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

by

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December, 1983

Prepared for
The U.S. Department of Energy
Report No. DOE/ER/60032-2

With support from the Climate Dynamics Program of the U.S. National Science Foundation Grant ATM70-25965 and the U.S. Department of Energy, Contract AT03-82ER-60032.

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Introduction

This report describes the system of carbon dioxide in air (CO_2-in-air) gas standards developed at the Scripps Institution of Oceanography. These gas mixtures are for the purpose of determining the corrections needed when air is compared with gas standards containing carbon dioxide in nitrogen (CO_2-in-N_2) using the nondispersive infrared gas analyzer installed at the Scripps Laboratory since 1956.

This is the second in a series of reports describing the reference gas standards developed by the Scripps Institution of Oceanography. An earlier report entitled "CO_2 Reference Gas System" [Bacastow et al., 1983] describes the system of CO_2-in-N_2 gas standards. It should be referred to for nomenclature and description of the Scripps Reference Gas System.

When CO_2-in-N_2 gases are employed to measure CO_2-in-air with the Scripps Applied Physics Corporation (APC) infrared analyzer installed at Scripps Laboratory, a correction of approximately 4 ppm must be made because of the difference in line broadening introduced by replacing 20.9% of the nitrogen by oxygen and 0.9% of the nitrogen by argon [Keeling et al., 1976; Griffith et al., 1982]. An additional correction of approximately 0.4 ppm must be made if the APC analyser is operated at lower ambient pressure, such as exists at Mauna Loa Observatory, Hawaii and the South Pole, where similar laboratory analyzers are or have been operated. A new determination of these corrections, made in connection with the 1981 calibration of the reference gas system, is described herein.

Manometric Air Standards

During 1980 and 1981, a suite of 12 cylinders were specially cleaned and then were filled with dry, filtered air at the Scripps Diving Locker. A Rix water lubricated piston compressor pump was used, and the air was pumped only during days when it was especially free of pollution. These gas mixtures are designated primary manometric standards for the Scripps CO_2-in-air reference gas system. They are stored in "white stripe" cylinders.

Before filling, the cylinders (standard 250 cubic foot chrome-molybedium steel tubes) were sent out to a commercial gas supply firm to be cleaned inside by a process that involves (1) tumbling with carborundum grit, (2) steam cleaning, and (3) etching with muriatic acid. There is some doubt that all of these procedures were actually carried out, but, in any case, all cylinders were probably treated in the same way. After the cylinders were returned to Scripps and filled, the air was rejected if it contained more than 10 ppm water vapor, as measured by a U.S. Bureau of Mines type dew point tester, and a new filling made. Those CO_2 gas mixtures retained after moisture testing were adjusted to the desired concentrations by removing CO_2 with ascarite or by adding reagent grade CO_2 gas (Airco grade 4).

These cylinders were manometrically analyzed, mostly in 1981, and their nitrous oxide (N_2O) concentration determined by Dr. Ray Weiss, of the Scripps Institution of Oceanography. The trace gas, N_2O, is included with CO_2 in the manometric analysis, so a correction of approximately 0.30 ppm was made for it to each cylinder. The N_2O data were obtained using a gas chromatograph with a flame ionization detector. The manometric data are listed in Tables 1a to 1d including, for completeness, measurements made in 1974 and of artificial as well as natural air. The manometric concentrations corrected for N_2O, are listed in Table 2a and 2b.

Infrared Analyzer Calibrations

Using the APC analyzer these 12 CO_2-in-air cylinders were compared by infrared analysis to the Principal Span and High Span CO_2-in-nitrogen reference gases of the Scripps reference gas system during five days between 18 August and 1 September, 1981 (Table 3a). The 12 manometric values, corrected for N_2O, have been fit to the obtained adjusted index values, J81, by a cubic relation:

$$X = \mathrm{CUB9}(J81) \tag{1}$$

$$= 86.984 + 0.523638(J81) + 5.0398\times10^{-4}(J81)^2 + 5.5214\times10^{-7}(J81)^3$$

where J81, refers to adjusted index values obtained at the time of the 1981 calibration.

Together with the 1980 calibration of CO_2-in-N_2 manometric standards, this calibration would provide all the information needed to establish a line broadening correction at standard atmospheric pressure, were it not for the problem of system drift in the CO_2-in-N_2 standards.

Drift of the CO_2-in-N_2 System between 1980 and 1981 Calibrations

Cylinders of CO_2-in-N_2 or CO_2-in-air may change in concentration with time for reasons that are thought to be related to surface interactions in the cylinder, fractionation effects associated with flow through the valves, or slow introduction of laboratory air into the cylinders at times of pressure regulator installations. In most cases, the compositions of Scripps primary standards when determined directly by a manometric technique have been found, however, to be reasonably stable.

Thus the drift is in the "system"; it involves changes with time of the relation between true concentration (X) and the Adjusted Index value (J), found by comparison to the reference gas system Principal and High Span standards to manometric standards. There is evidence that it is related to the procedure of determining new Principal and High Span standards by comparison to older Principal and High Span standards such that very small changes in concentration for individual standards yield a cumulative affect on the overlapping system [Bacastow et al., 1983]. In order to apply the 1981 CO_2-in-air calibration data generally, it is first necessary to correct J values for system drift relative to the 1980 CO_2-in-N_2 calibration, to which the CO_2-in-N_2 data are first adjusted.

Information to determine this system drift between 1980 and 1981 was obtained by infrared comparisons of four of the CO_2-in-N_2 manometric standards, made in conjunction with comparisons of five of the 12 CO_2-in-air primary manometric standards, near the time of the calibration of the 12 CO_2-in-air standards in 1981, as described above (Table 3b). These CO_2-in-N_2 standards have been shown to be stable between 1974 and

1980 [Bacastow et al., 1983]. The drift, J81 - J80, is summarized in Table 4 and a quadratic fit, shown in Figure 1, was found, as follows:

$$J81 - J80 = QUAD10(J80)$$

$$= -1.952 + 0.013966(J80) - 2.5281\times10^{-3}(J80)^2 \qquad (2)$$

For times of infrared analysis between the 1980 and 1981 calibrations, we use linear interpolation to determine J80 from the observed value, J:

$$J = J80 + (D - CD80)/(CD81 - CD80)\ QUAD10(J80) \qquad (3)$$

where CD81 denotes the central date for the 1981 calibration, 9 September 1981. The above equation is solved for J80 by iteration. For times before CD80, the central date of the 1980 calibration, we employ the drift correction described by Bacastow et al. [1983] to calculate J80. Afterwards all data, before or after CD80, are adjusted to J81 via Equation (2).

1981 Air Calculation

This is obtained by calculating the mole fraction X via Equation (1) from the J81 adjusted index values, calculated as just described. The reproducibility of equation (1) is illustrated by its goodness of fit to the 12 CO_2-in-air gas mixtures as shown in Table 5.

1974 WMO Air Correction

The 1974 WMO Scale air correction is represented as a factor with which the observed adjusted index value (J) is multiplied before using the cubic curve relating concentration (X) to analyzer response (J) for CO_2-in-N_2 gases. Specifically, for CO_2-in-air gases measured relative to CO_2-in-N_2 standards, Keeling et al. [1976] have reported the equation

$$X = CUBWMO(1.01201J) \qquad (4)$$

where CUBWMO is the originally determined 1974 CO_2-in-N_2 calibration curve:

$$\mathrm{CUBWMO}(J) = 76.582 + 0.584910(J) + 3.1151\mathrm{x}10^{-4}(J)^2 + 7.335\mathrm{x}10^{-7}(J)^3 \quad (5)$$

Equation (5) is essentially the same as

$$X = \mathrm{CUB1}(1.01201J) \quad (6)$$

where CUB1 is the CO_2-in-N_2 calibration curve for 1974 associated with the 1980 calibration:

$$\mathrm{CUB1}(J) = 77.455 + 0.573302(J) + 3.5735\mathrm{x}10^{-4}(J)^2 + 6.7618\mathrm{x}10^{-7}(J)^3 \quad (7)$$

CUB1 differs from CUBWMO only in that it is based on more manometric measurements of the CO_2-in-N_2 standards. Thus the air correction in current use, for J obtained any time during the project, is equivalent to:

$$\Delta J = 0.01201J \quad (8)$$

<u>Comparison of the 1981 Air Correction with Additional Data</u>

Table 6a and Figures 2 and 3 show a representation of the 1981 air correction in the same form as the 1974 air correction. Figure 2 displays only data from the 12 manometric CO_2-in-air standards described above. Figure 3 displays these data (as circles) plus additional data:

[1] Measurements (shown as plus marks) of five of the twelve CO_2-in-air manometric standards on the five days when four of the CO_2-in-N_2 standards were run to obtain data for the J81-J80 drift correction (Table 6b).

[2] Measurements (shown as crosses) of three air surveillance standards near the time of the 1980 CO_2-in-N_2 calibration (Table 6c).

[3] Measurements (shown as squares) of the three surveillance standards mentioned in [2] above, plus two others, near the time of the 1974 calibration (Table 6d). These are the data that led to the 1974 WMO Air Correction.

It is apparent from Figure 3 that the 1974 air measurements are about (0.0004)(330) = 0.13 ppm higher at 330 ppm than the 1980 air measurements.

Source Block Correction

On October 30, 1980, the ascarite trap on the source block was observed to be exhausted and ineffective. The trap is intended to remove CO_2 and water vapor from air in the source optical path where the infrared beam is split, part going through the reference cell and part through the sample cell. At this location, CO_2 might be expected to effect line broadening and, consequently, the air correction.

The trap is not easily accessed for ascarite replacement. Discussions with personnel responsible for the maintenance of the analyzer indicate that the ascarite in 1980 probably had not been replaced for the last six years.

An examination of data for CO_2-in-air surveillance standards (see Table 7) supports a small correction before October 30, 1980, raising J values approximately 0.11 ppm near air concentration. This correction would approximately bring the 1974 air correction data, depicted by squares in Figure 3, into accordance with the 1981 data. (Higher J values after correction result in a smaller carrier gas correction.)

Since the air correction, as indicated in Figure 3, is approximately proportional to J, the offset prior to October 30, 1980, has been represented by

$$\Delta J = 0.00033(J) \tag{9}$$

Pressure Correction to the Air Correction as Determined in 1974

A pressure broadening correction would be expected to vary with total pressure in the gas analyzer sample chamber, and indeed this has been found to be the case. Keeling et al. [1976] report a correction equivalent to

$$\frac{\Delta J}{J} = 0.003157 - 2.237\times10^{-6}(P) - 2.522\times10^{-9}(P)^2 \tag{10}$$

where P is the chamber pressure in mmHg. At the average Mauna Loa Observatory station pressure of 509.9 mm, the correction is $\Delta J/J$ = 0.00136. For a J value of 330 ppm, the correction is thus 0.45 ppm.

1981 Pressure Correction to the Air Correction

In 1981 more extensive data were obtained at two reduced pressures for CO_2-in-air and CO_2-in-N_2-and-O_2 standards (Table 8). The cell pressure was controlled with a cartesian diver manostat, as done for the 1974 data.

A simple equation has been fit to the 1981 data:

$$\Delta J = a_1 J(\Delta P)C(1 + a_2\Delta P)(1 + a_3 C) \tag{11}$$

where the a_i are coefficients to be determined by the fits, ΔP is the difference in pressure in mmHg from 760.46 mmHg, and

$$C = (\%O_2) + 1.5(\%A) \tag{12}$$

The factor of 1.5 in the above equation derives from information in Tables 10 and 11 of Guenther and Keeling [1981]. The correction for argon is approximately 0.26 ppm; its "effectiveness" relative to oxygen is thus approximately

$$\frac{0.26/0.93}{3.9/20.9} \sim 1.5 \qquad (13)$$

The form of Equation (11) is consistent with the observation that $\Delta J/J$ is approximately constant near air concentrations. Also, ΔJ should become zero if ΔP or C becomes zero. For large ΔP or C, a quadratic dependence is allowed.

The fit (Table 9) is quite good. Values of the fitted coefficients are

$$a_1 = (1.51 \pm 0.15) \times 10^{-7}$$
$$a_2 = (9.48 \pm 2.51) \times 10^{-4}$$
$$a_3 = (8.01 \pm 6.48) \times 10^{-4}$$

Clearly, a_3 is not significant and could have been omitted from the computation. The pressure correction at the average Mauna Loa Observatory pressure (509.9 monthly) is then $\Delta J/J = 0.00107$, or 0.35 ppm at 330 ppm.

The 0.10 difference between pressure corrections as found from 1974 and 1981 data is probably a result of more and better data in 1981.

Comparison with NBS Standards

During June of 1980 Dr. Ernest Hughes of the U.S. National Bureau of Standards visited the Scripps CO_2 Laboratory. He brought with him three cylinders of CO_2-in-air gas mixtures which had been compared by infrared and gas chromatographic analysis against primary gravimetric standards. The latter had been synthesized by a gravimetric procedure to be described in an article in preparation. Each gas mixture was analyzed twice by Peter Guenther at Scripps in the same manner as the other gas mixtures reported in Tables 1a - 1d. The results are listed in Table 1C. The contents of N_2O, analyzed in the laboratory of Dr. Ray Weiss, are listed in Table 2b, together with corrected CO_2 mole fractions. The agreement between the Scripps and NBS results is very close, as indicated by the comparisons listed in Table 10. On average the NBS mixtures were 0.09 ppm higher than the Scripps results. The standard deviation in the mean of the differences was 0.05 ppm.

Acknowledgements

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

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Table 1a. Manometric analyses of CO_2-in-air standards during 1974.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
35435	1	22 JAN 74	334.42 334.34	334.38	334.40	3
	2	23 JAN 74	334.46 334.50	334.48		
	3	7 MAR 74	334.29 334.37	334.33		
35405	1	10 APR 74	337.29 337.23	337.26	337.28	2
	2	11 APR 74	337.27 337.34	337.30		
34770	1	10 MAY 74	338.67 338.87	338.77	338.84	2
	2	15 MAY 74	338.90 338.90	338.90		
35401	Run Number 1 Contaminated					
	2	10 MAY 74	353.26 353.24	353.25	353.26	2
	3	15 MAY 74	353.21 353.36	353.28		
35378	1	7 MAY 74	355.82 355.93	355.88	355.93	2
	2	8 MAY 74	355.98 355.98	355.98		

Table 1b. Manometric analyses of CO_2-in-nitrogen-and-oxygen standards during 1974.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
44726	1	10 APR 74	309.48	309.56	309.57	2
			309.64			
	2	12 APR 74	309.59	309.58		
			309.58			
35452	1	13 FEB 74	323.82	323.80	323.86	2
			323.85			
			323.74			
			323.77			
	2	14 FEB 74	323.86	323.91		
			323.91			
			323.95			
35434	1	26 FEB 74	323.97	323.96	323.91	2
			323.99			
			323.92			
	2	27 FEB 74	323.87	323.86		
			323.85			
35442	1	5 MAR 74	326.96	327.02	327.02	2
			327.09			
	2	7 MAR 74	326.97	327.01		
			327.05			
35441	1	1 MAR 74	331.99	331.98	332.04	2
			331.96			
	2	1 MAR 74	332.12	332.10		
			332.08			
35389	1	27 FEB 74	335.21	335.30	335.36	2
			335.38			
	2	28 FEB 74	335.31	335.41		
			335.51			
44695	1	12 APR 74	351.98	352.00	351.92	2
			352.01			
	2	15 APR 74	351.75	351.84		
			351.94			

Table 1c. Manometric analysis of CO_2-in-air standards during 1980-1981.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
66556	1	18 JUN 80	101.40	101.39	101.36	2
			101.38			
	2	6 AUG 81	101.31	101.33		
			101.35			
71251	1	18 JUN 80	213.54	213.52	213.49	2
			213.50			
	2	6 AUG 81	213.48	213.46		
			213.43			
34819	1	7 AUG 81	251.95	251.92	251.96	2
			251.90			
	2	12 AUG 81	251.99	252.00		
			252.01			
71286	1	24 OCT 80	296.88	296.90	296.88	2
			296.91			
			296.91			
	2	7 AUG 81	296.88	296.86		
			296.85			
71341	1	12 AUG 81	322.72	322.70	322.76	2
			322.69			
	2	13 AUG 81	322.82	322.82		
			322.83			
66638	1	13 AUG 81	338.45	338.44	338.39	2
			338.43			
	2	14 AUG 81	338.35	338.34		
			338.32			
66625	1	14 AUG 81	344.90	344.86	344.91	2
			344.82			
	2	18 AUG 81	344.96	344.96		
66696	1	18 AUG 81	360.17	360.15	360.18	2
			360.13			
	2	19 AUG 81	360.21	360.22		
			360.22			
71308	1	26 AUG 81	376.87	376.84	376.80	2
			376.81			
	2	27 AUG 81	376.77	376.76		
			376.78			
			376.74			
			376.75			

Table 1c (Cont.).

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
71370	1	25 AUG 81	406.66 406.67	406.66	406.70	2
	2	26 AUG 81	406.75 406.72	406.74		
71479	1	24 AUG 81	453.73 453.72	453.72	453.70	2
	2	24 AUG 81	453.69 453.66	453.68		
67615	1	20 AUG 81	503.38 503.40	503.39	503.50	2
	2	20 AUG 81	503.63 503.61	503.62		
35405	1	16 MAY 80	337.32 337.33	337.32	337.27	2
	2	23 MAY 80	337.26 337.19	337.22		
34770	1	15 MAY 80	339.12 339.13	339.12		
	2	16 MAY 80	339.53 339.50	339.52		
	3	29 MAY 80	338.75 338.75	338.75	338.71	2*
	4	13 JUN 80	338.67 338.67	338.67		
35401	1	30 MAY 80	353.03 352.97	353.00	353.02	3
	2	30 MAY 80	353.07 353.03	353.05		
	3	5 AUG 81	353.02 353.03	353.02		
NBS Cylinders						
62206	1	3 JUN 80	333.56 333.51	333.54	333.50	2
	2	4 JUN 80	333.49 333.45	333.47		
61130	1	4 JUN 80	340.26 340.24	340.25	340.22	2
	2	10 JUN 80	340.22 340.15	340.18		
243988	1	30 MAY 80	347.00 346.91	346.96	346.97	2
	2	9 JUN 80	346.96 347.01	346.98		

* Runs 1 and 2 deleted due to instrumental problems

Table 1d. Manometric analyses of CO_2-in-nitrogen-and-oxygen standards during 1980.

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
75934	1	5 JUN 80	338.29 338.25	338.27		
	2	10 SEP 80	339.10 339.05	339.08	339.04	2*
	3	11 SEP 80	338.99 339.01	339.00		
127524	1	13 JUN 80	339.58 339.72	339.64		
	2	9 SEP 80	340.28 340.32	340.30	340.38	2*
	3	16 SEP 80	340.42 340.48	340.45		
127693	1	16 JUN 80	360.98 361.11	361.04		
	2	9 SEP 80	361.41 361.46	361.44	361.48	2*
	3	17 SEP 80	361.54 361.50	361.52		
35452	1	11 NOV 80	323.65 323.68	323.66	323.66	2
	2	12 NOV 80	323.66 323.64	323.65		
35441	1	13 NOV 80	331.94 331.88	331.91	331.90	2
	2	13 NOV 80	331.88 331.87	331.88		
35442	1	14 NOV 80	326.82 326.79	326.80	326.81	2
	2	14 NOV 80	326.83 326.82	326.82		
35389	1	18 NOV 80	335.55 335.50	335.52	335.48	2
	2	19 NOV 80	335.45 335.43	335.44		
35434	1	19 NOV 80	322.80 322.78	322.79		
	2	20 NOV 80	323.82 323.81	323.82	323.80	2†
	3	21 NOV 80	323.80 323.78	323.79		

*Run No. 1 deleted because of apparent drift in tank concentration
†Run No. 1 deleted because it is not consistent with other two

Table 2a. N_2O corrected concentration of CO_2-in-air standards manometrically analyzed during 1974.

Cylinder No.	Manometric Average* (ppm)	N_2O Concentration (ppm)	Corrected Concentration (ppm)
Red Stripe Cylinders			
35435	334.40	0.29	334.11
35405	337.28	0.29	336.99
34770	338.84	0.29	338.55
35401	353.26	0.30	352.96
35378	355.93	0.29	355.64

*See Table 1a

Table 2b. N_2O corrected concentration of CO_2-in-air standards manometrically analyzed during 1980-81.

Cylinder No.	Manometric Average* (ppm)	N_2O Concentration (ppm)	Corrected Concentration (ppm)
White Stripe Cylinders			
66556	101.36	0.37	100.99
71251	213.49	0.34	213.15
34819	251.96	0.24	251.72
71286	296.88	0.32	296.56
71341	322.76	0.31	322.45
66638	338.39	0.31	338.08
66625	344.91	0.29	344.62
66696	360.18	0.31	359.87
71308	376.80	0.32	376.48
71370	406.70	0.31	406.39
71479	453.70	0.30	453.40
67615	503.50	0.30	503.20
Red Stripe Cylinders†			
35405	337.27	0.29	336.98
34770	338.71	0.29	338.42
35401	353.02	0.30	352.72
NBS Cylinders			
62206	333.50	0.30	333.20
61130	340.22	0.31	339.91
243988	346.97	0.29	346.68

*See Table 1c

†N_2O values same as in Table 2a

Table 3a. Applied Physics infrared analyzer results from comparison to Scripps System CO_2-in-nitrogen standards for 12 manometrically analyzed CO_2-in-air standards during 1981 calibration. The entries, in ppm, are Index (I), except for the last column, which is Adjusted Index (J). The numbers in parentheses indicate the number of comparisons.

Cylinder No.	18 AUG	20 AUG	25 AUG	27 AUG	1 SEP	Average I	J
66556	77.20(10)	77.82(20)	77.15(12)	77.55(10)	76.18(10)	77.18	25.96
71251	216.61(10)	217.20(10)	216.50(10)	216.91(10)	216.25(10)	216.69	195.96
34819	255.14(10)	255.43(10)	255.11(10)	255.23(10)	254.95(10)	255.17	242.85
71286	295.47(10)	295.58(10)	295.51(10)	295.52(10)	295.39(10)	295.49	291.99
71341	316.90(10)	316.94(10)	316.98(10)	316.97(10)	316.85(10)	316.93	318.12
66638	329.65(10)	329.49(10)	329.50(10)	329.60(10)	329.56(10)	329.56	333.51
66625	334.58(12)	334.59(12)	334.63(10)	334.54(10)	334.63(10)	334.59	339.64
66696	346.24(10)	346.31(10)	346.32(10)	346.33(10)	346.30(10)	346.30	353.91
71308	358.46(10)	358.56(12)	358.59(10)	358.61(10)	358.54(12)	358.55	368.83
71370	379.82(10)	379.90(10)	379.96(10)	380.00(10)	379.93(10)	379.92	394.87
71479	411.36(10)	411.63(10)	411.51(10)	411.64(10)	411.33(10)	411.49	433.35
67615	442.20(10)	442.66(10)	442.41(10)	442.64(10)	442.26(10)	442.43	471.05

Table 3b. Applied Physics infrared analyzer results for 4 CO_2-in-nitrogen standards and 5 CO_2-in-air standards from comparison to Scripps System CO_2-in-nitrogen standards during time close to 1981 calibration. The entries, in ppm, are Index (I), except for the last column, which is Adjusted Index (J). The numbers in parentheses indicate the number of comparisons.

Cylinder No.	31 AUG	3 SEP	8 SEP	10 SEP	14 SEP	Average I	J
CO_2-in-nitrogen Standards							
2408	201.02(10)	200.95(10)	200.57(12)	200.96(10)	200.84(10)	200.87	176.68
7366	280.66(10)	280.70(10)	280.53(10)	280.70(10)	280.62(14)	280.64	273.89
39239	328.34(10)	328.39(10)	328.41(10)	328.44(10)	328.34(10)	328.38	332.07
35316	427.81(10)	427.81(10)	427.72(10)	427.87(10)	427.70(10)	427.78	453.20
CO_2-in-air Standards							
71251	216.64(10)	216.69(10)	216.28(10)	216.75(10)	216.44(10)	216.56	195.80
71286	295.41(10)	295.54(10)	295.41(10)	295.53(10)	295.45(10)	295.47	291.96
66638	329.58(10)	329.53(10)	329.54(10)	329.60(10)	329.56(10)	329.56	333.51
71370	379.89(10)	379.92(10)	379.84(10)	379.89(10)	379.78(10	379.86	394.80
67615	442.28(10)	442.33(10)	442.17(10)	442.33(12)	442.14(10)	442.25	470.83

Table 4. Data summary of 1981 correction for CO_2-in-nitrogen Reference Gas System drift between the central dates, CD80 and CD81. Adjusted index values (in ppm) in columns headed J80 and J81 are from special calibrations in 1980 [see Bacastow et al., 1983, Table 3] and 1981 (Table 3b), respectively.

Cylinder No.	J80	J81	J81-J80
CO_2-in-nitrogen Standards			
2408	176.96	176.67*	-0.29
7366	273.84	273.89	0.05
39239	332.24	332.07	-0.17
35316	454.01	453.20	-0.81

*Error detected in final proofing of report. See Table 3b. (Correct value, .01 ppm higher, is not shown and is not used in curve fits.)

Table 5. Summary of CO_2-in-air standards calibration relative to Scripps System CO_2-in-nitrogen standards. The column headed "Residual" is measured concentration less calculated concentration. The fitted equation is given in the text (Eq. (1)).

Cylinder No.	Concentration X (ppm)	Adjusted Index J (ppm)	Residual (ppm)
White Stripe Cylinders			
66556	100.99	26.08	0.00
71251	213.15	195.96	0.05
34819	251.72	242.85	-0.06
71286	296.56	291.99	-0.03
71341	322.45	318.12	0.11
66638	338.08	333.51	-0.08
66625	344.62	339.64	0.02
66696	359.87	353.97*	-0.10
71308	376.48	368.83	0.10
71370	406.39	394.87	0.06
71479	453.40	433.35	-0.08
67615	503.20	471.05	0.02

*Error detected in final proofing of report. See Table 3a. (Correct value, .06 ppm lower, is not shown and not used in curve fits.)

Table 6a. Comparison of 1981 CO_2-in-air calibration and 1980 CO_2-in-nitrogen calibration expressed in adjusted index, J, and mole fraction, X (both in ppm). The columns headed by "Points" and "Curve" refer to data plotted in Figures 2 and 3. The column labeled J81X is obtained by inverting CUB9(J), the CO_2-in-air curve (see Table 5). The column labeled J80X' is similarly obtained by inverting CUB2(J), the 1980 CO_2-in-nitrogen curve (the prime indicates that although the gas is CO_2-in-air we have used the CO_2-in-nitrogen curve). The column labeled J81X' is obtained by correcting J80X' for the system drift between 1980 and 1981 calibrations by use of QUAD10 (see Figure 1). All data are as obtained during the days in which all 12 CO_2-in-air standards were compared with Scripps System CO_2-in-nitrogen standards (see Table 3a).

	Measured		Calculated			Points		Curve	
Cylinder No.	J81	X	J81X	J80X'	J81X'	ΔJ_p = J81X'-J81	ΔJ_p/J81X	ΔJ_c = J81X'-J81X	ΔJ_c/J81X
66556	26.08	100.99	26.08	29.92	28.36	2.28	0.08742	2.28	0.08742
71251	195.96	213.15	196.02	198.35	198.17	2.21	0.01127	2.15	0.01097
34819	242.85	251.72	242.78	245.55	245.50	2.65	0.01092	2.72	0.01120
71286	291.99	296.56	291.95	295.34	295.31	3.32	0.01137	3.36	0.01151
71341	318.12	322.45	318.23	321.99	321.91	3.79	0.01191	3.68	0.01156
66638	333.51	338.08	333.43	337.42	337.30	3.79	0.01137	3.87	0.01161
66625	339.64	344.62	339.66	343.74	343.60	3.96	0.01166	3.94	0.01160
66696	353.97	359.87	353.88	358.17	357.98	4.01	0.01133	4.10	0.01159
71308	368.83	376.48	368.92	373.44	373.18	4.35	0.01179	4.26	0.01155
71370	394.87	406.39	394.92	399.83	399.42	4.55	0.01152	4.50	0.01140
71479	433.35	453.40	433.29	438.76	438.07	4.72	0.01089	4.78	0.01103
67615	471.05	503.20	471.06	477.06	476.02	4.97	0.01055	4.96	0.01053

Table 6b. Comparison of the 1980-81 air correction with measurements obtained for CO_2-in-air standards on days when CO_2-in-nitrogen primary standards were compared to give the J81-J80 correction (Table 3b, Figure 1). The nomenclature is as in Table 6a.

	Measured		Calculated				
Cylinder No.	J81	X	J81X	J80X'	J81X'	ΔJ_p = J81X'-J81	ΔJ_p/J81
71251	195.80	213.15	196.02	198.35	198.17	2.37	0.01209
71286	291.96	296.56	291.95	295.34	295.31	3.35	0.01148
66638	333.51	338.08	333.43	337.42	337.30	3.79	0.01137
71370	394.80	406.39	394.92	399.83	399.42	4.62	0.01170
67615	470.83	503.20	471.06	477.07	476.02	5.19	0.01102

Table 6c. Comparison of the 1980-81 air correction with measurements of CO_2-in-air gas mixtures measured near the central date of the 1980 CO_2-in-nitrogen calibration. Manometric measurements, X, are from Table 1c. Nomenclature is as in Table 6a.

Cylinder No.	J80†	X	Calculated J81X	Calculated J80X'	Calculated J81X'	Calculated J81	ΔJ_p = J81X'-J81	ΔJ_p/J81
35405	332.29	336.98	332.38	336.35	336.23	332.19	4.04	0.01215
34770	333.84*	338.42	333.76	337.75	337.63	333.73	3.90	0.01168
35401	347.40	352.72	347.26	351.46	351.29	347.25	4.04	0.01163

† Inclusive Dates:

35405	80 08 19 to 80 11 17	(8 calibrating days)	332.29
34770	80 09 10 to 80 11 17	(8 calibrating days)	333.84
35401	80 08 19 to 80 11 17	(8 calibrating days)	347.40

* Error detected in final proofing of report. Correct value (333.82 ppm) not used in curve fits.

Table 6d. Comparison of the 1980-81 air correction with the 1974 correction. Manometric measurements X are from Table 1a.* The nomenclature is as in Table 6a. The column headed "J81" is obtained by drift correcting the measured J74 in 1974 to the time of the 1981 CO_2-in-air calibration relative to CO_2-in-nitrogen standards. The column headed J74X' is obtained by inverting the 1974 calibration curve, CUB1(J), and J81X' results from drift correction of J74X' to the 1981 calibration time.

	Measured		Calculated				Points	
Cylinder No.	J74	X	J81X	J74X'	J81X'	J81	ΔJ_p = J81X'-J81	ΔJ_p/J81
35435	330.22	334.11	329.61	334.11	333.43	329.49	3.94	0.01195
35405	332.86	336.99	332.39	336.88	336.24	332.17	4.07	0.01224
34770	334.36	338.55	333.88	338.37	337.76	333.69	4.07	0.01219
35401	347.76	352.96	347.48	351.94	351.51	347.28	4.23	0.01217
35378	350.26	355.64	349.97	354.42	354.03	349.81	4.22	0.01206

* The adjusted index values, in the column headed 'J74', are from Guenther and Keeling, 1981 p. 70.

Table 7. Comparison of air and synthetic air CO_2 concentration data (X values in ppm) before and after replacement of the source block trap on October 30, 1980. In the column headed "Before" are summarized comparisons from January 1, 1980 to October 28, 1980. In the column headed "After" are summarized comparisons from October 30 through February 2, 1981. For these six standards, there are manometric measurements in 1974 and 1980.

	Cylinder No.	% O_2	Before	After	After-Before
CO_2-in-air Red Stripe Cylinders					
	35405	---	336.78±.02	336.91±.02	0.13±.03
	34770	---	338.37±.02	338.50±.02	0.13±.03
	35401	---	352.71±.02	352.80±.04	0.09±.04
CO_2-in-nitrogen and oxygen cylinders					
	35452	18.8	323.73±.01	323.83±.02	0.10±.02
	35434	18.8	323.77±.07	323.96±.04	0.19±.08
	35389	20.9	335.12±.06	335.22±.01	0.10±.06#
Wt. Av. Difference (in ppm):					
					0.11±.01

#Omitted from average because manometric measurements are almost 0.5 ppm above infrared concentration, indicating that there may be a contaminating gas present.

Table 8. Data for pressure correction to air correction.

Cylinder No.	% O_2	%A	Index I (ppm) 6 FEB 81, 760.46 mmHg	Index I (ppm) 4 FEB 81, 508.27 mmHg	Index I (ppm) 5 FEB 81, 255.18 mmHg	Adjusted Index J81 (ppm) 4 FEB 81, 508.27 mmHg	Adjusted Index J81 (ppm) 5 FEB 81, 255.18 mmHg
CO_2-in-air Red Stripe Cylinders							
34770	20.95	0.93	329.90	329.20	329.20	333.55	333.00
35401	20.95	0.93	341.11	340.73	340.20	347.03	346.38
CO_2-in-nitrogen-and Oxygen Standards							
127524	100	0.0	319.25	317.83	316.09	319.17	317.05
127693	100	0.0	334.84	333.41	331.40	338.12	335.68
75934	79.9	0.0	321.94	320.95	319.49	322.97	321.19
35442	60.0	0.0	315.10	314.38	313.34	314.97	313.70
35441	40.2	0.0	322.12	321.66	320.86	323.83	322.86
35434	18.8	0.0	318.83	318.53	318.25	320.02	319.68

Table 9. Fit of Equation (11) to pressure correction data summarized in Table 8. The column headed "ΔJ" is obtained by subtracting the Index (I) at pressure P (mmHg) from the Index at 760.46 (mmHg) and multiplying it by 1.2186, the ratio $\Delta J/\Delta I$.

Cylinder No.	J (ppm)	ΔJ (ppm)	ΔP (mmHg)	% O_2	%A	ΔJ FIT (ppm)	$\Delta J-\Delta J$ FIT (ppm)
34770	333.55	0.30	252.19	20.95	0.93	0.36	-0.06
35401	347.03	0.46	"	20.95	0.93	0.37	0.09
127524	319.17	1.73	"	100.00	0.0	1.63	0.10
127693	338.12	1.74	"	100.00	0.0	1.73	0.01
75934	322.97	1.20	"	79.9	0.0	1.30	-0.10
35442	314.97	0.88	"	60.0	0.0	0.94	-0.06
35441	323.83	0.56	"	40.2	0.0	0.63	-0.07
35434	320.02	0.37	"	18.8	0.0	0.29	0.08
34770	333.00	0.85	505.28	20.95	0.93	0.86	-0.01
35401	346.38	1.11	"	20.95	0.93	0.89	0.22
127524	317.05	3.85	"	100.00	0.0	3.87	-0.02
127693	335.68	4.18	"	100.00	0.0	4.10	0.08
75934	321.19	2.98	"	79.9	0.0	3.09	-0.11
35442	313.70	2.15	"	60.0	0.0	2.23	-0.08
35441	322.86	1.53	"	40.2	0.0	1.51	0.02
35434	319.68	0.71	"	18.8	0.0	0.69	0.02

Table 10. Comparisons of Manometric Analyses with NBS Gravimetric Standards

Cylinder No.	SIO Manometric Average Conc. (ppm)	NBS Gravimetric Conc. (ppm)	Difference (ppm)
62206	330.20	333.34	-0.14
61130	339.91	340.05	-0.14
243988	346.68	346.68	0.00
Average Difference (SIO-NBS)			-0.09 ± .05

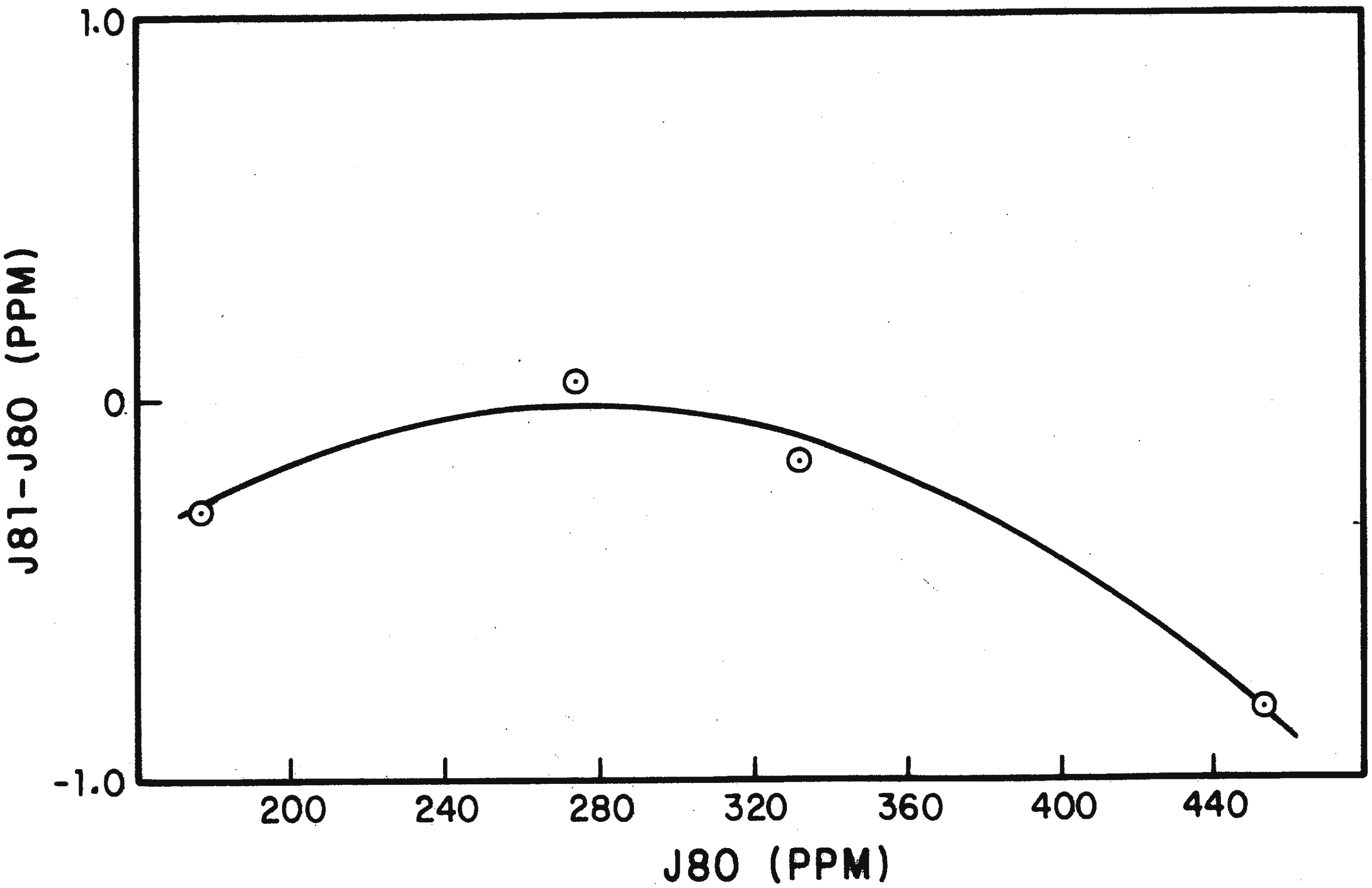

Fig. 1. System drift between 1980 and 1981 calibration periods (see Table 4). The equation for the curve is a quadratic least squares fit and is given in the text as equation (2).

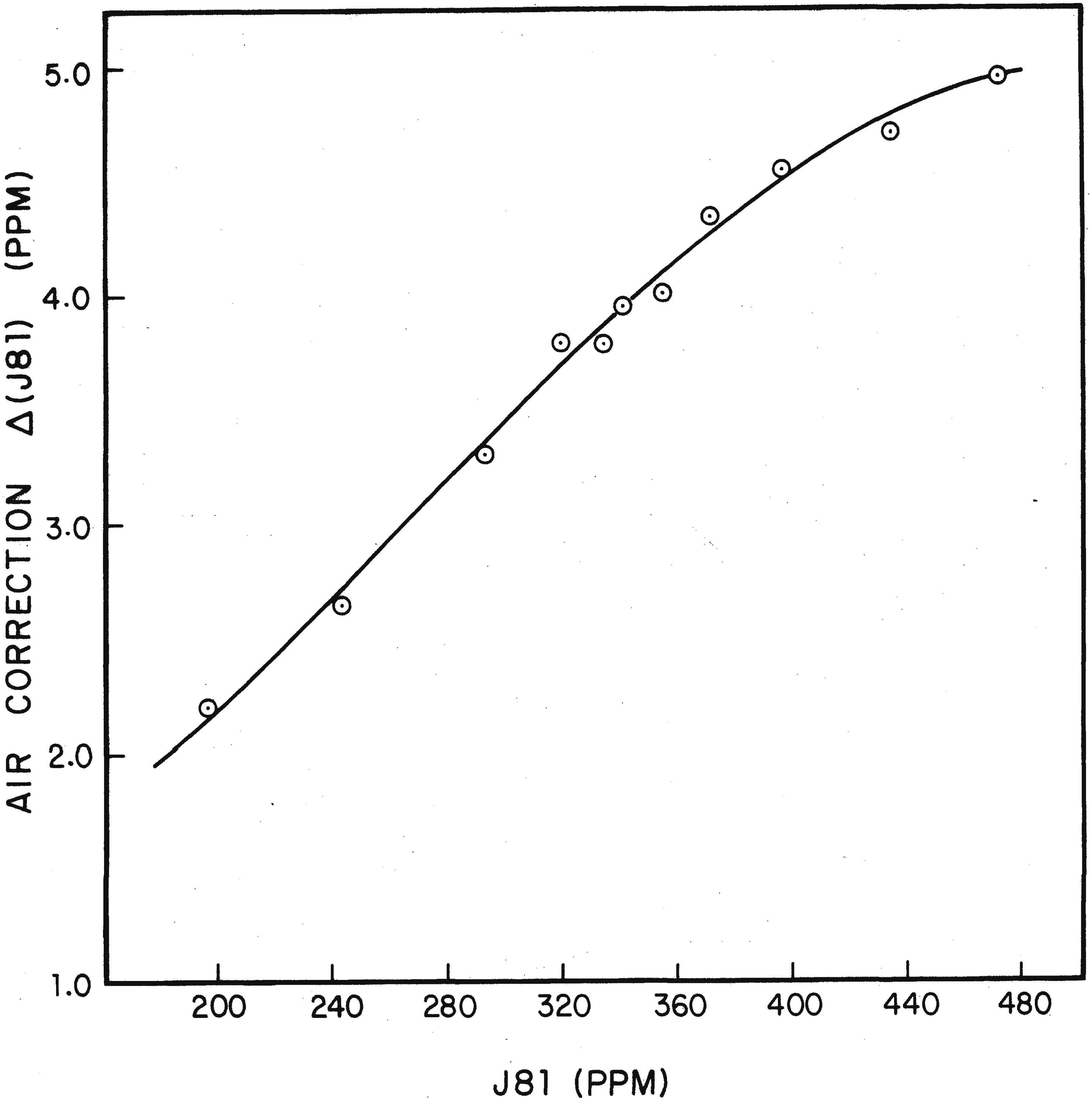

Fig. 2. Air correction obtained from 1980 and 1981 calibrations. Points are from CO_2-in-air manometrically analyzed cylinders, compared to Scripps span gases on same day (see Table 6a).

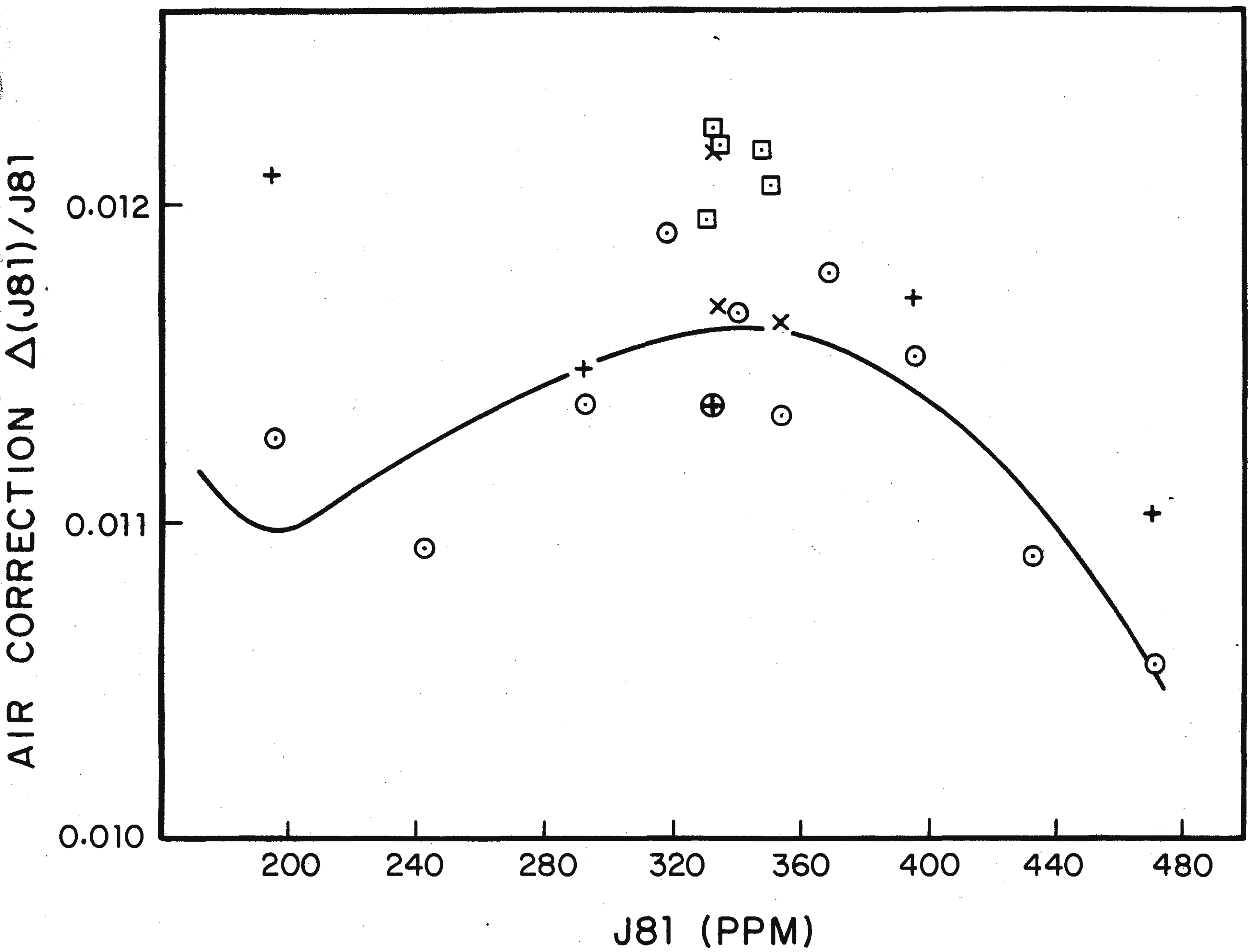

Fig. 3. Comparison of air corrections determined from calibrating data for different periods. The curve and the circled points (⊙) are for the same data as in Figure 2, and Table 6a. The pluses (+) represent additional comparisons near time of the 1981 CO_2-in-air calibration (Table 6b), the crosses (x) are for CO_2-in-air cylinders compared near the time of the 1980 CO_2-in-nitrogen calibration (Table 6c), and the squares (⊡) are for the comparisons that lead to the 1974 WMO air correction (Table 6d).