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

by

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Table of Contents

This report describes the system of CO_2-in-N_2 gas standards developed at Scripps Institution of Oceanography for the purpose of calibrating gas analyzers used to measure atmospheric CO_2. These standards were adopted by the World Meteorological Organization in 1976 to serve provisionally in their network of Base Line Monitoring stations until a system of CO_2-in-air standards is instituted. This report sets forth the procedures for revising the computations developed previously in connection with a calibration in 1974, and in use prior to completion of this 1980 calibration.

Brief History and Introduction

In preparation for atmospheric CO_2 measurements during the International Geophysical Year, 1957-58, C. D. Keeling assigned "Index" values to two gas mixtures of CO_2-in-N_2. The Index values were chosen to be close to true concentrations, in parts per million by volume (ppm), but were arbitrarily fixed irrespective of later data which permitted more accurate assignments. Other mixtures of CO_2-in-N_2, and CO_2-in-air, were then compared to these and assigned Index values through a linear interpolation or extrapolation based on the response of the Scripps Institution Applied Physics (AP) non-dispersive infrared analyzer. Later on these two original gas mixtures were used up and subsequently new mixtures were compared to previously assigned mixtures in an ever lengthening overlapping scheme of intercalibration.

Subsequent manometric calibrations of gas mixtures in 1959 through 1961, led C. D. Keeling to establish a second "Adjusted Index" scale, closer to true concentration. This scale is, however, still linear in the response of the Applied Physics analyzer and consequently also linear in the Index scale. We will here designate these concentration scales by the letters I and J, for Index and Adjusted Index, respectively. Many data have been reported on the J scale. However, the I scale continues to be used by the Scripps Institution, especially for routine, internally distributed, reports. The relationship between the scales is by definition:

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

Extensive calibrations have confirmed that this Adjusted Index scale, J, is close to true concentration in the region 310-340 ppm (parts per million by volume of dried gas), although it deviates at higher and lower concentrations owing to the nonliniarity of the response of the Applied Physics analyzer.

Since gas calibration mixtures that are directly compared to air at atmospheric CO_2 measuring stations are typically depleted within a few weeks, a hierarchy of gas standards was created to calibrate these so called "working gas" mixtures. Systematic procedures were developed to intercompare these additional reference gases and to create new ones. This hierarchy and these procedures are called the Scripps CO_2 Reference Gas System.

This system consists of manometric standards, Scripps reference gas system standards, assigned standards, and surveillance standards (Figure 1). The manometric standards, as their name suggests, have been analyzed manometrically and are primary standards used to calibrate all other gas mixtures, but especially the Scripps Reference Gas System standards. In recent years the latter have been two in number: a High Span (at ~340 ppm) and the Principal Span (at ~320 ppm). Assigned standards, prepared for use in atmospheric CO_2 measurement by the Scripps Institution or by other institutions, are routinely compared with the Scripps system standards. Surveillance standards, measured against the Scripps Reference Gas System standards, are intended to show any deviations in the long-term integrity of the Scripps System. In our laboratory parlance they have often been referred to as "quarterly tanks" because they were to be analyzed four times a year, although they have not usually been analyzed this often.

The operation of the system is schematically indicated in Figure 2. Overlaps and breaks in the time lines of individual gas mixtures illustrate the preparation of replacement Scripps Reference Gas System standards and their eventual succession as older standards become depleted.

In 1978 another level was added to the Scripps Reference Gas System by creation of a so-called User High Span and a User Principal Span. Assigned standards for other WMO members were then compared to these

User standards. However, these standards have been closely tied to the Scripps High Span and Principal Span through frequent comparisons during their lifetime, so this subsidary system is not further discussed in this report.

An extensive and systematic calibration of the Scripps Reference Gas System was accomplished in 1974 when a suite of ten manometric standards were compared to the Principal Span and High Span with the Applied Physics analyzer. Four of the ten manometric standards had already been manometrically analysed in 1970. All ten were manometrically analyzed in 1974 and from the data of these calibrations the Adjusted Index, J, was established as a function of the CO_2 mole fraction, X, over the range 210 to 450 ppm. The mole fraction values X were found to be well represented by a cubic function in J. A correction for the use of the CO_2-in-N_2 standards to measure CO_2-in-air was also determined in 1974, based on five manometrically analyzed CO_2-in-air gas mixtures (Guenther and Keeling, 1981), and an estimate obtained of the variation of this correction with pressure. In 1980 all ten manometric standards were reanalyzed manometrically, and further extensive calibrations were made against the Principal Span and High Span. CO_2-in-air standards were also calibrated, but we report below only the results for CO_2-in-N_2, since the CO_2-in-air calibrations are discussed in a further report (Bacastow, Keeling, Guenther, and Moss, 1982).

Were it not for a problem we refer to as "system drift" the results of these CO_2-in-N_2 calibrations would be expressed by a simple curve of concentration X vs. Adjusted Index, J. This curve, of course, would apply only to results obtained with the Applied Physics analyzer at Scripps, as used in the Scripps Reference Gas System, although it would be nearly valid for other Applied Physics analyzers, e.g. at Mauna Loa Observatory, Hawaii.

System drift refers to the observation that a gas mixture is found to have a progressively lower (or higher) Adjusted Index value, J, by comparison to the Principal Span and High Span standards. Since 1970, after four manometric standards were put into use, the drift has been observed to be "differential": lower concentration gas mixtures have

drifted downward faster than higher concentration mixtures. Above
approximately 370 ppm the drift is, in fact, positive after 1970. The
drift is apparently in the system; the suite of ten manometrically
analyzed gas mixtures have been essentially constant in manometric con-
centration, X, (see Table 3).

The objective of applying a drift correction is to correct the
adjusted index, measured at a given time, to the adjusted index which
would have been determined during the 1980 manometric calibration.
Thus, once the drift correction has been established, and a corrected J
value obtained, the corresponding mole fraction is found by applying the
1980 calibrating curve, irrespective of when that J value was originally
obtained.

We have applied three levels of correction to the adjusted index
values. Each successive level corresponds to a smaller correction near
the concentration of air and to a reduction in our estimate of the reli-
ability of the data on which it is based. The results of these three
corrections, in order of application, are called JA, JB, and JC. The
corresponding mole fractions are called respectively X80A, X80B, X80C.

The change from J to JA removes most of the drift; it uses only
information from gas mixtures which were compared directly with
manometric standards, close to the time of manometric calibrations in
1959-1961 (referred to as "1960"), 1974, and 1980. The correction from
JA to JB is based on further comparisons with these manometric gas stan-
dards during 1970, 1972, and 1977-78 (the latter referred to as the
"1978" calibration). The correction from JB to JC is based on comparis-
ons with surveillance standards, and only affects measurements prior to
1 July 1970.

Clearly, corrections could have been formulated in other ways. For
example, the data from 1970, 1972 and 1977-78 could have been treated as
calibrations on an equal basis to those in 1960, 1974 and 1980. How-
ever, the 1970 and 1972 data were for only four gases, and the 1977-78
data was obtained from comparisons involving usually only three to six
gases on any one day, and days were spread over about a year. Since
data from 1970, 1972 and 1977-78 are near the more thorough 1974 and

1980 calibrations, it was decided to treat them in second level of corrections.

Reliability of the System

The present study allows an estimate of how large might be the error which remains uncorrected, due to the unavailability of necessary data. We suggest that a reasonable upper limit on this error is the sum of the JB and JC corrections. In the general region of air concentration, 310-340 ppm, this sum is less than 0.22 ppm (see Table 14).

1960, 1974, and 1980 Calibrations

Manometric measurements during 1959-1961 and 1970 (Guenther, 1978), during 1974 (Guenther and Keeling, 1981), and during 1980 (unpublished results) are listed in Table 1a to 1d, and the results of corresponding Applied Physics analyzer comparisons are given in Table 2a to 2c. Ref. Gas Report No.'s refer to reference gas reports on file at the Scripps Institution of Oceanography. These reports list all reference gas comparisons by infrared analysis at Scripps together with subsidary calculations. Both sets of measurements are summarized together in Table 3. Infrared measurement dispersion data in 1974 and 1980 are shown in Figure 3 and discussed in the figure caption.

Calibration curves for 1974 and 1980 were obtained by making cubic fits of the averages of all the manometric measurements, X, from 1969 through 1980 for each gas mixture to the adjusted Index values, J, appropriate to each special period of calibration. These data are summarized in Table 3. Averages of both X and J are weighted according to the number of determinations. The 1980 calibration curve is shown in Figure 4. The difference between the 1974 and 1980 curves, which we attribute to drift in the Scripps Reference Gas System, is illustrated in Figure 5. In the caption to Figure 5, J74 denotes J for the 1974 calibration, J80 that for 1980. The 1974 calibration curve is not displayed because it would look almost identical to the 1980 curve shown in Figure 4.

A calibration curve for 1960 was obtained by assuming the same curve as for 1974, except for a correction for linear drift as shown in Figure 6.

The following nomenclature will be used to explain these calculations and the subsequent corrections from JA to JB and JC:

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.

X60   average CO_2 mole fraction based on manometric measurements during 1959-1961.

X80   average CO_2 mole fraction based on manometric measurements from 1969 through 1980 (T arbitrarily set equal to 80).

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.

JA Correction

The correction of J to JA uses only the data of Table 3 for three special calibrations with central dates in 1960, 1974, and 1980. A linear interpolation in time of cubic equations of X as a function of J is made between the central dates of each calibration period.

For the period between the central dates 15 August, 1974 and 19
September, 1980 (CD74 and CD80, respectively), calibration curves CUB1
and CUB2 were determined by least squares fits:

$$X80 = CUB1 (J74) \qquad (2)$$

$$X80 = CUB2 (J80) \qquad (3)$$

These two equations (whose coefficients are listed below in Table 12)
predict different relations between J and X. This is presumably owing
mainly to a drift in the Scripps reference gas system.

The drift then is in J, not X. However, the simplest calculation
to make for times between calibrations is a linear interpolation in time
of the values of X obtained at each calibration central date for the
observed J. Because the drift between calibrations is small, the rela-
tive time rate of change in J and X are very nearly equal, and the
difference in result in assuming a linear drift in X instead of in J is
negligible. Thus, between CD74 and CD80:

$$X1 = CUB1 (J) \qquad (4)$$

$$X2 = CUB2 (J) \qquad (5)$$

$$XINTERP1 = \left(\frac{CD80 - D}{CD80 - CD74}\right) X1 + \left(\frac{D - CD74}{CD80 - CD74}\right) X2 \qquad (6)$$

XINTERPI is, indeed, the sought after mole fraction based on assuming a
linear drift in time, but since we will apply a second, and possibly, a
third level of correction, and this will be done in the J system, we
next convert XINTERPI back to the adjusted index system via the
transformation:

$$JA = CUB2^{-1} (XINTERP1) \qquad (7)$$

where $CUB2^{-1}$ indicates the inversion of the 1980 calibration curve to

find J given X.

Data are inadequate to determine a cubic calibration curve for the 1960 special period. It was instead assumed that the 1974 curve was valid in 1960 except for a linear adjustment in J. A linear adjustment was deemed appropriate on the basis of a preliminary examination of the data. This adjustment was determined as follows:

First, from manometric data, X60, for the 1960 special period, corresponding J values were obtained based on the 1974 calibration:

$$J1 = CUB1^{-1} (X60) \tag{8}$$

These predicted J values were then compared with the observed J values, J60, and average differences, $\triangle$J60,

$$\triangle J60 = J1 - J60 \tag{9}$$

obtained for each manometric standard gas.

The pairs of values, ($\triangle$J60, J60), plotted in Figure 6, were fit to a straight line by least squares after excluding several apparently aberrant points. The resulting relation (whose coefficients are listed below in Table 12) is:

$$\triangle J60 = LIN3 (J60) \tag{10}$$

On the assumption, again, that the drift was linear in time with respect to X, the above equation was used with the calibration curve for 1974, CUB1, to calculate X from J for any given day D between the central dates of the 1960 and 1974 calibrations, CD60 and CD74. Specifically:

$$\triangle J = LIN3 (J) \tag{11}$$

$$X3 = CUB1 (J + \triangle J)$$

$$X1 = CUB1 (J) \tag{12}$$

$$\text{XINTERP2} = \left(\frac{\text{CD74} - \text{D}}{\text{CD74} - \text{CD60}}\right) \text{X3} + \left(\frac{\text{D} - \text{CD60}}{\text{CD74} - \text{CD60}}\right) \text{X1} \qquad (13)$$

Again, although XINTERP2 is the sought after mole fraction based on assuming a linear drift, we prepare for second and third level corrections, by convertion back to the J system via the 1980 calibration curve, i.e. we compute:

$$\text{JA} = \text{CUB2}^{-1} \; (\text{XINTERP2}) \qquad (14)$$

JB Correction

Second level corrections at central dates in 1970, 1972, and 1978 were calculated from Reference Gas System results for the manometric standards (Tables 6, 7, and 8; Figures 7, 8, and 9). First, JA values were calculated from data for each special calibration period, in accordance with the equations described above. Specifically the procedures used to find JA at the central dates in 1970, 1972, and 1980 are as follows:

For 1970:

$$\triangle\text{J} = \text{LIN3} \; (\text{J70}) \qquad (15)$$

$$\text{X3} = \text{CUB1} \; (\text{J70} + \triangle\text{J}) \qquad (16)$$

$$\text{X1} = \text{CUB1} \; (\text{J70}) \qquad (17)$$

$$\text{JA70} = \text{CUB2}^{-1} \left(\frac{\text{CD74} - \text{CD70}}{\text{CD74} - \text{CD60}} \, \text{X3} + \frac{\text{CD70} - \text{CD60}}{\text{CD74} - \text{CD60}} \, \text{X1}\right) \qquad (18)$$

For 1972 the same expressions were used with '72' replacing '70'.

For 1974 no interpolation was necessary since:

$$\text{JA74} = \text{CUB2}^{-1}(\text{CUB1}(\text{J74})) \qquad (19)$$

For 1980:

$$JA80 = J80 \qquad (20)$$

After JA had been calculated for each special period, a correction at each appropriate central date was found and represented by a quadratic in JA (whose coefficients are listed below in Table 12). The correction employed for any measurement was then obtained from a linear interpolation in time of corrections evaluated at the bracketing central dates.

Specifically, for the 1970 and 1972 corrections:

$$\triangle J70 = JA74 - JA70 \qquad (21)$$

$$\triangle J72 = JA74 - JA72 \qquad (22)$$

were first computed. Pairs of values $(\triangle J70, JA70)$ and $(\triangle J72, JA72)$ were fit to the quadratic expressions, QUAD4 and QUAD5, by least squares. The resulting relations:

$$\triangle J70 = QUAD4 \ (JA70) \qquad (23)$$

$$\triangle J72 = QUAD5 \ (JA72) \qquad (24)$$

were used to calculate JB for any given day between CD60 and CD74 by linear interpolation in time of $\triangle JT$. Between CD60 and CD70 (since there is no correction to JA for CD60):

$$JB = JA + \left(\frac{D - CD60}{CD70 - CD60}\right) QUAD4 \ (JA) \qquad (25)$$

Between CD70 and CD72:

$$JB = JA + \left(\frac{CD72 - D}{CD72 - CD70}\right) QUAD4 \ (JA) + \left(\frac{D - CD70}{CD72 - CD70}\right) QUAD5 \ (JA) \qquad (26)$$

Between CD72 and CD74 (since there is no correction to JA at CD74):

$$JB = JA + (\frac{CD74 - D}{CD74 - CD72}) \; QUAD5 \; (JA) \qquad (27)$$

For the calibration period 1978, the correction was based on depar-
tures of JA from 1980:

$$\triangle J78 = JA80 - JA78 \qquad (28)$$

Pairs of values ($\triangle J78$, JA78) were fit to a quadratic expression, QUAD6,
resulting in the relation:

$$\triangle J78 = QUAD6 \; (JA78) \qquad (29)$$

Between CD74 and CD78:

$$JB = JA + (\frac{D - CD74}{CD78 - CD74}) \; QUAD6 \; (JA) \qquad (30)$$

Between CD78 and CD80:

$$JB = JA + (\frac{CD80 - D}{CD80 - CD78}) \; QUAD6 \; (JA) \qquad (31)$$

JC Correction

Third level corrections at central dates in 1962 and 1966 were
obtained from data of four surveillance standards (two of which were
composites, as discussed below), by constructions similar to the con-
struction illustrated in Figure 11. The correction at each central date
(based on data listed in Tables 10 and 11) is represented by a linear
equation in JB (Figures 12 and 13). The coefficients are listed in
Table 12. The correction employed for any measurement is obtained from
a linear interpolation in time of corrections evaluated at the central
dates, and is assumed zero after the 1970 central date. The effect of
the correction for one of the surveillance gases is shown by comparison

of Figures 10 and 14.

The two composite standards, referred to above, were created by overlapping results for a pair of gas mixtures which were within 1 ppm of each other in concentration. One of each composite had adequate data for the period near 1960 but was used up in the late 1960's, while the other had data in the 1970's which were adequate to determine its mole fraction based on the manometric calibration period between 1970 and 1980. Index values, I, for the periods of overlap are listed in Table 9. To form the composites, the Index of the first listed gas mixture was adjusted by the difference shown in Table 9. Thus the I values of cylinder 4283 were lowered by 0.84 ppm, and those of cylinder 4287 were raised by 0.71 ppm.

Data taken from the surveillance standards were used to establish departures from JB between CD60 and CD70 on the basis of special periods in 1962 and 1966. First, JB values were calculated for each surveillance standard for the two special periods at the beginning and end of the calculation:

For 1960:

$$JB60 = JA60 \tag{32}$$

For 1970:

$$JB70 = JA70 + QUAD5 \; (JA70) \tag{33}$$

Since a zero correction to JB is assumed to apply at both CD60 and CD70, but the JB values of each surveillance standard on these two dates are not identical, owing, for example, to possible change in concentration over the ten year period, the corrections are defined as the departures in 1962 and 1966 from a linear variation in JB between 1960 and 1970, as illustrated in Figure 11:

$$\triangle J62 = JB60 - JB62 + (JB70 - JB60) \frac{(CD62 - CD60)}{CD70 - CD60} \qquad (34)$$

$$\triangle J66 = JB60 - JB66 + (JB70 - JB60) \frac{(CD66 - CD60}{CD70 - CD60} \qquad (35)$$

Pairs of values ($\triangle J62$, JB62) and ($\triangle J66$, JB66) were fit to linear expressions LIN7 and LIN8 by least squares. The resulting relations:

$$\triangle J62 = LIN7 \ (JB62) \qquad (36)$$

$$\triangle J66 = LIN8 \ (JB66) \qquad (37)$$

were used to calculate JC for any given day between CD60 and CD70 by linear interpolation analogous to the interpolation formulas developed earlier for JB. The JC correction is non zero only between CD60 and CD70. After CD70:

$$JC = JB \qquad (38)$$

Verification of 1960 Calibration

The four surveillance standards just discussed were used to check the 1960 calibration discussed in the section headed "JA Correction" (see Table 5). Firstly, that part of the set of original infrared analysis data for these surveillance gas mixtures which were obtained during and after the special calibration in 1970 were assembled and JB values were calculated from the original I values. From the average of JB for each gas mixture, JBS (where S signifies a surveillance gas standard), a mole fraction XS was calculated on the basis of the 1980 calibration curve:

$$XS = CUB2 \ (JBS) \qquad (32)$$

Secondly, that part of the original data for the surveillance gas mixtures obtained near the time of the 1960 calibration were assembled,

and averages, JS60, computed. Thirdly, adjusted index values, J1S, were calculated from the derived mole fractions XS on the basis of the 1974 calibration curve:

$$J1S = CUB1^{-1} (XS) \tag{33}$$

Differences, $\triangle$JS60, between J1S and the J values of the surveillance standards for the special period 1960, JS60:

$$\triangle JS60 = J1S - JS60 \tag{34}$$

are plotted versus JS60, in Figure 6 (as triangles). The agreement with the selected manometric data (shown by circles) is good. No direct use, however, is made of the differences $\triangle$JS60. These are used only as evidence that the surveillance standards are consistent with the manometric calibration data.

Implementation

The above described corrections are implemented by the Fortran program MAPCOR2 listed in Table 13. The effect of each of the three corrections is shown separately in Table 14, and together in Table 15. Table 16 lists the differences between the mole fraction XC, calculated from all the corrections discussed above, i.e.,

$$XC = CUB2 (JC) \tag{42}$$

and the mole fraction XWMO, calculated on the 1974 Manometric Scale as adopted by WMO:

$$XWMO = 76.582 + 0.584910 (J') + 3.1151 \times 10^{-4} (J')^2 \tag{43}$$

$$+ 7.3225 \times 10^{-7} (J')^3$$

where

$$J' = J - 1.050 + 0.060t \qquad (44)$$

t being the time in years since the beginning of 1957. Table 17 lists the differences between the mole fraction XC and the Adjusted Index J.

Drift Model

The differential drift between 1974 and 1980 is consistent with a model in which each new Scripps system standard (Principal Span or High Span) is assigned an Adjusted Index value 0.07 ppm too low (see Figure 15). The drift is greater at the Principal Span concentration than at the High Span concentration, in this model, because the Principal Span was replaced more often. New Scripps system standards are compared directly to the Principal Span, thus depleting it before the High Span. Assigned standards are compared directly to a transfer standard that is well known with respect to the Principal Span.

This same 0.07 ppm error per change of cylinder is also more or less consistent with the drift observed between 1960 and 1970. The Principal Span was replaced about once per year, and the Low Span and High Span each about half as often. We suppose, in this model, that the use of a Low Span counterbalanced the use of the High Span during this period, and the Principal Span drift then propagated to all concentrations in the range of the calibration.

The cause of the system drift is not well understood. The effect is consistent with a small increase in concentration (the order of 0.1 ppm) of each reference system standard during its lifetime. Since these standards have been prepared mainly by comparison to the preceding set of standards, the overall effect has been cumulative. Thus it is to be expected that the drift would be considerably reduced if all system standards were prepared by direct comparison to a long lasting set of higher standards, or to manometrically analyzed standards.

Several phenomena have been suggested as the ultimate cause of the drift:

(1) A chemical reaction that slowly produces CO_2, for example, by oxidation of a film of oil on the cylinder walls.

(2) A surface chemical reaction. Newly filled cylinders of gas are sometimes observed to rapidly decrease in CO_2 concentrations for a few months, possibly due to a chemical reation involving the cylinder walls, then stabilize. As pressure is reduced in the cylinder, such a reaction might reverse and thereby enrich the mixture.

(3) Fractionation due to the accelerations of the gas molecules in leaving the cylinder. There is an approximately 1 square millimeter orifice at the entrance to the Hoke pressure regulators used until 1978. It seems reasonable to assume that all fractionation takes place in entering the regulator; the geometry is such that all molecules that gain entrance are probably eventually swept downstream. The flow rate in the APC analyzer was ordinarily 0.5 liter per minute. Thus, assuming an average cylinder pressure of 1100 psi, the gas molecules had to accelerate from an average velocity of 0 to

$$\frac{(0.5)(1000)(14.7)}{(0.01)(60)(1100)} = 11 \, cm/sec$$

in entering the regulator. One would expect the heavier CO_2 molecules to be preferentially left behind and thereby enrich the remainder of the gas.

(4) Introduction of laboratory air into the cylinder when a pressure regulator is installed and the main valve of the cylinder opened, since this allows laboratory air to diffuse into the cylinder. Owing to the high pressure in the cylinder, the effect is negligibly small for a single installation, but since the regulators are installed and removed on each day of calibration, a significant cumulative effect is possible.

References

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R. B. Bacastow, C. D. Keeling, P. R. Guenther, and D. J. Moss, "Correction for Measurement of air Relative to Nitrogen Standards for APC Analyzer", in preparation.

Table 1a. Manometric analyses of CO_2-in-N_2 standards during 1959-1961.

Cylinder No.	Year	Run No.	Individual Determinations (ppm)	Average (ppm)	No. of Analyses
164	1961	1	284.13[a]	285.43	1
		2	285.43		
3758	1959	1	284.90	284.98	2
		2	285.06		
6071	1959	1	309.82	309.89	2
		2	309.96		
3760	1959	1	314.68[a]	314.68[a]	1
6071[b]	1961	1	318.38[a]	315.63	1
		2	315.63		
4269	1959	1	334.01[a]	323.04[a]	1
		2	323.73[a]		
		3	323.04[a]		
2425	1959	1	349.82	349.84	2
	1961	1	349.86		

[a]Analysis judged to be in error because of large departure from expected value (see Figure 6).

[b]Cylinder refilled in 1960.

Table 1b. Manometric analyses of CO_2-in-nitrogen standards during 1970 (Guenther, 1978).

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Average (ppm)	No. of Analyses
7366	1	12 MAY 70	276.48	276.57	3
	2	12 MAY 70	276.60		
	3	13 MAY 70	276.63		
6078	1	2 DEC 69	310.86	310.95	7
	2	2 DEC 69	311.01		
	3	9 DEC 69	310.62		
	4	10 DEC 69	311.00		
	5	12 DEC 69	310.93		
	6	10 MAR 70	311.07		
	7	15 MAY 70	311.14		
2399	1	4 DEC 69	324.12	324.19	8
	2	5 DEC 69	324.57		
	3	12 MAR 70	323.99		
	4	12 MAR 70	324.46		
	5	24 APR 70	324.10		
	6	29 APR 70	324.09		
	7	14 MAY 70	324.19		
	8	15 MAY 70	323.98		
10069	1	11 DEC 69	355.71	355.64	4
	2	24 APR 70	355.74		
	3	28 APR 70	355.46		
	4	14 MAY 70	355.65		

Table 1c. Manometric analyses of CO_2-in-nitrogen standards during 1974 (Guenther and Keeling, 1981).

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Analyses
2408	1	22 MAY 74	196.93 196.85	196.89	196.90	2
	2	22 MAY 74	196.91 196.89	196.90		
3753	1	11 FEB 74	246.03 246.05	246.04	246.02	2
	2	13 FEB 74	246.00 245.99	246.00		
7366	1	7 FEB 74	276.82 276.66 276.90	276.79	276.80	2
	2	8 FEB 74	276.76 276.85	276.80		
6078	1	18 JAN 74	310.78 310.81	310.80	310.82	3
	2	21 JAN 74	310.84 310.91	310.88		
	3	21 FEB 74	310.79 310.79	310.79		
2399	1	25 JAN 74	323.90 323.68 323.89	323.82	324.05	4
	2	28 JAN 74	324.19 324.23	324.21		
	3	30 JAN 74	324.06 324.07	324.06		
	4	8 MAR 74	324.08 324.17	324.12		
39239	1	15 OCT 74	332.64 332.80 332.87	332.77	332.78	2
	2	16 OCT 74	332.83 332.76	332.80		
10069	1	31 JAN 74	355.69 355.61	355.65	355.60	2
	2	1 FEB 74	355.55 355.53	355.54		
1540	1	15 OCT 74	380.50 380.51	380.50	380.56	2
	2	17 OCT 74	380.63 380.62	380.62		

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Analyses
35299	1	24 MAY 74	415.19 415.07	415.13	415.06	2
	2	24 MAY 74	414.91 415.05	414.98		
35316	1	23 MAY 74	473.03 472.98	473.00	472.97	2
	2	23 MAY 74	472.91 472.97	472.94		

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

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Analyses
2408	1	10 SEP 80	196.74 196.75	196.74	196.80	2
	2	17 SEP 80	196.85 196.86	196.86		
3753	1	26 JUN 80	246.00 246.01	246.00	245.99	2
	2	27 JUN 80	245.99 245.97	245.98		
7366	1	5 OCT 79	276.74 276.66	276.70	276.67	2
	2	19 OCT 79	276.65 276.64	276.64		
6078	1	18 SEP 79	310.90 310.91	310.90	310.96	2
	2	19 SEP 79	311.07 210.97	311.02		
2399	1	24 SEP 79	324.12 324.10	324.11	324.15	2
	2	25 SEP 79	324.21 324.17	324.19		
39239	1	18 JUN 80	332.63 332.66	332.64	332.72	2
	2	19 JUN 80	332.80 332.82	332.81		
10069	1	3 OCT 79	355.89 355.88	355.88	355.82	2
	2	5 OCT 79	355.81 355.70	355.76		
1540	1	19 JUN 80	380.03* 380.02*	380.02*	380.45	2
	2	24 JUN 80	380.45 380.50	380.48		
	3	17 SEP 80	380.42 380.42	380.42		

* Run No. 1 deleted

Cylinder No.	Run No.	Date	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Analyses
35299	1	24 JUN 80	414.90 414.90	414.90	414.94	2
	2	25 JUN 80	415.00 414.94	414.97		
35316	1	25 JUN 80	471.67[†] 471.67[†]	471.67[†]	472.72	4
	2	26 JUN 80	472.65 472.74	472.70		
	3	23 SEP 80	472.32[†] 472.29[†]	472.30[†]		
	4	23 SEP 80	472.69 472.67	472.68		
	5	22 OCT 80	472.79 472.81	472.80		
	6	23 OCT 80	472.69 472.70	472.70		

[†] Runs Nos. 1 and 3 deleted

Table 2a. Applied Physics infrared analyzer
results in Index units, I, for gas mixtures
analyzed manometrically in 1958-1961. Number
of comparisons are shown in parentheses.

Cyl. No. 164 (from Ref. Gas Report No. 3, p. 50)

25 AUG 59	290.64 (10)
9 NOV 59	290.26 (12)
9 NOV 59	290.31 (11)
10 NOV 59	290.31 (14)
10 NOV 59	290.25 (11)
11 NOV 59	290.32 (11)

Cyl. No. 3758 (from Ref. Gas Report No. 3, p. 60)

18 JUN 59	290.09 (10)
28 AUG 59	289.97 (10)
12 NOV 59	289.95 (7)
22 DEC 59	289.98 (14)

Cyl. No. 6071 (from Ref. Gas Report No. 3, p. 60)

6 JUL 59	311.14 (10)
28 AUG 59	311.15 (10)
4 DEC 59	311.41 (10)
22 DEC 59	311.16 (11)
10 NOV 60	311.25 (10)

Cyl. No. 3760 (from Ref. Gas Report No. 2, p. 34)

20 NOV 58	314.52 (10)
20 NOV 58	314.52 (10)
18 DEC 58	314.50 (11)
18 DEC 58	314.54 (10)

19 DEC 58	314.59 (11)
19 DEC 58	314.69 (10)
13 JAN 59	314.71 (10)
13 JAN 59	314.83 (9)
6 FEB 59	314.59 (10)
6 FEB 59	314.61 (12)
13 MAR 59	314.57 (10)
13 MAR 59	314.59 (10)
17 APR 59	314.66 (11)
17 APR 59	314.61 (10)
17 APR 59	314.60 (10)
29 APR 59	314.60 (10)
29 APR 59	314.54 (11)
30 APR 59	314.55 (11)
30 APR 59	314.62 (10)
13 MAY 59	314.72 (10)
13 MAY 59	314.48 (10)
19 MAY 59	314.55 (9)
19 MAY 59	314.64 (11)
5 JUN 59	314.73 (11)
5 JUN 59	314.53 (10)
6 JUN 59	314.51 (10)
6 JUN 59	314.57 (10)
18 JUN 59	314.59 (11)
18 JUN 59	314.58 (10)

Cyl. No. 6071[b] (from Ref. Gas Report No. 4, p. 30-31)

16 MAR 61	316.21 (11)
16 MAR 61	316.30 (10)
17 MAR 61	316.28 (11)
17 MAR 61	316.13 (9)

17 MAR 61	316.36 (10)
13 APR 61	316.01 (11)
13 APR 61	316.13 (10)
14 APR 61	316.09 (14)
14 APR 61	316.09 (10)
18 APR 61	316.13 (10)
18 APR 61	315.98 (10)
27 APR 61	316.08 (8)
27 APR 61	316.04 (10)
28 APR 61	316.08 (10)
28 APR 61	316.24 (10)
1 MAY 61	316.05 (10)
1 MAY 61	315.92 (12)
9 JUN 61	316.19 (11)
9 JUN 61	316.16 (10)
15 JUN 61	316.02 (11)
15 JUN 61	316.09 (10)
22 JUN 61	316.09 (10)
22 JUN 61	316.15 (10)
26 JUN 61	315.89 (11)
26 JUN 61	315.82 (10)
27 JUN 61	316.14 (10)
27 JUN 61	316.29 (11)
2 AUG 61	315.99 (11)
2 AUG 61	315.98 (10)
3 AUG 61	316.00 (11)
3 AUG 61	316.06 (10)
10 AUG 61	315.94 (10)
10 AUG 61	315.89 (10)
15 AUG 61	316.04 (10)
15 AUG 61	316.18 (11)
16 AUG 61	315.96 (11)

16 AUG 61	316.00 (10)
22 AUG 61	316.14 (11)
22 AUG 61	316.22 (10)

[b]Cylinder refilled in 1960.

Cyl. No. 4269 (from Ref. Gas Report No. 3, p. 63)

30 APR 59	321.54 (10)
15 MAY 59	321.58 (10)
18 MAY 59	321.63 (10)
18 MAY 59	321.48 (11)
31 AUG 59	321.65 (10)
9 NOV 59	321.63 (10)
10 NOV 59	321.67 (10)
11 NOV 59	321.65 (10)
30 JUN 60	321.76 (10)
10 OCT 60	321.70 (12)
11 NOV 60	321.59 (10)

Cyl. No. 2425 (from Ref. Gas Report No. 3, p. 49)

25 AUG 59	343.18 (10)
28 AUG 59	343.18 (11)
28 AUG 59	343.34 (10)
31 AUG 59	343.23 (11)
31 AUG 59	343.42 (10)
1 SEP 59	343.17 (11)
1 SEP 59	343.26 (10)
9 SEP 59	343.27 (8)
9 SEP 59	343.30 (10)
16 SEP 59	343.40 (11)
16 SEP 59	343.36 (10)
9 OCT 59	344.53# (13)

9 OCT 59	344.63$^{\#}$ (10)
19 OCT 59	343.00 (10)
19 OCT 59	343.26 (10)
3 NOV 59	343.21 (12)
3 NOV 59	343.24 (10)
3 NOV 59	343.32 (6)

$^{\#}$Omitted from average.

Table 2b. Applied Physics infrared analyzer results in Index units, I, for the ten manometrically analyzed standards during special calibration in 1974. The number of comparisons is shown in parentheses. Information is from Ref. Gas Reports No. 25 and 26.

Cyl. No.	23 MAY	30 MAY	20 JUN	27 JUN	11 JUL	5 AUG	22 AUG	9 SEP
2408	204.78 (10)	204.98 (9)	205.29 (10)	203.88 (10)	203.55 (10)	204.31 (12)	204.74 (10)	202.84 (10)
	204.92 (9)	205.17 (10)	205.25 (10)	203.86 (10)	203.59 (11)	204.46 (10)	204.71 (10)	202.90 (10)
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)
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)
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)
35316	426.90 (10)	427.33 (9)	426.55 (10)	427.60 (10)	427.78 (10)	426.84 (10)	426.59 (10)	428.20 (10)
	427.08 (9)	426.94 (10)	426.25 (10)	427.62 (10)	427.75 (10)	426.83 (10)	426.53 (10)	428.00 (10)

Cyl. No.	24 MAY	31 MAY	21 JUN	28 JUN	12 JUL	6 AUG	23 AUG	10 SEP
2408	205.20 (10)	205.29 (9)	205.64 (10)	203.55 (10)	204.25 (10)	203.64 (10)	203.80 (10)	202.64 (10)
	205.25 (10)	205.12 (11)	205.47 (10)	203.58 (10)	204.29 (10)	203.49 (10)	203.62 (10)	202.72 (10)
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)
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)
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)
35316	426.54 (9)	426.76 (11)	426.17 (10)	428.13 (8)	427.23 (10)	427.77 (10)	427.44 (10)	428.41 (10)
	426.70 (10)	426.86 (10)	426.42 (10)	427.92 (10)	427.27 (10)	427.81 (11)	427.60 (10)	428.18 (10)

Cyl. No.	10 OCT	14 OCT	17 OCT	22 OCT	30 OCT	31 OCT	1 NOV	4 NOV
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)
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)
39239	328.97 (10)	329.00 (9)	329.01 (9)	329.00 (10)	329.03 (10)	329.02 (10)	329.01 (10)	328.95 (10)
	328.94 (10)	329.11 (9)	329.05 (9)	328.92 (10)	329.04 (11)	329.02 (10)	328.96 (10)	328.93 (10)
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)
1540	365.23 (14)	365.35 (10)	365.66 (10)	365.31 (10)	365.02 (10)	365.36 (10)	365.12 (10)	365.26 (10)
	365.07 (11)	365.46 (10)	365.60 (10)	365.36 (14)	364.99 (10)	365.38 (10)	365.11 (9)	365.10 (10)
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)

Table 2c. Applied Physics analyzer results in Index units, I, for the ten manometrically analyzed standards during 1980 calibration. The number of comparisons is shown in parentheses. Information is from Ref. Gas Report No. 38.

1980 CALIBRATION (INDEX I)

Cyl. No.	4 AUG	25 AUG	22 SEP	25 SEP	30 SEP	2 OCT	7 OCT	9 OCT
2408	201.04 (10)	201.50 (9)	200.70 (9)	200.91 (11)	201.23 (9)	201.20 (9)	200.96 (9)	201.35 (9)
						201.23 (9)		201.15 (9)
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)
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)
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)
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)
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)
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)
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)
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)
35316	428.31 (11)	427.48 (9)	428.28 (9)	428.44 (9)	428.89 (9)	428.81 (9)	428.68 (9)	428.53 (9)
							428.62 (9)	

Table 3. Summary of Calibration data on CO_2-in-N_2 from Tables 1 and 2. The number of manometric measurements is shown in parentheses. The dates shown in the heading are central calibrating dates (see text).

SUMMARY OF CO_2-IN-N_2 CALIBRATION DATA

Cyl. No.	Av. Manometric Concentration (ppm) 1960 (X60)	Adjusted Index J (ppm) 1 JUL 1960 (J60)
164	285.43(1)	285.71
3758	284.98(2)	385.30
6071	309.89(2)	311.16
3760	314.68(1)	315.38
6071a	315.63(1)	317.09
4269	323.04(1)	323.84
2425	349.84(2)	350.20

Cyl. No.	Av. Manometric Concentration (ppm)				Adjusted Index J (ppm)		
	1970	1974	1980	Wt. Av. (X80)	1 JUL 1970 (J70)	15 AUG 1974 (J74)	19 SEP 1980 (J80)
2408		196.90(2)	196.80(2)	196.85		180.83	176.96
3753		246.02(2)	245.99(2)	246.00		241.32	238.93
7366	276.57(3)	276.80(2)	276.67(2)	276.66	275.88	275.55	273.84
6078	310.95(7)	310.82(3)	310.96(2)	310.92	311.49	311.17	310.23
2399	324.19(8)	324.05(4)	324.15(2)	324.14	324.56	324.23	323.54*
39239		332.78(2)	332.72(2)	332.75		332.82	332.24*
10069	355.64(4)	355.60(2)	355.82(2)	355.68	354.38	354.47	354.37*
1540		380.56(2)	380.45(2)	380.50		377.02	377.07
35299		415.06(2)	414.94(2)	415.00		406.55	407.18†
35316		472.97(2)	472.72(4)	472.80		452.55	454.01#

* Small error detected in final proofing of report (correct value, .01 ppm lower, is not shown and not used in curve fits).

† Ditto except .01 ppm higher.

Ditto except .03 ppm lower.

a Cylinder refilled.

Table 4a. Data for 1960 calibration. The best information is deemed to be from the gas mixtures in cylinders No. 3758, 6071, and 2425, for which two manometric measurements agreed closely. The column headed J60 is the average of Reference Gas System comparisons from the years 1958-1961 (see Table 2a). Data in column headed J1 are obtained from by inverting the 1974 calibration curve.

1960 Calibration

Cylinder No.	X (ppm)	J60 (ppm)	J1 (ppm)	J1 - J60 (ppm)
164	284.13[a]	285.71	283.52	-2.19[a]
	285.43		284.90	-0.81
3758	284.90	285.30	284.34	-0.96
	285.06		284.51	-0.79
6071	309.82	311.16	310.16	-1.00
	309.96		310.30	-0.86
3760	314.68[a]	315.28	315.04	-0.24[a]
6071[b]	318.38[a]	317.09	318.73	1.64[a]
	315.63		315.99	-1.10
4269	334.01[a]	323.84	334.01	10.17[a]
	323.73[a]		324.01	0.17[a]
	323.04[a]		323.33	-0.51[a]
2425	349.82	350.20	349.01	-1.19
	349.86		349.05	-1.15

[a] Judged to be in error owing to large departure from value expected by linear curve through data of cylinders 3758, 6071, and 2425.

[b] Cylinder refilled.

Table 4b. Summary of 1974 CO_2-in-nitrogen calibration. Column headed "Concentration" is average of manometric measurements in 1970, 1974, and 1980. Column headed "Residual" is manometrically measured concentration less concentration calculated from J and the fitted cubic equation.

Cylinder No.	Concentration X (ppm)	Adjusted Index J (ppm)	Residual (ppm)
2408	196.85	180.83	0.04
3753	246.00	241.32	-0.12
7366	276.66	275.55	-0.05
6078	310.92	311.17	0.10
2399	324.14	324.23	0.19
39239	332.75	332.82	-0.02
10069	355.68	354.47	-0.01
1540	380.50	377.02	-0.13
35299	415.00	406.55	-0.03
35316	472.80	452.55	0.04

Table 4c. Summary of 1980 CO_2-in-nitrogen calibration. Column headed "Residual" is measured concentration less calculated concentration.

Cylinder No.	Concentration X (ppm)	Adjusted Index J (ppm)	Residual (ppm)
2408	196.85	176.96	0.02
3753	246.00	238.93	−0.09
7366	276.66	273.84	0.01
6078	310.92	310.23	0.07
2399	324.14	323.54	0.14
39239	332.75	332.24	−0.03
10069	355.68	354.37	−0.13
1540	380.50	377.07	0.00
35299	415.00	407.18	0.00
35316	472.80	454.01	0.01

Std. Error: 0.092

Table 5. Check of 1960 calibration data. Cylinder numbers are for sur-
veillance standards measured against Reference Gas System standards be-
ginning in 1961, or earlier, to 1970 or later, that do not apparently drift
in JB after mid-1970. We are better able to judge true concentration
drift after 1970 because of the continued use of the same manometric
standards. The column headed JS60 is the average of Adjusted Index
measurements during the special period 1960. The column headed JBS is the
average of corrected Adjusted Index values (weighted by number of com-
parisons) obtained after the 1970 central date CD70, and XS is the calculated
corresponding mole fraction. The data in the column headed J1S are obtained
from inversion of the 1974 calibration curve. The entries CMPL and CMPH
under "cylinder number" each refer to composites of two gas mixtures
(see Table 9 below).

Surveillance Standard Check of 1960 Calibration

Cyl. No.	JS60	JBS	XS	J1S	J1S - JS60
CMPL	290.91	288.70	290.32	290.07	-0.84
2401	308.78	306.58	307.31	307.62	-1.16
6073	312.05	310.08	310.71	311.06	-0.99
CMPH	349.19	347.95	349.03	348.27	-0.92

Table 6. Data summary for the 1970 correction. The column headed JA70
is the average of Reference Gas System results, J70, (not weighted by number
of comparisons), converted to JA, for 1970. The column headed JA74 is the
average of infrared analyzer results for the 1974 calibration (as summarized
in Table 3), converted to JA.

1970 Correction

Cyl. No.	JA74	JA70	JA74 - JA70
3753	238.96	238.99	−0.03
7366	273.91	274.00[#]	−0.09
6078	310.20	310.22	−0.02
2399	323.49	323.53	−0.04
10069	354.26	353.83	0.43

[#]Measurement of 18 May 1970 omitted.

Table 7. Data summary for the 1972 correction. The column headed JA72
is the average of Reference Gas System results, J72, (not weighted by number
of comparisons), converted to JA, for 1972. The column headed JA74 is
obtained as described in Table 6 caption.

1972 Correction

Cyl. No.	JA74	JA72	JA74 - JA72
3753	238.96	239.28	−0.32
7366	273.91	274.12	−0.21
6078	310.20	310.50	−0.30
2399	323.49	323.66	−0.17
10069	354.26	353.93	0.33

Table 8. Data summary for the 1978 correction. The column headed JA78 is the average of Reference Gas System results, J78, (not weighted by number of comparisons), corrected to JA, for late 1977 and during 1978. The column headed JA80 is identical to J measured for the 1980 calibration (see Table 3) since JA80 = J80.

1978 Correction

Cyl. No.	JA78	JA80	JA80 - JA78
2408	176.80	176.96	0.16
3753	238.84	238.93	0.09
7366	273.82	273.84	0.02
6078	310.33	310.23	-0.10
2399	323.62	323.54	-0.08
39239	332.23	332.24	0.01
10069	354.34	354.37	0.03
1540	377.34	377.07	-0.27
35299	407.44	407.18	-0.26
35316	454.71	454.01	-0.70

Table 9. Index values, I, for the individual gas mixtures which were combined to form composite surveillance standards CMPL and CMPH. The number of comparisons is shown in parentheses. The computed differences in I between each pair of gas mixtures are shown below for each composite.[#]

CMPH

Index I (ppm)

Cyl. No.	4283	3751
5 MAR 64	343.07(10)	342.19(10)
9 MAR 64	342.94(10)	342.11(10)
10 MAR 64	342.84(10)	342.03(10)
Average	342.95	342.11

Difference (Correction to cylinder 4283) -0.84

CMPL

Index I (ppm)

Cyl. No.	4287	6074
10 DEC 65	293.21(9)	293.97(10)
13 DEC 65	293.22(11) 293.21(10)	293.93(10)
14 DEC 65	293.28(9)	293.94(10)
Average	293.23	293.95

Difference (Correction to cylinder 4287) +0.72

[#]The correction made to cylinder 4287 Index values (I), to make CMPL, was +0.71, instead of the difference +0.72 as indicated in this table. This is because the calculation was originally done in Adjusted Index, J, and the differences converted back to the Index scale by dividing by 1.2186. Difference in rounding resulted in a 0.01 ppm difference.

Table 10. Data summary for the 1962 correction. The column headed JB62 is the average of Reference Gas System results, corrected to JB, for 1962 (not weighted by number of comparisons). Third column is the correction determined as indicated in Figure 12 caption.

1962 Correction

Cyl. No.	JB62	JC62 – JB62
CMPL	288.71	-0.05
2401[#]	306.70	0.10
6073	310.20	-0.17
CMPH	347.43	0.27

[#]Because there were no measurements during 1962 for this standard, four measurements in March and April of 1963 are averaged.

Table 11. Data summary for the 1966 correction. The column headed JB66 is the average of Reference Gas System results, corrected to JB, for 1966 (not weighted by number of comparisons). Third column is the correction determined as indicated in Figure 12 caption.

1966 Correction

Cyl. No.	JB66	JC66 – JB66
CMPL	288.05	0.56
2401	306.59	0.10
6073	309.96	0.10
CMPH	347.94	-0.07

Table 12. Constants used in the drift correction and calibration procedures. 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.

CALIBRATION CONSTANTS

Year	Central Date	Y_{out}	Y_{in}	Name	C_0	C_1	C_2	C_3	Limits of Validity of J	
1960	1 JUL 60	J74-J60	J60	LIN3	0.576	-0.005011			285	350
1974	15 AUG 74	X	J74	CUB1	77.455	0.573302	3.5735×10^{-4}	6.7618×10^{-7}	181	453
1980	19 SEP 80	X	J80	CUB2	84.370	0.542223	4.2284×10^{-4}	5.8862×10^{-7}	177	454

CORRECTION CONSTANTS

Year	Central Date	Y_{out}	Y_{in}	Name	C_0	C_1	C_2	C_3	Limits of Validity of J	
1970	1 JUL 70	JB-JA	JA	QUAD4	7.036	-0.051734	0.93176×10^{-4}		239	354
1972	28 SEP 72	JB-JA	JA	QUAD5	6.566	-0.051026	0.93967×10^{-4}		239	354
1978	18 FEB 78	JB-JA	JA	QUAD6	-0.444	0.005385	-0.12695×10^{-4}		177	455
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

Table 13. Fortran program that makes Table 16, and with slight modifi-

cation, Tables 14, 15, and 17.

```
$BATCH
C..PGM PRINTS X80C - XM74
      DIMENSION IDEL(25), ICOR1(25), ICOR2(25)
      COMMON/CAL/CD59, CD62, CD66, CD70, CD72, CD74, CD78, CD80
C
 1000 FORMAT(1H1,'                     X80C - XM74')
 1001 FORMAT(1H0, 'YEAR      57    58     59     60     61     62     63     64',
      X '   65    66    67    68    69    70    71    72    73    74    75',
      Y '   76    77    78    79    80    81')
 1002 FORMAT(1H ,'   J')
 1003 FORMAT(1H , I3, 2X, 25I5)
 1004 FORMAT(1H , 5X, 25I5)
 1005 FORMAT(1H )
C
      CALL CALDAY
      WRITE(6, 1000)
      WRITE(6, 1001)
      WRITE(6, 1002)
      DAY74=DAYNO(74, 7, 1)
      DO 100 J=170, 450, 10
      Y59=J
      DO 20 IY=57, 81
      DAYN=DAYNO(IY, 7, 1)
      CALL CALIB(DAYN, Y59, AJ80)
      CALL CORR1(DAYN, AJ80, BJ80)
      CALL CORR2(DAYN, BJ80, CJ80)
      YC59=Y59+0.06*(DAYN-DAY74)/365.25
      XM74=CUBM74(YC59)
      X80C=CUB80(CJ80)
      DEL=100.*(X80C-XM74)
      DD=ABS(DEL)+.5
      IDEL(IY-56)=SIGN(DD, DEL)
   20 CONTINUE
C
      WRITE(6, 1003)Y59, IDEL
  100 CONTINUE
C
      END
```

```
      SUBROUTINE CALDAY
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80
C
      CD59=DAYNO(60,7,1)
      CD62=DAYNO(62,7,1)
      CD66=DAYNO(66,7,1)
      CD70=DAYNO(70,7,1)
      CD72=DAYNO(72,9,28)
      CD74=DAYNO(74,8,15)
      CD78=DAYNO(78,2,18)
      CD80=DAYNO(80,9,19)
      RETURN
      END
```

```
      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
```

```
      SUBROUTINE CALIB(DAYN,Y59,AJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80
C
      IF(DAYN.GT.CD74)GO TO 20
      X59=CUB59(Y59)
      X74=CUB74(Y59)
      XX=(X74*(DAYN-CD59)+X59*(CD74-DAYN))/(CD74-CD59)
      GO TO 50
C
   20 CONTINUE
      X74=CUB74(Y59)
      X80=CUB80(Y59)
      XX=(X80*(DAYN-CD74)+X74*(CD80-DAYN))/(CD80-CD74)
C
   50 CONTINUE
      AJ80=CUB80I(XX)
      RETURN
      END


      FUNCTION CUB59(A59)
      DJ=0.576-0.005011*A59
      A74 = A59 + DJ
      CUB59=CUB74(A74)
      RETURN
      END


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


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


      FUNCTION CUBM74(YJ)
      CUBM74=76.582+YJ*(0.584910+YJ*(3.1151E-4+7.3225E-7*YJ))
      RETURN
      END


      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
```

```fortran
      SUBROUTINE CORR1(DAYN,AJ80,BJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80
      QUAD70(AJ) = 7.036 + AJ*(-0.051734 + 0.000093176*AJ)
      QUAD72(AJ) = 6.565 + AJ*(-0.051026 + 0.000093967*AJ)
      QUAD78(AJ) = -.444 + AJ*(0.005385 - 0.000012695*AJ)
C
      DJ=0.
C
      IF(DAYN.GT.CD70)GO TO 10
      IF(DAYN.LT.CD59)GO TO 50
      DJ70=QUAD70(AJ80)
      DJ=(DAYN-CD59)/(CD70-CD59)*DJ70
      GO TO 50
C
   10 IF(DAYN.GT.CD72)GO TO 20
      DJ70=QUAD70(AJ80)
      DJ72=QUAD72(AJ80)
      DJ=(DJ72*(DAYN-CD70)+DJ70*(CD72-DAYN))/(CD72-CD70)
      GO TO 50
C
   20 IF(DAYN.GT.CD74)GO TO 30
      DJ72=QUAD72(AJ80)
      DJ=(CD74-DAYN)/(CD74-CD72)*DJ72
      GO TO 50
C
   30 IF(DAYN.GT.CD78)GO TO 40
      DJ78=QUAD78(AJ80)
      DJ=(DAYN-CD74)/(CD78-CD74)*DJ78
      GO TO 50
C
   40 CONTINUE
      IF(DAYN.GT.CD80)GO TO 50
      DJ78=QUAD78(AJ80)
      DJ=(CD80-DAYN)/(CD80-CD78)*DJ78
C
   50 BJ80=AJ80+DJ
      RETURN
      END




      SUBROUTINE CORR2(DAYN,BJ80,CJ80)
      COMMON/CAL/CD59,CD62,CD66,CD70,CD72,CD74,CD78,CD80
      STLN62(BJ) = -1.736 + .005661*BJ
      STLN66(BJ) = 3.059 - .009219*BJ
C
      DJ=0.
C
      IF(DAYN.GT.CD62)GO TO 10
      IF(DAYN.LT.CD59)GO TO 50
      DJ62=STLN62(BJ80)
      DJ=(DAYN-CD59)/(CD62-CD59)*DJ62
      GO TO 50
C
   10 IF(DAYN.GT.CD66)GO TO 20
      DJ62=STLN62(BJ80)
      DJ66=STLN66(BJ80)
      DJ=(DJ66*(DAYN-CD62)+DJ62*(CD66-DAYN))/(CD66-CD62)
      GO TO 50
C
   20 CONTINUE
      IF(DAYN.GT.CD70)GO TO 50
      DJ66=STLN66(BJ80)
      DJ=(CD70-DAYN)/(CD70-CD66)*DJ66
C
   50 CJ80=BJ80+DJ
      RETURN
      END
```

Table 14. Corrections JA - J, JB - JA, and JC - JB to be applied to J for 1 July of each year between 1957 and 1981. All differences above have been multiplied by 100. See Table 13 for a program which calculates JA, JB, and JC. Values for 1981 are tentative. All J values are in ppm.

JA - J
JB - JA
JC - JB

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
280	-259	-252	-246	-240	-234	-228	-222	-216	-210	-204	-198	-192	-186	-180	-174	-168	-162	-156	-133	-108	-82	-57	-31	-6	20
	0	0	0	0	-1	-3	-4	-6	-7	-9	-10	-12	-13	-15	-24	-33	-21	-2	2	4	6	6	3	1	0
	0	0	0	0	-8	-16	0	17	33	50	37	25	12	0	0	0	0	0	0	0	0	0	0	0	0
290	-245	-238	-232	-226	-219	-213	-207	-200	-194	-188	-181	-175	-169	-162	-156	-150	-143	-137	-117	-94	-72	-50	-27	-5	17
	0	0	0	0	-1	-3	-4	-5	-7	-8	-9	-11	-12	-13	-22	-31	-20	-2	1	3	4	4	2	0	0
	0	0	0	0	-5	-11	2	15	28	40	30	20	10	0	0	0	0	0	0	0	0	0	0	0	0
300	-232	-225	-219	-212	-205	-199	-192	-185	-179	-172	-165	-158	-152	-145	-138	-132	-125	-118	-101	-81	-62	-43	-24	-4	15
	0	0	0	0	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10	-19	-27	-17	-2	1	2	2	3	1	0	0
	0	0	0	0	-2	-5	4	13	22	31	23	15	8	0	0	0	0	0	0	0	0	0	0	0	0
310	-220	-213	-206	-199	-192	-185	-178	-170	-163	-156	-149	-142	-135	-128	-121	-114	-107	-100	-85	-69	-52	-36	-20	-4	13
	0	0	0	0	-1	-1	-2	-2	-3	-3	-4	-4	-5	-5	-13	-21	-14	-1	0	0	1	1	0	0	0
	0	0	0	0	0	1	6	11	16	22	16	11	5	0	0	0	0	0	0	0	0	0	0	0	0
320	-208	-201	-193	-186	-178	-171	-164	-156	-149	-141	-134	-127	-119	-112	-104	-97	-90	-82	-70	-56	-43	-30	-16	-3	10
	0	0	0	0	0	0	0	0	1	1	1	1	1	1	-6	-13	-9	-1	0	-1	-2	-2	-1	0	0
	0	0	0	0	3	7	8	9	11	12	9	6	3	0	0	0	0	0	0	0	0	0	0	0	0
330	-197	-189	-181	-173	-165	-158	-150	-142	-134	-127	-119	-111	-103	-96	-88	-80	-72	-65	-54	-44	-34	-23	-13	-2	8
	0	0	0	0	1	2	3	4	5	6	7	8	9	10	3	-3	-3	0	-1	-3	-4	-4	-2	0	0
	0	0	0	0	6	12	10	8	5	3	2	1	1	0	0	0	0	0	0	0	0	0	0	0	0
340	-185	-177	-169	-161	-153	-145	-136	-128	-120	-112	-104	-96	-88	-80	-72	-63	-55	-47	-39	-32	-24	-17	-9	-2	6
	0	0	0	0	2	4	6	8	10	12	14	17	19	21	15	9	4	0	-2	-4	-7	-7	-4	-1	0
	0	0	0	0	9	18	12	6	0	-7	-5	-3	-2	0	0	0	0	0	0	0	0	0	0	0	0
350	-174	-166	-157	-149	-140	-132	-123	-115	-106	-98	-89	-81	-72	-64	-55	-47	-39	-30	-25	-20	-15	-11	-6	-1	4
	0	0	0	0	3	6	10	13	16	20	23	27	30	33	28	22	13	1	-3	-6	-9	-10	-5	-1	0
	0	0	0	0	12	24	14	4	-6	-16	-12	-8	-4	0	0	0	0	0	0	0	0	0	0	0	0
360	-163	-155	-146	-137	-128	-119	-110	-102	-93	-84	-75	-66	-57	-49	-40	-31	-22	-13	-10	-8	-6	-4	-2	-1	1
	0	0	0	0	5	9	14	19	24	28	33	38	43	48	43	38	22	2	-4	-8	-12	-13	-7	-1	0
	0	0	0	0	15	30	16	2	-12	-25	-19	-13	-6	0	0	0	0	0	0	0	0	0	0	0	0
370	-153	-143	-134	-125	-116	-107	-97	-88	-79	-70	-61	-51	-42	-33	-24	-15	-5	4	4	3	3	2	1	0	-1
	0	0	0	0	6	13	19	25	32	38	45	51	58	64	60	56	33	4	-5	-10	-16	-16	-9	-2	0
	0	0	0	0	18	35	18	0	-17	-35	-26	-18	-9	0	0	0	0	0	0	0	0	0	0	0	0
380	-142	-132	-123	-113	-104	-94	-85	-75	-65	-56	-46	-37	-27	-18	-8	1	11	21	19	15	12	8	4	1	-3
	0	0	0	0	8	16	24	33	41	49	58	66	74	83	79	75	45	5	-6	-12	-19	-20	-11	-2	0
	0	0	0	0	20	41	20	-1	-23	-44	-33	-22	-11	0	0	0	0	0	0	0	0	0	0	0	0

Table 15. Total correction JC - J to be applied to J for 1 July of each year between 1957 and 1981. All differences JC-J have been multiplied by 100. See Table 13 for computer program which calculates JC. Values for 1981 are tentative. All J values are in ppm.

JC - J

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
170	-456	-454	-452	-450	-478	-506	-435	-364	-294	-224	-250	-276	-302	-328	-341	-353	-383	-417	-358	-286	-214	-144	-79	-14	54
180	-432	-430	-427	-425	-452	-478	-413	-347	-283	-219	-244	-270	-294	-319	-332	-343	-364	-389	-332	-265	-197	-132	-73	-13	50
190	-410	-407	-404	-402	-427	-451	-392	-333	-272	-213	-239	-262	-287	-311	-323	-334	-347	-361	-308	-245	-181	-122	-66	-12	46
200	-389	-386	-383	-380	-403	-426	-372	-317	-262	-208	-232	-255	-279	-302	-313	-322	-329	-335	-284	-225	-167	-111	-61	-11	43
210	-369	-364	-362	-359	-380	-402	-352	-303	-253	-204	-226	-247	-270	-292	-302	-311	-312	-310	-262	-207	-153	-102	-56	-10	40
220	-351	-347	-343	-339	-358	-379	-334	-288	-243	-196	-219	-240	-261	-281	-290	-298	-295	-287	-241	-190	-140	-93	-51	-9	36
230	-333	-329	-325	-321	-338	-355	-315	-274	-234	-193	-213	-232	-251	-270	-278	-285	-277	-263	-221	-174	-128	-84	-46	-8	33
240	-316	-312	-307	-303	-318	-333	-297	-261	-224	-189	-206	-223	-239	-256	-264	-270	-259	-241	-201	-159	-116	-77	-42	-8	31
250	-301	-295	-291	-286	-299	-311	-279	-246	-215	-183	-198	-213	-228	-243	-249	-255	-240	-220	-183	-144	-105	-70	-38	-7	28
260	-286	-280	-275	-270	-280	-289	-261	-233	-205	-176	-190	-203	-216	-228	-233	-239	-223	-198	-166	-130	-95	-63	-34	-6	25
270	-271	-266	-260	-255	-261	-268	-244	-218	-195	-170	-181	-192	-201	-212	-217	-221	-204	-178	-148	-116	-86	-57	-31	-5	22
280	-258	-252	-246	-240	-243	-247	-226	-205	-184	-163	-171	-179	-187	-195	-198	-201	-183	-158	-131	-104	-76	-51	-28	-5	20
290	-245	-238	-232	-226	-225	-227	-209	-190	-173	-156	-160	-166	-171	-175	-178	-181	-163	-139	-116	-91	-68	-46	-25	-5	17
300	-232	-225	-219	-212	-208	-206	-191	-176	-162	-147	-149	-151	-153	-155	-157	-159	-142	-120	-100	-79	-60	-40	-23	-4	15
310	-220	-213	-206	-199	-193	-185	-174	-161	-150	-137	-137	-135	-135	-133	-134	-135	-121	-101	-85	-69	-51	-35	-20	-4	13
320	-208	-201	-193	-186	-175	-164	-156	-147	-137	-128	-124	-120	-115	-111	-110	-110	-99	-83	-70	-57	-45	-32	-17	-3	10
330	-197	-189	-181	-173	-158	-144	-137	-130	-124	-118	-110	-102	-93	-86	-85	-83	-75	-65	-55	-47	-38	-27	-15	-2	8
340	-185	-177	-169	-161	-142	-123	-118	-114	-110	-107	-95	-82	-71	-59	-57	-54	-51	-47	-41	-36	-31	-24	-13	-3	6
350	-174	-166	-157	-149	-125	-102	-99	-98	-96	-94	-78	-62	-46	-31	-27	-25	-26	-29	-28	-26	-24	-21	-11	-2	4
360	-163	-155	-146	-137	-108	-80	-60	-81	-81	-81	-61	-41	-20	-1	3	7	0	-11	-14	-16	-18	-17	-9	-2	1
370	-153	-143	-134	-125	-92	-59	-60	-63	-64	-67	-42	-18	7	31	36	41	28	8	-1	-7	-13	-14	-8	-2	-1
380	-142	-132	-123	-113	-76	-37	-41	-43	-47	-51	-21	7	36	65	71	76	56	26	13	3	-7	-12	-7	-1	-3
390	-132	-122	-112	-102	-59	-15	-20	-24	-29	-35	-1	33	67	101	107	114	85	43	26	12	-3	-10	-5	-1	-5
400	-121	-111	-100	-90	-42	8	2	-4	-11	-16	21	60	99	138	146	153	116	62	39	21	3	-8	-4	-1	-7
410	-110	-100	-89	-78	-24	30	24	16	9	2	45	89	133	177	187	195	147	81	53	30	8	-6	-4	0	-9
420	-100	-89	-78	-67	-7	54	46	38	30	22	70	120	169	219	228	238	180	98	65	38	12	-4	-2	-1	-11
430	-89	-78	-66	-55	11	78	69	60	52	42	98	152	207	263	273	284	214	117	78	47	17	-3	-2	0	-14
440	-79	-67	-55	-43	30	102	93	85	75	65	126	186	246	307	320	332	249	136	92	56	21	-1	0	0	-16
450	-68	-55	-43	-31	48	126	118	108	99	88	155	222	288	355	368	381	286	156	105	65	25	0	0	0	-18

Table 16.   Comparison of XC = CUB2(JC), where CUB2 is the 1980 calibration curve, and XWMO, the 1974 Manometric value (see Equation (43) of text), for values of J for each year between 1957 and 1981. The 1974 Manometric value is based on assuming a drift for all concentrations of −0.06 ppm (J) per year, from 1 July 1974. The cubic parameters are from a fit of 1974 analyzer data to 1974 manometric data alone, and thus are slightly different from the 1974 curve used to make the JA correction. All differences XC−XWMO have been multiplied by 100. Values for 1981 are tentative. All J and X values are in ppm.

$$XC - XWMO$$

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
170	47	44	41	37	13	−12	35	82	129	176	152	129	105	92	68	54	28	−2	37	85	134	180	223	267	312
180	42	39	37	34	9	−15	29	73	117	160	137	113	90	66	53	39	19	−4	34	80	126	170	210	250	293
190	38	35	33	30	6	−17	23	64	105	146	122	99	75	52	39	26	11	−5	31	75	118	159	197	234	274
200	34	31	29	27	4	−19	18	56	94	131	108	85	62	39	26	14	3	−6	29	70	111	149	184	218	256
210	30	28	25	23	1	−21	14	48	83	117	95	72	50	28	15	3	−3	−6	27	65	104	140	171	203	238
220	26	24	22	20	−1	−22	10	41	73	104	82	61	39	17	5	−7	−8	−7	25	61	97	130	159	188	220
230	22	20	18	17	−3	−22	6	35	63	91	71	50	29	8	−3	−15	−13	−7	23	57	90	121	147	174	204
240	18	16	15	14	−4	−22	3	29	54	79	60	40	20	1	−10	−21	−17	−7	22	52	83	111	136	160	187
250	13	12	11	10	−6	−22	1	23	45	68	49	31	13	−6	−16	−27	−19	−6	20	48	76	102	124	145	170
260	9	8	8	7	−7	−21	−1	18	37	57	40	23	7	−10	−20	−30	−21	−6	19	44	69	92	112	131	154
270	5	4	4	3	−8	−20	−3	13	30	46	31	16	2	−13	−23	−32	−22	−5	17	39	62	82	100	117	137
280	0	0	0	0	−9	−18	−4	9	23	36	24	11	−2	−15	−24	−32	−21	−4	15	35	54	72	88	103	120
290	−5	−5	−4	−4	−10	−16	−5	6	16	27	17	6	−4	−15	−23	−31	−20	−3	13	30	46	62	75	89	103
300	−10	−9	−9	−8	−11	−14	−6	2	10	19	11	3	−5	−13	−20	−27	−18	−2	11	25	38	51	62	74	86
310	−15	−14	−14	−13	−12	−11	−6	0	5	11	6	1	−4	−9	−16	−22	−14	−1	9	19	29	39	49	58	68
320	−21	−20	−19	−17	−13	−8	−5	−2	0	3	1	0	−2	−3	−9	−15	−9	0	7	13	20	27	35	43	50
330	−28	−26	−24	−23	−14	−5	−4	−4	−4	−4	−2	0	2	5	−1	−6	−4	1	4	7	10	14	20	27	31
340	−34	−32	−30	−28	−15	−1	−3	−5	−7	−10	−4	2	8	14	10	6	4	2	1	0	−1	−4	5	10	12
350	−42	−39	−36	−34	−16	3	−1	−6	−10	−15	−5	6	16	26	23	20	12	2	−3	−8	−13	−14	−11	−8	−8
360	−49	−46	−43	−40	−17	7	1	−6	−13	−20	−5	10	25	40	38	36	22	3	−7	−16	−25	−30	−28	−26	−30
370	−58	−54	−51	−47	−18	12	3	−6	−14	−23	−3	17	37	57	56	55	33	4	−11	−25	−38	−47	−46	−46	−52
380	−66	−63	−59	−55	−19	17	6	−4	−15	−26	−1	25	51	76	76	76	45	5	−16	−34	−53	−64	−65	−66	−75
390	−76	−72	−67	−63	−21	22	10	−3	−16	−28	3	35	66	98	99	100	59	5	−22	−45	−68	−84	−86	−88	−99
400	−86	−82	−77	−72	−22	28	14	−1	−15	−30	8	46	84	123	125	127	75	5	−28	−57	−85	−104	−107	−110	−125
410	−97	−92	−87	−81	−24	34	18	2	−14	−30	15	60	105	150	153	157	92	5	−35	−69	−103	−126	−130	−134	−151
420	−109	−103	−97	−91	−26	40	23	6	−11	−29	23	75	128	181	185	190	111	5	−43	−82	−122	−149	−154	−159	−180
430	−122	−115	−109	−102	−28	46	28	10	−8	−27	33	93	153	214	220	226	131	5	−51	−97	−143	−174	−180	−186	−210
440	−135	−128	−121	−114	−31	53	34	15	−4	−24	44	113	181	251	258	265	154	4	−60	−113	−165	−200	−207	−214	−241
450	−150	−142	−134	−127	−33	60	41	21	0	−20	57	135	213	291	300	309	178	3	−70	−129	−188	−228	−236	−244	−274

Table 17. Comparison of XC = CUB2(JC), where CUB2 is the 1980 calibration curve, and J, for values of J for each year between 1957 and 1981. All differences XC-J have been multiplied by 100. Values for 1981 are tentative. All J and X values are in ppm.

XC − J

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
170	1831	1833	1834	1836	1816	1796	1847	1899	1950	2001	1982	1963	1944	1925	1916	1907	1885	1860	1903	1956	2009	2060	2108	2156	2206
180	1587	1589	1590	1592	1572	1553	1601	1650	1698	1747	1728	1709	1690	1671	1662	1653	1637	1619	1661	1712	1762	1811	1856	1901	1948
190	1356	1359	1361	1363	1344	1325	1370	1416	1461	1506	1488	1469	1450	1432	1423	1415	1404	1393	1434	1482	1530	1576	1618	1660	1705
200	1141	1143	1146	1148	1130	1112	1154	1196	1239	1281	1263	1245	1226	1208	1200	1192	1187	1182	1222	1268	1313	1357	1396	1435	1477
210	940	943	946	948	931	914	953	993	1032	1072	1054	1036	1019	1001	994	986	985	987	1025	1068	1112	1152	1189	1226	1265
220	755	758	761	764	748	732	769	805	842	878	861	844	828	811	804	797	800	807	844	885	925	964	998	1032	1069
230	586	589	592	596	581	567	601	634	667	701	685	669	654	638	631	625	632	643	678	717	755	791	823	854	889
240	432	436	440	444	431	419	449	480	510	541	526	512	497	483	477	471	481	496	529	565	601	635	664	693	725
250	296	300	304	309	298	287	315	342	370	398	385	372	358	345	340	335	347	366	397	431	464	495	522	549	579
260	177	181	186	190	182	173	198	223	248	273	261	250	238	227	222	218	232	253	283	313	344	373	397	422	450
270	75	80	85	90	84	78	100	122	144	166	156	147	137	128	124	120	136	158	185	213	241	267	290	313	338
280	-9	-4	1	7	4	0	19	39	58	77	70	63	55	48	45	42	58	81	106	131	156	180	201	222	245
290	-75	-69	-64	-58	-58	-58	-42	-25	-9	8	3	-2	-6	-11	-14	-16	1	23	45	68	90	111	130	149	169
300	-123	-116	-110	-103	-100	-97	-84	-70	-56	-42	-44	-46	-48	-50	-51	-53	-37	-16	3	23	42	60	77	95	113
310	-151	-144	-137	-130	-124	-117	-105	-94	-83	-71	-70	-69	-68	-67	-68	-69	-55	-36	-20	-3	13	28	44	60	75
320	-159	-152	-145	-138	-127	-116	-107	-98	-90	-81	-76	-72	-67	-63	-63	-62	-51	-36	-23	-10	3	16	30	44	57
330	-148	-141	-133	-125	-110	-95	-88	-82	-75	-69	-61	-53	-44	-36	-35	-34	-26	-15	-6	3	12	23	35	48	59
340	-117	-109	-100	-92	-72	-52	-48	-44	-40	-36	-24	-11	1	13	15	18	21	26	31	37	42	50	61	72	80
350	-65	-56	-47	-38	-14	11	13	15	17	19	36	52	69	86	89	92	91	88	89	91	92	97	106	116	122
360	8	17	27	36	67	97	97	97	97	96	118	139	161	183	187	191	183	172	168	166	163	165	173	181	185
370	102	112	122	132	169	205	203	201	199	197	223	250	277	304	309	315	300	278	269	262	255	254	261	268	269
380	219	229	240	251	293	336	332	328	324	320	352	385	417	450	457	463	439	406	392	380	369	364	370	376	374
390	357	368	379	391	440	490	484	479	473	467	506	544	583	622	629	637	604	556	536	520	504	496	501	506	501
400	518	530	542	554	610	667	660	653	646	639	683	729	774	819	828	838	793	730	704	683	662	650	654	658	650
410	702	715	727	740	804	869	861	852	844	835	887	939	991	1044	1054	1065	1007	928	895	868	842	826	829	832	822
420	910	923	936	950	1022	1096	1086	1076	1067	1057	1116	1176	1235	1295	1307	1319	1248	1150	1109	1077	1045	1025	1028	1030	1017
430	1141	1155	1169	1183	1265	1347	1336	1326	1315	1303	1371	1439	1506	1575	1588	1602	1515	1396	1347	1309	1271	1248	1249	1250	1234
440	1397	1411	1426	1441	1532	1623	1612	1601	1589	1577	1653	1729	1806	1883	1898	1913	1809	1667	1610	1566	1521	1493	1494	1495	1475
450	1677	1692	1708	1723	1824	1926	1914	1902	1890	1877	1962	2047	2133	2219	2236	2253	2130	1963	1897	1846	1795	1763	1763	1763	1741

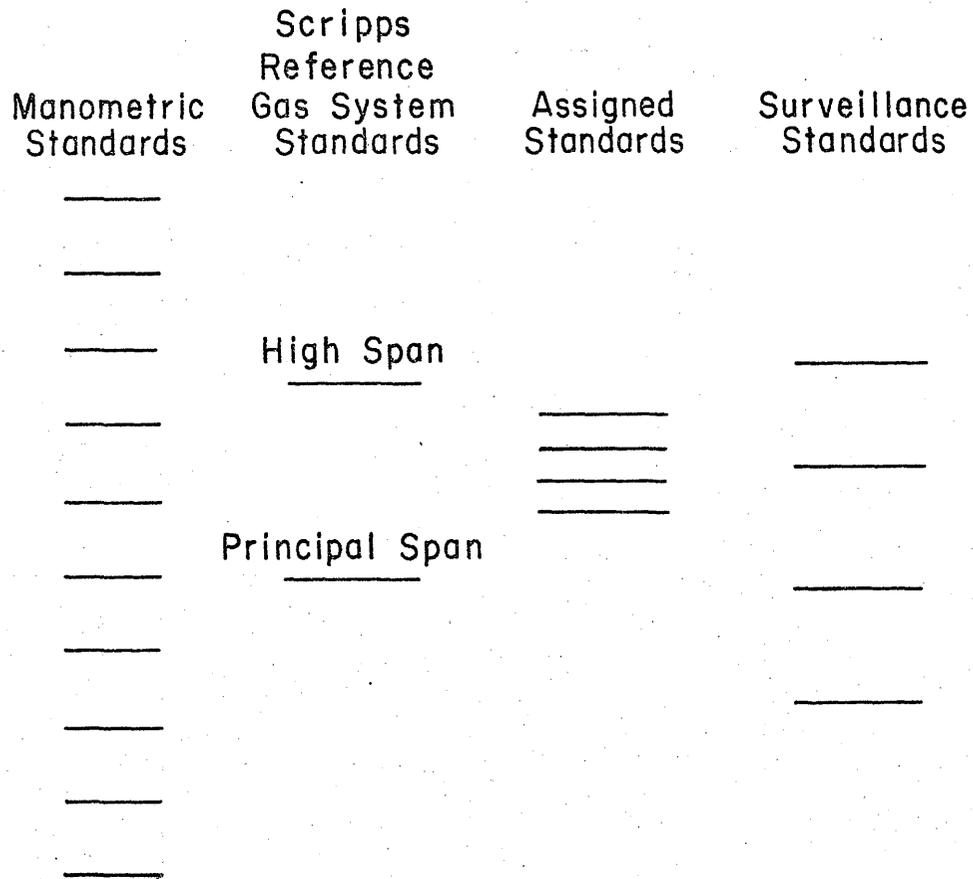| | Scripps Reference Gas System Standards | | |
| Manometric Standards | | Assigned Standards | Surveillance Standards |

High Span

Principal Span

Figure 1. The CO_2 Reference Gas System consists of 10 manometric

standards, two Scripps reference gas system standards called the

Principal Span and the High Span, and numerous assigned standards

and surveillance standards. All of these gas mixtures are CO_2-in-N_2,

except for some assigned standards consisting of CO_2-in-air. All are

stored in commercially available 250 cu. ft. chrome-molybdenum steel

cylinders.
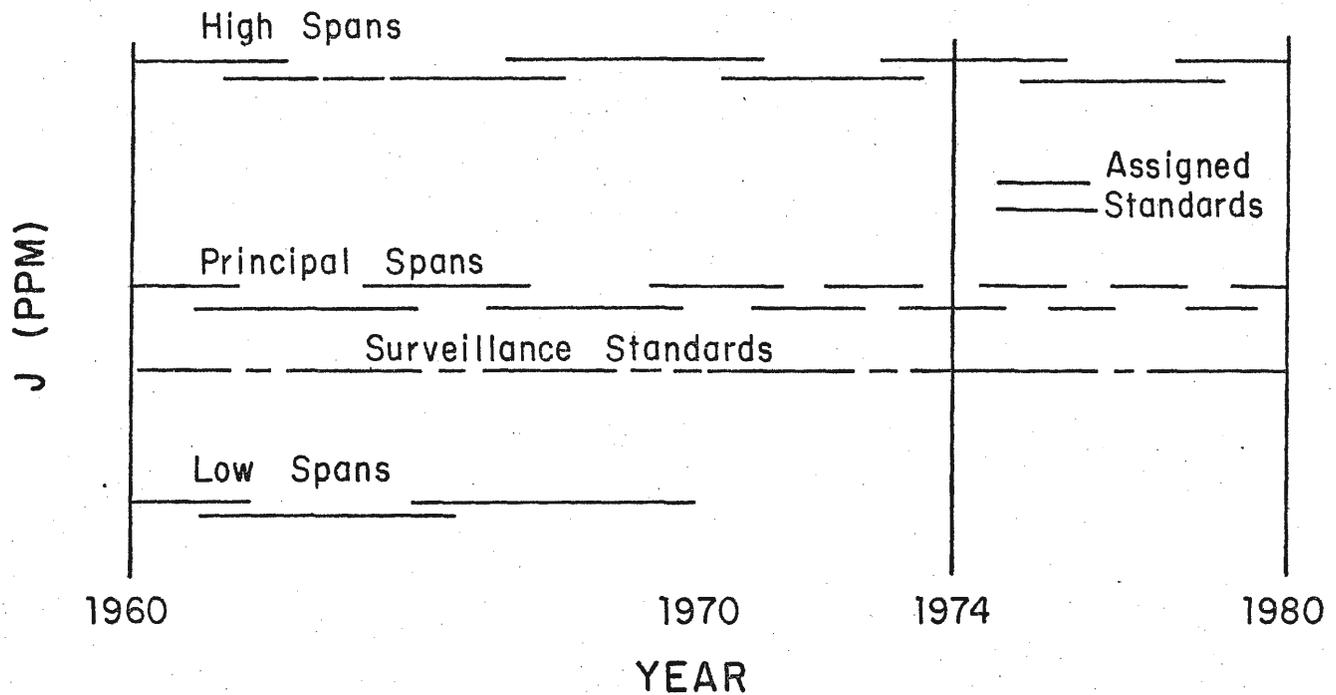
Figure 2. Operation of the CO_2 Reference Gas System: horizontal lines represent cylinders of gas, plotted versus time with respect to their Adjusted Index values, J; solid vertical lines indicate times of manometric calibrations. Assigned standards are prepared by comparison with the Principal Span and High Span standards. Prior to 1970, a Low Span standard was used with the Principal Span standard for part of the preparation of low concentration gas mixtures. New Scripps system standards are created by comparison with older Scripps system standards. The plot is schematic to illustrate the system, since actually, many more replacements occurred between 1960 and 1980 than are shown.
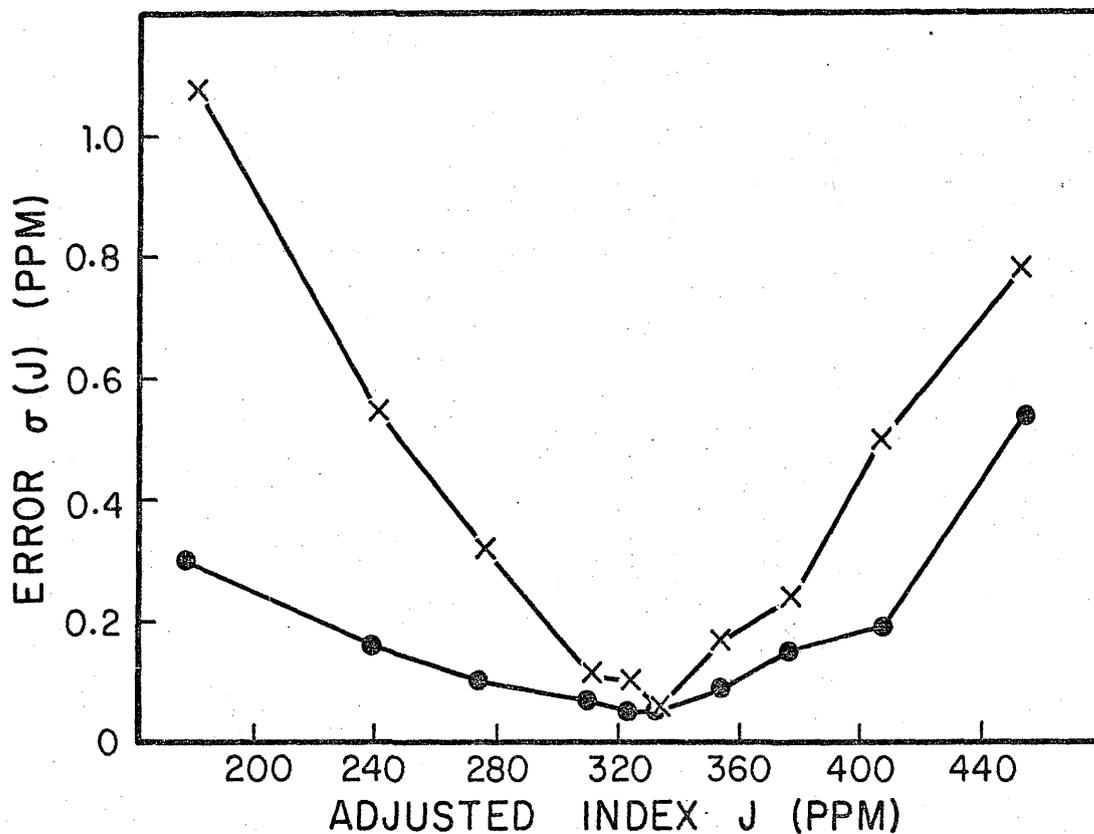
Figure 3. Standard deviation σ of infrared analyzer measurements: crosses, 1974 calibration: dots, 1980 calibration. One would expect the dispersion to be greater for extreme concentrations because the sensitivity is determined by the Principal Span to High Span difference. By basing the sensitivity on all the gas mixtures compared during the day, the average standard deviation was reduced to 0.16 ppm and 0.12 ppm for the 1974 and 1980 calibrations, respectively, but the means were essentially unchanged. All the standards were run together on each day for the 1980 calibration, whereas they were run in three overlapping groups in 1974. Also, data for the 1980 infrared calibration were all recorded digitally. These two differences probably explain the lower dispersions obtained in 1980.
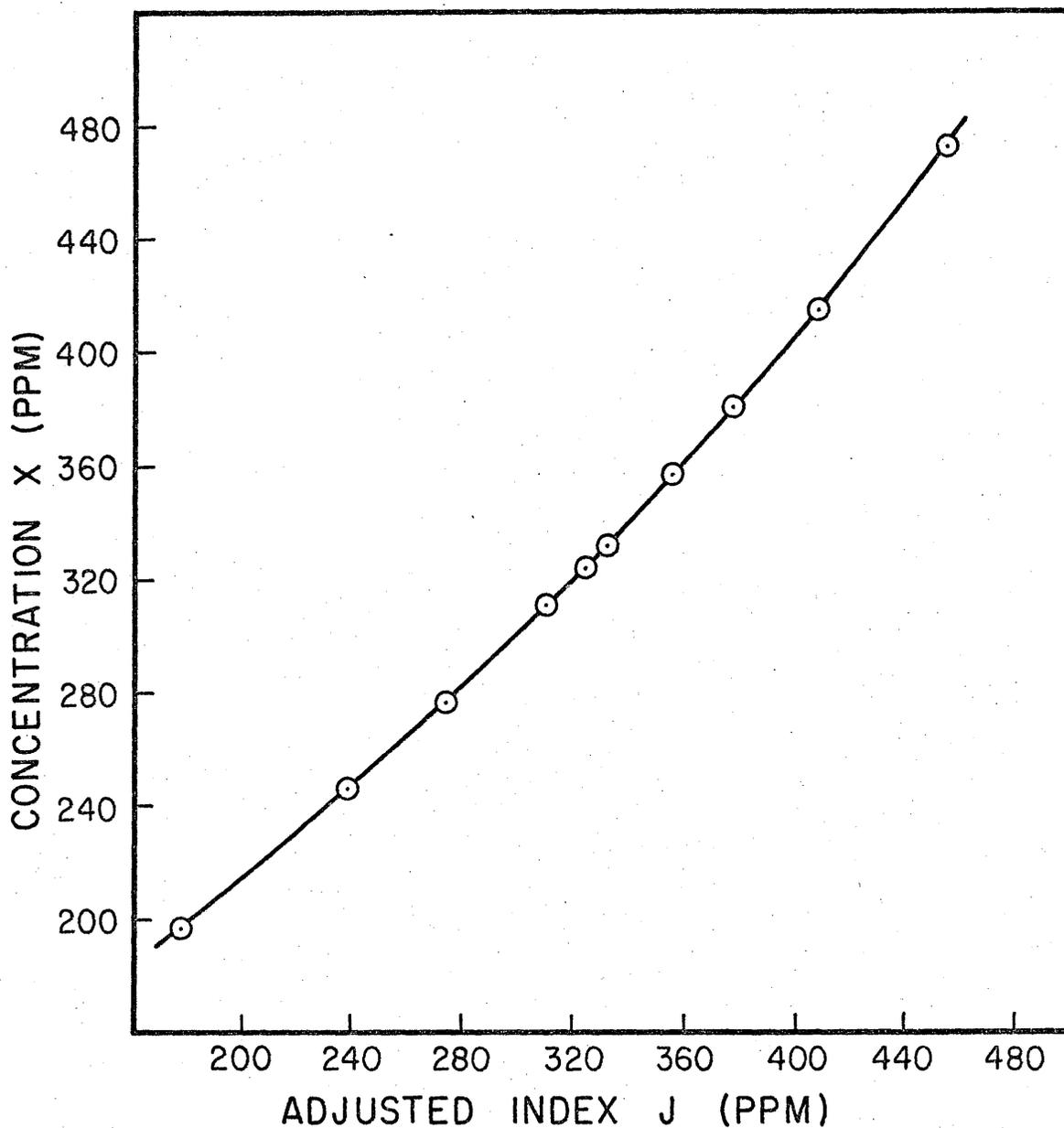
Figure 4. Calibration points and the fitted curve for the 1980 calibration. The values of X used are the weighted average of 1980, 1974, and 1970 measurements (see Table 1). The curve is that of X as a cubic function of J with the assumed error equal for all points. The best-fit constants are listed in Table 12.
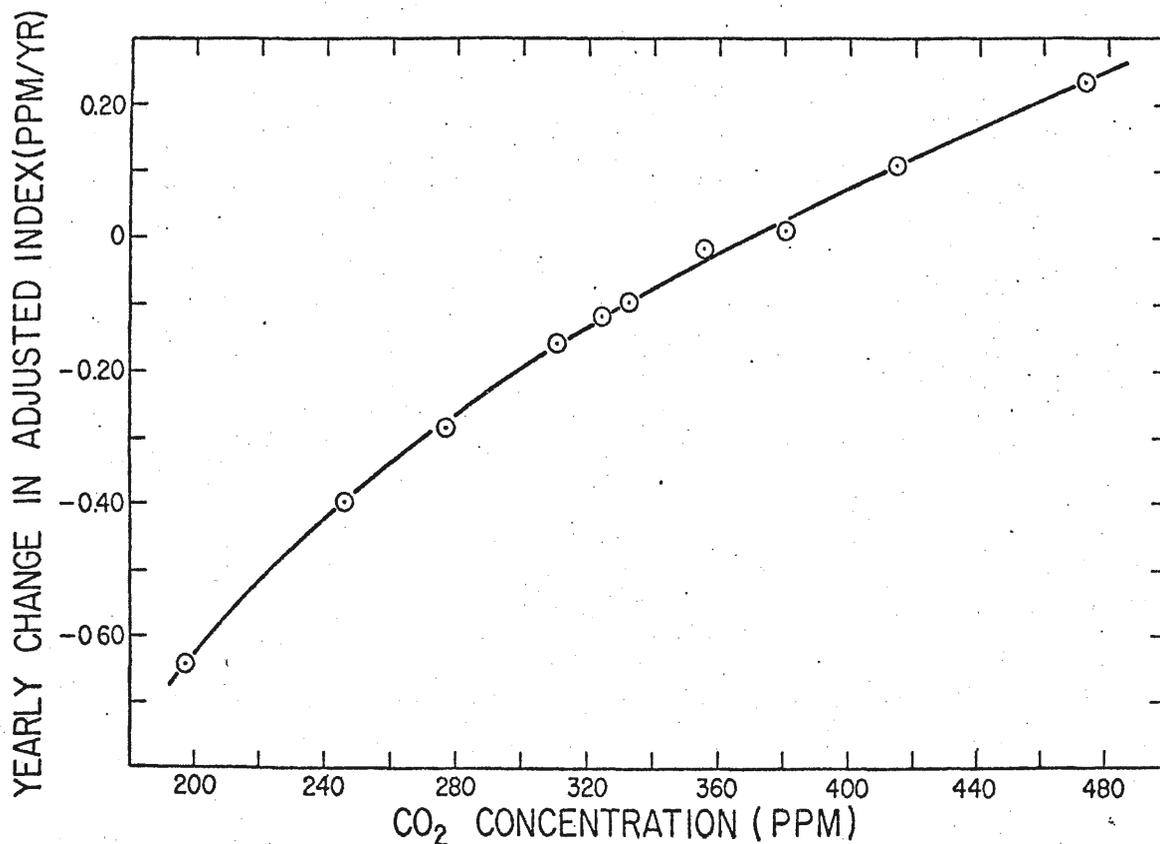
Figure 5. System drift per year, between 1974 and 1980. The drift expressed by differences, (J80 - J74) divided by 6, is plotted on the vertical axis. The circles represent observed values plotted versus the average concentration in X of each manometric standard. The smooth curve is obtained from the fitted calibration curves (see Figure 4 for the 1980 curve). A tangent to this curve at 330 ppm has a slope of approximately 0.0027 per year (this observation is used for comparison with a model estimate in Figure 15).
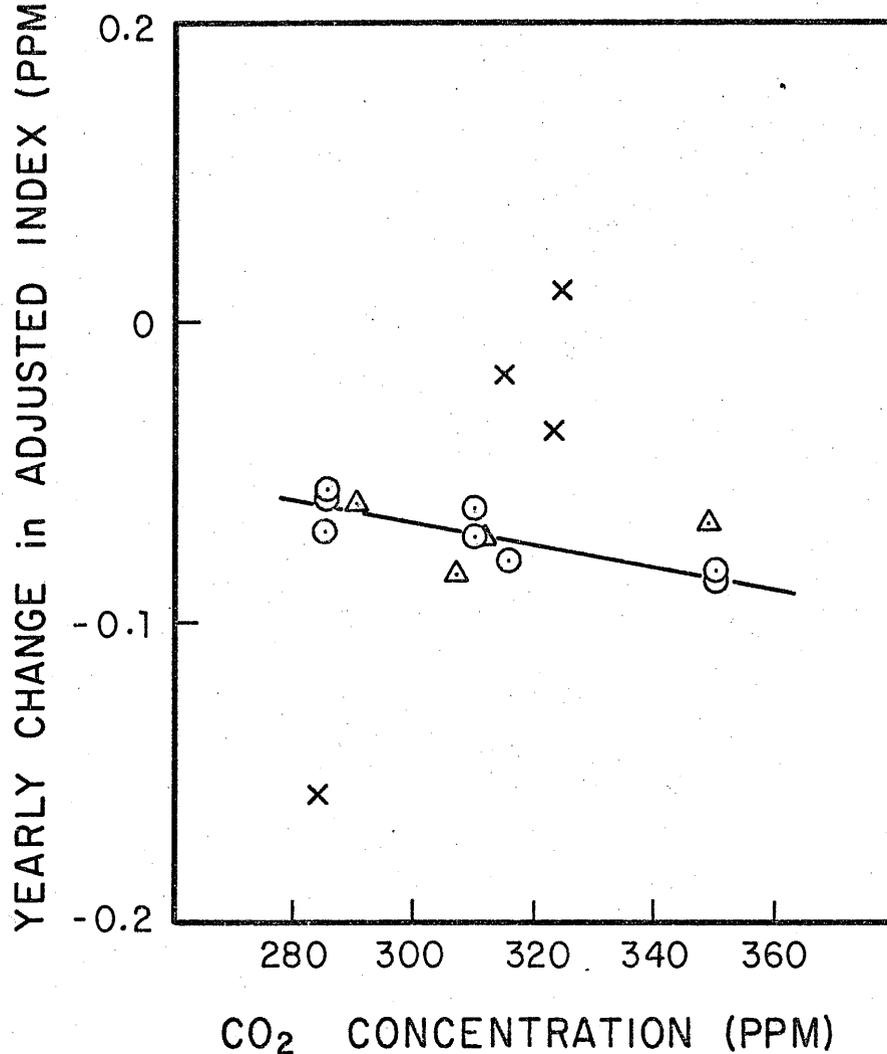
Figure 6. System drift per year between 1960 and 1974. The circles and crosses are from calibration data given in Table 4a. The circles and crosses are differences, (J1 - J60) divided by 14, from Table 4 for each manometric standard, where J1 is the Adjusted Index value, based on the manometric measurement X60, and is obtained by inverting the 1974 calibration curve. The difference is thus a construction to approximate the difference (J74 - J60)/14, which could not be computed directly because no gas analyzer data exist for these gases in 1974. They are plotted against the CO_2 concentration measured in 1960. The straight line is a linear regression fit to data represented by circles; data represented by crosses are judged to be in error (two additional rejected data, off scale are not plotted). The surveillance standards differences (J1S - JS60)/14, from Table 5, denoted by triangles, and discussed below in the text, are an independent check on the regression line, and were not included in the fit. The regression fit is actually to points (J1 - J60, J60) but is here displayed vs X60. The difference between J60 and X60 on the horizontal axis is negligible.
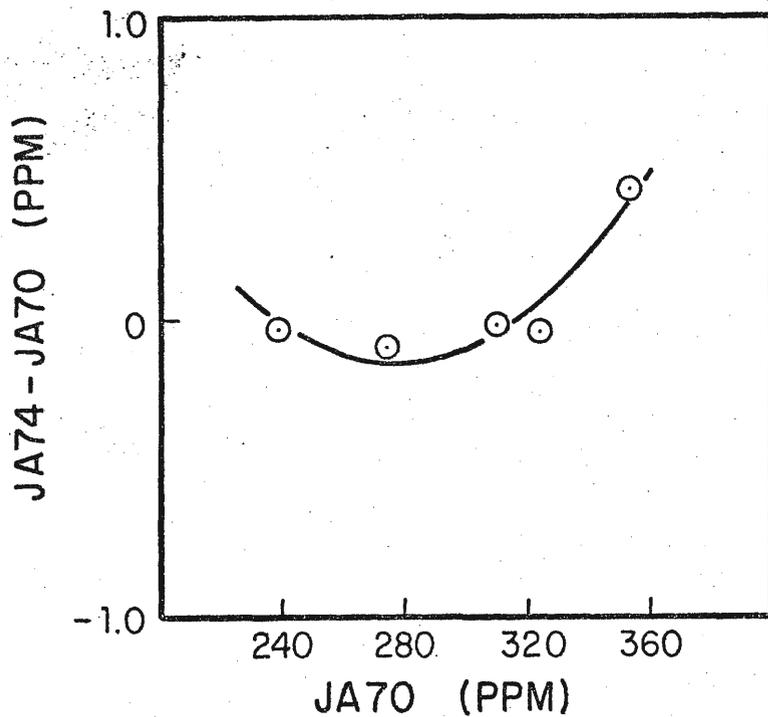
Figure 7.   JB correction in 1970, data from Table 6.
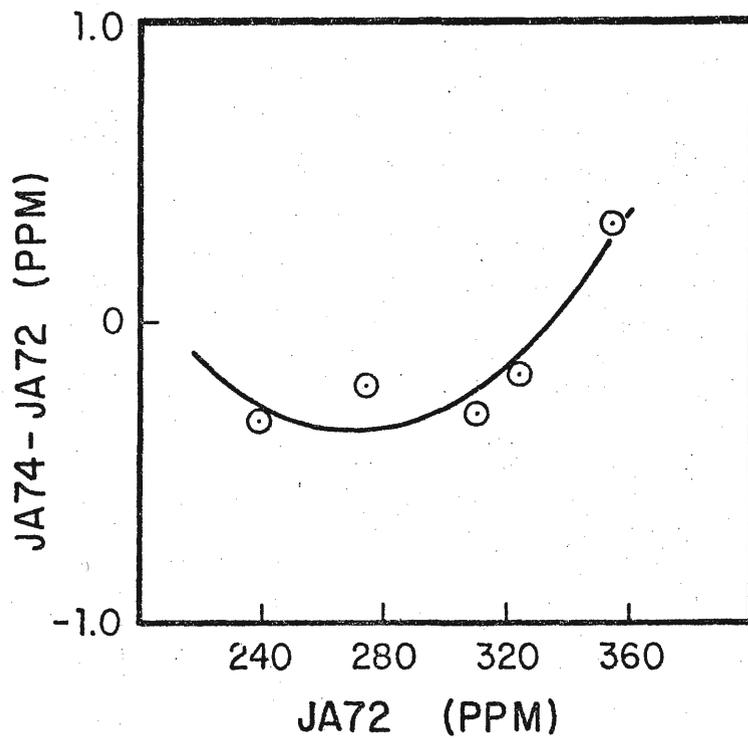
Figure 8.   JB correction in 1972, data from Table 7.
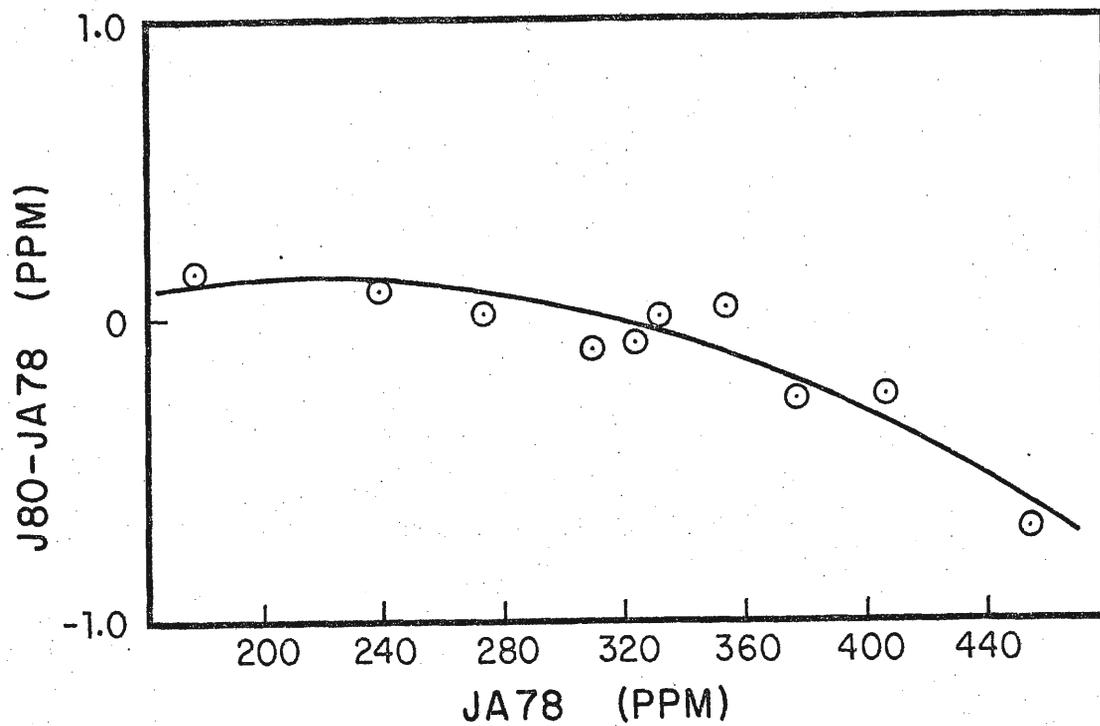
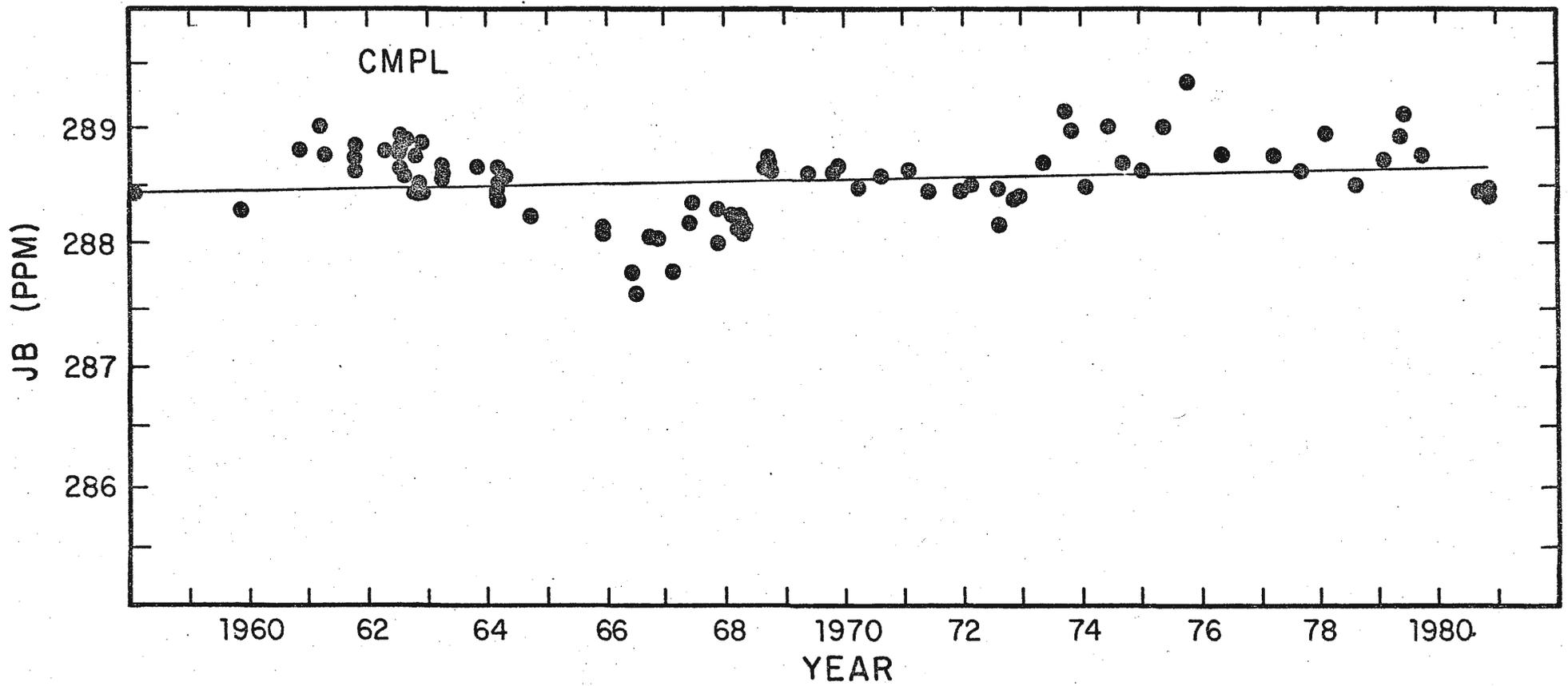Figure 9.   JB Correction in 1978, data from Table 8.

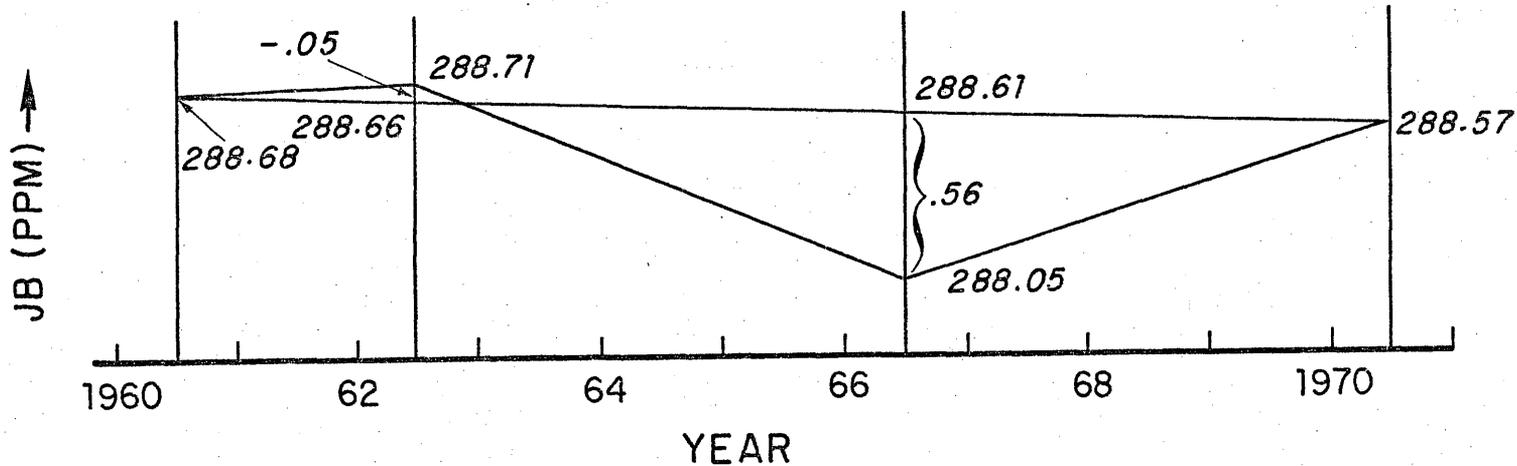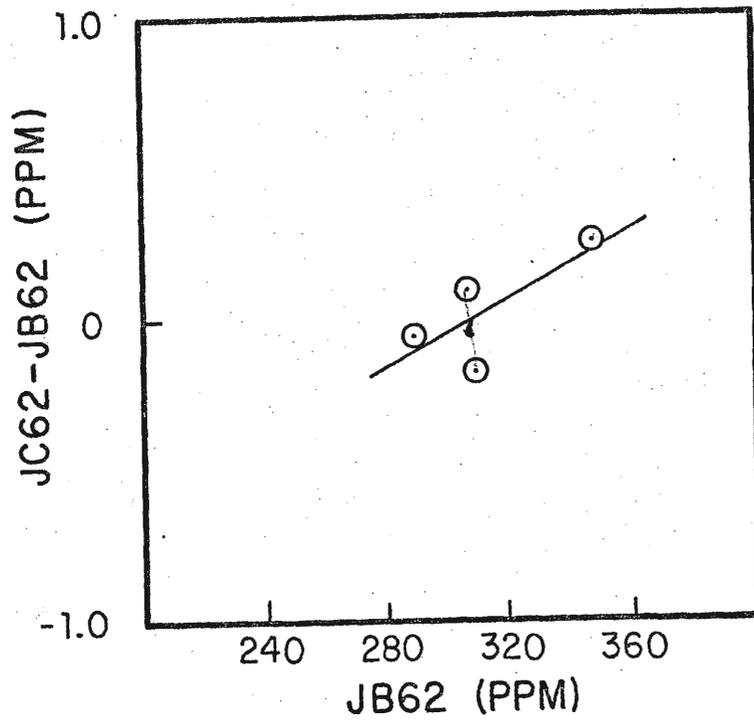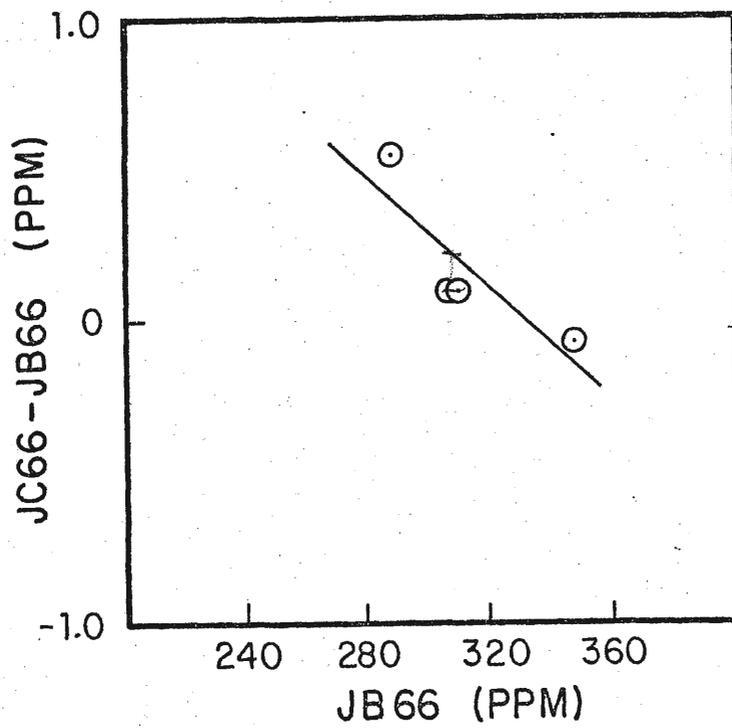Figure 10. Infrared analyzer data for composite surveillance standard CMPL, expressed by the corrected index, JB.

Figure 11. Construction used to determine a JC-JB correction based on data from the composite surveillance standards CMPL (see Figure 10). The value 288.68 ppm plotted on the time axis at 1960.5 years is the average of results for 1959-61. The value 288.57 ppm plotted at 1970.5 is the average results for 1969-71. The values 288.66 ppm at 1962.5 and 288.61 ppm at 1966.5 are from linear interpolation between values at 1960.5 and 1970.5; 288.71 ppm is the observed average of JB during 1962, and 288.05 ppm is the observed average of JB during 1965-67.

Figure 12. JC correction in 1962, data from Table 10.

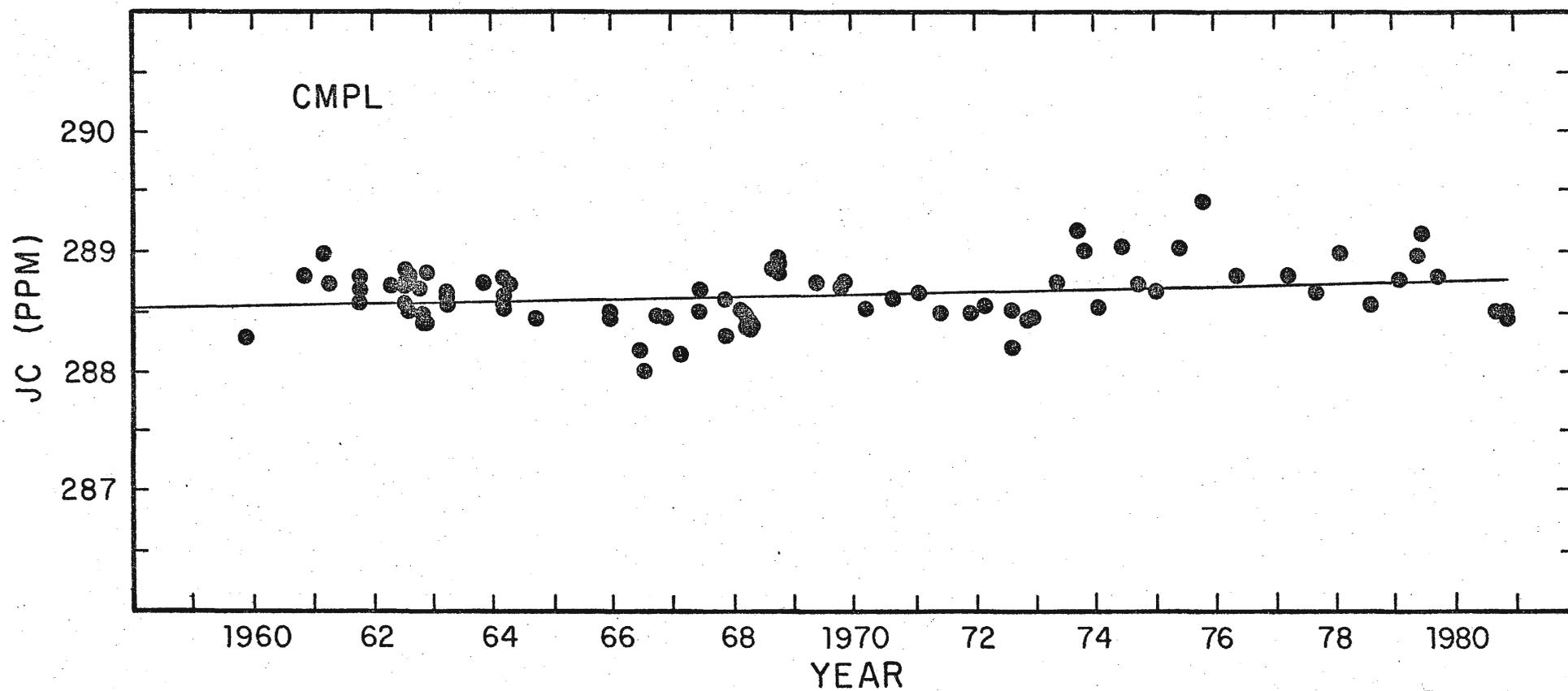Figure 13. JC correction in 1966, data from Table 11.

Figure 14. Infrared analyzer data for composite surveillance standard CMPL corrected to JC. (Compare with Figure 10).
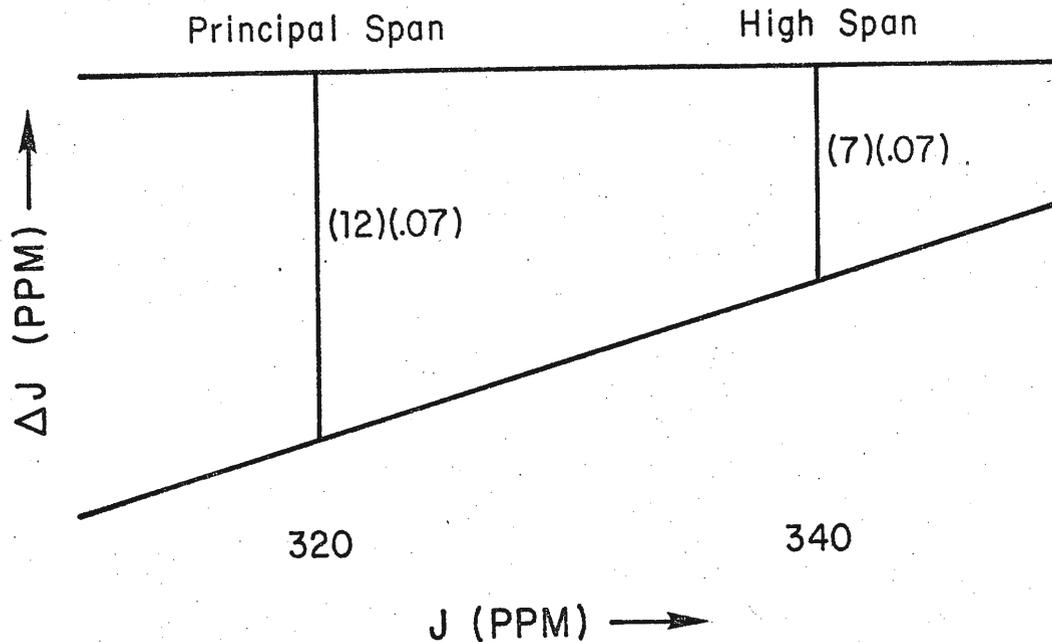
Figure 15. Drift model. Both the magnitude of the drift and its change with concentration are consistent with a model in which each replaced Scripps system standard is assigned a concentration of 0.07 ppm too low. Between 1974 and 1980, there were 12 replacements of the Principal Span standard (~320 ppm) and 7 replacements of the High Span standard (~340 ppm). The expected magnitude of the drift at 340 ppm is thus (7) (0.07)/6 = 0.08 per year, and the expected differential drift is:

$$\frac{(12 - 7)(.07)}{(340 - 320)(6)} = 0.0029 \text{ (ppm per year) per ppm}$$

The observed drift at 340 ppm is approximately 0.08 ppm and the observed differential drift at 330 ppm is approximately 0.0027 per year.