SCRIPPS REFERENCE GAS CALIBRATING SYSTEM

FOR CARBON DIOXIDE IN AIR STANDARDS: REVISION OF 1983

A REPORT PREPARED FOR THE ENVIRONMENTAL MONITORING PROGRAM

OF THE WORLD METEOROLOGICAL ORGANIZATION

by

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January, 1984

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1. Introduction

This report describes extensive calibrations carried out in October and November, 1983. These calibrations establish a new system of carbon dioxide in air (CO_2-in-air) primary reference gas standards to be used in the Base Line Monitoring Program of the World Meteorological Organization (WMO). This set of standards supercedes carbon dioxide in nitrogen (CO_2-in-N_2) standards in use since the beginning of the Scripps carbon dioxide program in 1957. The WMO provisionally adopted these CO_2-in-N_2 standards to calibrate non-dispersive infrared gas analyzers used to measure atmospheric carbon dioxide at a worldwide network of stations under the name "BAPMoN" (for Baseline Atmospheric Pollution Monitoring Network).

Since 1 January, 1983 the Scripps Carbon Dioxide Program has been under Contract with the United States Bureau of Standards to maintain primary reference gases. This report is submitted as an annual summary of activities under this contract.

The 1983 calibrations, here reported, involve extensive measurements of both CO_2-in-air and CO_2-in-N_2 standards. These measurements provide a close comparison of the two types of standards at the time of change over to the new standards. As such, they also provide detailed new data on the CO_2-in-N_2 system, in prior use. We intend to carry out one additional set of calibrations of the CO_2-in-N_2 standards in 1984 before discontinuing there use, but this final determination will be mainly to guarantee their performance as standards during the coming interim period when these CO_2-in-N_2 standards, necessarily still in use, are retired and replaced with the new standards. The present

calibrations, extensive and closely tied to the CO_2-in-air standards, will serve to provide final concentration values and calibration equations for CO_2-in-air standards for the period up to 18 November, 1983, the central date of the 1983 calibration. Such final values for 1983, however, will not be determined until after the 1984 calibration, because of the need for post-calibration data to verify the stability of performance of the manometer in 1983. Changes in the reported 1983 data will probably be too small, however, to affect field calibrations in any significant way.

The present report is written primarily to describe the new 1983 data. The terminology and mathematical development follow closely three previous reports [Bacastow et al., 1983a, b, and Keeling et al., 1983] to which the reader is referred for background information. By way of summary, however, some of the tables of data recapitulate tables appearing in the three previous reports, and in additional earlier manometric reports [Guenther, 1978a, b, 1981, and Guenther and Keeling, 1981]. A few small errors in tabular entries found in the three previous calibration reports are corrected. These errors have been noted in revisions of the earlier reports. The latter are, indeed, being finally issued contemporaneously with this fourth report.

2. Manometric Calibrations

All of the gas mixtures involved in the 1983 infrared analyzer calibration were analyzed manometrically during 1983, between 16 August and 9 November. In all cases these mixtures have been previously measured manometrically: most of the CO_2-in-N_2 mixtures in 1980, and all of the CO_2-in-air mixtures in 1981. It was necessary to replace one of the

CO_2-in-N_2 mixtures in 1982, and at that time one additional CO_2-in-N_2 mixture was also introduced.

The manometric data of 1983 are listed in Tables 1a to 1b. These data are subject to small adjustments (maximum 0.02 ppm) because only preliminary meniscus corrections were used. Also, as noted below, the manometric 4/5000 cc volume ratio used in the computations is provisional. The entire set of manometric calibrations of Scripps primary gas standards from 1970 through 1983 are summarized in Tables 1c to 1e. The measurements are reported as mole fractions in parts per million by volume (ppm). The CO_2-in-air standards were obtained by pumping air at the Scripps Diving Locker Facility using a Rix water lubricated piston compressor pump [Keeling et al., 1983]. The air was pumped only on days when it was essentially free of industrial pollution. Ascarite was used to reduce the CO_2 concentration for the lower concentration mixtures, and CO_2 from commercial compressed CO_2 (derived from limestone) was used to prepare the higher concentrations.

The manometric determinations were made by first expanding gas from the high pressure cylinders into a 5000cc calibrated glass volume where the pressure and temperature were determined. This aliquot of the gas mixture was then passed through a concentric spherical trap chilled with liquid nitrogen which removed CO_2, N_2O, and water vapor. The trapped gases were sublimed into a glass U trap using liquid nitrogen refrigerant, and subsequently sublimed three more times at dry ice temperature to remove water vapor. The dried sample was then transferred with liquid nitrogen to the inside of another chamber of the manometer. The gas was warmed and confined to a volume of approximately 4 cc by bring-

ing a column of mercury to a glass pointer. The pressure and tempera-
ture were measured and the mole fraction determined using the equations
of state of air and CO_2. For additional details see Guenther [1978a].

The amount of N_2O in the sample was determined by gas chromotogra-
phy in the laboratory of Dr. Ray Weiss at Scripps, and this amount was
subtracted to produce the mole fraction data in Tables 1c-1e. The ori-
ginal mole fractions and N_2O concentrations are listed in the reports of
Bacastow et al. [1983b] and Keeling et al. [1983].

The ratio we found for the 4 cc to the 5000 cc volumes of the
manometer has been determined several times. The same average value
(1320.61 cc) was used in all of the determinations reported prior to
1983. In 1982, using this volume ratio, we found for six gas mixtures
furnished by the National Bureau of Standards manometric mole fractions
in close agreement with gravimetric determinations made at the Bureau.
There is no evidence, as indicated by the data in Tables 1c and 1d, that
the volume ratio changed significantly between 1970 and 1982, thus con-
firming the validity of this ratio to a high precision. In 1983 both
CO_2-in-N_2 and CO_2-in-air gas mixtures showed a small shift towards lower
manometric concentrations, however. This shift was roughly proportional
to mole fraction. The 5000cc volume was not checked, but it is highly
unlikely that it changed significantly. The 4cc volume, on the other
hand, showed evidence of change on the basis of comparisons with 1cc and
16cc volumes of the same manometer. Pending a redetermination of the 4
cc volume, we have applied a correction to the volume to reduce to zero
the average shift in concentration of the 23 gas mixtures measured in
1983 relative to the average mole fractions found previously. The

volume ratio thus used for 1983 is 1319.61 cc.

Prior to October 1978 the manometer was used only very infrequently and almost entirely for measuring primary gas standards. It then was put to use to measure CO_2 collected from sea water samples with a large number of samples measured from 1981 through July, 1983. The mercury surfaces of the columns have shown increasing discoloration during this time, and we believe that contamination from sea water samples has begun to affect the manner of approach of the mercury column to the glass pointer, which can be influenced by static electric charges [Guenther, 1978b]. We intend to put into use a second manometric system, already constructed, for analysis of sea water, in order to avoid further risk of contamination of the manometer used for calibrating standard gases.

The manometer performed well in 1983. The standard deviation of replicate analyses of CO_2-in-N_2 and CO_2-in-air combined (23 sets) was 0.041 ppm down from 0.048 ppm in 1982 (12 sets), 0.071 ppm in 1981 (12 sets), and 0.058 ppm in 1980 (24 sets, including CO_2-in-N_2+O_2).

3. Infrared Analyzer Calibrations

All 23 of the gas mixtures of the 1983 calibration were compared with three gas mixtures of the Scripps CO_2-in-N_2 standard system on five special test periods, each lasting approximately 22 hours. The same Applied Physics Corporation (APC) nondispersive infrared gas analyzer was used as in the previous calibrations. No significant alterations to the optical system of the analyzer were made through the entire period from the 1980 to the 1983 calibration, except for replacement of the ascarite absorption tube on the source block on 30 October, 1980. As

reported by Bacastow et al. [1983a] this replacement produced a change in the relative sensitivity of the instrument to CO_2-in-air compared to CO_2-in-N_2. The shift was estimated to be 0.11 ppm for mixtures near natural air in concentration. (CO_2-in-air gas mixtures analyzed higher after the replacement.) The extent of this shift is redetermined in section 9, below.

The infrared data are expressed in index units, I, proportional to the response of the APC analyzer, as explained by Bacastow et al., [1983a]. For mixtures near the concentration of natural air, a computation of an adjusted index scale, J, brings these values close to the manometric mole fractions, the latter denoted by the symbol, X. The data for all calibrations of primary standards from 1974 through 1983 are listed in Tables 2a to 2h. Averages for each test period (individual days except in 1983) are shown with the number of individual comparisons against the Scripps System gases listed within parentheses. Nonweighted index averages have been calculated in preference to weighted averages on the grounds that systematic shifts in instrument performance from test period to test period were more likely to influence the results than random shifts. The nonweighted averages in index units, I, are converted to adjusted index units, J, by the formula:

$$J = 1.2186 \ (I - 3.11.51) + 311.51 \qquad (1)$$

which defines the J scale, and has been in use since 1959.

In preparing these new tables, we have not been able to reproduce exactly the averages obtained by Bacastow et al. [1983a and b]. For data prior to the central date of the 1980 calibration (19 September,

1980) we have not modified the formulation of Bacastow et al. [1983a] because the differences are too small to affect significantly the calibration adjustment equations employed. It is possible, that we will subsequently reexpress these formula in a simpler form for more efficient computations. If we do so, we will then employ the averages of J listed in this report.

As discussed below, all calibration equations subsequent to the 1980 calibration central date are redetermined in this report. The equations of Bacastow et al. [1983b] and Keeling et al. [1983] are therefore no longer recommended for use.

In 1981 and 1982 the CO_2-in-air gas mixtures were measured in two sets in order to achieve test periods terminating in one working day. Tables 2d and 2f indicate the averages for each set followed by combined averages for those cases where varying numbers of cylinders were calibrated on alternating days. The latter averages are used subsequently for curve fitting, as discussed below. The data for 1983 are based on a preliminary computation of the data of Reference Gas Report 44. Because the average adjusted index values, as listed in Tables 1e and 1h, changed only negligibly (by not over 0.03 ppm) when a final computation was made, it was not deemed necessary to incorporating these changes in the present report. Some additional infrared data not obtained on special calibrating dates, are listed in Table 3 and discussed in Section 6, below.

4. System Drift

The principal gas mixtures, used during routine calibrating at Scripps, consist of a principal span and high span gas with concentrations lying, respectively, below and above natural air as measured over the time period 1959 to 1983. A secondary gas with a concentration close to that of the principal span gas is also used.

The special calibrations with the APC analyzer at Scripps as reported here also employ these three gas standards. These special calibrations thus serve to establish the correct concentrations of these standards at the time of the calibrations. Over the course of the project these standards became depleted and were replaced by new ones measured against the previous set. This overlap, indeed, produces what we call our "system" of gas standards, as explained by Bacastow et al. [1983a].

We have found that this system drifts in index, I (and thus also in J), and that the rate tends to be proportional to the number of replacements. Between 1959, when the first manometric calibration took place, and 1974, the third such calibration, the apparent drift rate for concentrations of CO_2-in-N_2 gases near the mole fraction of natural air was on average 0.06 ppm per year. As shown in Table 4, the rate from 1974 until 1980 was on average 0.10 ppm per year, while it was 0.16 ppm per year from 1980 to 1983.

The recently increased rate reflects, evidently, the greater amount of calibrating activity since 1980.

To allow for this drift in the Scripps system, we have not combined the data of Tables 2a to 2h into grand averages, but have made separate use of the data for each individual calibration period, as we will now explain.

5. Nomenclature and symbols

To explain the calculations used in this report we use the same terminology as previously. The main terms and their definitions are as follows:

J   adjusted index (proportional to Applied Physics Analyzer response).

T   designator of a special period of calibration (e.g. $T = 60$, 74, 80 for the periods in 1960, 1974, and 1980 used to determine JA as described in the next section).

JT   average adjusted index obtained for a given gas mixture during special period, T.

X   observed CO_2 mole fraction of a gas mixture based on manometric measurements.

X83   average CO_2 mole fraction based on manometric measurements from 1970 through 1983, as quoted in Tables, 1c to 1e in the column labeled "average".

CDT   central date of special period, T. This central date is a weight average date for a special period of calibration under consideration.

D   date of a given determination of J not necessarily occurring
during a special period.

6. Equations to Correct for System Drift

Since the system drift has occurred in the overlapping Scripps
principal span and high span gas standards, it applies only to gas mix-
tures of CO_2-in-N_2. (This will now change as we adopt a new system
employing CO_2-in-air standards in 1984). Of the eleven CO_2-in-N_2 mix-
tures measured in the special calibration of 1983, nine were also
included in the 1980 calibration. The other two were at that time
second level surveillance standards analyzed approximately every three
months. The infrared comparisons obtained on nearby three-monthly test
days permit us to determine their J values close to the time of the 1980
special calibration. These data are summarized in Table 3. Using the
drift corrections as prescribed by Bacastow et al. [1983b], we find
that the weighted averages are altered by, at most, 0.03 ppm, if drift
corrected. Therefore, we have accepted the data without correction as
though the gas mixtures had been run on the special calibrating days.

With J values now assigned for all 11 CO_2-in-N_2 mixtures in 1980
and 1983, we establish the system drift between the central dates (CD's)
of the 1980 and 1983 calibrations. The best estimate of this drift
involves taking advantage of the smoothing inherent when we fit the J
values of each calibration to the manometric data. The latter are taken
as single, time independent, values for each gas mixture, i.e. the same
manometric values are assigned to both 1980 and 1983. We obtain excel-
lent fits to the data by assuming that these time independent values,
X83, are a cubic power series in J.

Our first step is thus to fit, by least squares, J80 and J83 versus X83. We obtain the relations:

$$X83 = CUB9 \ (J80) \qquad\qquad (2)$$

$$X83 = CUB10 \ (J83) \qquad\qquad (3)$$

where we continue the numbering of equations from those employed by Bacastow et al. [1983a]. (We disregard the numbering of equations by Bacastow [1983b] and Keeling et al. [1983]). The coefficients of these expressions are listed in Table 5. Owing to drift, as shown in Figure 1, they predict significantly different relations between J and X for 1980 and 1983.

We remove most of the drift in the system by assuming it to be linear with time between CD80 and CD83. To make use of equations (2) and (3) we perform the interpolation in X83 units instead of J. Because the drift is over a range less than 2 ppm, the time rate of change in J and X at any given mole fraction is very nearly equal between CD80 and CD83. Thus we carry out the interpolation by computing:

$$X9 = CUB9 \ (J) \qquad\qquad (4)$$

$$X10 = CUB10 \ (J) \qquad\qquad (5)$$

$$XINTERP = \left(\frac{CD83 - D}{CD83 - CD80}\right) X9 + \left(\frac{D - CD83}{CD83 - CD80}\right) X10 \qquad (6)$$

XINTERP is, indeed, the sought after mole fraction based on assuming a linear drift in time. But, since we will apply a second level of correction based on the 1981 and 1982 calibrations in the J system, we next convert XINTERP back to the adjusted index system via the transformation:

$$JA = CUB10^{-1}(XINTERP) \qquad (7)$$

where $CUB10^{-1}$ is the inversion of the 1983 calibration curve to find J given X. By using CUB10 instead of CUB9 we obtain J values consistent with the most recent and, for CO_2-in-N_2 gas mixtures, presumably final calibration curve for the Scripps APC analyzer.

For infrared data obtained prior to CD80 the formulation of Bacastow et al. [1983a] produces JA values which correct the system drift to CD80. The final step of Bacastow et al. inverts XINTERP via cubic expression, CUB2, which was obtained from the 1980 calibration, as is CUB9. The cubic, CUB2, however, employed only 9 of the 11 gas mixtures used in CUB9, plus one additional one not in the set of 11. Also the manometric data used in obtaining CUB2 were based on measurements only through 1980 rather than through 1983 (i.e. X80 instead of X83). Finally the J values of CUB2 in some cases were slightly different owing to unexplained differences in averaging, as noted above.

The computations to obtain JA do no more than drift correct J values between the designed central dates. Since the 10 gas mixtures of CUB2 were also used in 1974 to obtain CUB1, it is consistent, to employ CUB2 when interpolating before CD80, and CUB9 after CD80. Consequently for infrared analyses made prior to CD80 the formulation of Bacastow et al. [1983a] is suitable to obtain JA values based on CUB2. We will make use of this approach, as discussed below.

The calibrating data of 1981 and 1982 involve respectively 4 and 6 CO_2-in-N_2 gas mixtures. They produce less precise calibrating curves for CD81 and CD82 than for CD80 and CD83. To allow for this we employ

these data only to make second level corrections after first computing first level corrections via JA. The latter values, corrected via equations (4) through (7) are designated JA81 and JA82. The average J values for the special calibration of 1983, equal to JA, are designated JA83.

First, the differences:

$$\triangle J81 = JA83 - JA81 \tag{8}$$

$$\triangle J82 = JA83 - JA82 \tag{9}$$

were computed for each gas mixture. Then pairs of values ($\triangle J81$, JA81, and $\triangle J82$, JA82) were fitted to quadratic expressions, QUAD11 and QUAD12, by least squares. The resulting relations, whose coefficients are listed in Table 5,

$$\triangle J81 = QUAD11 \ (JA81) \tag{10}$$

$$\triangle J82 = QUAD12 \ (JA82) \tag{11}$$

fit the data closely (see Table 6).

The expressions (10) and (11) were then used to calculate second level corrected J values, JB, for any given day between the appropriate central dates by linear interpolation in time. Between CD80 and CD81 (since there is no correction to JA for CD80):

$$JB = JA + (\frac{D - CD80}{CD81 - CD80}) \ QUAD11 \tag{12}$$

Between CD81 and CD82:

$$JB = JA + (\frac{CD82 - D}{CD81 - CD81})QUAD11 + (\frac{D - CD81}{CD81 - CD81})QUAD12 \tag{13}$$

Between CD82 and CD83 (since there is no correction to JA at CD83):

$$JB = JA + (\frac{CD83 - D}{CD82 - CD82}) \; QUAD12 \qquad (14)$$

For dates before the 1970 calibration (CD70) a third level corrected index, JC, is computed as explained by Bacastow et al. [1983a]. Between CD70 and 1980 this correction is nil, i.e.

$$JC = JB. \qquad (15)$$

Assuming now, that all data before CD80 have been fully corrected to the JC scale and noting that, since the formulism of Bacastow et al. [1980a] has been employed, this scale is drift corrected only to CD80, we now convert all data prior to and including the date, CD80, to the new scale via the expressions

$$XSHIFT = CUB2 \; (JC) \qquad (16)$$

$$JF = CUB10^{-1}(XSHIFT) \qquad (17)$$

For data after CD80 up to and including the date, CD83, the data are fully drift corrected by equation (14), hence:

$$JF = JC = JB \qquad (18)$$

7. Equations to Convert Index Values to Mole Fractions

The special calibration of 1983 presents us with the most detailed set of data obtained so far in the Scripps program for the purpose of determining the nonlinear instrument response of the APC analyzer. For CO_2-in-N_2 gas mixtures this calibration, however, principally serves as a reference for defining Scripps system drift. In effect, the conversion from J to X depends equally on the CO_2-in-N_2 calibration data

obtained for each year of special calibrations. For analyses of gas mixtures made after central date CD80, in which the drift corrections up to CD83 have been made directly, we apply the equation:

$$XN_2 = CUB10 \ (JB) \tag{19}$$

where XN_2 indicates that the mole fraction is for CO_2-in-N_2 gas mixtures. Since from (7)

$$XINTERP = CUB10 \ (JA) \tag{20}$$

we would have obtained the final calculated value by equation (6) were it not for the second level correction to obtain JB, computed in adjusted index units.

For CO_2-in-N_2 analyses on or before CD80, and especially for those on or before CD70, the corrections are more extensive. But once these corrections have been made, the data all refer to the same central date, CD80. Without computing JF, we may immediately apply the equation:

$$XN_2 = CUB2 \ (JC) \tag{21}$$

It can be seen that XN_2 and XSHIFT are identical in value for CO_2-in-N_2 gas mixtures analyzed on or before CD80.

For CO_2-in-air gas mixtures, the 1983 calibration is the most reliable basis for determining mole fractions. It is therefore necessary to carry the drift correction forward to CD83 for all analysis dates. The final calculation is:

$$XAIR = ACUB13 \ (JF) \tag{22}$$

where XAIR indicates that the mole fraction is for CO_2-in-air gas mixtures and ACUB13 is a cubic equation obtained by a least squares fit of J to X for the 12 air cylinders whose data are listed in Tables 1d and 2h.

For infrared analyses carried out before October 30, 1980 a correction is applied to JF to allow for a change in the APC analyzer's source block, as discussed in section 9, below. The corrected values, JF, are obtained by the substitution

$$JF = 1.00033 \ JF \qquad (23)$$

This substitution, for concentrations near normal air, is equivalent to raising JF by 0.11 ppm. The factor is as derived by Bacastow et al. [1983b]. The results of using the above formulism to calculate mole fractions for the special CO_2-in-air calibrations of 1981, 1982, and 1983 are compared with the direct manometric data in Tables 7a to 7c. The agreement is highly satisfactory.

8. Test of the Validity of the Formulation

A critical test of the reliability of the formulation of the previous two sections is to compute mole fractions for the CO_2-in-air gas standards analyzed on the APC infrared gas analyzer prior to central date, CD83. In previous reports by Bacastow et al. [1983b] and Keeling et al. [1983] this comparison was done indirectly and expressed by a carrier gas correction factor. The new formulation provides a means for a straight forward computation of XAIR which can be compared directly with manometric data, not only for the primary standards (white stripe cylinders) but also for the special set of 1982 standards (blue strip

and NOAA cylinders) and miscellaneous standards analyzed as early as 1973 (red stripe cylinders). The data for the latter are assembled in Table 8.

First, annual average values of the difference between the infrared analyses, XAIR, and (time invarient) manometric long term average data, XMANO, are listed. For CO_2-in-air mixtures the differences are all small, as expected since the computations of XAIR are based on a calibrating curve for CO_2-in-air mixtures. For CO_2-in-N_2+O_2 mixtures the differences, XAIR-XMANO, reflect varying mole fractions of oxygen. For cylinder nos. 35452 and 35434, which contain less oxygen than air, the differences are approximately 0.60 ppm more positive, reflecting the smaller shift in infrared analyzer response, from CO_2-in-N_2, than for air. For cylinder nos. 35441 and 35442, with approximately two and three times the oxygen fraction of air, respectively, the differences, XAIR-XMANO are negative by circa 3 and 7 ppm, respectively. These results are especially useful to check on changes in infrared analyzer response because they amplify the change compared to that of CO_2-in-air mixtures.

To obtain comparable results for all mixtures listed, the mean departures of XAIR-XMANO from their long term averages are computed. The departures for the two high oxygen mixtures are computed separately so that they can be compared with the other six mixtures, having normal or near-normal oxygen mole fractions. It can be seen that annual average departures from the long term means from 1973 through 1983 are negligibly small (i.e. less than 0.10 ppm) for all years. A satisfactory result could be seen for 1981 and 1982 from the data of Tables 7a

and 7b. This eleven year history is more important, however; it indi-
cates that both the analyzer optical system and the gas mixtures them-
selves have remained stable over a long time period.

9. Source Block Correction

As discussed by Bacastow et al. [1983b] the ascarite trap on the
APC analyzer source block was replaced on 30 October, 1980. Bacastow et
al. applied a correction factor of 1.00033 to drift corrected J as com-
puted from data assembled in their Table 7. We have not been able to
verify the data of this table because records were not kept of the
analysis dates for which the 'before' and 'after' mean values were cal-
culated. In Table 9 we list a new version of the data, and we recompute
this shift. We used computed values of JF in which we reverse the
correction already made by raising the observed difference by 0.11 ppm
(i.e. .00033 times J) in the column labeled "$\triangle$J + 0.11". In Table 9 we
have included data for two gas mixtures containing two and three times
normal oxygen, data not so used by Bacastow et al. [1983b]. For these
mixtures, the shift in drift corrected index ($\triangle$JF) is reduced, in the
entries appearing in the final column, by the ratio of oxygen concentra-
tions in normal air to oxygen concentration in the mixture. The new
factor (1.00031) is nearly identical with the previous when the data
again are weighted by σ^{-2}. In our computations of XAIR we have, for
convenience, retained the previous factor, since the new result is
negligibly different.

To establish a date on which the source block correction should
begin, we have searched our laboratory records for indications of
replenishment of the ascarite. The last indication found was entered in

a laboratory notebook on 20 November, 1970. Records of Mr. David Moss, engineer of the CO_2 project, indicate that the entire optical system of the APC analyzer was replaced on 15 February, 1972. A few months later, on 19 June, 1972, the detectors of that replaced system were themselves replaced causing a further change in the optical system which could influence the difference in response of the analyzer to CO_2-in-air when calibrated with CO_2-in-N_2 standards. Subsequently no important optical changes have occurred; the detectors have been no. "119a" in the sample path, and no. "IV" in the reference path up to the present time (January, 1984). Thus 19 June, 1972 is the earliest date on which the present method of computing XAIR directly applies. It is likely that the ascarite trap was working properly at the time of installation of the new optical system, since a spent trap would have been obvious to the installer. Thus a source block correction is not justified in early, 1972, and probably not for at least a year after that time.

On several occasions between 19 June, 1972 and 19 September, 1975 electrical adjustments were made which resulted in abrupt shifts in instrument sensitivity. Nevertheless (see Table 8), XAIR values of red stripe cylinders, based on analyses as early as December, 1972, indicated no systematic shifts associated with these changes in sensitivity. Indeed, averages for XAIR for each period of constant electrical setting, agree within 0.10 ppm as do the annual averages of Table 8, from 1973 onward. These data are more consistent when a source block correction is applied back to the beginning of the analyses of the red stripe cylinders.

Therefore, whether the consistency of the data of Table 8 is a result of a need for a source block correction or some unidentified compensating change in the APC analyzer, we retain the source block correction back to 19 June, 1972. Before that date, because the optical system was different, there is no basis for a further backward projection. Accordingly the correction is applied between the dates 19 June, 1972 and 30 October, 1980. (To convert drift corrected adjusted index values to XAIR before 19 June, 1972 Keeling [1984] has established "period corrections" which are applied to the adjusted index, J, before computing XAIR.)

10. Pressure Correction of XAIR

In 1975 measurements were carried out at reduced pressure. These data indicate the relative responses of the APC analyzer to standards of varying carrier gas composition as the sample cell pressure is varied. The results are summarized in Table 4 of an article by Griffith et al. [1982]. The original data do not appear in any previous Scripps Report, however, and, to make them more generally available, they are shown in Tables 10 and 11. Table 10 lists the index data obtained with the APC analyzer, and Table 11 summarizes the calculations appearing in Table 4 of Griffith et al. We will not further discuss these data because of more recent data to be considered next.

In 1981 Bacastow et al. [1983b] report additional data at reduced pressure. The sources of the data are described in that report, but it is convenient to summarize them here in a form useful for computing concentrations of CO_2 in air. We recommend their use in place of the earlier data available to Griffith et al.

The newer data were found to fit the equation:

$$\triangle J/J = a_1 C(1 + a_2 C)\triangle P(1 + a_3\triangle P) \tag{23}$$

where $\triangle J$ (in ppm) is the correction to be applied to the adjusted index, J; the a_1 are coefficients determined by the least squares fitting procedure, $\triangle P$ denotes the difference in pressure (in mmHg) from ambient assumed to be 760.46 mmHg, and:

$$C = (\%O_2) + 1.5(\%A) \tag{24}$$

where $\%O_2$ and $\%A$ denote, respectively, the mole fractions of oxygen and argon in the gas mixture after removing all water vapor. The coefficients were found to have the values:

$$a_1 = 1.51 \times 10^{-7}$$
$$a_2 = 8.01 \times 10^{-4}$$
$$a_3 = 9.48 \times 10^{-4}$$

while, for normal air:

$$\%O_2 = 20.946$$
$$\%A = 0.934$$

Hence the parameter C is equal to 22.347 and the equation for normal air is:

$$\triangle J/J = 3.43 \times 10^{-6} \triangle P(1 + 9.48 \times 10^{-4} \triangle P) \tag{25}$$

No additional information was obtained at reduced pressure in 1982 or 1983. Accordingly, it is recommended to employ the above equations in connection with the computations of this report.

11. Comparison with previous calibration

The results of computing XAIR from J by the formulism of sections 6 and 7, above, are compared in Table 12 with a similar computation based on the 1982 calibration as reported by Keeling et al. [1983]. For prescribed values of J, in increments of 10 ppm from 170 to 450 ppm, XAIR was computed both ways. The differences (1983 calibration minus 1982 calibration) are listed in Table 12 for 1 July of each year from 1957 to 1983. It can be seen that the differences are invarient from 1957 through 1980 and, in the range of CO_2 concentration in normal air, are between 0.02 to 0.05 ppm. The cause of these differences being nonzero is the substitution of a cubic equation for converting JF to XAIR based on the 1983 calibrating curve of CO_2-in-air rather than the 1981 curve and a new cubic equation for CO_2-in-N_2 for 1980 (CUB9) to produce the drift correction from 1980 to 1983. The effect of the latter substitutions is seen in Table 13 which lists similar differences for XN2. For the concentration range of normal air the differences from 1957 to 1980 are 0.01 to 0.03 ppm for CO_2-in-N_2 mixtures. Thus, none of the changes when replacing the 1982 calibration with that for 1983 are significant for normal air computed up to the central date of the 1980 calibration.

For 1981, 1982 and 1983 the differences are larger, but are still scarcely significant except for 1983. This demonstrates that the recomputed drift corrections for 1981 and 1982 are not significantly different from those of Bacastow et al. [1983b] and Keeling et al. [1983]. The implimentation, for the first time, of a drift correction after the central date of the 1982 calibration has produced a change from assuming

no drift at all. The drift correction for normal air is approximately +0.20 ppm on 1 July, 1983.

For air data already reported using the 1982 calibration scale, there is thus no justification for a recomputation using the 1983 scale, provided that analyses precede the central date of the 1982 calibration, and are near the CO_2 concentration range of normal air (320-360 ppm).

12. Computer program

At the end of this report we list a FORTRAN subroutine which executes the calculations described in Sections 6 and 7, above. The main parameters of the program and their equivalent symbols, as given in this report, are listed.

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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.

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Keeling, C. D., "Adjustments to Applied Physics Infrared Analyzer Data to Allow for Differences in Response of the Various Detectors Used", Scripps Institution of Oceanography, 1984.

Table 1a. Manometric analyses of CO_2-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	196.86 196.89	196.88	196.84	3
	2	25 OCT 83	196.76 196.84	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	276.55	2
	2	30 SEP 83	276.50 276.53	276.52		
6078	1	29 AUG 83	310.81 310.71	310.76	310.75	2
	2	30 AUG 83	310.74 310.73	310.74		
2399	1	20 SEP 83	324.00 324.06	324.03	324.00	2
	2	20 SEP 83	323.94 324.02	323.98		
39239	1	16 AUG 83	332.75 332.77	332.76	332.71	5
	2	26 SEP 83	332.74 332.71	332.72		
	3	27 OCT 83	332.69 332.73	332.71		
	4	8 NOV 83	332.69 332.73	332.71		
	5	8 NOV 83	332.67 332.66	332.66		
39256	1	22 AUG 83	345.88 345.81 345.82	345.84	345.80	2
	2	22 AUG 83	345.96 345.65 345.70	345.77		
39272	1	17 AUG 83	360.60 360.59	360.60	360.59	2
	2	17 AUG 83	360.66 360.51	360.58		

Table 1a. (cont.)

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
1540	1	28 SEP 83	380.47 380.47	380.47	380.44	2
	2	28 SEP 83	380.43 380.42	380.42		
35299	1	4 OCT 83	415.02 414.98	415.00	415.01	2
	2	5 OCT 83	415.11 414.92	415.02		
35316	1	20 OCT 83	472.79 472.67	472.73	472.72	2
	2	21 OCT 83	472.76 472.69	472.72		

Table 1b. Manometric analyses of CO_2-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	101.40 101.40	101.40	101.37	2
	2	31 OCT 83	101.36 101.31	101.34		
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	297.01 296.92	296.96	296.99	2
	2	29 SEP 83	297.00 297.03	297.02		
71341	1	23 AUG 83	322.56 322.56	322.56	322.54	2
	2	23 AUG 83	322.53 322.50	322.52		
66638	1	24 AUG 83	338.53 338.51	338.52	338.52	2
	2	29 AUG 83	338.51 338.53	338.52		
66625	1	30 AUG 83	344.76 344.74	344.75	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	344.90 344.86	344.88		
66696	1	21 SEP 83	360.17 360.21	360.19	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	376.52 376.49	376.50		

Table 1b. (cont.)

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
71370	1	3 OCT 83	406.75 406.67	406.71	406.72	2
	2	4 OCT 83	406.71 406.72	406.72		
71479	1	7 OCT 83	453.58 453.58	453.58	453.66	2
	2	20 OCT 83	453.73 453.76	453.74		
67615	1	26 OCT 83	503.94 503.93	503.94	503.92	2
	2	26 OCT 83	503.95 503.84	503.90		

Table 1c. 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 CYLINDERS

CYL.NO.	1970	1974	1980	1982	1983	AVERAGE
2408		196.90 (2)	196.80 (2)		196.84 (3)	196.85 (7)
3753		246.02 (2)	245.99 (2)		246.08 (2)	246.03 (6)
7366	276.57 (3)	276.80 (2)	276.67 (2)		276.55 (2)	276.64 (9)
6078	310.95 (7)	310.82 (3)	310.96 (2)		310.75 (2)	310.90 (14)
2399	324.19 (8)	324.05 (4)	324.15 (2)		324.00 (2)	324.13 (16)
39239		332.78 (2)	332.72 (2)	332.64 (2)	332.71 (5)	332.71 (11)
39256				345.57 (3)	345.80 (2)	345.66 (5)
10069	355.64 (4)	355.60 (2)	355.82 (2)			355.68 (8)
39272				360.49 (3)	360.59 (2)	360.53 (5)
1540		380.56 (2)	380.45 (2)		380.44 (2)	380.48 (6)
35299		415.06 (2)	414.94 (2)		415.01 (2)	415.00 (6)
35316		472.97 (2)	472.72 (4)		472.72 (2)	472.78 (8)

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

CO2-IN-AIR CYLINDERS (RED STRIPES)

CYL.NO.	1974	1980	AVERAGE
35435	334.11 (3)		334.11 (3)
35405	336.99 (2)	336.98 (2)	336.98 (4)
34770	338.55 (2)	338.42 (2)	338.48 (4)
35401	352.96 (2)	352.72 (3)	352.82 (5)
35378	355.64 (2)		355.64 (2)

CO2-IN-N2+O2 CYLINDERS (RED STRIPES)

CYL.NO.	1974	1980	AVERAGE
44726	309.57 (2)		309.57 (2)
35452	323.86 (2)	323.66 (2)	323.76 (4)
35434	323.91 (2)	323.80 (2)	323.86 (4)
35442	327.02 (2)	326.81 (2)	326.92 (4)
35441	332.04 (2)	331.90 (2)	331.97 (4)
35389	335.36 (2)	335.48 (2)	335.42 (4)
75934		339.04 (2)	339.04 (2)
127524		340.38 (2)	340.38 (2)
44695	351.92 (2)		351.92 (2)
127693		361.48 (2)	361.48 (2)

CO2-IN-AIR CYLINDERS (WHITE STRIPES)

CYL.NO.	1981	1983	AVERAGE
66556	101.00 (2)	101.00 (2)	101.00 (4)
71251	213.15 (2)	213.16 (2)	213.16 (4)
34819	251.72 (2)	251.81 (2)	251.76 (4)
71286	296.56 (2)	296.67 (2)	296.62 (4)
71341	322.45 (2)	322.23 (2)	322.34 (4)
66638	338.08 (2)	338.21 (2)	338.14 (4)
66625	344.62 (2)	344.53 (4)	344.56 (6)
66696	359.87 (2)	359.92 (2)	359.90 (4)
71308	376.48 (2)	376.20 (2)	376.34 (4)
71370	406.39 (2)	406.41 (2)	406.40 (4)
71479	453.40 (2)	453.36 (2)	453.38 (4)
67615	503.20 (2)	503.62 (2)	503.41 (4)

Table 1e. Summary of manometric measurements (in ppm) of gas mixtures in Blue Stripe cylinders (SIO) and miscellaneous cylinders (NOAA). The number of determinations are shown in parentheses. Averages are weighted by the number of determinations.

CO2-IN-AIR CYLINDERS

CYL.NO.	1982			TYPE
34891	297.92	(	2)	SIO
3082	316.32	(	2)	NOAA
3074	329.08	(	2)	NOAA
62807	338.36	(	2)	SIO
3091	341.62	(	2)	NOAA
3071	352.40	(	2)	NOAA
62817	365.35	(	2)	SIO
3092	366.63	(	2)	NOAA
62814	424.92	(	2)	SIO

TABLE 2a. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1974 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.	23 MAY	30 MAY	30 JUN	27 JUN	11 JUL	05 AUG	22 AUG	09 SEP	AVG. I	AVG. J
2408	204.85 (19)	205.08 (19)	205.27 (20)	203.87 (20)	203.57 (21)	204.39 (22)	204.72 (20)	202.87 (20)	204.33	180.90
3753	253.95 (10)	254.41 (10)	254.39 (10)	253.60 (10)	253.59 (10)	253.93 (10)	254.28 (10)	253.14 (10)	253.91	241.32
7366	282.13 (10)	282.28 (10)	282.31 (10)	281.82 (10)	281.78 (10)	282.06 (10)	282.07 (10)	281.58 (10)	282.00	275.55
6078	311.17 (10)	311.34 (9)	311.27 (10)	311.17 (10)	311.16 (10)	311.28 (10)	311.27 (10)	310.98 (10)	311.21	311.14
35316	426.99 (19)	427.14 (19)	426.40 (20)	427.61 (20)	427.76 (20)	426.84 (20)	426.56 (20)	428.10 (20)	427.18	452.47
AVERAGE:	295.82	296.05	295.93	295.61	295.57	295.70	295.78	295.33		

CYL. NO.	24 MAY	31 MAY	21 JUN	28 JUN	12 JUL	06 AUG	23 AUG	10 SEP	AVG. I	AVG. J
2408	205.22 (20)	205.20 (20)	205.56 (20)	203.56 (20)	204.27 (20)	203.56 (20)	203.71 (20)	202.68 (20)	204.22	180.77
2399	321.91 (10)	321.94 (12)	322.00 (10)	322.02 (10)	321.94 (10)	321.98 (10)	322.06 (10)	321.87 (10)	321.97	324.26
10069	346.59 (11)	346.76 (10)	346.63 (10)	346.98 (10)	346.52 (10)	346.85 (10)	346.69 (10)	346.95 (10)	346.75	354.45
35299	389.15 (12)	389.24 (10)	388.94 (10)	390.02 (10)	389.40 (10)	389.84 (10)	389.70 (10)	390.08 (10)	389.55	406.61
35316	426.62 (19)	426.81 (21)	426.30 (20)	428.03 (18)	427.25 (20)	427.79 (21)	427.52 (20)	428.30 (20)	427.33	452.65
AVERAGE:	337.90	337.99	337.89	338.12	337.88	338.00	337.94	337.98		

CYL. NO.	10 OCT	14 OCT	17 OCT	22 OCT	30 OCT	31 OCT	01 NOV	04 NOV	AVG. I	AVG. J
6078	311.28 (10)	311.33 (9)	311.19 (11)	311.15 (10)	311.32 (10)	311.31 (10)	311.24 (10)	311.27 (10)	311.26	311.21
2399	321.83 (10)	322.05 (10)	321.95 (10)	321.96 (9)	322.13 (10)	321.87 (10)	321.88 (10)	321.88 (10)	321.94	324.22
39239	328.96 (20)	329.06 (18)	329.03 (18)	328.96 (20)	329.04 (21)	329.02 (20)	328.98 (20)	328.94 (20)	329.00	332.82
10069	346.70 (12)	346.86 (14)	346.91 (10)	346.88 (10)	346.68 (10)	346.74 (10)	346.63 (10)	346.76 (10)	346.77	354.48
1540	365.15 (25)	365.40 (20)	365.63 (20)	365.34 (24)	365.00 (20)	365.37 (20)	365.12 (19)	365.18 (20)	365.27	377.02
35299	389.04 (12)	389.83 (10)	390.12 (12)	389.69 (10)	389.06 (10)	389.65 (10)	389.13 (10)	389.13 (11)	389.46	406.50
AVERAGE:	343.83	344.09	344.14	344.00	343.87	343.99	343.83	343.86		

Summary of Adjusted Index averages (J) for the 1974 calibration.

CYL. NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	180.83	1.10	16
3753	241.32	0.55	8
7366	275.55	0.32	8
6078	311.17	0.11	16
2399	324.23	0.10	16
39239	332.82	0.05	8
10069	354.47	0.17	16
1540	377.02	0.24	8
35299	406.55	0.50	16
35316	452.55	0.78	16

TABLE 2b. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1980 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.	04 AUG	25 AUG	22 SEP	25 SEP	30 SEP	02 OCT	07 OCT	09 OCT	AVG. I	AVG. J
2408	201.04 (10)	201.50 (9)	200.70 (9)	200.91 (11)	201.23 (9)	201.22 (18)	200.96 (9)	201.25 (18)	201.10	176.96
3753	251.76 (10)	252.08 (9)	251.74 (9)	251.98 (9)	252.03 (9)	251.97 (9)	252.00 (9)	252.05 (9)	251.95	238.93
7366	280.44 (10)	280.65 (9)	280.54 (9)	280.57 (9)	280.68 (9)	280.59 (9)	280.62 (9)	280.67 (9)	280.60	273.84
6078	310.34 (10)	310.43 (9)	310.51 (9)	310.46 (9)	310.50 (9)	310.47 (9)	310.50 (9)	310.51 (9)	310.46	310.23
2399	321.31 (10)	321.34 (9)	321.31 (9)	321.41 (9)	321.41 (9)	321.35 (9)	321.41 (9)	321.40 (9)	321.37	323.53
39239	328.52 (10)	328.54 (9)	328.54 (9)	328.55 (9)	328.51 (9)	328.50 (9)	328.49 (9)	328.44 (9)	328.51	332.23
10069	346.77 (10)	346.54 (9)	346.62 (9)	346.75 (9)	346.64 (11)	346.65 (13)	346.70 (9)	346.67 (9)	346.67	354.36
1540	365.34 (10)	365.08 (9)	365.20 (9)	365.37 (9)	365.37 (9)	365.41 (9)	365.33 (9)	365.41 (9)	365.31	377.07
35299	390.07 (12)	389.67 (9)	389.92 (9)	390.10 (9)	390.15 (9)	390.06 (9)	390.14 (9)	390.10 (9)	390.03	407.19
35316	428.31 (11)	427.48 (9)	428.28 (9)	428.44 (9)	428.89 (9)	428.81 (9)	428.65 (18)	428.53 (9)	428.42	453.98
AVERAGE:	322.39	322.33	322.34	322.45	322.54	322.50	322.48	322.50		

Summary of Adjusted Index averages (J) for the 1980 calibration.

CYL. NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	176.96	0.30	8
3753	238.93	0.16	8
7366	273.84	0.10	8
6078	310.23	0.07	8
2399	323.53	0.06	8
39239	332.23	0.05	8
10069	354.36	0.09	8
1540	377.07	0.15	8
35299	407.19	0.19	8
35316	453.98	0.54	8

TABLE 2c. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1981 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.	31 AUG	03 SEP	08 SEP	10 SEP	14 SEP	AVG. I	AVG. J
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
AVERAGE:	309.46	309.46	309.31	309.49	309.38		

Summary of Adjusted Index averages (J) for the 1981 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	176.68	0.22	5
7366	273.89	0.09	5
39239	332.07	0.05	5
35316	453.20	0.09	5

TABLE 2d. Applied Physics analyzer results in Index units, I, for mano-
metrically analyzed standards during 1982 calibration. The number of
comparisons is shown in parentheses. Averages, not weighted, are ex-
pressed 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 2e. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1983 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.	12 AUG		16 SEP		23 SEP		28 SEP		06 OCT		AVG. I	AVG. J
2408	200.32	(10)	199.74	(14)	199.65	(10)	199.48	(10)	199.87	(14)	199.81	175.39
3753	251.55	(10)	251.31	(10)	251.19	(10)	251.10	(10)	251.44	(10)	251.32	238.16
7366	280.29	(10)	280.08	(12)	280.05	(10)	280.00	(10)	280.22	(10)	280.13	273.27
6078	310.07	(10)	310.02	(10)	309.99	(10)	309.99	(10)	310.18	(10)	310.05	309.73
2399	320.98	(10)	320.97	(10)	320.97	(10)	320.98	(10)	321.11	(10)	321.00	323.07
39239	328.11	(10)	328.04	(10)	328.05	(14)	328.08	(10)	328.13	(10)	328.08	331.70
39256	338.40	(10)	338.39	(10)	338.44	(10)	338.34	(10)	338.48	(10)	338.41	344.29
39272	349.91	(10)	349.81	(10)	349.81	(10)	349.79	(10)	349.91	(10)	349.85	358.23
1540	364.86	(10)	364.85	(10)	364.83	(10)	364.77	(10)	364.83	(10)	364.83	376.49
35299	389.37'	(10)	389.32	(10)	389.37	(10)	389.26	(10)	389.29	(10)	389.32	406.33
35316	427.39	(10)	427.23	(10)	427.26	(14)	427.23	(10)	427.29	(10)	427.28	452.59

AVERAGE: 323.75 323.61 323.60 323.55 323.70

Summary of Adjusted Index averages (J) for the 1983 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
2408	175.39	0.39	5
3753	238.16	0.22	5
7366	273.27	0.15	5
6078	309.73	0.10	5
2399	323.07	0.07	5
39239	331.70	0.05	5
39256	344.29	0.06	5
39272	358.23	0.07	5
1540	376.49	0.05	5
35299	406.33	0.06	5
35316	452.59	0.09	5

TABLE 2f. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1981 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 (WHITE STRIPES)

CYL.NO.	18 AUG	20 AUG	25 AUG	27 AUG	01 SEP	AVG. I	AVG. 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	318.11
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
AVERAGE:	313.64	313.84	313.68	313.80	313.51		

CYL.NO.	31 AUG	03 SEP	08 SEP	10 SEP	14 SEP	AVG. I	AVG. J
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
AVERAGE:	332.76	332.80	332.65	332.82	332.67		

Summary of Adjusted Index averages (J) for the 1981 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
66556	25.96	0.76	5
71251	195.89	0.35	10
34819	242.85	0.22	5
71286	291.98	0.07	10
71341	318.11	0.06	5
66638	333.51	0.06	10
66625	339.64	0.05	5
66696	353.91	0.05	5
71308	368.83	0.07	5
71370	394.84	0.09	10
71479	433.35	0.18	5
67615	470.94	0.22	10

TABLE 2g. Applied Physics analyzer results in Index units, I, for mano-
metrically analyzed standards during 1982 calibration. The number of
comparisons is shown in parentheses. Averages, not weighted, are ex-
pressed 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 2h. Applied Physics analyzer results in Index units, I, for manometrically analyzed standards during 1983 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

CYL.NO.	12 AUG		16 SEP		23 SEP		28 SEP		06 OCT		AVG. I	AVG. J
71251	215.95	(10)	215.57	(10)	215.42	(10)	215.32	(10)	215.63	(10)	215.58	194.61
34819	254.68	(10)	254.42	(12)	254.33	(10)	254.28	(10)	254.54	(10)	254.45	241.98
71286	295.17	(10)	295.09	(10)	295.04	(10)	295.00	(10)	295.15	(10)	295.09	291.50
71341	316.46	(10)	316.44	(10)	316.41	(10)	316.36	(10)	316.53	(10)	316.44	317.52
66638	329.32	(10)	329.27	(10)	329.28	(10)	329.30	(10)	329.36	(10)	329.31	333.20
66625	334.29	(10)	334.27	(10)	334.28	(10)	334.24	(16)	334.37	(10)	334.29	339.27
66696	346.10	(10)	346.06	(10)	346.04	(10)	346.00	(10)	346.18	(10)	346.08	353.64
71308	358.19	(10)	358.15	(14)	358.11	(10)	358.13	(10)	358.19	(10)	358.15	368.35
71370	379.72	(10)	379.63	(10)	379.62	(10)	379.58	(10)	379.63	(10)	379.64	394.53
71479	411.10	(10)	410.86	(10)	410.96	(16)	410.90	(10)	411.00	(10)	410.96	432.70
67615	441.93	(10)	441.74	(10)	441.83	(10)	441.70	(10)	441.92	(10)	441.82	470.31
AVERAGE:	334.81		334.68		334.67		334.62		334.77			

Summary of Adjusted Index averages (J) for the 1983 calibration.

CYL.NO.	AVG. J	SIGMA	NO. OF DAILY SETS
71251	194.61	0.29	5
34819	241.98	0.19	5
71286	291.50	0.09	5
71341	317.52	0.07	5
66638	333.20	0.05	5
66625	339.27	0.06	5
66696	353.64	0.09	5
71308	368.35	0.05	5
71370	394.53	0.06	5
71479	432.70	0.11	5
67615	470.31	0.12	5

TABLE 3. Applied Physics analyzer results in Index units, I, for three-monthly analyzed standards around the 1980 calibration. The number of comparisons is shown is parentheses. Averages, not weighted, are expressed in Index units, I, and Adjusted Index units, J.

CYL. NO.	14 AUG 1979	06 NOV 1980	04 NOV 1980	21 OCT 1980	26 SEP 1981	AVG. I	AVG. J
39256	338.59 (10)	338.84 (9)	338.77 (9)	338.89 (9)	338.78 (10)	338.77	344.73

CYL. NO.	14 AUG 1979	07 NOV 1980	04 NOV 1980	11 SEP 1980	26 SEP 1981	AVG. I	AVG. J
39272	350.09 (10)	350.35 (10)	350.28 (9)	350.29 (10)	350.22 (10)	350.25	358.71

Table 4. 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)	(J80−J74)/6	(J83−J80)/3
CO_2-IN-NITROGEN CYLINDERS							
2408	196.85		180.83	176.96	175.39	−0.65	−0.52
3753	246.03		241.32	238.93	238.16	−0.40	−0.26
7366	276.64	275.88	275.55	273.84	273.27	−0.29	−0.19
6078	310.90	311.49	311.17	310.23	309.73	−0.16	−0.17
2399	324.13	324.56	324.23	323.53	323.07	−0.12	−0.15
39239	332.71		332.82	332.23	331.70	−0.10	−0.18
39256	345.66			344.73	344.29		−0.15
10069	355.68	354.38	354.47	354.36		−0.02	
39272	360.53			358.71	358.23		−0.16
1540	380.48		377.02	377.07	376.49	0.01	−0.19
35299	415.00		406.55	407.19	406.33	0.11	−0.29
35316	472.78		452.55	453.98	452.59	0.24	−0.46

* 1970 and 1974 data are as they appear in Table 3 of Bacastow et al. 1983a.

Table 5. Coefficients used in computing mole fractions from infrared data

Year	Central Date	Y_{out}	Y_{in}	Name	C_0	C_1	C_2 $\times 10^4$	C_3 $\times 10^7$	Limits of Validity of J	
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
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 6. Data summary for 1981 and 1982 corrections for CO_2-in-Nitrogen standards
(All listed values are in ppm)

Cylinder No.	J81	JA81	JA83	JA83–JA81	Residuals from fit
1981 Calibration					to QUAD11:
2408	176.68	175.63	176.39	−0.24	.01
7366	273.89	273.50	273.25	−0.23	−.03
39239	332.07	331.76	331.70	−0.06	.02
35316	453.20	452.27	452.59	0.32	−.01
				Standard error:	.043

	J82	JA82	JA83	JA83–JA82	
1982 Calibration					to QUAD12:
7366	273.84	273.68	273.27	−0.41	−.01
39239	331.91	331.78	331.70	−0.08	.02
39256	344.43	344.31	344.29	−0.02	.04
39272	358.44	358.30	358.23	−0.07	−.04
35299	406.56	406.33	406.33	0.00	−.02
35316	453.01	452.63	452.59	−0.04	.01
				Standard error:	.038

Table 7a. Comparison of Manometric and Infrared calibrating data for Scripps CO_2 Project gas standards during the 1981 calibration. Quoted values are in ppm.

CO2-IN-AIR (WHITE STRIPES)

CYLINDER NO.	J	JA	(JA-J)	JF	(JF-JA)	XN2	XAIR	XAIR-XN2	XMANO	XAIR-XMANO
66556	25.96	23.37	-2.59	23.40	0.03	99.75	101.21	1.46	101.00	0.21
71251	195.89	195.01	-0.88	194.76	-0.25	211.37	213.26	1.89	213.16	0.10
34819	242.85	242.32	-0.53	242.08	-0.23	249.43	251.89	2.46	251.76	0.13
71286	291.98	291.64	-0.34	291.47	-0.17	293.38	296.61	3.22	296.62	-0.01
71341	318.11	317.81	-0.30	317.68	-0.12	318.63	322.32	3.69	322.34	-0.02
66638	333.51	333.20	-0.31	333.11	-0.09	334.16	338.13	3.98	338.14	-0.01
66625	339.64	339.33	-0.31	339.25	-0.07	340.47	344.57	4.10	344.56	0.01
66696	353.91	353.57	-0.34	353.53	-0.04	355.48	359.87	4.39	359.90	-0.03
71308	368.83	368.45	-0.38	368.45	0.01	371.65	376.35	4.69	376.34	0.01
71370	394.84	394.34	-0.50	394.43	0.09	401.03	406.29	5.26	406.40	-0.11
71479	433.35	432.59	-0.76	432.83	0.24	447.43	453.57	6.14	453.38	0.19
67615	470.94	469.83	-1.11	470.24	0.41	496.25	503.30	7.05	503.41	-0.11

Table 7b. Comparison of Manometric and Infrared calibrating data for Scripps CO_2 Project gas standards during the 1982 calibration. Quoted values are in ppm.

CO2-IN-AIR (BLUE STRIPES AND NOAA CYLINDERS)

CYLINDER NO.	J	JA	(JA-J)	JF	(JF-JA)	XN2	XAIR	XAIR-XN2	XMANO	XAIR-XMANO
34891	293.27	293.13	-0.14	292.85	-0.28	294.68	297.93	3.24	297.92	0.01
3082	312.02	311.90	-0.12	311.71	-0.18	312.76	316.33	3.58	316.32	0.01
3074	324.62	324.50	-0.12	324.37	-0.13	325.29	329.10	3.81	329.08	0.02
62807	333.55	333.42	-0.13	333.33	-0.10	334.37	338.36	3.98	338.36	0.00
3091	336.74	336.61	-0.13	336.53	-0.08	337.66	341.70	4.05	341.62	0.08
3071	346.89	346.76	-0.13	346.70	-0.05	348.25	352.50	4.25	352.40	0.10
62817	358.82	358.68	-0.14	358.65	-0.02	360.97	365.47	4.49	365.35	0.12
3092	360.01	359.86	-0.15	359.84	-0.02	362.26	366.78	4.51	366.63	0.15
62814	410.23	409.99	-0.24	410.01	0.02	419.41	425.02	5.61	424.92	0.10

Table 7c. Comparison of Manometric and Infrared calibrating data for Scripps CO_2 Project gas standards during the 1983 calibration. Quoted values are in ppm.

CO2-IN-AIR (WHITE STRIPES)

CYLINDER NO.	J	JA	(JA-J)	JF	(JF-JA)	XN2	XAIR	XAIR-XN2	XMANO	XAIR-XMANO
71251	194.61	194.61	0.00	194.61	0.00	211.25	213.14	1.89	213.16	-0.02
34819	241.98	241.98	0.00	241.98	0.00	249.34	251.80	2.46	251.76	0.04
71286	291.50	291.50	0.00	291.50	0.00	293.41	296.63	3.22	296.62	0.01
71341	317.52	317.52	0.00	317.52	0.00	318.47	322.15	3.68	322.34	-0.19
66638	333.20	333.20	0.00	333.20	0.00	334.24	338.22	3.98	338.14	0.08
66625	339.27	339.27	0.00	339.27	0.00	340.49	344.59	4.10	344.56	0.03
66696	353.64	353.64	0.00	353.64	0.00	355.60	359.98	4.39	359.90	0.08
71308	368.35	368.35	0.00	368.35	0.00	371.54	376.23	4.69	376.34	-0.11
71370	394.53	394.53	0.00	394.53	0.00	401.14	406.40	5.26	406.40	0.00
71479	432.70	432.70	0.00	432.70	0.00	447.26	453.40	6.14	453.38	0.02
67615	470.31	470.31	0.00	470.31	0.00	496.34	503.39	7.05	503.41	-0.02

Table 8. Annual averages of XAIR-XMANO (in ppm) of gas mixtures containing oxygen

Cyl. No:	CO$_2$-IN-AIR			CO$_2$-IN-N$_2$ + O$_2$				Av.	HIGH O$_2$ MIXTURES				Av.
%O$_2$:	35405 20.9	34770 20.9	35401 20.9	35452 18.8	35434 18.8	35389 20.9	Av.	Departure	35442 58.0	35441 41.0	35442 Reduced Departures from Average†	35441 Reduced Departures from Average†	Departure
1973	-0.04	-0.01	0.27	0.65	0.72	-0.18	0.24	0.05	-7.07	-3.31	0.02	0.05	0.04
1974	-0.23	-0.04	0.02	0.59	0.56	-0.16	0.12	-0.07	-7.34	-3.58	-0.08	-0.09	-0.08
1975	-0.01	-0.01	0.17	0.61	0.58	-0.10	0.21	0.02	-7.19	-3.52	-0.03	-0.06	-0.04
1976	-0.18	-0.07	-0.10	0.59	0.51	-0.07	0.11	-0.08	-7.27	-3.51	-0.05	-0.06	-0.06
1977	-0.19	-0.03	-0.04	0.62	0.61	0.04	0.17	-0.02	-7.19	-3.41	-0.03	-0.01	-0.02
1978	-0.08*	0.03	-0.11	0.62	0.67	0.05	0.20	0.01	-7.07	-3.42	0.02	-0.01	0.00
1979	-0.03	0.03	-0.01	0.70	0.69	0.12	0.25	0.06	-7.00	-3.26	0.04	0.07	0.06
1980	-0.07	0.02	0.02	0.66	0.62	0.02	0.21	0.02	-7.07	-3.35	0.02	0.03	0.02
1981	-0.06	0.04	-0.01	0.61*	0.79	-0.06*	0.22	0.03	-6.86	-3.23	0.09	0.09	0.09
1982	-0.11	0.00	-0.01	0.59	0.60	0.03	0.18	-0.01	-7.02	-3.32	0.04	0.04	0.04
1983	-0.05	0.01	0.06	0.59	0.61	0.10	0.22	0.03	-6.97	-3.26	0.05	0.07	0.06
Wt. Av.	-0.08	-0.01	0.05	0.61	0.61	-0.06	0.19	0.00	-7.12	-3.40			0.00

† Departures from Average divided by percent O$_2$ times 20.9.

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

Table 9. Date used to verify correction for change in the source block optical path (adjusted index values, JF and ΔJF in ppm, standard deviations shown in parentheses).

| Cylinder No. | Inclusive Dates (yr/mo/day) | | Average JF | | $\frac{\Delta J}{}$ After-minus before | $\Delta J +$ 0.11 | O_2 ratio | ΔJF corrected for O_2 variation |
	Before	After*	Before	After				
CO_2-IN-AIR CYLINDERS								
35405	800410–801028	801117–810929	331.94	331.94	0.00	0.11		0.11
			(.014)	(.007)	(.016)			(.016)
34770	" "	" "	333.47	333.47	0.00	0.11		0.11
			(.021)	(.012)	(.024)			(.024)
35401	800417– "	" "	347.03	346.99	−0.04	0.07		0.07
			(.022)	(.052)	(.056)			(.056)
CO_2-IN-N_2+O_2 CYLINDERS								
35452	790221–801029	801110–801114	319.78	319.78	0.00	0.11		0.11
			(.015)	(.026)	(.030)			(.030)
35434	" –800819	" –810206	319.83	319.90	−0.07	0.18		0.18
			(.066)	(.030)	(.072)			(.072)
35389	" "	" –801114	330.55	330.56	0.01	0.12		0.12
			(.075)	(.015)	(.076)			(.076)
35442	" –801029	" –800206	315.21	315.35	0.14	0.25	20.9/	0.09
			(.050)	(.031)	(.059)		58.0	(.021)
35441	" "	" "	323.92	323.94	0.02	0.13	20.9/	0.07
			(.046)	(.025)	(.052)		41.0	(.027)

Unweighted average:		0.108
Average weighted by σ^{-2}:		0.101
Weighted average concentration:		327
Correction factor:		0.00031

* Data for 810204 and 810205 omitted, because analyses were at reduced pressure.

Table 10. Applied Physics Analyzer results to obtain adjusted index data of Table 11.

(All Data are obtained from Reference Gas Report No. 27.)

Cylinder No.	Interval	Index (in ppm)	No. of Det'ns	No. of Run Days	Interval Date	Date	Adjusted Index (in ppm)	Remarks
2401	Before	308.48	135	14	10/14/69	11/14/74		Refgas Subcum Av.
	After	308.21	32	3	4/ 8/75	4/22/75		" " "
	Wt. Av.	308.43	167	17			307.76	Not in Refgas
39232	Before	314.87	161	14	12/21/72	11/14/74		Refgas Cum. Av.
	After	314.71	32	3	4/10/75	4/22/75		" Subcum. Av.
	Wt. Av.	314.84	193	17			315.57	Not in Refgas
3756	Before	321.39	168	17	1/ 9/75	3/15/75		Refgas Cum. Av.
	After	321.45	83	8	4/ 7/75	4/24/75		" " "
	Wt. Av.	321.41	251	25			323.57	Not in Refgas
4287	Before	328.61	139	14	4/20/73	11/15/74		Refgas Cum. Av.
	After	328.67	29	3	4/ 8/75	4/23/75		" Subcum. Av.
	Wt. Av.	328.62	168	17			332.36	Not in Refgas.
10077	Before	341.83	115	11	9/27/73	3/13/75		Refgas Cum. Av.
	After	341.98	20	2	4/14/75	4/18/75		" Subcum. Av.
	Wt. Av.	341.85	135	13			348.48	Not in Refgas
34816	Before	307.52	92	9	6/26/74	3/12/75		Refgas Cum. Av.
	After	307.50	20	2	4/ 8/75	4/16/75		" " "
	Wt. Av.	307.52	112	11			306.65	Not in Refgas
39382	Before	319.62	40	4	1/ 8/75	2/20/75		Refgas Cum. Av.
	After	319.58	22	2	4/10/75	4/16/75		" " "
	Wt. Av.	319.60	62	6			321.37	Not in Refgas
35260	Before	321.74	52	5	11/27/74	3/13/75		Refgas Cum. Av.
	After	321.82	24	2	4/10/75	4/11/75		" " "
	Wt. Av.	321.76	76	7			324.00	Not in Refgas
35380	Before	325.20	62	6	4/18/74	3/12/75		Refgas Cum. Av.
	After	325.31	20	2	4/ 8/75	4/16/75		" " "
	Wt. Av.	325.23	82	8			328.23	Not in Refgas
35405	Before	329.05	107	10	10/11/73	3/12/75		Refgas Cum. Av.
	After	329.11	21	2	4/8/75	4/16/75		" " "
	Wt. Av.	329.06	128	12			332.90	Not in Refgas

Table 10. (cont.)

Cylinder No.	Interval	Index (in ppm)	No. of Det'ns	No. of Run Days	Interval Date	Date	Adjusted Index (in ppm)	Remarks
35401	Before	341.27	212	21	10/11/73	3/12/75		Refgas Cum. Av.
	After	341.36	20	2	4/ 8/75	4/16/75		" " "
	Wt. Av.	341.28	232	23			347.79	Not in Refgas
35442	Before	315.54	137	13	4/20/73	3/13/75		Refgas Cum. Av.
	After	315.38	21	2	4/ 9/75	4/17/75		" " "
	Wt. Av.	315.52	158	15			316.40	Not in Refgas
35441	Before	322.56	141	13	4/20/73	3/13/75		Refgas Cum. Av.
	After	322.32	26	2	4/ 9/75	4/17/75		" " "
	Wt. Av.	322.52	167	15			324.93	Not in Refgas

Table 11. Data obtained in 1974 to determine the pressure correction to the computation of CO_2 concentrations in air when CO_2-in-N_2 standards are used with the Scripps Applied Physics Analyzer.

Cylinder No.	Gas Type	Atmospheric Pressure*		700 mb or 511 mm Hg**		350 mb or 256 mm Hg***	
		No. of Comparisons	Measured Infrared Adjusted Index (J) (ppm)	No. of Comparisons	ΔJ (ppm)	No. of Comparisons	ΔJ (ppm)
2401	CO_2 in N_2	167	307.76	66	−.14	21	+.05
39232	"	193	315.57	10	−.08	11	−.14
3756	"	251	323.57	94	+.41	12	+.31
4287	"	168	332.36	45	+.28		
10077	"	135	348.48	40	+.14		
				Av of 8 CO_2 in N_2 = +.10		σ_i = .22	
34816	Compressed Air	112	306.65	44	−.42		
39382	"	62	321.37	10	−.33	10	−.53
35260	"	76	324.00	10	−.32	10	−.58
35380	"	82	328.23	56	−.50		
35405	"	128	332.90	46	−.48		
35401	"	232	347.79	46	−.26		
				Av of 6 = −.38		σ_i = .10	
35442	CO_2 in 60% O_2, 40% N_2	158	316.40	40	−1.10	20	−2.05
35441	CO_2 in 40% O_2, 60% N_2	167	324.93	30	−.80	20	−1.61

* Measured before and after reduced pressure calibrations (see Table 10)

** Measured on 3/26/65, 3/27/75, 3/28/75, 3/31/75 and 4/2/75

*** Measured on 4/4/75

Table 12. Comparison of XAIR computed in 1982 and 1983, (1983 minus 1982) in hundredth of a ppm.

J	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83
170	28	28	28	28	28	28	28	28	27	27	27	27	28	28	28	28	28	28	28	27	27	27	27	27	26	16	112
180	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	25	25	25	25	24	16	106
190	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	23	23	22	15	100
200	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	21	20	15	93
210	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	18	14	86
220	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	16	13	80
230	17	17	17	17	17	17	17	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	14	12	73
240	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	14	14	14	14	14	12	11	67
250	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	12	12	10	10	60
260	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	8	9	54
270	10	10	10	10	10	10	10	10	9	9	9	9	9	9	9	10	10	9	9	9	9	9	9	9	6	8	49
280	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	5	7	43
290	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	6	6	6	6	6	3	6	38
300	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	2	5	34
310	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	0	4	30
320	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	26
330	3	3	3	3	3	3	3	3	3	3	3	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	3	23
340	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	2	21
350	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-3	2	19
360	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	2	19
370	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	3	19
380	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	20
390	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	0	4	22
400	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	1	5	25
410	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	4	7	29
420	10	10	10	10	10	11	11	10	10	10	11	11	11	11	11	11	11	11	11	10	10	10	10	10	6	8	34
430	13	13	13	13	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	13	13	13	9	11	40
440	17	17	17	17	17	17	17	17	17	17	18	18	18	18	18	18	18	18	17	17	17	17	17	17	13	13	48
450	21	21	21	21	21	22	22	22	22	22	22	22	22	23	23	23	22	22	22	21	21	21	21	21	17	16	57

Table 13. Comparison of "XN2" computed in 1982 and 1983, (1983 minus 1982) in hundredth of a ppm.

YEAR J	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83
170	1	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	-9	86
180	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	-9	81
190	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	-8	75
200	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	-7	70
210	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	-6	65
220	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	-5	61
230	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	-4	56
240	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	-4	51
250	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-3	-3	47
260	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-2	-2	43
270	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-3	-1	39
280	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-3	-1	35
290	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-2	0	32
300	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-2	1	29
310	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-2	1	26
320	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	2	24
330	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	2	22
340	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	3	21
350	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-2	3	20
360	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	19
370	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	19
380	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	19
390	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	3	20
400	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	2	22
410	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-1	2	23
420	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	-2	1	26
430	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	0	29
440	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	-2	-2	32
450	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-3	-4	36

```
C*********************************************************************
C
C
C
C          SUBROUTINES TO COMPUTE MOLE FRACTION FOR CO2-IN-N2 AND
C          CO2-IN-AIR BASED ON THE 1983 CALIBRATION.
C               A SINGLE CALL TO CALDAY IS NECESSARY BEFORE CALLING
C          CAL83.  CAL83 CAN THEN BE CALLED AS MANY TIMES AS DESIRED.
C            INPUTS TO CAL83 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 CAL83:
C                 DAYN: DAY NUMBER (REAL) DAYS SINCE 1 JAN. 1955.
C                 FJ: DRIFT CORRECTED "J" VALUE (REAL)
C                 X: MOLE FRACTION VALUE (REAL)
C
C
C
C.....TABLE OF VARIABLES, ARRAYS, AND FUNCTIONS:
C
C       NAME (DATA TYPE)         DESCRIPTION IN 1983 CALIBRATION REPORT
C
C       ACUB83 (REAL            "ACUB13".
C              FUNCTION)
C       AJ     (REAL)           "JA"="J" AFTER FIRST LEVEL DRIFT CORRECTION.
C       BJ     (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       CDSBO  (REAL)           START DATE FOR SOURCE BLOCK CORRECTION, EXPRESSED
C                               AS THE NUMBER OF DAYS SINCE 1/1/55.
C       CJ     (REAL)           "JC"="J" AFTER THIRD LEVEL DRIFT CORRECTION.
C       CUB60  (REAL            "CUB1(J+LIN3(J))".
C              FUNCTION)
C       CUB74  (REAL            "CUB1".
C              FUNCTION)
C       CUB80  (REAL            "CUB2".
C              FUNCTION)
C       CUB83  (REAL            "CUB10".
C              FUNCTION)
C       CUB83I (REAL            INVERSE OF "CUB10".
C              FUNCTION)
C       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       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       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      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      X60    (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".
C
       SUBROUTINE CAL83(ID,GAS,Y59,DAYN,FJ,X)
       COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
      &              DAY74,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') 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,
      &              DAY74,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)
```

```fortran
      CD80=DAYNO(80,9,19)
      CD81=DAYNO(81,9,7)
      CD82=DAYNO(82,11,18)
      CD83=DAYNO(83,09,17)
      CDSB=DAYNO(80,10,30)
C.....THIS STATEMENT NOT REFERENCED
C     DAY74=DAYNO(74,7,1)
      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 CORR1(DAYN,Y59,AJ)
      COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
     &           DAY74,CDSB
C
C.....THIS PROCEDURE EXTRAPOLATES PRIOR TO CD60.
      IF(DAYN.GT.CD74)GO TO 20
      X60=CUB60(Y59)
      X74=CUB74(Y59)
      XX=(X74*(DAYN-CD60)+X60*(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=CUBQ80(Y59)
```

```fortran
      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
      FUNCTION CUB60(A60)
      DJ=0.576-0.005011*A60
      A74 = A60 + DJ
      CUB60=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 CUBM74(YJ)
C.....THIS FUNCTION IS NOT REFERENCED IN THIS PROGRAM.
C     CUBM74=76.582+YJ*(0.584910+YJ*(3.1151E-4+7.3225E-7*YJ))
C.    RETURN
C     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 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
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 CUB83(A83)
```

```
      CUB83=86.946+A83*(0.537883+A83*(3.8471E-4+6.8562E-7*A83))
      RETURN
      END
C
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
      SUBROUTINE CORR2(DAYN,AJ,BJ)
      COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
     &          DAY74,CDSB
      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)
      QUAD81(AJ) =   0.110 + AJ*(-0.003606 + 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 80
      DJ70=QUAD70(AJ)
      DJ=(DAYN-CD60)/(CD70-CD60)*DJ70
      GO TO 80
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 80
C
   20 IF(DAYN.GT.CD74)GO TO 30
      DJ72=QUAD72(AJ)
      DJ=(CD74-DAYN)/(CD74-CD72)*DJ72
      GO TO 80
C
   30 IF(DAYN.GT.CD78)GO TO 40
      DJ78=QUAD78(AJ)
      DJ=(DAYN-CD74)/(CD78-CD74)*DJ78
      GO TO 80
C
   40 CONTINUE
      IF(DAYN.GT.CD80)GO TO 50
      DJ78=QUAD78(AJ)
      DJ=(CD80-DAYN)/(CD80-CD78)*DJ78
      GO TO 80
C
   50 CONTINUE
      IF (DAYN.GT.CD81) GO TO 60
      DJ81=QUAD81(AJ)
      DJ=DJ81*(DAYN-CD80)/(CD81-CD80)
```

```fortran
         GO TO 80
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 80
C
   70 CONTINUE
      IF (DAYN.GT.CD83) GO TO 80
      DJ82=QUAD82(AJ)
      DJ=DJ82*(CD83-DAYN)/(CD83-CD82)
C
   80 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,
     &            DAY74,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,
     &            DAY74,CDSB
C
      IF (DAYN.GT.CD80) GO TO 10
      XXX=CUBQ80(CJ)
      XN2=XXX
      FJ=CUB83I(XXX)
      GO TO 20
C
   10 FJ=CJ
      XN2=CUB83(FJ)
```

```
  C
     20 CONTINUE
        RETURN
        END
  C
  C
        SUBROUTINE CORR5(DAYN,FJ,XAIR)
        COMMON/CAL/CD60,CD62,CD66,CD70,CD72,CD74,CD78,CD80,CD81,CD82,CD83,
       &          DAY74,CDSB
  C
  C.....ASCARITE TRAP CLEANED ON CDSBO, CONTAMINATED AND NOT CLEANED
  C     AGAIN UNTIL CDSB.
  C
        CDSBO=DAYNO(72,06,19)
        IF ((DAYN.LT.CDSB) .AND. (DAYN.GE.CDSBO))
       &FJ=FJ+0.00033*FJ
        XAIR=ACUB83(FJ)
  C
        RETURN
        END
  C
  C
        FUNCTION ACUB83(C83)
        ACUB83=88.574 + C83*(0.529183+C83*(4.42387E-4+6.5448E-7*C83))
        RETURN
        END
  C
  C       END OF X83 SUBROUTINES
  C
  C******************************************************************************
```
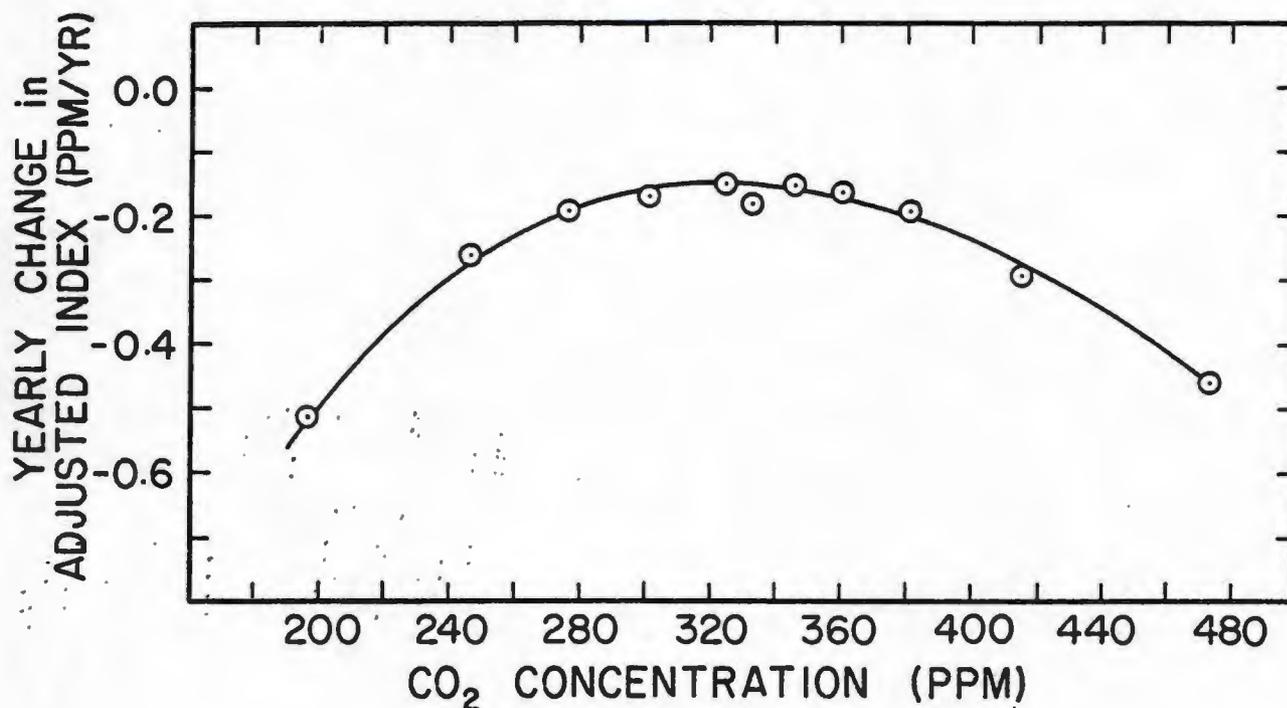
Figure 1. System drift in CO_2-in-N_2 gas standards between 1980 and 1983 calibration periods based on the change in adjusted index of 11 standards (see final column of Table 4). The smooth curve is a plot of the difference between cubic equations, CUB9 and CUB10, fit separately to the data for 1980 and 1983, respectively. The actual differences are divided by three to establish the annual drift rate.
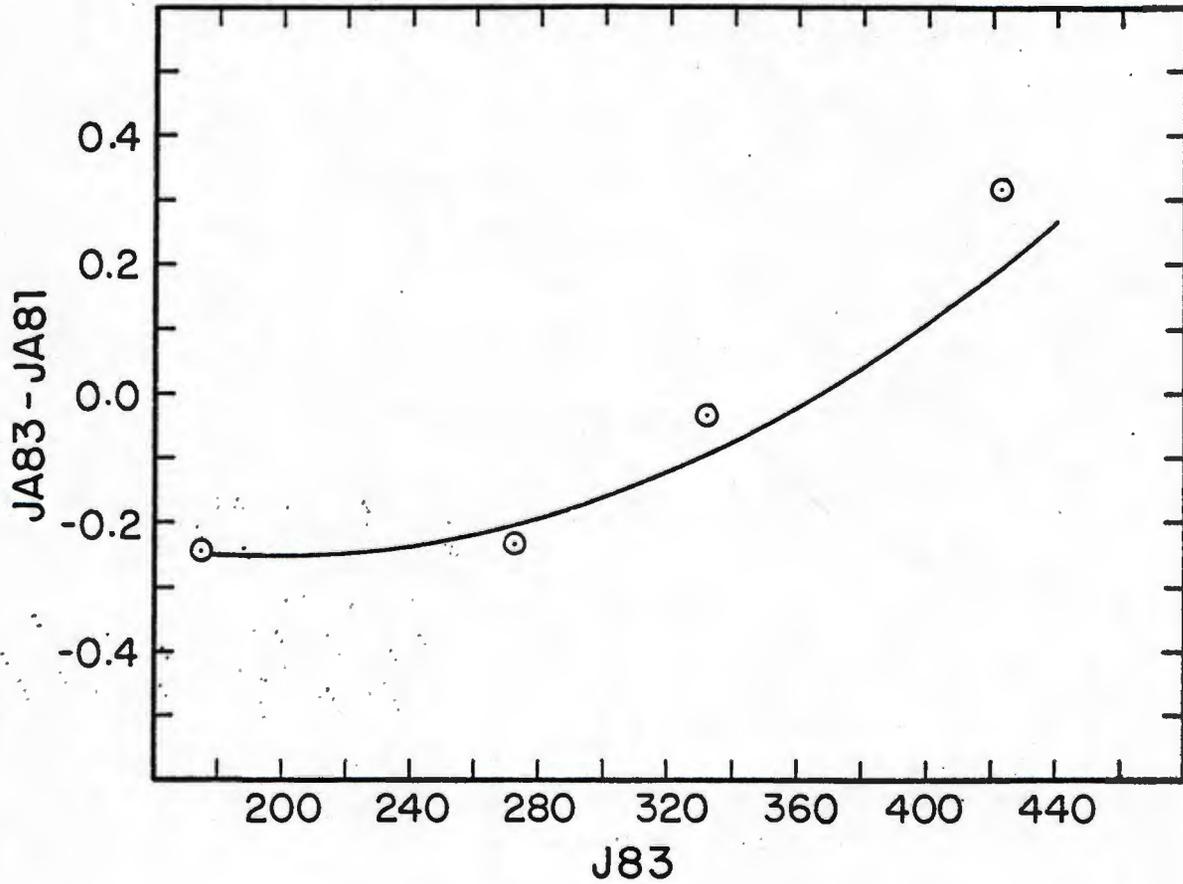
Figure 2. - Second level correction for the special calibration period of 1981. The circles indicate data from Table 6. The smooth curve represents QUAD11, a quadratic fit of the differences, JA83-JA81. The data on both axes are expressed in ppm.
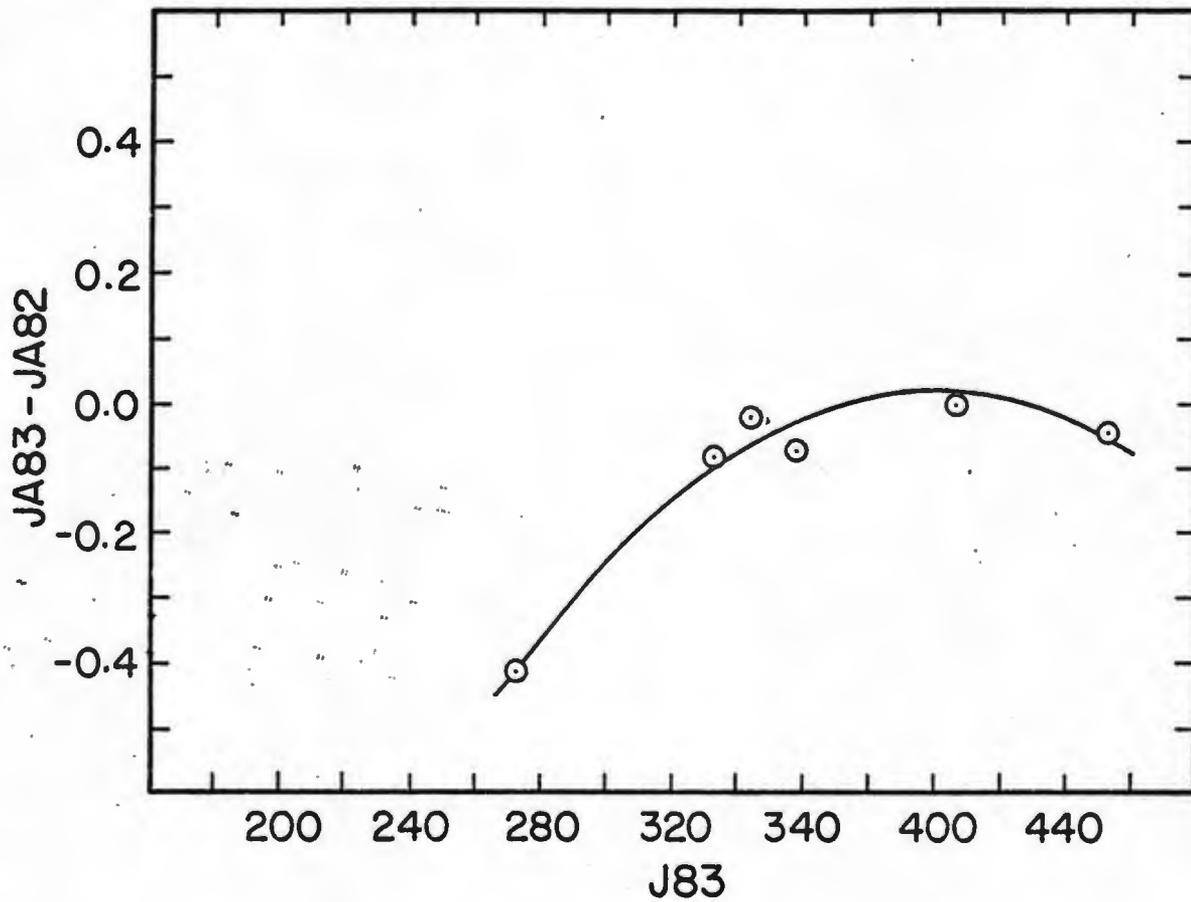
Figure 3. Second level correction for the special calibration period of 1982. The circles indicate data from Table 6. The smooth curve represents QUAD12, a quadratic fit to the differences, JA83-JA82. The data on both axes are expressed in ppm.