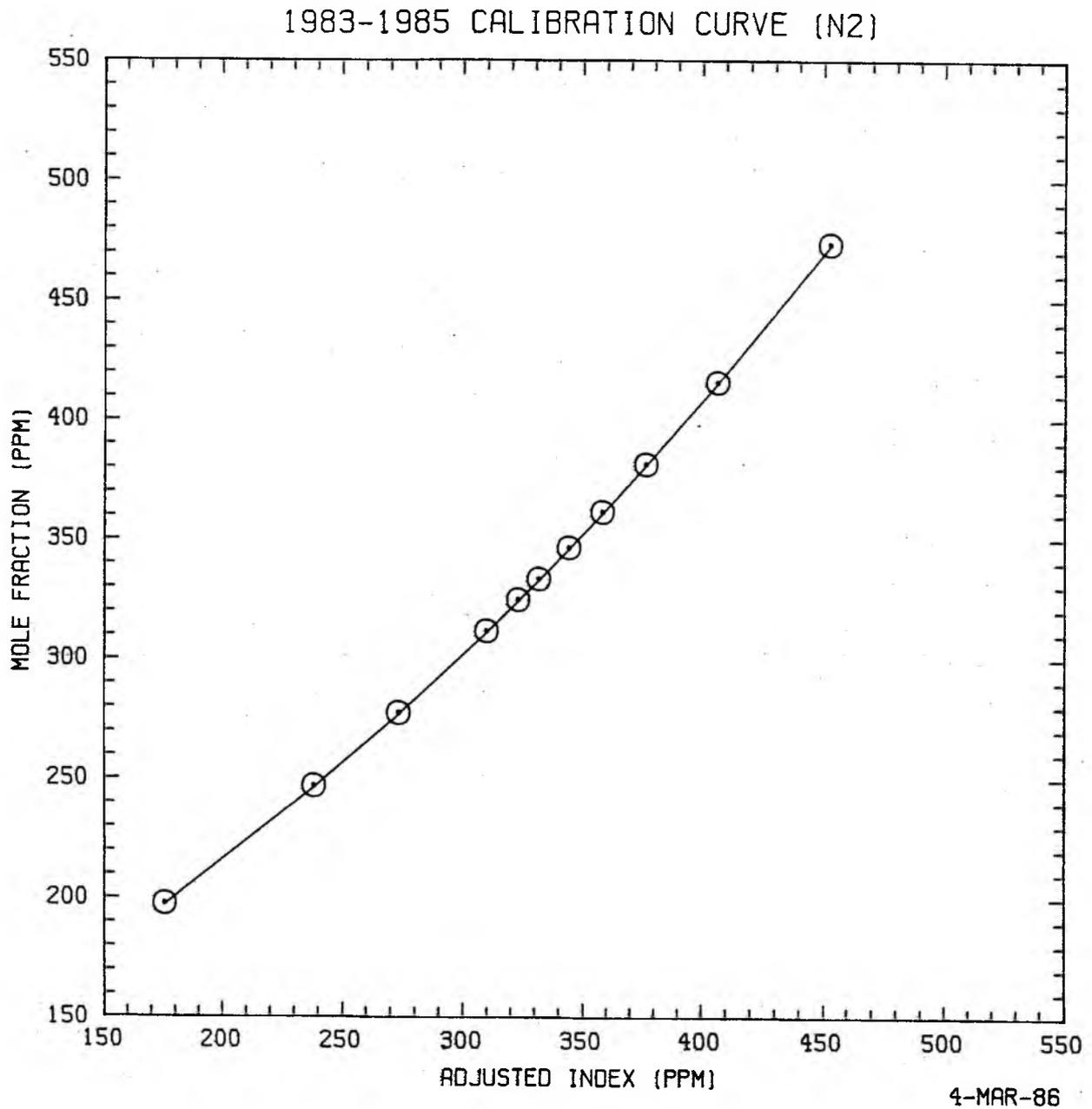


Figure 4. Plot of the calibration curve linking manometric mole fraction (vertical axis) and infrared adjusted index (horizontal axis) of carbon dioxide in gas mixtures of CO₂-in-nitrogen, based on the combined analyses of 1983 and 1985. The smooth curve is a least squares fit of the data (in ppm) to a cubic power series according to equation (7.1).

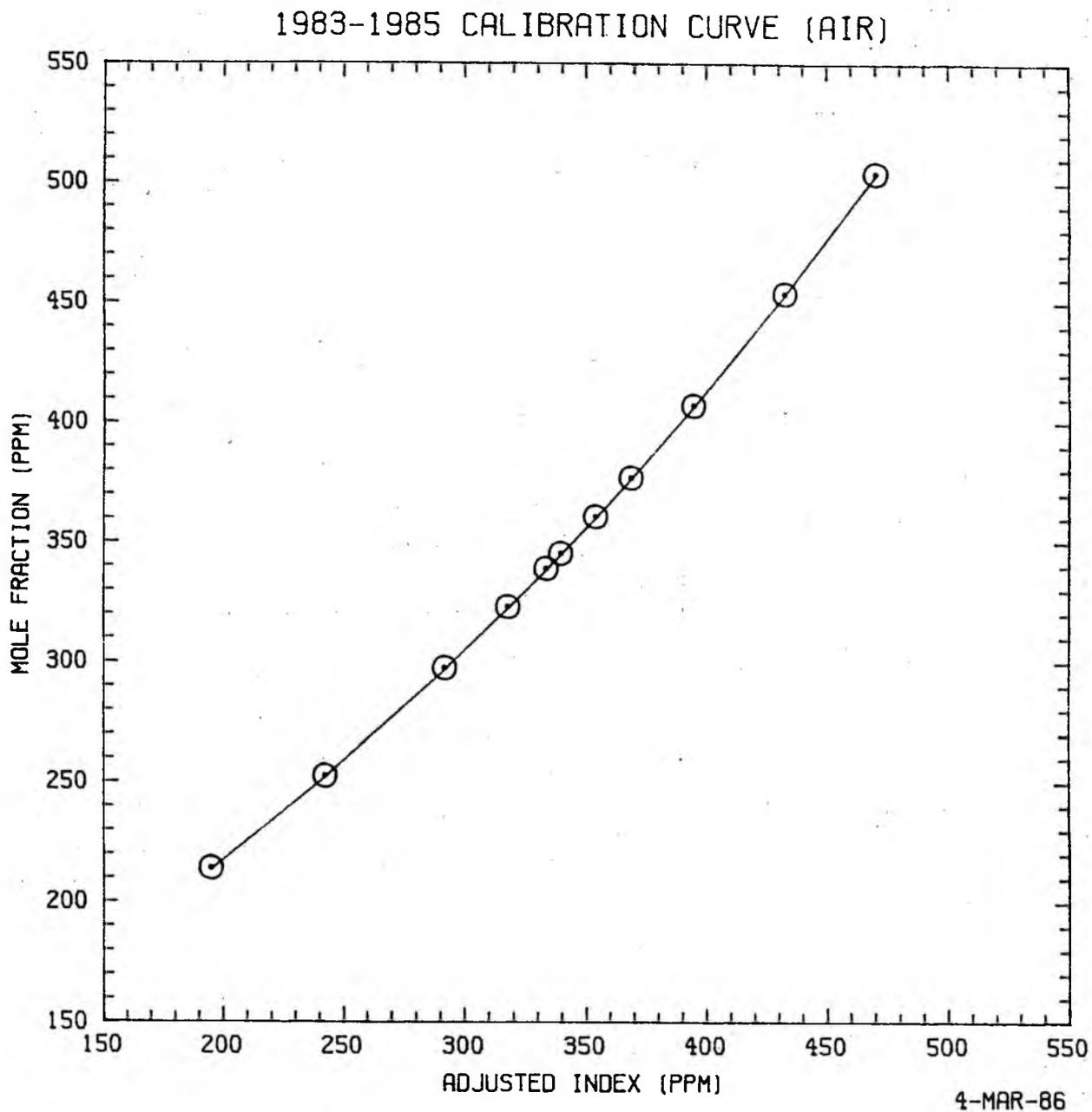


Figure 5. Same as Figure 4 except for CO₂-in-air mixtures.

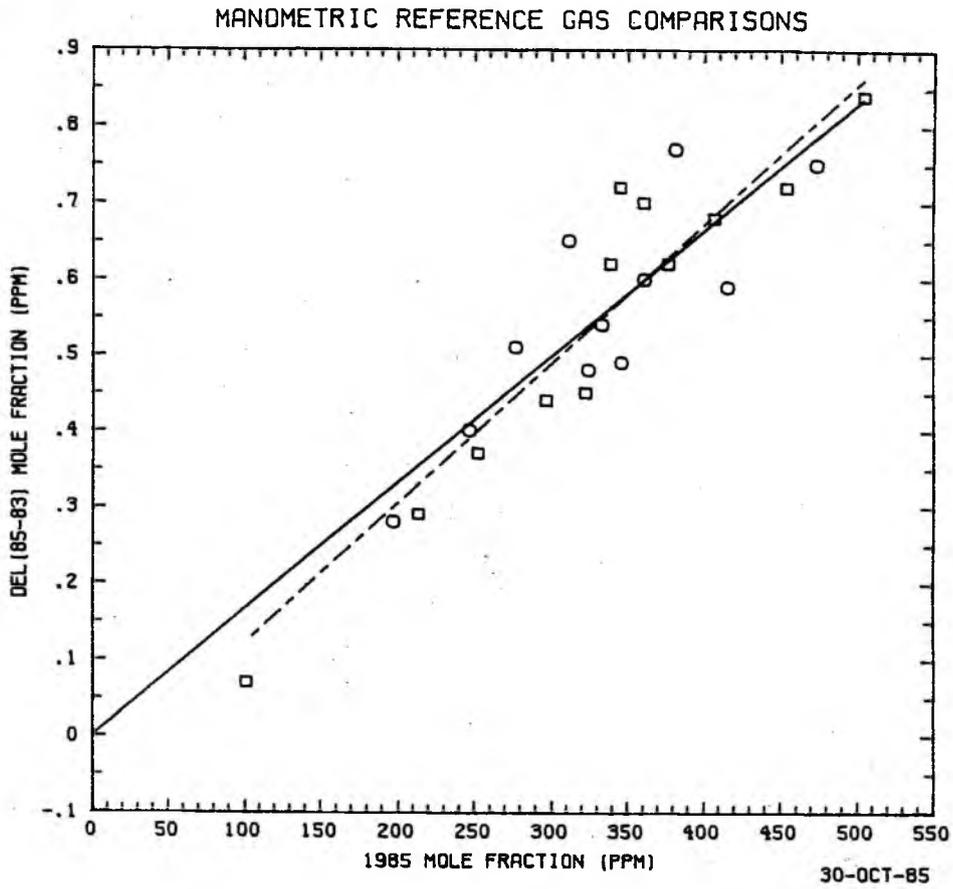


Figure 6. Plot of the difference in mole fraction, in ppm, between the manometric calibrations of primary standard gas mixtures during 1983 and 1985 as a function of mole fraction in 1985. The solid straight line is a least squares fit forced through the origin according to equation (7.3). The dashed curve, shown for comparison, is a least squares fit with the slope determined by the fit. Both CO₂-in-nitrogen (circles) and CO₂-in-air mixtures (squares) are plotted and included in the straight line fits.

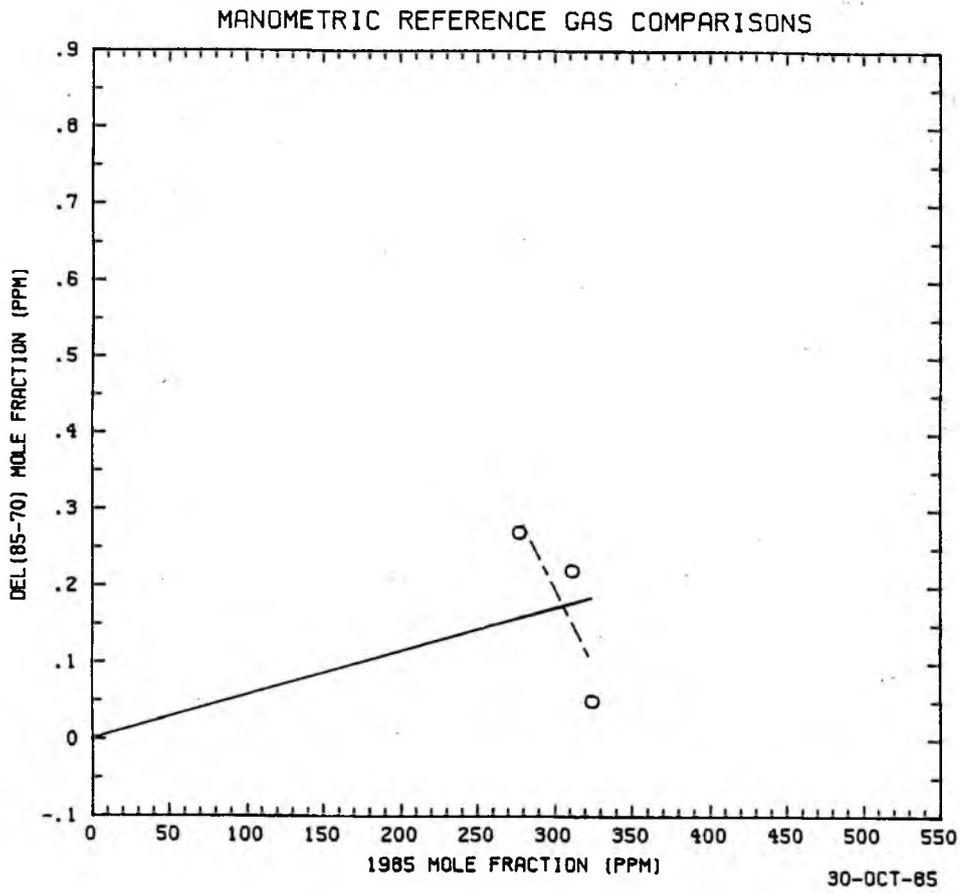


Figure 7. Same as Figure 6 except that 1970 calibrations are compared with 1985 and are based solely on CO₂-in-nitrogen mixtures.

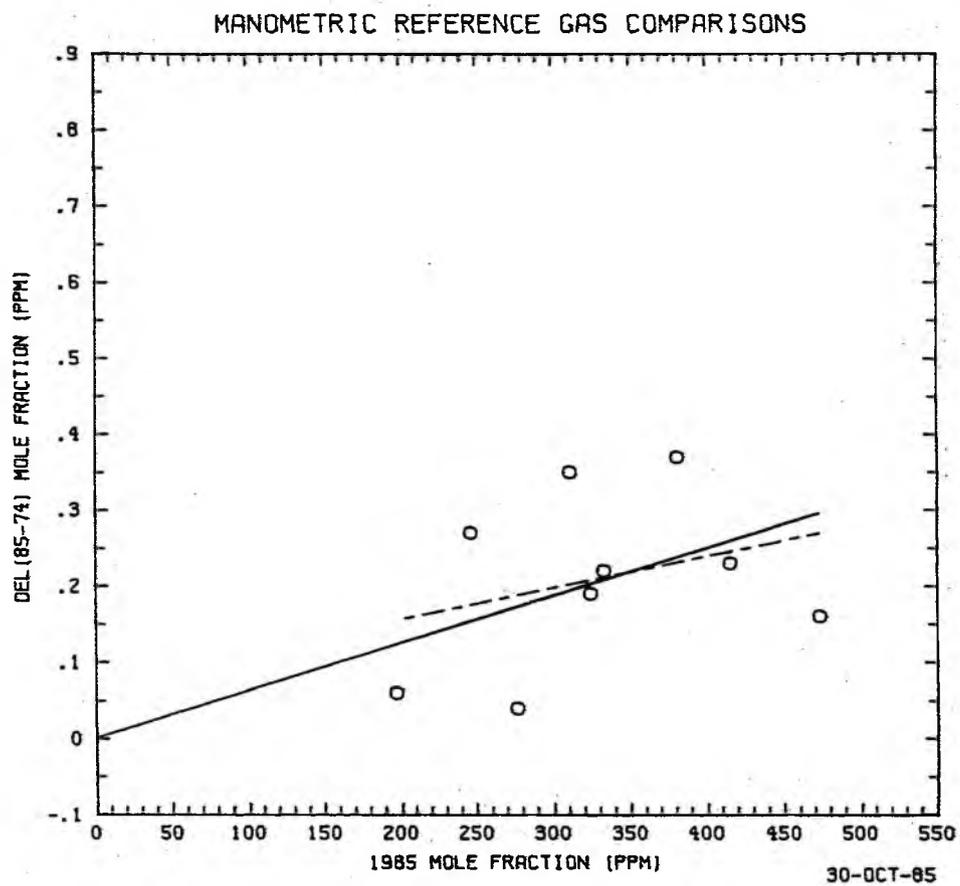


Figure 8. Same as Figure 6 except that 1974 calibrations are compared with 1985 and are based solely on CO₂-in-nitrogen mixtures.

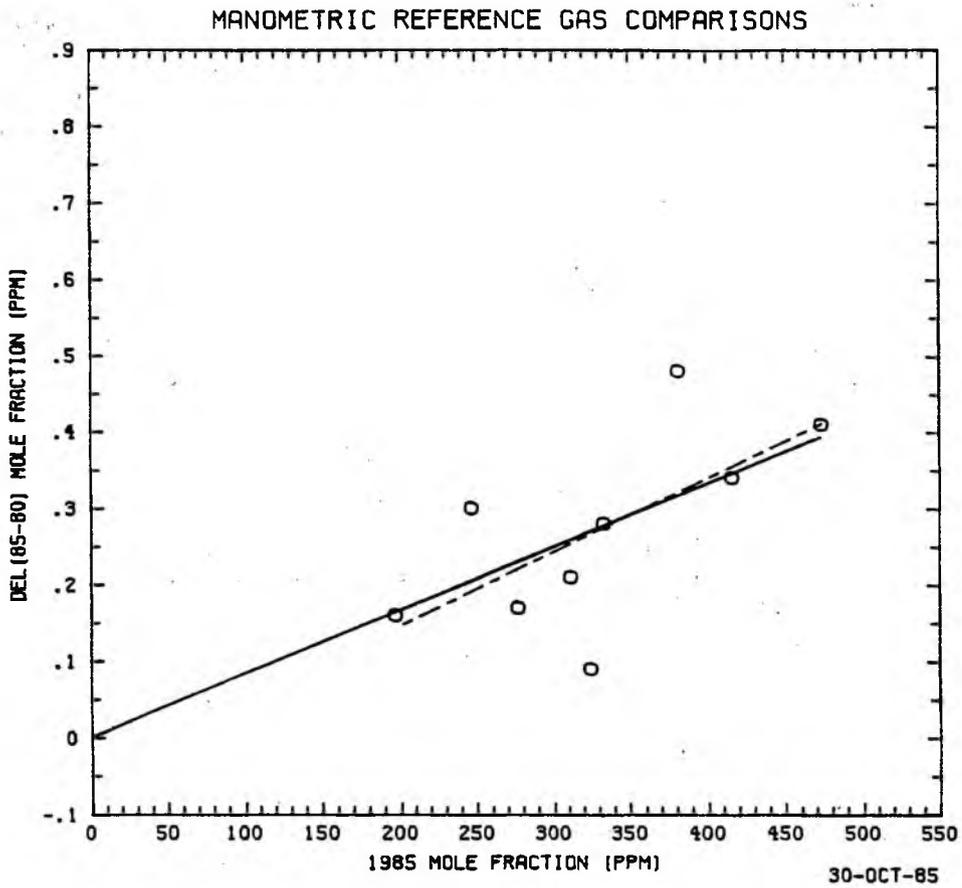


Figure 9. Same as Figure 6 except that 1980 calibrations are compared to 1985 and are based solely on CO₂-in-nitrogen mixtures.

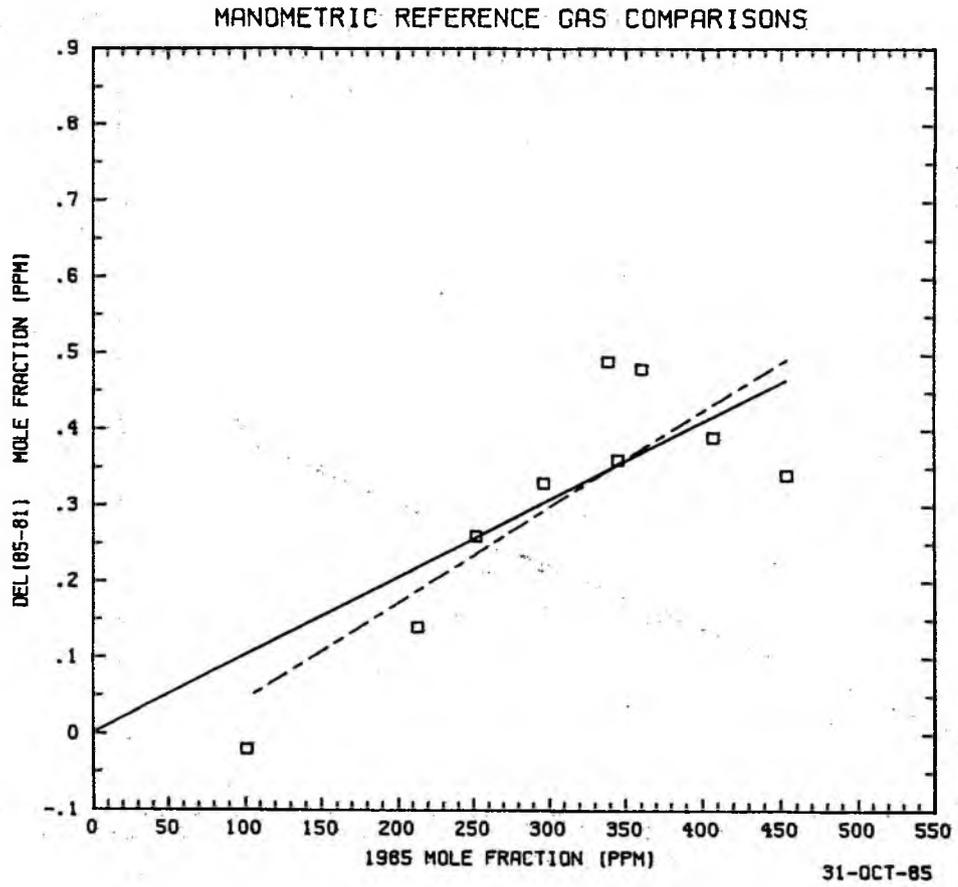


Figure 10. Same as Figure 6 except that 1981 calibrations are compared to 1985 and are based solely on CO₂-in-air mixtures.

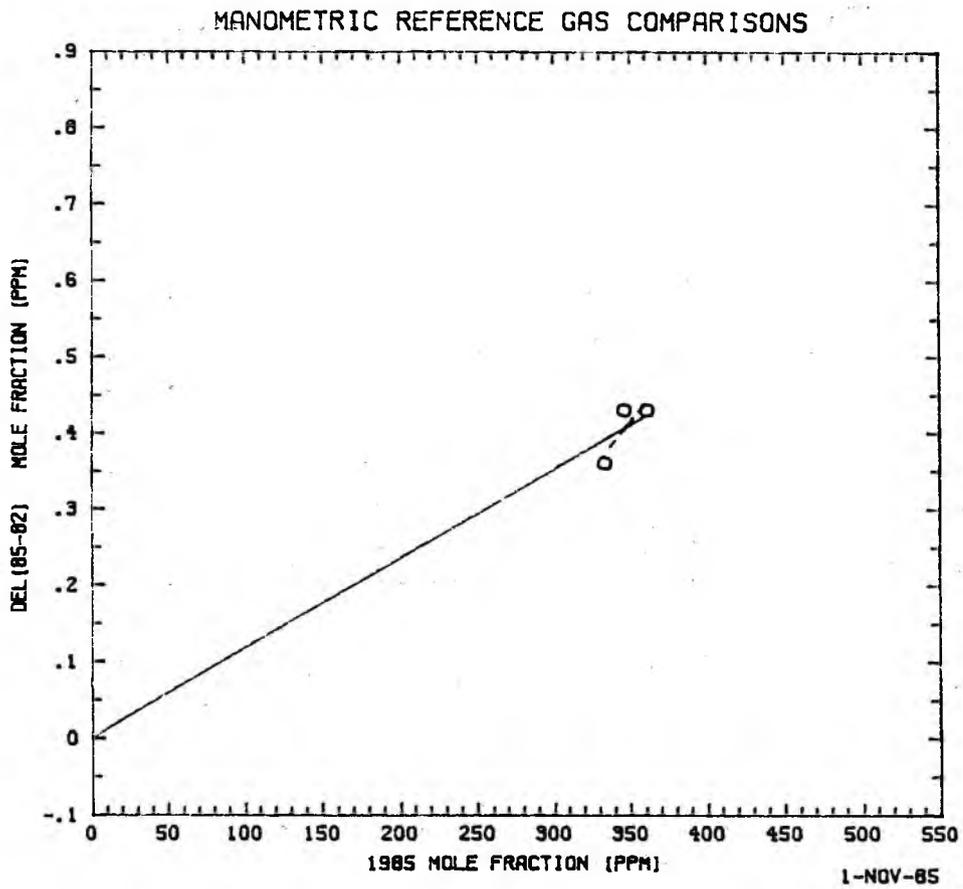


Figure 11. Same as Figure 6 except that 1982 calibrations are compared to 1985 and are based solely on CO₂-in-air mixtures.

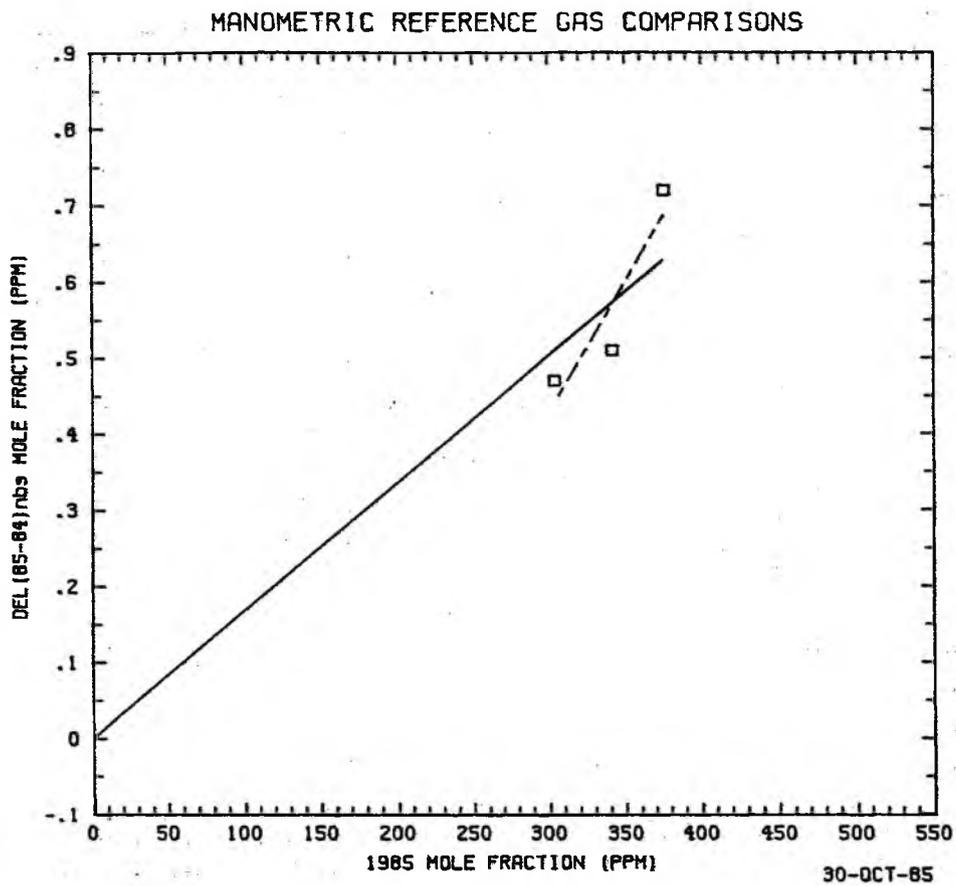


Figure 12. Same as Figure 6 except that 1984 calibrations are compared to 1985 and are based solely on CO₂-in-air mixtures.

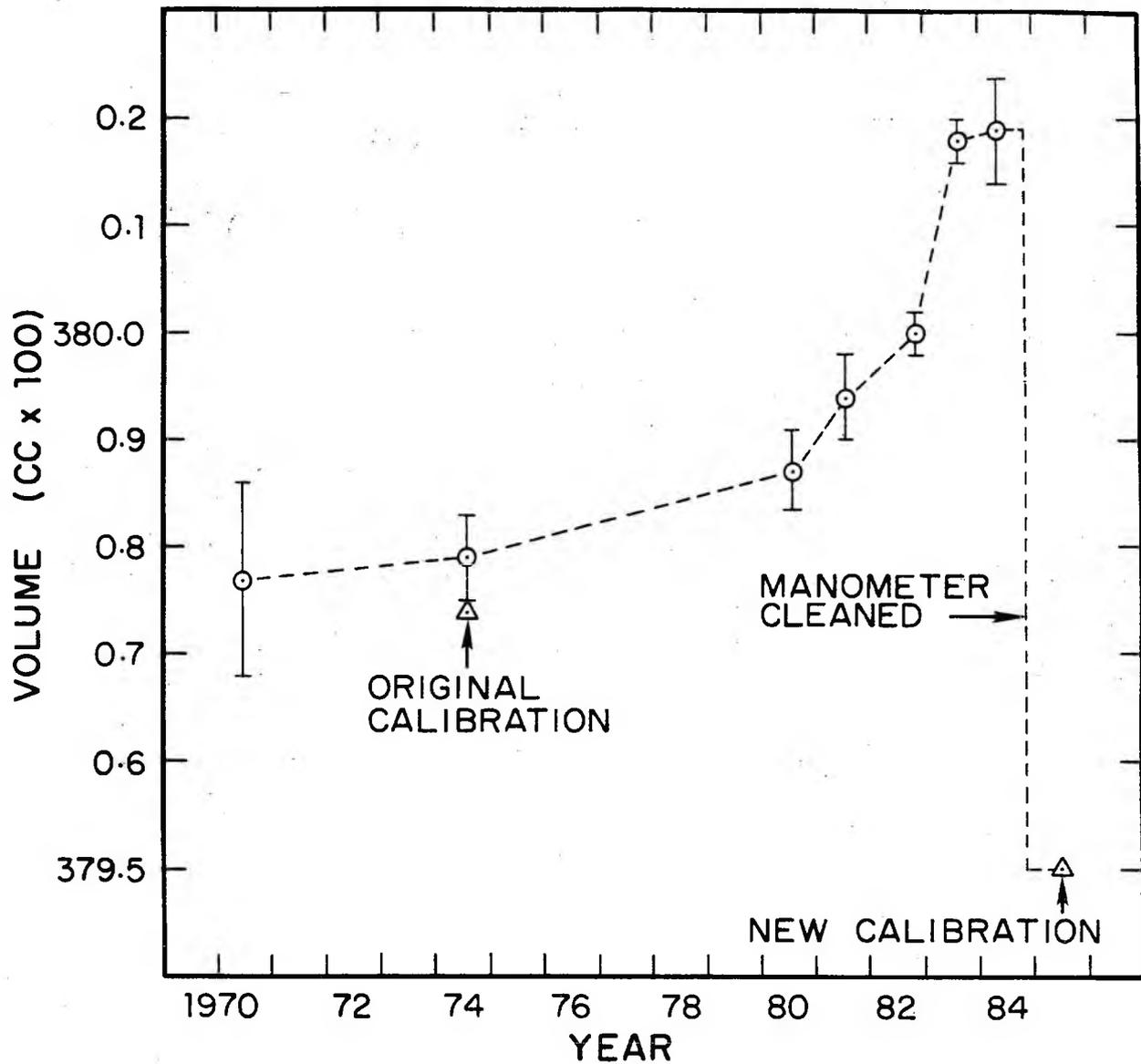


Figure 13. Change in volume of the 4 cc chamber of the small volume manometer, in cc. x 100, as determined indirectly from comparisons of calibrations of primary standard gas mixtures (circles) and by direct measurements using glass plenums (triangles). The indirect determinations assume that the direct measurement in 1985 is correct, and are shown with error bars indicating \pm one standard error, as listed in Table 12. A dashed line connects the indirect determinations to show the progressive change in volume from 1970 to 1985 and the abrupt shift when the manometer was cleaned in early 1985.

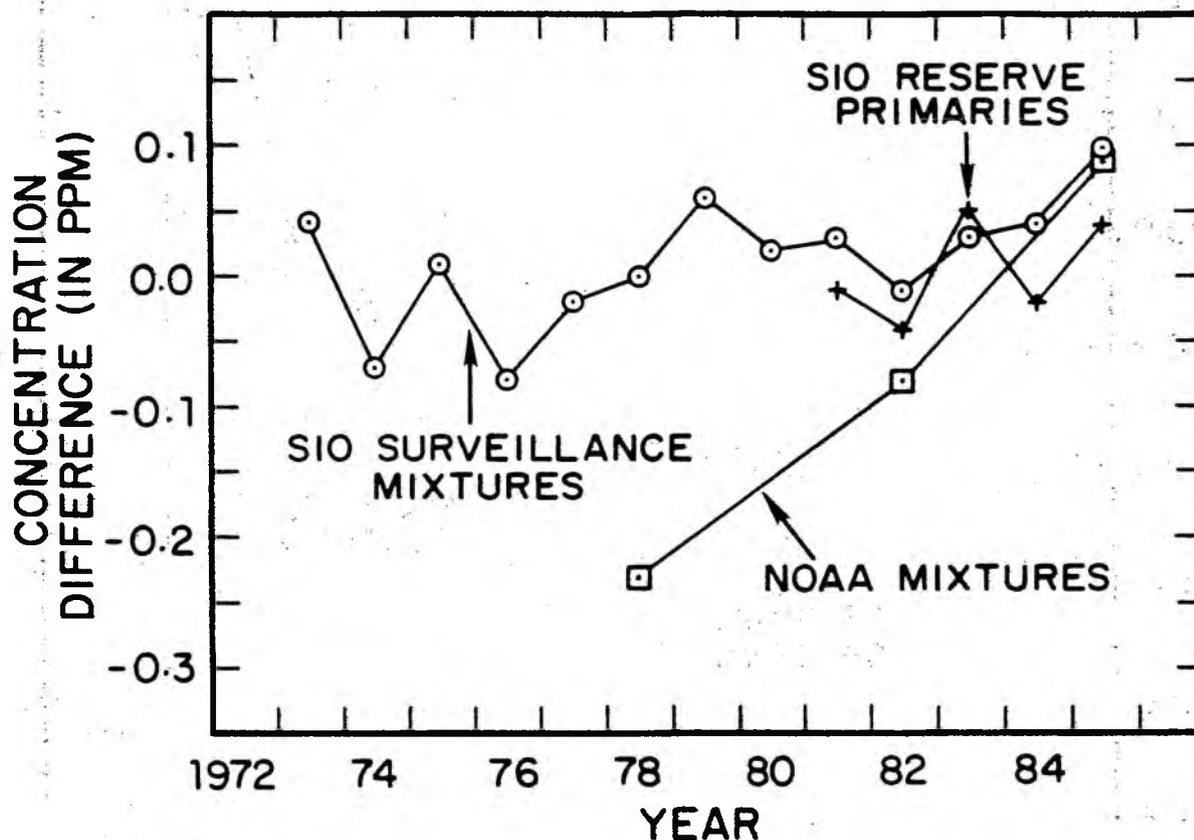


Figure 14. Indication of the stability of CO₂-in-air gas mixtures stored in large chrome-molybdenum steel cylinders. Concentration differences, as defined in the text, are plotted in ppm.

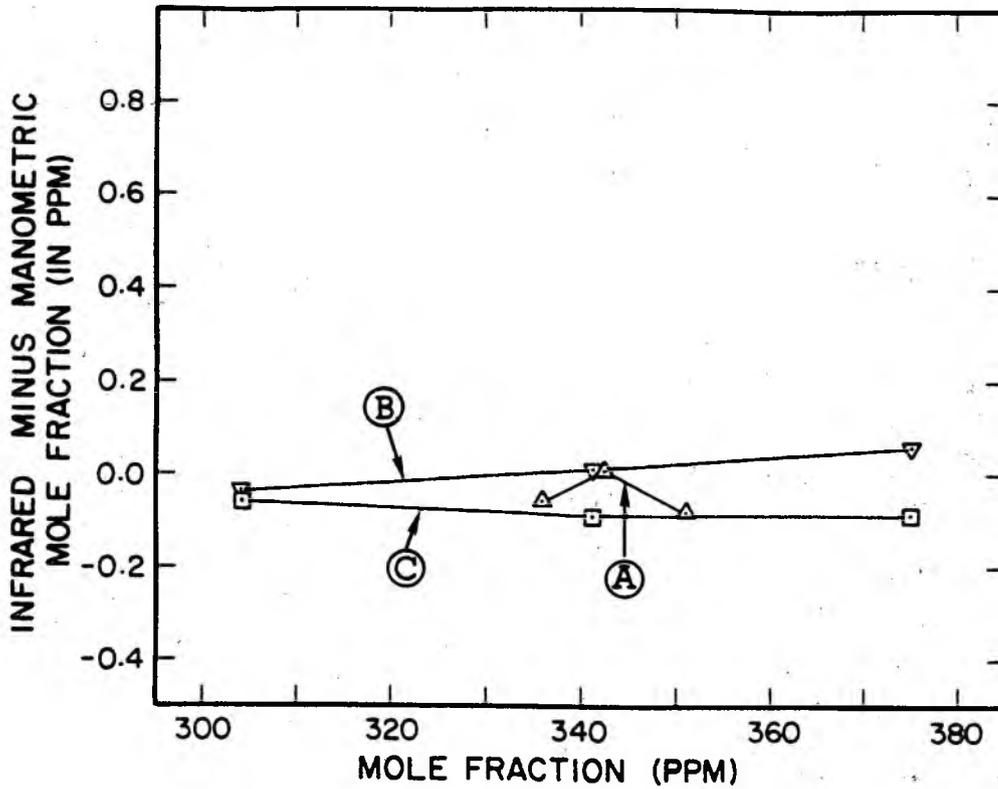


Figure 15. Comparison of infrared and manometric analyses (expressed in ppm) measured at the Scripps laboratory on CO₂-in-air mixtures supplied by the National Bureau of Standards. Differences are plotted with respect to manometric mole fraction. A: mixtures prepared in 1982 in small cylinders, B: mixtures prepared in 1984 in small cylinders, C: mixtures prepared in 1984 in large cylinders.

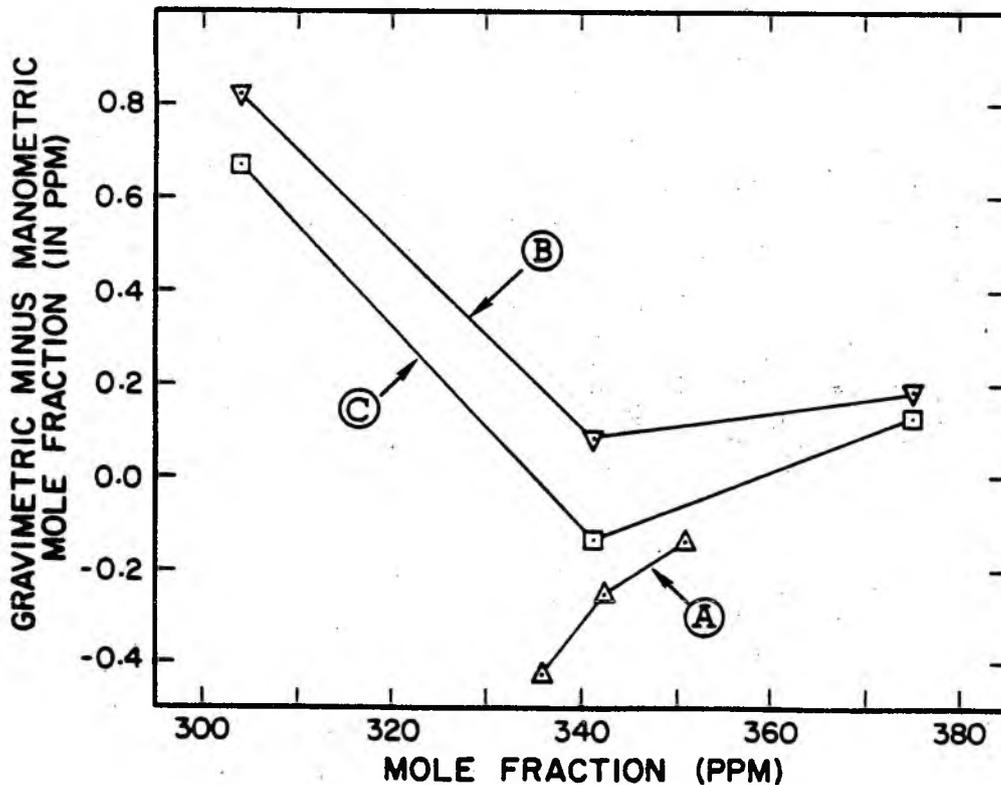


Figure 16. Same as Figure 15 except that gravimetric data from the National Bureau of Standards are substituted for the Scripps infrared data.

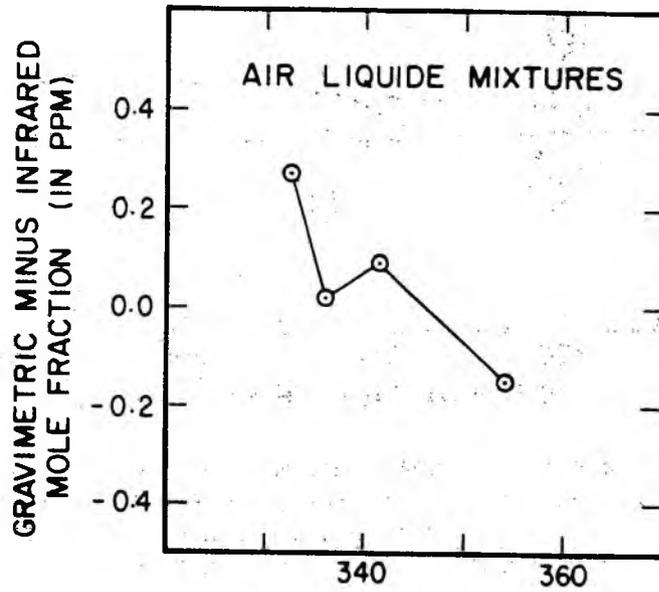


Figure 17. Comparison of gravimetric data from Air Liquide of France with Scripps infrared analyses (in ppm) for CO₂-in-air mixtures prepared by Air Liquide in large cylinders. Differences are plotted with respect to manometric mole fraction.

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