SCRIPPS REFERENCE GAS CALIBRATING SYSTEM FOR CARBON DIOXIDE IN AIR STANDARDS: REVISION OF 1982

A REPORT PREPARED FOR THE ENVIRONMENTAL MONITORING PROGRAM

OF THE WORLD METEOROLOGICAL ORGANIZATION

by

C. D. Keeling, R. B. Bacastow, P. R. Guenther, and D. J. Moss

Central CO_2 Laboratory

of the World Meteorological Organization

Scripps Institution of Oceanography

La Jolla, California 92093

December, 1983

Prepared for

The U.S. Department of Energy

Contract No. AT03-82ER-60032

Report No. DOE/ER/60032-3

Table of Contents

This report describes calibrations carried out in 1982 to maintain the primary reference gas standards developed at the Scripps Institution of Oceanography for the Base Line Monitoring Program of the World Meteorological Organization. This organization adopted these primary standards in 1976 to calibrate infrared gas analyzers used in the measurement of atmospheric carbon dioxide at a worldwide network of stations.

A more extensive set of calibrations has since been carried out to establish a new system of carbon dioxide in air (CO_2-in-air) standards. In 1984 these will replace the carbon dioxide in nitrogen (CO_2-in-N_2) standards in current use. The 1982 calibration is, however, a link in the maintenance of the Scripps primary standard system, and has resulted in an interim 1982 calibration scale on which some data have been reported to the public. Thus it is desirable to describe the 1982 calibration even though most of the adopted equations will be superceded when the 1983 calibration data are worked up.

The terminology and mathematical development follow closely two previous reports [Bacastow et al., 1983a, b] to which the reader is referred for background information.

Manometric Calibrations

As with the 1981 calibrations, only a subset of the ten Scripps CO_2-in-N_2 primary standards were used in 1982. This reduction in number of standards was to allow, during a single day's calibration, the combining of these gas mixtures with a subset of the Scripps CO_2-in-air primary standards also under calibration. In 1981 four CO_2-in-N_2 standards were used. Their concentrations were widely spaced (197, 277, 333, 473 ppm, where "ppm" refers to the mole fraction of CO_2 per million parts of dry air). This spacing was chosen to control drift in the adjusted index values of the Scripps CO_2-in-N_2 system of standards over a wide range, on the assumption that the higher order terms of the characteristic response function of the infrared gas Applied Physics Corporation (APC) analyzer would not have changed significantly since 1980 when ten CO_2-in-N_2 gas mixtures were employed. It turned out, however, that the two middle concentration gas mixtures did not fit a calibration curve as well as expected during the 1981 calibration [see Bacastow et al., 1983b, Figure 1]. As a result, in 1981 the relationship between CO_2-in-N_2 response and CO_2-in-air response was not determined in the range of atmospheric CO_2 concentration to the highest precision possible with the APC analyzer.

Although, for the sake of uniformity, it would have been desirable to use the same four CO_2-in-N_2 gases in 1982, it seemed preferable not to repeat the wide spacing of the 1981 calibration. Instead a narrower spacing was chosen in order to optimize the calibration in the vicinity of natural CO_2-in-air concentrations. This narrowing was further justified, because the set of CO_2-in-air standard gases used in 1982 were also in a narrower range.

One of the primary standards used in 1980 (Cylinder No. 10069) could not be used in 1982 owing to low gas pressure. To add to the number of gas mixtures near natural CO_2 concentration levels, not only was this gas mixture replaced, but a new mixture was also put into the calibration. As a control on the performance of the constant volume manometer, one gas mixture, measured in 1980, was remeasured, making a total of three CO_2-in-N_2 gas mixtures determined manometrically in 1982.

The results are listed in Table 1a. The redetermined mixture was in cylinder No. 39239. The result of two new determinations (332.64 ppm) is in good agreement with the average of two previous determinations in 1980 (332.72 ppm) as shown in Table 1d of Bacastow et al. [1983a].

The new Scripps CO_2-in-air primary standards, still under development, are contained in twelve high pressure cylinders, designated "white stripe" cylinders. It was deemed desirable to hold these gas mixtures for two years (from 1981 until 1983) to test them for stability. To avoid depleting them in the meantime, they were not employed during the 1982 calibration. Instead four second level CO_2-in-air standards, called "blue stripe" cylinders, were manometrically calibrated for the first time in 1982 together with five cylinders supplied by the National Oceanographic and Atmospheric Administration (NOAA). The latter cylinders were returned to NOAA to serve as standards in their atmospheric CO_2 base line station program. The manometric data for the blue stripe gas mixtures are listed in Table 1b, those for the NOAA cylinders in Table 1c. Also listed there are manometric determinations of six gas mixtures supplied in small cylinders by the National Bureau of Standards. These mixtures, whose concentrations were established gravimetrically by NBS, will be discussed separately at the end of this report.

Manometric concentrations corrected for nitrous oxide (N_2O) are listed in Table 2. The N_2O data for the blue stripe mixtures are from measurements made in the laboratory of Dr. Ray Weiss using a gas chromatograph with an electron capture detector.

It can be seen that the replicate manometric determinations agree satisfactorily. We define the standard deviation of an individual determination, σ, by:

$$\sigma = \sqrt{\Sigma d_i^2/(N_a - N_S)}$$

where:

d_i denotes the deviation of an individual analysis from the mean for that gas mixture

N_a denotes the number of analyses

N_g denotes the number of gas mixtures analyzed

In this series of measurements (12 sets) σ was found to be 0.048 ppm.

Infrared Analyzer Calibrations

The four blue stripe and the five NOAA CO_2-in-air mixtures were compared with the APC analyzer against six CO_2-in-N_2 primary standards on six special calibrating days during November, 1982. The six CO_2-in-N_2 standards consisted of three gas mixtures taken from the set of ten primary standards used in the 1980 calibration plus the three mixtures listed in Table 1c. The three CO_2-in-N_2 standards not listed in Table 1a (cylinders No. 7366, 35299, 35316) did not receive new manometric determinations in 1982. Instead, the 1980 manometric data were relied upon. Three of the six mixtures (Nos. 7366, 39239, and 35316) were the same as the three highest concentration mixtures used in 1981.

Two calibrating sequences were used alternately in 1982. On the first, third, and fifth calibrating days, the highest concentration CO_2-in-N_2 mixture was deleted, and the five remaining CO_2-in-N_2 mixtures were compared with the five NOAA CO_2-in-air gases. On the second, fourth, and sixth days, all six CO_2-in-N_2 mixtures were compared against four blue stripe Scripps CO_2-in-air gases. As in all previous special calibrations, the gases were run in a sequence involving the principal and high span standards and the secondary gas standard of the Scripps CO_2-in-N_2 system. These are the same three gas mixtures used as standards during routine calibrating. The infrared data are listed in Table 3a and 3b as Scripps index, or "I", values. Averages are also listed in adjusted index or "J" units [for definition see Bacastow et al., 1983a, Equation (1)]. The data are taken from Scripps Reference Gas Report No. 41. The standard deviations of the infrared measurements, as a function of concentration are similar to those obtained in 1974 and 1980 [see Figure 3 of Bacastow et al., 1983a].

<u>Drift of the Scripps CO_2-in-N_2 System between the 1980 and 1982 Calibrations</u>

Because a different set of CO_2-in-N_2 standards were used in 1982 than in 1981, it is preferable to express changes in adjusted index, J, relative to the detailed calibration of 1980 rather than the 1981 calibration. Two of these mixtures, however, were not part of the special calibration of 1980, although they had been analyzed repeatedly at other times. (They were, in 1980 and earlier, designated as Scripps quarterly cylinders. See Bacastow et al. [1983a] for definition of these gas mixtures.) In the 1983 calibration we will make use of these quarterly data to estimate adjusted index values for 1980, but for the 1982 calibration, an indirect approach was adopted. Since the 1983 calibration scale will make obsolete the 1982 scale developed here, it is not worthwhile to revise the 1982 scale in this report. We, therefore, describe this indirect approach and its subsequent use to establish the 1982 scale.

The relation between the adjusted index, J, and the manometric mole fraction, X, was established in 1980 by a least squares fit of the J and X data resulting in the cubic equation [see Bacastow et al., 1983a, Equation (3)]:

$$X82 = CUB2\ (J80). \tag{1}$$

The manometric concentration data (X values) for the three mixtures redetermined in 1982 (see Table 1a) were averaged into the earlier set of manometric data (used to determine CUB2), and new average X values used to derive J values for 1980 for all six mixtures using the calibration curve versus X as a basis.

Specifically, these derived values, designated J80X′, are obtained from the relation:

$$J80X' = CUB2^{-1}\ (X82) \tag{2}$$

where X82 denotes the updated average X values (three of which are indeed identical to X80 values) and $CUB2^{-1}$ is the inverse of the function CUB2. The relevant data are listed in Table 4 including the J values obtained in 1980 (shown only for comparison to J80X′) and in 1982. The latter are designated "J82" and are copied from the second column of the summary listings of Table 3a. The corresponding "J80" data are listed as they will appear in 1983 calibration report. They differ slightly for those reported by Bacastow et al. [1983a].

The system drift, J82-J80X′, of each gas mixture, is also listed in Table 4. A quadratic least squares fit, shown in Figure 1, was determined between the drift data and J80X′:

$$\begin{aligned} J82-J80X' &= QUAD11(J80X') \qquad (3) \\ &= -0.9098 + 0.085096(J80X') - 1.9177\times 10^{-3}(J80X')^2 \end{aligned}$$

This equation is the basis for determining the system drift for dates between the 1980 and 1982 calibrations.

Specifically, to find by interpolation the drift correction between central dates CD81 AND CD82 (9 September, 1981 and 18 November, 1982):

$$J - J80X' = (J81 - J80X') + R(J82 - J81) \qquad (4)$$

where J denotes the observed value for any date, D, J81 denotes J for CD81,

$$J81 - J80X' = QUAD10\ (J80X') \qquad (5)$$

and

$$R = (D - CD81)/(CD82 - CD81) \qquad (6)$$

Since:

$$J82 - J81 = QUAD11\ (J80X') - QUAD10\ (J80X') \qquad (7)$$

it follows that:

$$J - J80X' = (1-R)\ QUAD10\ (J80X') + (R)\ QUAD11\ (J80X') \qquad (8)$$

The above equation is solved for J80X′ by iteration.

1982 Air Correction

The data for CO_2-in-air gas mixtures are used here merely to check on the validity of the 1981 CO_2-in-air calibration function in current use. This function, CUB9, [See Bacastow et al., 1983b, Equation 1] corrects J values obtained when CO_2-in-N_2 reference gases are compared with air samples or gas mixtures of CO_2-in-air in cylinders. This approach is an interim procedure until the 1983 calibration is worked up. At that time a more rigorous expression based in the intercomparison of 10 CO_2-in-N_2 standards with 12 CO_2-in-air standards will be adopted as the principal function.

Basically the air correction, expressed on the J scale, is obtained by comparing the observed J value of a CO_2-in-air gas mixture with that calculated from the observed manometric mole fraction using the relation of J to X for CO_2-in-N_2 gas mixtures. Owing to system drift, the procedure is made more complicated, but the principal is unaltered.

The relevant observations and calculated J and X values are listed in Table 5 for the CO_2-in-air gas mixtures measured in 1982. The N_2O corrections to the manometric concentrations, listed in Table 2, were not available when these calculations were performed. As an interim procedure, a constant correction of 0.31 ppm was used. The resulting errors using 0.31 ppm are negligible except in the case of the lowest concentration gas (0.24 ppm).

First, from the N_2O corrected manometric concentration, X82, adjusted index values for CO_2-in-air are derived on the basis of the

1981 calibration. These values are called "J81X" where:

$$J81X = CUB9^{-1}\ (X82) \tag{9}$$

Secondly, J values for CO_2-in-N_2 are calculated on the basis of the 1980 calibration. These values are called "J80X′" where (identically with equation (2)):

$$J80X' = CUB2^{-1}\ (X82) \tag{10}$$

The prime indicates that the gas mixture is here treated as though it contained only nitrogen as the carrier gas even though it actually contained air. Thirdly, the J80X′ values are corrected for system drift so as to apply to 1981 via the 1980-1981 CO_2-in-N_2 data. These are called "J81X′" values where:

$$J81X' = J80X' + QUAD10\ (J80'X) \tag{11}$$

The air correction is equal to J81X′ - J81X. The correction is alternatively expressed by a factor:

$$FACTOR = (J81X' - J81X)/J81X \tag{12}$$

The differences, ΔJ = J81X′ - J81X, are shown in Table 5 and the correction factors, defined by equation (12), are plotted and compared in Figure 2 with those obtained previously. The smooth curve was obtained as a locus of points of the quantity, "FACTOR" of equation (12) versus a horizontal axis scaled in adjusted index. The procedure was to compute J81X and J81X′ for selected values of X82 via equations (9), (10), and (11). Then "FACTOR" was computed and plotted versus J81X′.

Comparison with NBS Standards

During April of 1982 Dr. Earnest Hughes of the U.S. National Bureau of Standards visited the Scripps CO_2 laboratory. He brought with him six aliqotes of CO_2-in-air mixtures derived, pairwise, from three batches of standard gases undergong preparation as standard materials by the bureau. As in the case of three gas mixtures which he had brought to Scripps in 1980 [see Bacastow et al. 1983a] each batch had been analyzed at NBS against primary gravimetric standards synthesized by Dr. Hughes. Each of the six aliquotes was analyzed once by Peter Guenther at Scripps in the same manner as the other gas mixtures reported in Tables 1a-1c. The results are listed in Table 1c. The contents of N_2O, analyzed at the N.B.S., are listed in Table 2, together with corrected CO_2 mole fractions. The agreement between the Scripps and NBS results, as indicated by the comparisons listed in Table 6, is even closer than in 1980. On average the mixtures agree to 0.01 ppm. The standard deviation in the mean of the differences is 0.02 ppm. In comparison, the NBS mixtures analyzed in 1980 were 0.09 ± 0.05 ppm higher than the Scripps results. It may be concluded that the Scripps and NBS methods for determinating the concentration of CO_2 in primary tandards agree within the detectability of CO_2 by any existing means of instrumental analysis.

Computer Program

At the end of this report we list a FORTRAN subroutine which executes the calculations described above. The main parameters of the program and their equivalent symbols, as given in this report, are also listed.

Acknowledgements

We thank Dr. Ray Weiss and Mr. Rick vanWoy for making the N_2O measurements reported in Table 2.

References

Bacastow, R. B., C. D. Keeling, P. R. Guenther, and D. J. Moss, "Scripps Reference Gas Calibrating System for Carbon Dioxide in Nitrogen Standards: Revision of 1980", A report prepared for the Environmental Monitoring Program of the World Meteorological Organization, Scripps Institution of Oceanography, 1983a.

Bacastow, R. B., C. D. Keeling, P. R. Guenther, and D. J. Moss, "Scripps Reference Gas Calibrating System for Carbon Dioxide in Air Standards: Revision of 1981", A report prepared for the Environmental Monitoring Program of the World Meteorological Organization, Scripps Institution of Oceanography, 1983b.

Table 1a. Manometric analyses of CO_2-in-N_2 standards during 1982.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
39239	1	3 NOV 82	332.46	332.46		
			332.47			
	2	10 NOV 82	332.62	332.61	332.64	2*
			332.60			
	3	12 NOV 82	332.70	332.66		
			332.62			
39256	1	5 NOV 82	345.47	345.50	345.57	3
			345.52			
	2	10 NOV 82	345.68	345.66		
			345.64			
	3	15 NOV 82	345.57	345.56		
			345.56			
39272	1	8 NOV 82	360.46	360.46	360.49	3
			360.46			
	2	10 NOV 82	360.50	360.48		
			360.46			
	3	11 NOV 82	360.57	360.54		
			360.52			

*Run No. 1 deleted (detectable uptake in gas delivery line)

Table 1b. Manometric analyses of CO_2-in-air secondary standards (blue striped cylinders) during 1982.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
Blue stripe Cylinders						
34891	1	19 NOV 82	298.14	298.16	298.16	2
			298.19			
	2	20 NOV 82	298.15	298.16		
			298.16			
62807	1	21 NOV 82	338.65	338.64	338.65	2
			338.62			
	2	22 NOV 82	338.65	338.66		
			338.67			
62817	1	22 NOV 82	365.61	365.61	365.63	2
	2	23 NOV 82	365.67	365.65		
			365.63			
62814	1	23 NOV 82	425.20	425.22	425.23	2
			425.24			
	2	23 NOV 82	425.23	425.24		
			425.25			

Table 1c. Manometric analyses of CO_2-in-air secondary standards obtained from NOAA and NBS.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
NBS Cylinders						
18207	1	19 APR 82	335.68 335.66	335.67	335.67	1
18040	1	20 APR 82	335.52	335.52	335.52	1
18067	1	20 APR 82	342.47 342.40	342.44	342.44	1
16410	1	21 APR 82	351.06 351.06	351.06	351.06	1
18042	1	23 APR 82	342.77 342.67	342.72	342.72	1
16417	1	23 APR 82	351.16 351.18	351.17	351.17	1
NOAA Cylinders						
3082	1	12 NOV 82	316.71 316.64	316.68	316.62	2
	2	15 NOV 82	316.57 316.55	316.56		
3074	1	15 NOV 82	329.41 329.35	329.38	329.38	2
	2	16 NOV 82	329.38 329.36	329.37		
3071	1	16 NOV 82	352.70 352.65	352.68	352.70	2
	2	17 NOV 82	352.74 352.71	352.72		
3091	1	17 NOV 82	341.93 341.92	341.92	341.92	2
	2	18 NOV 82	341.93 341.91	341.92		
3092	1	18 NOV 82	366.99 366.98	366.98	366.93	2
	2	19 NOV 82	366.89 366.88	366.88		

Table 2. N_2O corrected concentration of CO_2-in-air standards manometrically analyzed during 1982

Cylinder No.	Manometric Average * (ppm)	N_2O Concentration (ppm)	Corrected Concentration (ppm)
Blue Stripe Cylinders [1]			
34891	298.16	.24	297.92
62807	338.65	.29	338.36
62817	365.63	.28	365.35
62814	425.23	.31	424.92
NOAA Cylinders [2]			
3082	316.62	.30 [3]	316.32
3074	329.38	.30	329.08
3091	341.92	.30	341.62
3071	352.70	.30	352.40
3092	366.93	.30 [3]	366.63
NBS Cylinders [4]			
18207	335.67	.06	335.61
18040	335.52	.06	335.46
18067	342.44	.08	342.36
18042	342.72	.08	342.64
16410	351.06	.03	351.03
16417	351.17	.03	351.14

[1] [N_2O] determined by SIO as in 1981 and before
[2] [N_2O] determined by NOAA
[3] [N_2O] assumed
[4] [N_2O] determined by NBS
* See Tables 1b and 1c

TABLE 3a. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1982 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 CYLINDERS

CYL.NO.	09 NOV	16 NOV	23 NOV	AVG. I	AVG. J
7366	280.62 (10)	280.62 (10)	280.55 (10)	280.60	273.84
39239	328.26 (12)	328.27 (11)	328.24 (10)	328.26	331.92
39256	338.55 (10)	338.53 (10)	338.52 (10)	338.53	344.44
39272	350.00 (10)	350.03 (10)	349.99 (10)	350.01	358.43
35299	389.50 (10)	389.56 (10)	389.47 (10)	389.51	406.56
AVERAGE:	337.39	337.40	337.35		

CYL.NO.	11 NOV	17 NOV	01 DEC	AVG. I	AVG. J
7366	280.60 (10)	280.65 (10)	280.54 (10)	280.60	273.84
39239	328.23 (10)	328.31 (10)	328.19 (10)	328.24	331.90
39256	338.51 (10)	338.53 (10)	338.52 (14)	338.52	344.42
39272	350.00 (10)	350.05 (14)	350.03 (12)	350.03	358.45
35299	389.46 (10)	389.58 (10)	389.48 (10)	389.51	406.56
35316	427.51 (10)	427.77 (10)	427.61 (10)	427.63	453.01
AVERAGE:	352.39	352.48	352.40		

Summary of Adjusted Index averages (J) for the 1982 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
7366	273.84	0.05	6
39239	331.91	0.05	6
39256	344.43	0.01	6
39272	358.44	0.02	6
35299	406.56	0.06	6
35316	453.01	0.16	3

TABLE 3b. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1982 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 CYLINDERS (NOAA)

CYL.NO.	09 NOV	16 NOV	23 NOV	AVG. I	AVG. J
3082	311.95 (10)	311.94 (10)	311.90 (12)	311.93	312.02
3074	322.27 (12)	322.29 (10)	322.24 (10)	322.27	324.62
3091	332.21 (10)	332.22 (10)	332.19 (10)	332.21	336.74
3071	340.52 (10)	340.56 (10)	340.53 (10)	340.54	346.89
3092	351.31 (10)	351.32 (12)	351.30 (10)	351.31	360.01
AVERAGE:	331.65	331.67	331.63		

CO2-IN-AIR CYLINDERS (BLUE STRIPES)

CYL.NO.	11 NOV	17 NOV	01 DEC	AVG. I	AVG. J
34891	296.58 (10)	296.54 (10)	296.51 (12)	296.54	293.27
62807	329.60 (10)	329.62 (14)	329.58 (10)	329.60	333.55
62817	350.34 (10)	350.39 (12)	350.27 (10)	350.33	358.82
62814	392.47 (10)	392.64 (10)	392.46 (10)	392.52	410.23
AVERAGE:	342.25	342.30	342.21		

Summary of Adjusted Index averages (J) for the 1982 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
34891	293.27	0.05	3
3082	312.02	0.04	3
3074	324.62	0.04	3
62807	333.55	0.02	3
3091	336.74	0.02	3
3071	346.89	0.02	3
62817	358.82	0.07	3
3092	360.01	0.01	3
62814	410.23	0.12	3

Table 4. Data summary of 1982 corrections for CO_2-in-N_2 Reference Gas System drift between the central dates, CD80 and CD82. Adjusted index values in the column headed J80Y' are from a calculation based on manometric data as explained in the text. The values in the column headed J80 are observed values as listed in Table 3. Numbers in parentheses indicate number of manometric determinations averaged.

Cylinder No.	J82 (ppm)	X80 (ppm)	New Manometric Data	X82 (ppm)	J80 (ppm)	J80X'	J82 - J80X'
7366	273.84	276.66(7)		276.66(7)	273.84	273.85	-0.01
39239	331.91	332.75(4)	332.64(2)	332.71(6)	332.23	332.17	-0.26
39256	344.44*		345.57(3)	345.57(3)		344.65	-0.21
39272	358.44		360.49(3)	360.49(3)		338.75	-0.31
35299	406.56	415.00(4)		415.00(4)	407.19	407.19	-0.63
35316	453.02*	472.80(6)		472.80(6)	453.98	454.02	-1.00

*Small error detected in final proofing of report (Correct value .01 ppm lower, see Table 3a).

Table 5. Summary of data to compute the air correction for the Applied Physics Corporation analyzer during the special calibration of 1982. The derivation of the calculated quantities, J81X, J80X', and J82X' are explained in the text. ΔJ denotes the difference J81X' - J81.

Cylinder No.	Manometric conc. (ppm)	Assumed N_2O conc. (ppm)	X82 (ppm)	J82 (ppm)	J81X (ppm)	J80X' (ppm)	J81X' (ppm)	ΔJ (ppm)	$\frac{\Delta J}{J81X}$	ΔJ for J = 330 (ppm)
CO_2-in-air in Blue Strip Cylinders										
34891	298.16	0.31	297.85	293.27	293.30	296.71	296.68	3.38	0.01152	3.80
62807	338.65	"	338.34	333.55	333.68	337.67	337.55	3.90	0.01169	3.86
62817	365.63	"	365.32	358.82	358.86	363.23	363.02	4.07	0.01134	3.74
62814	425.23	"	424.92	410.23	410.39	415.53	415.02	4.62	0.01126	3.72
CO_2-in-air in NOAA Cylinders										
3082	316.62	"	316.31	312.02	312.12	315.80	315.74	3.65	0.01169	3.86
3074	329.38	"	329.07	324.62	324.72	328.58	328.49	3.78	0.01164	3.84
3091	341.92	"	341.61	336.74	336.80	340.84	340.71	3.87	0.01149	3.79
3071	352.70	"	352.39	346.89	346.95	351.14	350.97	3.96	0.01141	3.77
3092	366.93	"	366.62	360.01	360.05	364.43	364.21	4.07	0.01130	3.73
	Av.									3.79
										$\sigma = 0.05_4$

Table 6. Comparison of Manometric Analyses with N.B.S. Gravimetric Data

Cylinder No.	SIO Manometric Conc. (ppm)	NBS Gravimetric Conc. (ppm)	Difference (ppm)
18207	335.61	335.61	0.00
18040	335.46	335.49	-0.03
18067	342.36	342.31	+0.05
16410	342.64	342.65	-0.01
18042	351.03	351.08	-0.05
16417	351.14	351.11	+0.03
Average Difference (SIO-NBS)			-0.00 ± .02

```
C
C  SUBROUTINES TO COMPUTE MOLE FRACTION FOR CO2-IN-N2 AND
C  CO2-IN-AIR BASED ON THE 1982 CALIBRATION.
      SUBROUTINE X82CON(IDATE,GAS,Y59,DAYN,X)
C.....TABLE OF VARIABLES, ARRAYS, AND FUNCTIONS:
C
C     NAME (DATA TYPE)        DESCRIPTION IN 1982 CALIBRATION REPORT
C
C     ACUB81 (REAL          "ACUB9".
C            FUNCTION)
C     AJ80   (REAL)         "JA"="J" AFTER FIRST LEVEL DRIFT CORRECTION.
C     BJ80   (REAL)         "JB"="J" AFTER SECOND LEVEL DRIFT CORRECTION.
C     CDyy   (REAL)         CENTRAL DATE FOR CALIBRATION OR CORRECTION
C                           OF YEAR 19yy EXPRESSED AS NUMBER OF DAYS SINCE
C                           1/1/55.
C     CDSB   (REAL)         END DATE FOR SOURCE BLOCK CORRECTION, EXPRESSED AS
C                           THE NUMBER OF DAYS SINCE 1/1/55.
C     CJ80   (REAL)         USED IN TWO WAYS: FOR DATA UP TO AND INCLUDING CD80
C                           DENOTES "JC", i.e. "J" AFTER THIRD LEVEL CORRECTION;
C                           FOR DATA AFTER CD80 DENOTES "J80X'"="J" AFTER A
C                           SINGLE LEVEL DRIFT ACCORDING TO EQUATION (8) OF TEXT.
C     CJ80T  (REAL)         TRIAL VALUE OF CJ80.
C     CJ81   (REAL)         "J81"="J" OR "JC" DRIFT CORRECTED FROM CD80 TO CD81.
C     CUB60  (REAL          "CUB1(J+LIN3(J))".
C            FUNCTION)
C     CUB74  (REAL          "CUB1".
C            FUNCTION)
C     CUB80  (REAL          "CUB2".
C            FUNCTION)
C     CUB80I (REAL          INVERSE OF "CUB2".
C            FUNCTION)
C     DJ     (REAL)         "DELTA J".
C     DJyy   (REAL)         IN GENERAL: DJyy=QUADyy(AJ) OR DJyy=STLNyy(BJ).
C     DJ62   (REAL)         "DELTA J62".
C     DJ66   (REAL)         "DELTA J66".
C     DJ70   (REAL)         "DELTA J70".
C     DJ72   (REAL)         "DELTA J72".
C     DJ78   (REAL)         "DELTA J78".
C     DAYN   (REAL)         DATE OF ANALYSIS, EXPRESSED AS NUMBER OF DAYS
C                           SINCE 1/1/55.
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          "QUAD10", SOLVED BY ITERATION.
C            FUNCTION)
C     QUAD82 (REAL          "QUAD11" (OF 1982 REPORT ONLY),
C            FUNCTION)      SOLVED BY ITERATION.
C     R      (REAL)         "R"=INTERPOLATING FACTOR.
C     STLN62 (REAL          "LIN7".
C            FUNCTION)
C     STLN66 (REAL          "LIN8".
C            FUNCTION)
C     X      (REAL)         MOLE FRACTION VALUE RETURNED BY ROUTINE.
C     Xyy    (REAL)         IN GENERAL: Xyy = CUByy(Y59).
C     X59    (REAL)         "X3".
```

```
C      X74    (REAL)        "X1".
C      X80    (REAL)        "X9".
C      XX     (REAL)        "XINTERP".
C      Y59    (REAL)        "J".
C
C
C..PGM READS DATE, I OR J, AND GAS FROM CONSOLE AND PRINTS X
C..LINK WITH FLKINSB--
C..WRITTEN BY R. BACASTOW
C..LAST MODIFIED 8 MAR 82
C..INCLUDES SOURCE BLOCK CORRECTION APPROPRIATE ONLY FOR
C....AIR LAB APC
      DIMENSION IDATE(3)
      LOGICAL IINDEX
      DATA AIR,GN2/'A','N'/
C
      CALL CAL80(IDATE(1),Y59,DAYN,CJ80,CJ81)
C
      IF(GAS.EQ.AIR)GO TO 40
C
      IF(GAS.NE.GN2)WRITE(6,1016)
      X=CUB80(CJ80)
      GO TO 100
C
   40 CONTINUE
      IF(DAYN.LT.CDSB)CJ81=CJ81+0.00033*CJ81
      X=ACUB81(CJ81)
C
  100 CONTINUE
      RETURN
C
      END
C
C  SUBROUTINES FOR FLKIN,MLOIN, AND SPOIN
C  LAST MODIFIED 29 MARCH 1983
C
      SUBROUTINE CAL80(ID,Y59,DAYN,CJ80,CJ81)
      DIMENSION ID(3)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
C
      DAYN=DAYNO(ID(1),ID(2),ID(3))
      IF(DAYN.LT.CD80)GO TO 20
C
      CALL CORR3(DAYN,Y59,CJ80,CJ81)
      GO TO 30
C
   20 CONTINUE
C.....THE FOLLOWING 3 CALLS APPLY    ONLY TO DATA UP TO AND INCLUDING CD80
      CALL CALIB(DAYN,Y59,AJ80)
      CALL CORR1(DAYN,AJ80,BJ80)
      CALL CORR2(DAYN,BJ80,CJ80)
C.....THE FOLLOWING CALL APPLIES ONLY TO DATA AFTER CD80
      CALL CORR3(DAYN,Y59,CJ80,CJ81)
C
   30 CONTINUE
      RETURN
      END
C
C
      SUBROUTINE CALDAY
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
```

```
      CD59=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)
      RETURN
      END
C
C
      FUNCTION DAYNO(MYEAR,MONTH,MDAY)
C      THIS SUBROUTINE CALCULATES THE NO.  OF DAYS FROM JAN 1,1955
      DIMENSION MONTHR(12),IDATE(3)
      DATA MONTHR/31,28,31,30,31,30,31,31,30,31,30,31/
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 CALIB(DAYN,Y59,AJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
C
      IF(DAYN.GT.CD74)GO TO 20
      X59=CUB59(Y59)
      X74=CUB74(Y59)
      XX=(X74*(DAYN-CD59)+X59*(CD74-DAYN))/(CD74-CD59)
      GO TO 50
C
   20 CONTINUE
      X74=CUB74(Y59)
      X80=CUB80(Y59)
      XX=(X80*(DAYN-CD74)+X74*(CD80-DAYN))/(CD80-CD74)
C
   50 CONTINUE
      AJ80=CUB80I(XX)
      RETURN
      END
C
C
```

```
      FUNCTION CUB59(A59)
      DJ=0.576-0.005011*A59
      A74 = A59 + DJ
      CUB59=CUB74(A74)
      RETURN
      END
C
C
      FUNCTION CUB74(A74)
      CUB74=77.455+A74*(0.573302+A74*(3.5735E-4+6.7618E-7*A74))
      RETURN
      END
C
C
      FUNCTION CUB80(A80)
      CUB80=84.370+A80*(0.542223+A80*(4.2284E-4+5.8862E-7*A80))
      RETURN
      END
C
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
C
      FUNCTION CUBM74(YJ)
      CUBM74=76.582+YJ*(0.584910+YJ*(3.1151E-4+7.3225E-7*YJ))
      RETURN
      END
C
C
      SUBROUTINE CORR1(DAYN,AJ80,BJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
      QUAD70(AJ) = 7.036 + AJ*(-0.051734 + 0.93176E-4*AJ)
      QUAD72(AJ) = 6.566 + AJ*(-0.051026 + 0.93967E-4*AJ)
      QUAD78(AJ) = -0.444 + AJ*(0.005385 - 0.12695E-4*AJ)
C
      DJ=0.
C
      IF(DAYN.GT.CD70)GO TO 10
      IF(DAYN.LT.CD59)GO TO 50
      DJ70=QUAD70(AJ80)
      DJ=(DAYN-CD59)/(CD70-CD59)*DJ70
      GO TO 50
C
   10 IF(DAYN.GT.CD72)GO TO 20
      DJ70=QUAD70(AJ80)
      DJ72=QUAD72(AJ80)
      DJ=(DJ72*(DAYN-CD70)+DJ70*(CD72-DAYN))/(CD72-CD70)
      GO TO 50
C
   20 IF(DAYN.GT.CD74)GO TO 30
```

```
      DJ72=QUAD72(AJ80)
      DJ=(CD74-DAYN)/(CD74-CD72)*DJ72
      GO TO 50
C
   30 IF(DAYN.GT.CD78)GO TO 40
      DJ78=QUAD78(AJ80)
      DJ=(DAYN-CD74)/(CD78-CD74)*DJ78
      GO TO 50
C
   40 CONTINUE
      IF(DAYN.GT.CD80)GO TO 50
      DJ78=QUAD78(AJ80)
      DJ=(CD80-DAYN)/(CD80-CD78)*DJ78
C
   50 BJ80=AJ80+DJ
      RETURN
      END
C
C
      SUBROUTINE CORR2(DAYN,BJ80,CJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
      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.CD59)GO TO 50
      DJ62=STLN62(BJ80)
      DJ=(DAYN-CD59)/(CD62-CD59)*DJ62
      GO TO 50
C
   10 IF(DAYN.GT.CD66)GO TO 20
      DJ62=STLN62(BJ80)
      DJ66=STLN66(BJ80)
      DJ=(DJ66*(DAYN-CD62)+DJ62*(CD66-DAYN))/(CD66-CD62)
      GO TO 50
C
   20 CONTINUE
      IF(DAYN.GT.CD70)GO TO 50
      DJ66=STLN66(BJ80)
      DJ=(CD70-DAYN)/(CD70-CD66)*DJ66
C
   50 CJ80=BJ80+DJ
      RETURN
      END
C
C
      SUBROUTINE CORR3(DAYN,Y59,CJ80,CJ81)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82
      QUAD81(CJ) = -1.952 + CJ*(0.013966 - 0.25281E-4*CJ)
      QUAD82(CJ) = -0.910 + CJ*(0.008510 - 0.19177E-4*CJ)
 1001 FORMAT(1H0,'CORR3 FAILED TO CONVERGE, DAYN AND J59 =',
     X  I6,F10.2)
C
      IF(DAYN.LT.CD80)GO TO 60
      IF(DAYN.GT.CD81)GO TO 20
C
      R=(DAYN-CD80)/(CD81-CD80)
      CJ80T=Y59
      DO 10 I=1,20
```

```
      CJ80=Y59-R*QUAD81(CJ80T)
      IF(ABS(CJ80-CJ80T).LT..001)GO TO 60
      CJ80T=CJ80
   10 CONTINUE
      WRITE(6,1001)DAYN,Y59
      GO TO 60
C
   20 CONTINUE
      R=(DAYN-CD81)/(CD82-CD81)
C  DO NOT EXTRAPOLATE CORRECTION
      IF(R.GT.1.0) R=1.0
      CJ80T=Y59
      DO 30 I=1,20
      CJ80=Y59-(1.-R)*QUAD81(CJ80T)-R*QUAD82(CJ80T)
      IF(ABS(CJ80-CJ80T).LT..001)GO TO 60
      CJ80T=CJ80
   30 CONTINUE
      WRITE(6,1001)DAYN,Y59
C
   60 CJ81=CJ80+QUAD81(CJ80)
      RETURN
      END
C
C
      FUNCTION ACUB81(C81)
      ACUB81=86.984+C81*(0.523638+C81*(5.0398E-4+5.5214E-7*C81))
      RETURN
      END
```

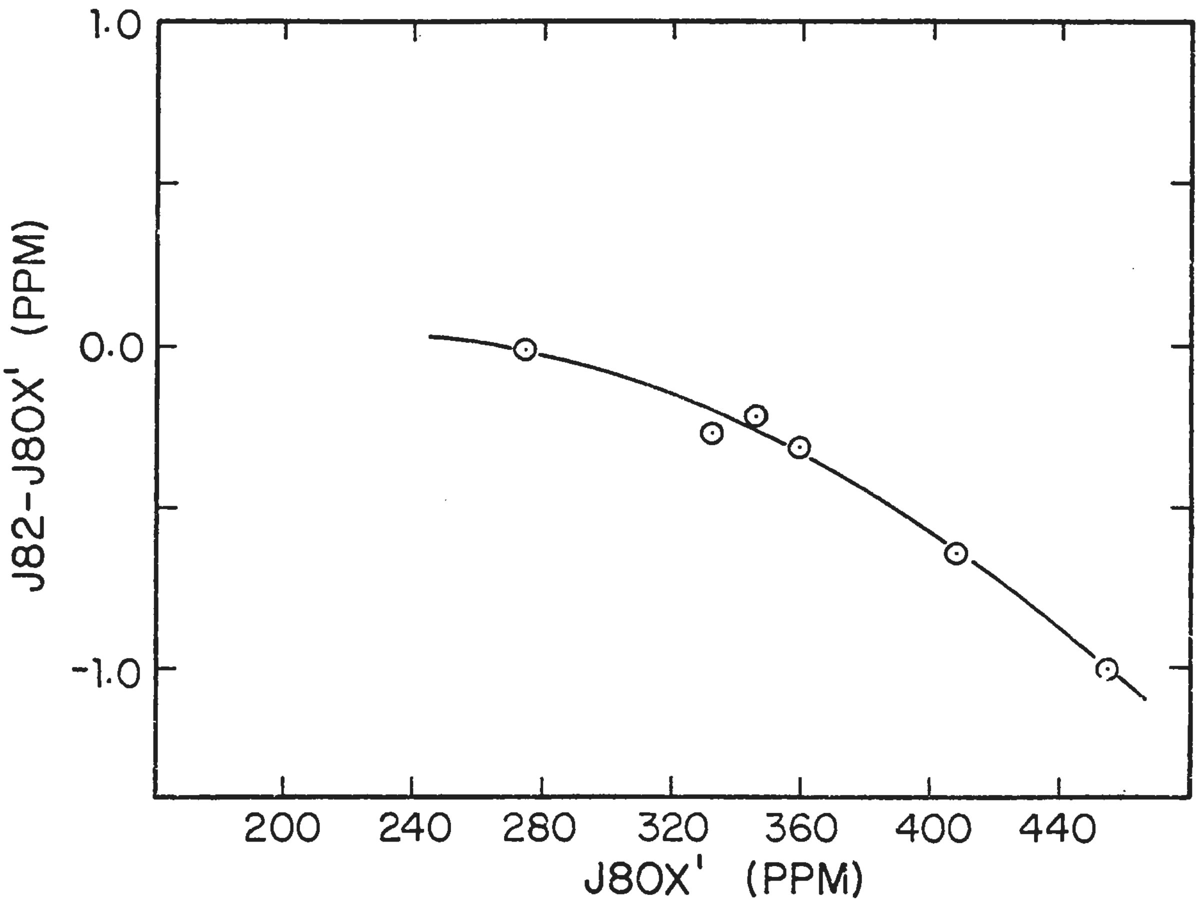

Figure 1. System drift in CO_2-in-N_2 gas standards between 1980 and 1982 calibration periods (see last column of Table 4). The equation for the curve is a quadratic leasts squares fit and is given in the text as Equation (3).

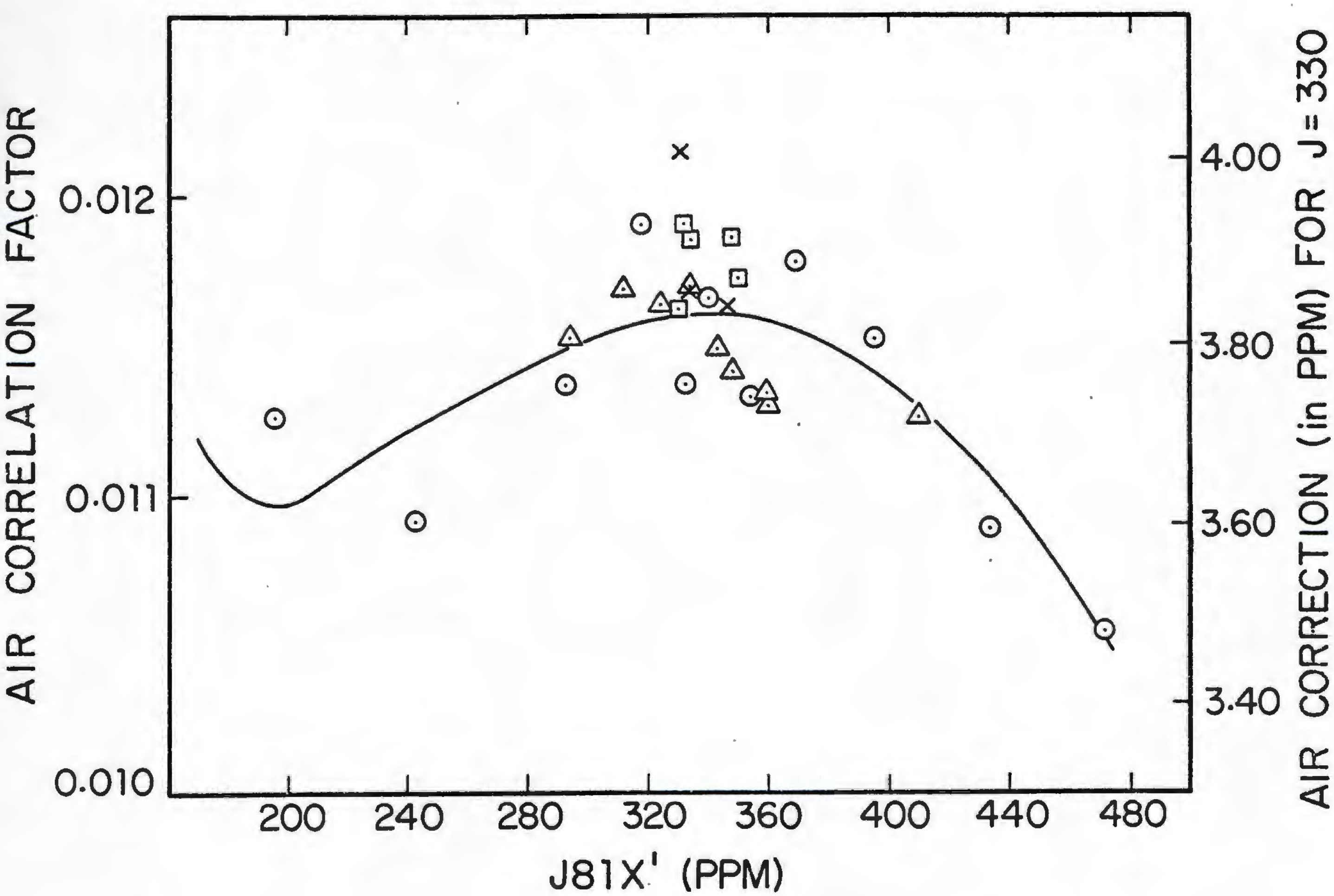

Figure 2. Comparison of air corrections determined from calibrating data for different periods. The data obtained in 1982, as listed in Table 5, are shown as triangles. Corrections based on earlier measurements are shown as follows: 1974 data by squares (J81 data of Table 6d of Bacastow et al., [1983b] are reduced by 0.11 ppm to allow for source block correction), 1980 data by crosses, 1981 data by circles. The latter three sets as listed respectively in Tables 6a, 6b, and 6c of Bacastow et al., [1983b]. The smooth curve is a fit of the 1981 data computed as explained in the text.