VOLUMETRIC REPORT I

J. Alexander Adams
Carbon Dioxide Project
Scripps Institution of Oceanography
La Jolla, California 92093

August 27, 1975

Revised March 18, 1977

I. Introduction

During 1974 an independent check was made on the manometric calibration of the non-dispersive infrared (IR) analyzer (Applied Physics Corporation (APC) Model No. 55) located in 2317 Ritter Hall, used in this project for CO_2 analysis (reported in Manometer Report III, Guenther, 1976 a). Precise synthetic mixtures of CO_2 in N_2, O_2, and Ar were prepared and analyzed versus reference gases used in the manometric studies.

This study was suggested in 1972 when, in the course of test-at Scripps two UNOR analyzers made by Maihak Corporation, Hamburg, Germany, and an URAS 1 made by Hartmann and Braun Corporation, Frankfurt, Germany, it was found that when mixtures of CO_2 in N_2 used as reference gases were compared with air, infrared index values deduced for air with the UNORs were distinctly higher than those obtained from an APC analyzer run in parallel. The difference was approximately 4 ppm for one of the UNORs and 6 ppm for the other. A close check on the performance of an URAS analyzer also being tested at the same time showed a difference on the order of 0.3 ppm from the same APC analyzer, the URAS giving, however, a lower index value than the APC. These differences are probably a result of a differential pressure broadening effect on the CO_2 IR absorption band when the reference gas contains a carrier gas different from the air being analyzed. To establish this pressure broadening effect accurately for several carrier gases, the present study was undertaken.

In the experiments now to be described, seven pyrex glass flasks of approximately five liter capacity, and seven pyrex glass plenums with volumes between 1.3 and 2.3 cc, were employed to prepare synthetic mixtures of CO_2 in nitrogen, oxygen, and argon. The flask volumes were calibrated with water, and the plenum volumes with mercury, as described in Appendix A to this report. Each plenum was filled to ambient pressure with CO_2, the gas being prepared by acidifying an aqueous solution of Na_2CO_3 in a reaction vessel attached to a high vacuum system. This method insured that the CO_2 was free of other gaseous contaminants such as N_2O. The gas from an individual plenum was transferred, as described below, into a five liter flask and combined there with the selected carrier gas. While the flask temperature was controlled to within 0.01°C, the ambient pressure was measured to the nearest 0.1 mm. CO_2 infrared index values, based on comparisons with Scripps primary reference gas standards, were then determined using the APC analyzer.

The CO_2 concentrations of the gas mixtures ranged from approximately 240 to 430 ppm.

II. Experimental Procedures

A. Preparation of CO_2 Gas

An aqueous solution, approximately 0.56M in Na_2CO_3, was prepared in a one liter volumetric flask by weighing out 59 grams of Baker reagent anhydrous Na_2CO_3 and dissolving it in single distilled water obtained from Dr. Joris Gieskes's quartz distillery at 3255

Sverdrup Hall. Weighings were made on an Ohaus Triple Beam balance with a sensitivity of 0.5 g. Since the concentration was not critical, the Na_2CO_3 was not dried.

A solution of 1.6M H_3PO_4 was prepared by diluting 105 ml of Mallinckrodt reagent 85% H_3PO_4 solution of density 1.76 in one liter of single distilled water.

The apparatus used to prepare CO_2 gas is depicted in Figure 1.   Fig. 1

The procedure used to fill the plenums was as follows. Stopcock S3 was closed, and all the rest of the stopcocks were opened, including those on the plenums. Stopcock S7 was then opened to the line. The system between the stopcock S3 and stopcock S8 was pumped down for three to four hours. This removed CO_2 adsorbed onto the glass walls and hydrocarbon joint and stopcock grease in the vacuum system. At the end of this period, the pressure of the vacuum system was measured by an Autovac Pirani-gauge conductance bridge with four individual gauge probes, and found to be less than 1.0 millitorr. Then a reaction vessel with a special funnel was attached as shown in Figure 1, and 50 ml of 0.56M Na_2CO_3 solution was pipetted via the funnel into the reaction vessel from a calibrated open ended standard pipette. A teflon coated magnetic stirring bar was inserted into the solution and the top assemblage of the reaction vessel was installed. This assemblage consisted of a special 40 ml capacity pipette closed at both ends with a 4 mm 120° curved bore stopcocks (S1 and S2), and with a 30 ml open ended chamber above. Stopcock S2 was opened, stopcock S1 was closed, and

CO₂ SAMPLE PREPARATION RACK
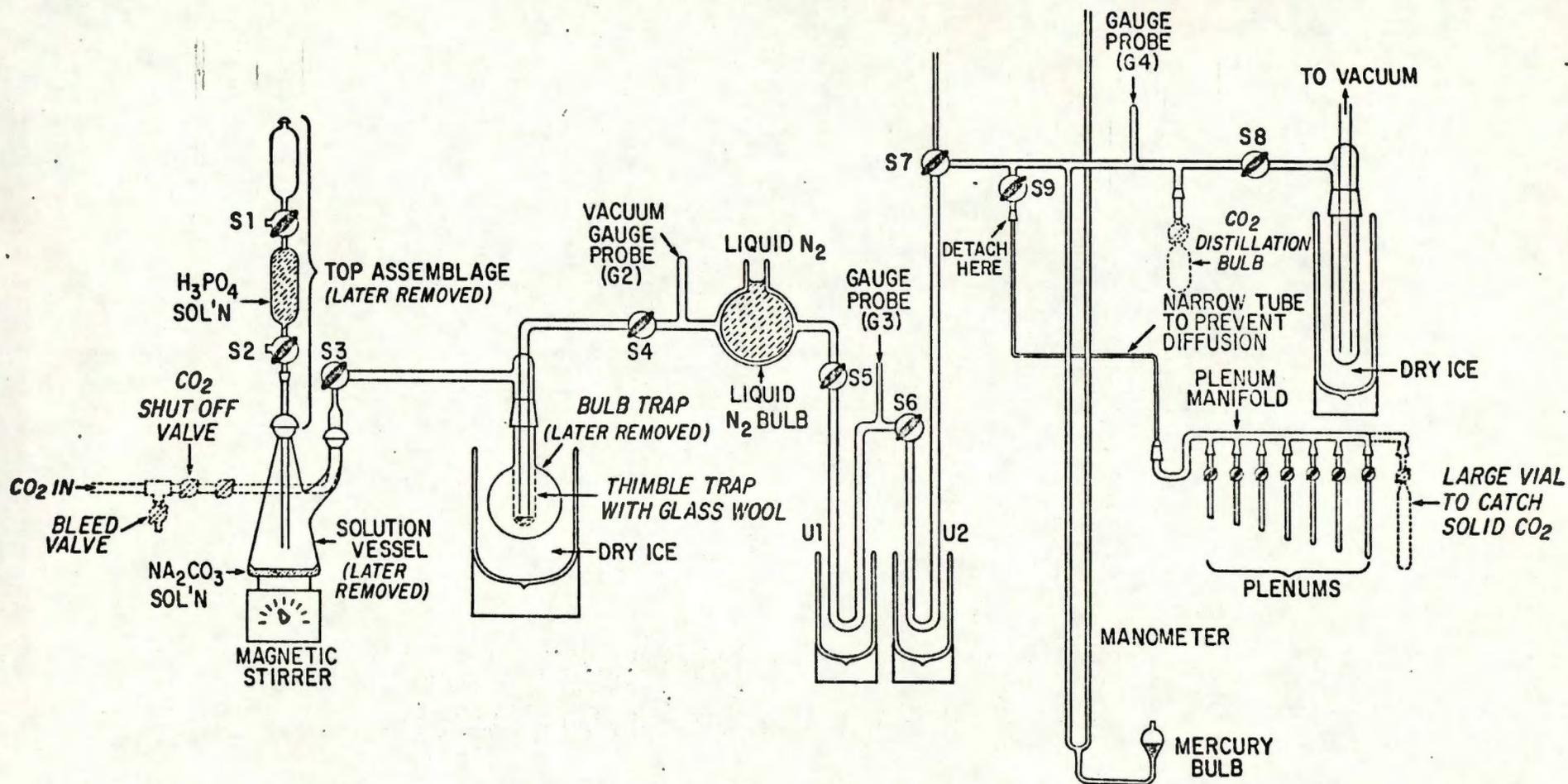
.Figure 1. Apparatus housed in 2328 Ritter Hall for preparation of CO₂ gas for volumetric samples. The parts drawn in broken lines were added to the system after the experiment began (See section IV, C) Parts removed at this time are also indicated.

the magnetic stirrer was turned on. Thirty ml of the previously prepared 1.6M H_3PO_4 was introduced into the open ended chamber above the reaction vessel. Stopcock S9 was closed, stopcock S3 opened, and after the line pressure at Pirani-gauge G2 had fallen to 1 mm or less, stopcock S2 was closed and stopcock S1 opened to drop the H_3PO_4 into a pipette between stopcock S1 and stopcock S2. Enough additional H_3PO_4 solution was carefully added via the open-ended chamber to fill the pipette without allowing any bubbles of air to enter the pipette. Then stopcock S1 was closed and stopcock S2 opened slowly to let the H_3PO_4 drip onto the Na_2CO_3. About three minutes were allowed for the addition of the acid to the salt. The pressure, as measured by Pirani-gauge G2, was not allowed to rise above 2 mm during this process. Stopcock S2 was closed for a few seconds if the pressure at Pirani-gauge G2 rose too high. A spherical trap, chilled to dry ice temperature in tandem with the reaction chamber, removed the bulk of the water vapor from the CO_2 stream. The CO_2 was frozen out in a concentric spherical liquid nitrogen trap beyond the water trap. After all detectable CO_2 had been driven from the Na_2CO_3 solution and the solution had frozen, stopcocks S3 and S4 were closed, and a liquid nitrogen bath was placed around U-trap U1. Stopcock S8 was then closed, the liquid nitrogen removed from the bulb, and the CO_2 sublimed into U-trap U1. This process required about fifteen minutes. Stopcock S5 was then closed and stopcock S8 opened to pull out any non-condensible gases. When

the pressure at Pirani-gauge G4 fell below 1 millitorr, a liquid
nitrogen bath was placed around U-trap U2. Stopcock S8 was then
closed and the liquid nitrogen bath on U-trap U1 replaced with dry
ice. About twenty minutes later, with CO_2 sublimed into U-trap U2,
stopcock S6 was closed and stopcock S8 opened. When the vacuum at
Pirani G4 fell below 1 millitorr, stopcock S9 was opened and stop-
cock S8 closed. A liquid nitrogen bath was then placed around one
of the long plenums. The liquid nitrogen bath on U-trap U2 was then
replaced with dry ice.

After about twenty minutes, with the CO_2 now sublimed into the
plenum, chilled with liquid N_2, stopcock S7 was closed and the liquid
nitrogen trap taken off the plenum so that it could warm. Just as the
CO_2 released from that plenum reached atmospheric pressure in the line
and all of the other plenums, stopcock S7 was opened to the atmosphere
so that excess CO_2 could vent. When the thawing in the plenum was
complete, the plenum manifold and tube were detached from the line at the
standard taper glass joint immediately below stopcock S9. The pur-
pose of the long narrow tube from stopcock S9 to the plenum manifold
was to prevent back diffusion of lab air into the plenums while
allowing the plenums to be in equilibrium with atmospheric pressure.
The plenum manifold was placed in a controlled temperature bath for
five minutes with all plenum stopcocks still open. The bath tem-
perature was measured with a Beckman mercury thermometer calibrated

by Walter Bryan of NORPAX against a NBS calibrated thermometer. It was controlled with a mercury contract switch that operated a 50 watt light bulb to heat the bath. Cooling was furnished by circulating water about one-half degree C cooler than the bath through a coil of copper tubing immersed in the bath. The ambient pressure was measured with a mercury wall barometer to 0.1 mm. With the apparatus at temperature equilibrium, the plenum stopcocks were closed and the temperature and pressure recorded. The plenums were immersed in liquid nitrogen for storage.

B. <u>Preparation</u> <u>of</u> <u>Gas</u> <u>Mixtures</u>

The apparatus used for gas mixture preparation is shown in Figure 2.   Fig. 2

Carrier gas was obtained commercially as follows. Nitrogen was Liquid Carbonic Corporation's Water Pump Nitrogen, 99.98% purity. Argon was also from Liquid Carbonic. The personnel at Liquid Carbonic felt that it was probably 99.99% pure. Oxygen was Liquid Carbonic's Commercial Grade, 99.5% pure.

Stopcock S10 was opened to allow carrier gas from a high pressure steel cylinder to flow through the apparatus via an ascarite trap to insure that the carrier gas was free of CO_2. After three minutes, stopcocks S10 and S11 were opened to the vacuum line and the gas was vented through stopcock S12. A five-liter flask was im-

CALIBRATION GAS PREPARATION RACK
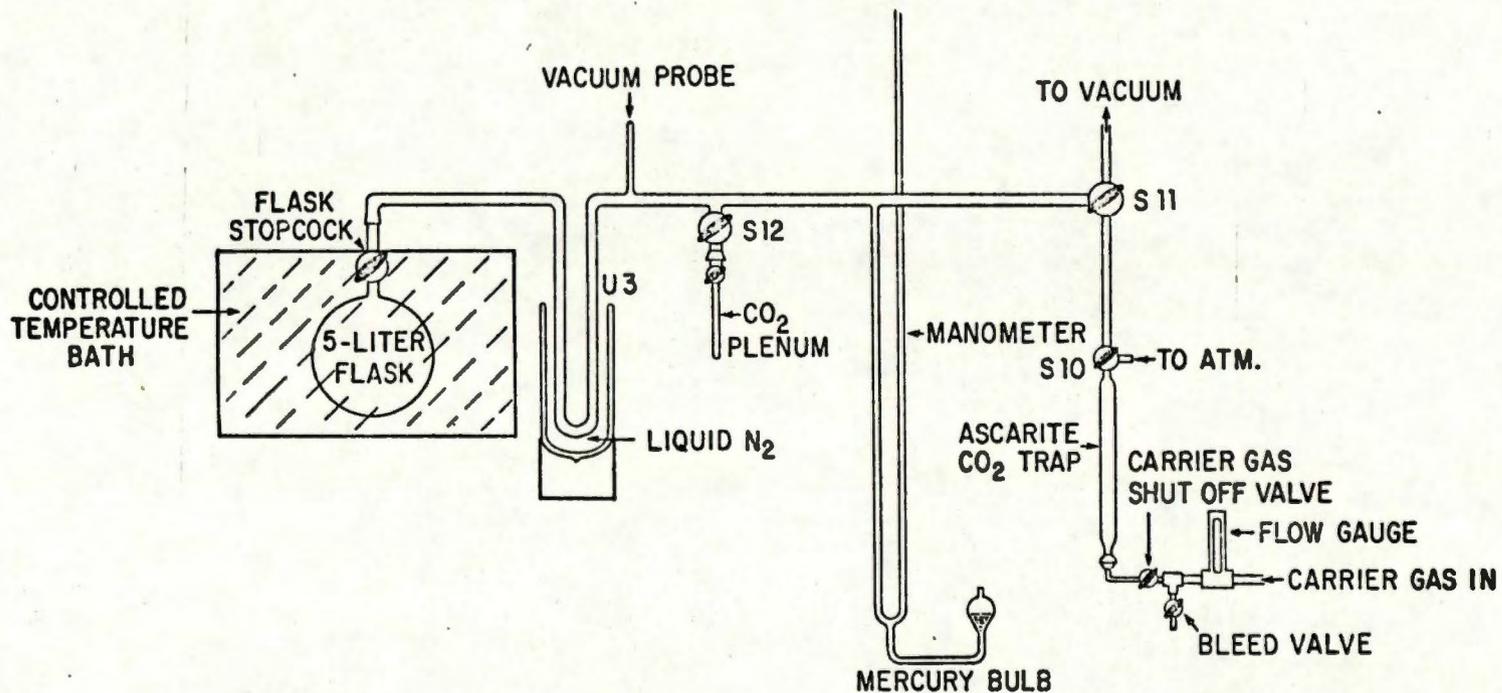
Figure 2. Apparatus housed in 2328 Ritter Hall for making volumetric gas mixtures, the

volume... gas mixture ... a 5-liter ...

mersed in the controlled temperature bath and connected to the apparatus as shown. Then stopcock S11 was closed and a CO_2 plenum to be paired with the flask installed. Stopcock S10 was opened from the carrier gas cylinder to continue the flushing through the line. Stopcock S12 was then opened and the vacuum line as far as the flask stopcock was evacuated to less than 1 millitorr after opening stopcock S11. Then stopcock S11 was closed. A liquid nitrogen bath was placed on U-trap U3 and the plenum stopcock was opened. After the CO_2 had completely sublimed from the plenum into U-trap U3 as indicated by the vacuum returning to less than 1 millitorr, stopcock S12 was closed and the flask stopcock opened. The liquid nitrogen was removed from U-trap U3 and the CO_2 expanded into the line and the five-liter flask. Stopcock S11 was then opened to the carrier gas line. The CO_2 was swept into the flask in a stream of CO_2-free carrier gas. As the carrier gas filled the line, the bulb on the mercury manometer was raised to prevent CO_2 from being trapped in the manometer tube as the mercury was pushed down. Filling to atmospheric pressure took ten to fifteen minutes. When the flask pressure was about 1 mm less than ambient, stopcock S10 was opened to the atmosphere and the flask was equilibrated in the controlled temperature bath for ten minutes. A pressure in the system slightly less than ambient before opening to atmospheric assured that no CO_2 would be lost from the flask into the line upon equilibrating the system with the outside. Then

the flask stopcock was closed and pressure and temperature recorded in the same manner as with the plenum filling. Each flask so filled was allowed to stand overnight or longer to allow thorough mixing of CO_2 with the carrier gas. Flasks were stored in the dark to prevent photo-oxidation of the Apiezon "N" stopcock grease and resulting addition of CO_2 to the sample. As discussed below, each flask containing oxygen or argon was analyzed four times on the APC analyzer. Flasks containing nitrogen were analyzed six times each.

III. Results and Discussion

The plenums were paired with five-liter flasks inversely according to volume, e.g. the smallest plenum with the largest flask. This maximized the CO_2 concentration range in the prepared gas mixtures. Seven gas mixtures were obtained for each carrier gas.

Table 1 lists the index values obtained for the gas mixtures Table 1 from the APC analyzer. Listed are the index values from the 1956 Scripps index scale and the 1959 adjusted index values. The latter were used in all data interpretations. Table 2 summarizes these Table 2 numbers.

Four aliquots of gas were run against the reference gases routinely used as flask standards with adjusted index values of 319.30 and 355.44 ppm. From the CO_2-N_2 samples and additional two aliquots were run against two selected manometric standards with adjusted index values of 311.17 and 354.47 ppm. Aliquots of gas from the low manometric reference gas, adjusted index value 180.83 ppm, and

from the high manometric reference gas, adjusted index value 345.55 ppm,
were also analyzed with the CO_2-O_2 mixtures. Uncertainties in the
index values of the reference gases and in recorder scale factor
were responsible for the minor differences in computed index values
of the aliquots run against flask standards and those run against
manometric standards. Since the manometric standards were used only
in connection with CO_2-N_2 mixtures, comparisons based on these
standards were omitted from the averages listed in Table 2.

Table 3 lists the laboratory data from the volumetric synthe- Table 3
ses of gas mixtures. Table 4 lists the gas pressure data and calcu- Table 4
lated gas pressures. Table 5 lists the volumetric data and volumetric Table 5
CO_2 concentrations.

The volumetric concentrations were calculated according to the
formula:

$$\frac{n_1}{n_2} = \frac{10^6 V_1 B_2(T_2)}{V_2 B_1(T_1)} \cdot \frac{1 - \sqrt{1 + \dfrac{4P_1 B_1(T_1)}{RT_1}}}{1 - \sqrt{1 + \dfrac{4P_2 B_2(T_2)}{RT_2}}} \tag{1}$$

which derives from

$$P_i V_i = n_i R T_i + B_i(T_i) \frac{n_i}{V_i} \tag{2}$$

where: subscript 1 is CO_2

subscript 2 is carrier gas

subscript i is either gas

n is number of moles of gas

$\dfrac{n_1}{n_2}$ is CO_2 mole fraction in ppm

V is volume of gas vessel in cc

T is gas temperature in °K

R is gas constant in erg/mole-K°

P is gas pressure in dynes/cm^2, obtained by setting $P = \rho gh$, where h is the observed height in cm of the column of mercury in the barometer; g is the local acceleration of gravity (979.558 cm/sec^2), ρ is density of mercury in the barometer, obtained from linear interpolation of tabulated mercury densities in "Handbook of Chemistry and Physics", 43rd edition, p. 2157, Chemical Rubber Publishing Co., 1962. Handbook values were divided by 1.000027 to convert g/ml to g/cc.

B(T) is the second density virial coefficient of gas at temperature T, obtained by quadratic interpolation of values of virials from tables in "Pressure-Volume-Temperature Relationships of Gases Virial Coefficients", Heat Division, National Bureau of Standards, Washington, D.C., 1971 (the virial at the lowest tabulated temperature higher than T plus the virials at the two highest tabulated temperatures lower than T were used in the interpolation). Units are cc/mole.

Table 6 lists the adjusted index values and volumetric CO_2
concentrations for the various gas mixtures.

The volumetric concentrations were plotted as functions of
adjusted index values by computer (see Figure 3). The computer
constructed a cubic curve by least squares to run through the points.
The cubic function fit the data points better than any other form
of function tried. One curve was drawn for each carrier gas.
They were of the form

$$V = A_0 + A_1 \cdot J + A_2 \cdot J^2 + A_3 \cdot J^3 \tag{3}$$

where V was volumetric CO_2 concentration and J was 1959 adjusted
index value. Table 7 lists the coefficients A_i for each carrier gas.

The programs indicated that the best way to relate the changes
in index values caused by changing carrier gas was to assume that
the quotient:

$$\frac{J_{N_2} - J_X}{J_{N_2}}$$

was constant, where J_{N_2} was adjusted index value for N_2 carrier
gas and J_X was adjusted index value for other carrier gases. In
other words, the substitution of any carrier gas for N_2 depressed the
adjusted index value by a constant factor independent of CO_2-concentration.
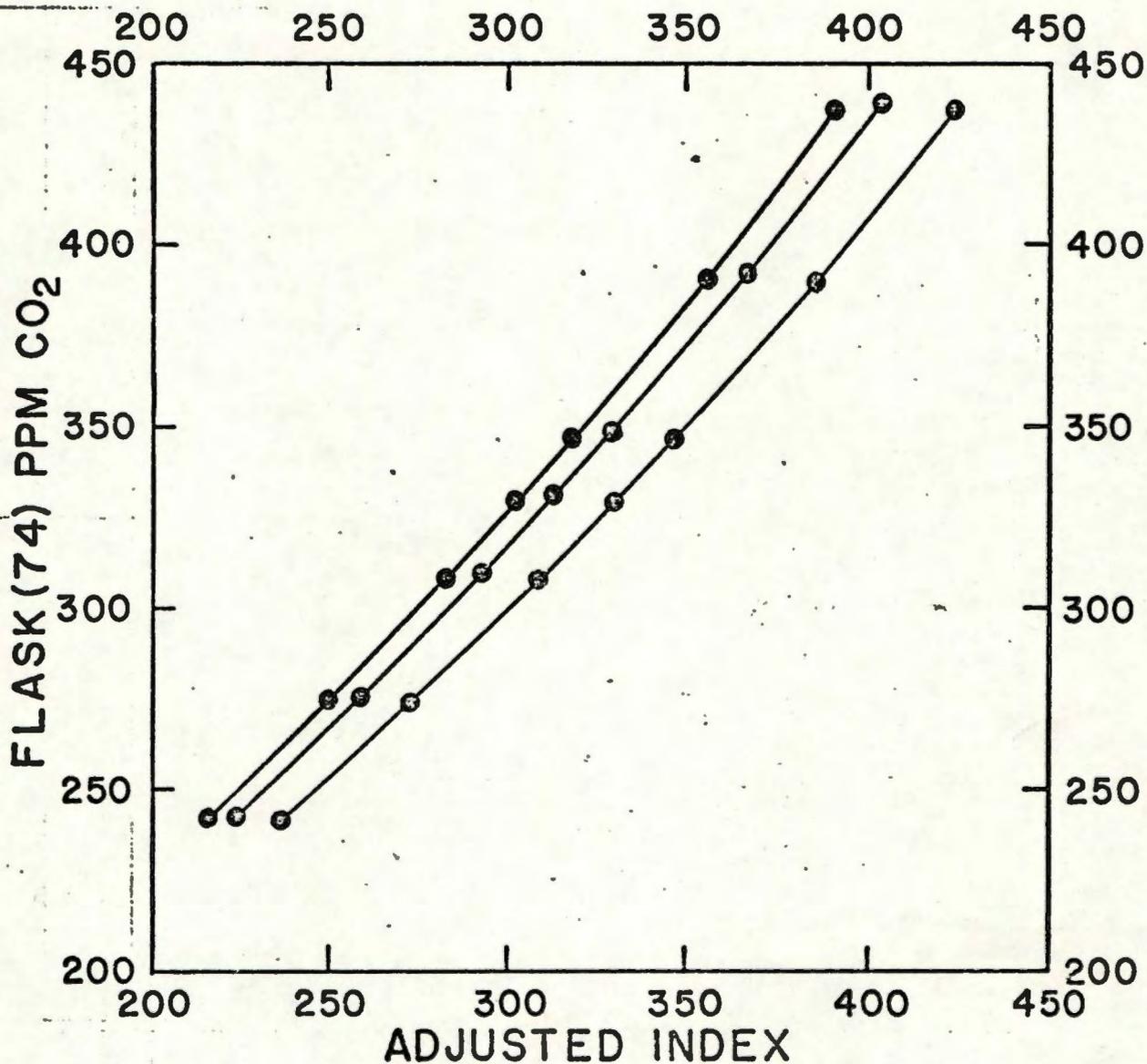
Figure 3. Calibration curves for CO_2 in various carrier gases. Volumetric CO_2 concentration is plotted vs. 1959 Adjusted Index value. The curve furthest to the right is from CO_2-N_2 mixtures; the middle curve is from CO_2-O_2 mixtures; and the curve furthest to the left is from CO_2-Ar mixtures.

Table 8 lists the values of this factor for various CO_2 mole fractions, where J_{N_2}, J_{Ar}, and J_{O_2} were computed from equation (3) using the coefficients of Table 7.

The average depression in adjusted index value caused by replacing N_2 with Ar was 8.24% with an absolute standard deviation (σ) of 0.26%. Adjusted index values for O_2-CO_2 averaged 5.26% lower than those for N_2-CO_2 with an absolute standard deviation of 0.18%.

If it is assumed that these depressions in adjusted index values are linear with mole fraction of the non-N_2 carrier gas, the depression in index value caused by replacing N_2 with air, if air is 0.934% Ar and 20.946% O_2, can be calculated by the formula

$$\frac{J_{N_2}-J_{Air}}{J_{N_2}} = 0.00934 \cdot 0.0824 + .20946 \cdot 0.0526 = 1.18\%$$

An independent method of measuring the depression in 1959 adjusted index value caused by the presence of O_2 and Ar in air was performed by P. R. Guenther of the Scripps laboratory research group using a constant volume manometer in 2317 Ritter Hall. As opposed to the volumetric method of synthesizing gas mixtures and determining the CO_2 concentration on the APC analyzer, the manometric method was to analyze a gas mixture from a compressed gas cylinder by removing an aliquot, measuring its volume, pressure and temperature, and extracting the CO_2 and measuring its volume, pressure and temperature. These gas mixtures were also run extensively on the APC analyzer. Manometric analyses done on CO_2-N_2 and

CO_2-air mixtures indicated a lowering of the adjusted index value on the APC analyzer of 1.20% (see Manometric Report III, Guenther, 1976). Thus the air corrections measured by the two methods agree quite well.

Guenther also analyzed some artificial air mixtures, containing about 330 ppm CO_2, prepared by Liquid Carbonic Corporation and certified at 20% O_2 in N_2. He obtained O_2 mole fractions on the artificial air by a paramagnetic comparison with real air with its precisely know O_2 mole fraction. He normalized the measured O_2-caused depression in 1959 adjusted index value for artificial air to real air O_2-mole fraction. The argon caused depression, deduced from the difference in depression between artificial and real air, agreed very closely with the direct volumetric determination.

It is concluded that the adjusted index value obrained for an air sample with the Scripps APC analyzer in 2317 Ritter Hall should be corrected by adding 1.2% to its value to obtain the adjusted index value the APC analyzer would yield if only N_2 were present in the sample as carrier gas (called virtual adjusted index by Guenther). Both this virtual adjusted index and the actually obtained adjusted index value can be converted to CO_2 mole fraction using the relationship between adjusted index value and mole fraction for CO_2-N_2 mixtures. The difference between the two mole fractions obtained is the error in CO_2 concentration read by the APC analyzer which results from comparing air samples to CO_2-N_2 standards. The contribution to

this error of O_2 and Ar in the air can also be calculated from

the CO_2-O_2 and CO_2-Ar mixture comparisons with CO_2-N_2 mixtures

in the volumetric experiment (Table 7) and the manometric artificial

air analyses. Table 9 lists the errors in CO_2 mole fraction caused   Table 9

by the different air carrier gases at 1959 adjusted index values

of 310, 320, and 330 ppm. The results of both volumetric and

manometric measurements are included.

IV.   Supplemental Experiments

    A.   Influence of N_2O on the Infrared CO_2 Analyzer

         An experiment was conducted to determine the effect of

N_2O on the response of the APC infrared analyzer to CO_2. The

plenums were filled to ambient pressure directly from a cylinder of

medical grade (99.9%) N_2O from L & V Industrial Supply Inc., Encinitas,

California, on the vacuum line used for CO_2-N_2 mixtures. They were

then placed in the controlled temperature bath described earlier.

After waiting for five minutes to achieve temperature equilibrium,

the plenums were placed in the liquid N_2 bath for storage described

earlier. The N_2O was not purified because it was assumed that the

APC analyzer would be so insensitive to N_2O that minor impurities would

not detectably affect the APC analyzer's response to N_2O.

         After warming a given plenum, the N_2O in it was swept into

a five liter flask with N_2 gas according to the procedure for

CO_2 in N_2 described above. The resulting mixture was then analyzed

on the APC analyzer. A vacuum pen trace was first obtained and

the displacement from the vacuum trace caused by N_2O noted when the N_2O-N_2 mixture was put into the analyzer cell. The laboratory data are recorded in Table 10. The lowest concentration mixture, 240 ppm of N_2O, caused a barely readable displacement of 0.2 scale divisions, and the highest concentration mixture, 430 ppm N_2O, caused a displacement of 0.3 scale divisions. At the given span setting, CO_2-N_2 mixtures of similar concentration caused displacements of 60 and 90 scale divisions, respectively. These were the low manometric standard, cylinder No. 2408, manometric CO_2 concentration 196.90 ppm, and the high manometric standard, cylinder No. 34316, manometric CO_2 concentration 472.97 ppm. Therefore, the analyzer was approximately 300 times as sensitive to CO_2 as to N_2O at these low concentrations.

Another experiment was run with higher N_2O concentrations. Medical grade N_2O was expended into each of three previously evacuated 5-liter flasks to a specific pressure. The flask stopcocks were closed and the connecting vacuum line was pumped to less than 1 millitorr, then filled with a CO_2-N_2 reference gas from a high pressure cylinder to a pressure greater than that of the N_2O in the flask. Thus when the flask stopcock was opened, no N_2O was lost into the vacuum line. With the stopcock open the flask was filled to ambient pressure with the CO_2-N_2 mixture. The result was a CO_2-N_2 sample considerably contaminated with N_2O. Pressures were measured on a mercury column read with a meter stick. Table 11 lists the results. The N_2O pressures of the mixtures were 5.1 mm Hg,

9.3 mm Hg, and 18.1 mm Hg. The reference gas used for the first
two mixtures were from cylinder No. 6071 with an adjusted index
value of 318.40 ppm CO_2. For the third mixture the reference gas
came from cylinder No. 4285 with an adjusted index value of 349.90
ppm CO_2. All the CO_2 adjusted index values were converted to
mole fractions using the cubic relationship, in equation (3), for
CO_2-N_2 mixtures with the coefficients listed in Table 7. The CO_2
mole fractions were corrected for the dilution caused by the added
N_2O by the relationship

$$\text{mole fraction(corrected)} = CO_2 \ N_2 \text{ mole fraction} \times \frac{\text{Total pressure} - N_2O \text{ pressure}}{\text{Total pressure}}.$$

Concentrations of N_2O were computed to by 6696, 12208, and 23756 ppm
by the ratios of N_2O pressure to ambient pressure. The response
ratios found by infrared analysis were approximately 550, 740, and
950 ppm N_2O/ppm CO_2, respectively. Therefore, the N_2O response of
the APC analyzer is not linear with CO_2 response but decreases with
increasing concentration of N_2O. This result is consistent with
finding a ratio of 300 at low N_2O concentration. It is concluded
that normal air, which contains about 0.3 ppm N_2O, can be analyzed
for CO_2 by the infrared method without making any correction for the
infrared absorption of N_2O, since air N_2O would cause a pen displace-
ment on the recorder equivalent to approximately 0.001 ppm CO_2.

B. **Influence of H_2O on the Infrared CO_2 Analyzer**

The influence of water vapor on APC analyzer response was
also determined. About 5 cc of single distilled water was injected into
four previously evacuated 5-liter flasks and the flasks brought to
ambient pressure with reference gases as described above. Two
flasks were filled with reference gas from cylinder No. 6071 and
two were filled from cylinder No. 4285. The samples were run
on the APC analyzer with and without dry ice on the
cold trap on the line leading to the analyzer cell. The water
vapor was assumed to be in equilibrium with liquid water at the
ambient temperature. The vapor pressure was calculated from
data listed in the Handbook of Chemistry and Physics, 43rd edition,
p. 2361-2364, Chemical Rubber Publishing Company, 1962. Tables 10
and 12 list the results of this experiment.   Table 12

As with the N_2O sensitivity experiment, adjusted index values
were converted to mole fractions by the volumetric cubic relation-
ship, and mole fractions were corrected for dilution by the added
interfering gas, in this case, water vapor. At the laboratory ambient
temperature of 22.0°C, the H_2O concentration (the ratio of vapor
pressure of liquid water to ambient pressure) was approximately
26300 ppm. The average ppm H_2O/ppm CO_2 response ratio was found
to be 660. When 319 ppm CO_2 was present, the ratio was 680; when
350 ppm CO_2 was present the ratio was 630.

It can concluded that water vapor, as well as N_2O, does not interfere significantly with the analyzer during routine air CO_2 measurements. Since water vapor in equilibrium with water ice at dry ice temperature is about 0.7 ppm, and the response ratio for water was 660 to 1, the recorder pen displacement caused by water is equivalent to approximately 0.001 ppm CO_2, provided that the dry ice trap is removing all water vapor above the equilibrium vapor pressure.

C. Manometer Volume Calibration

The 4 cc chamber in the manometric system in Room 2317 Ritter Hall was calibrated with volume-calibrated CO_2 plenums used in the experiments described above. The largest and smallest plenums were used. At first the same procedure was used for filling them with CO_2 as previously described. However, discrepancies occurred between results obtained from the small and large plenums. The large plenum results indicated a larger volume for the 4 cc chamber. The liquid N_2 bath was placed on the larger plenum to trap purified CO_2 prior to subliming it into the plenums and plenum manifold. If the purification described above had failed to remove all of the water vapor, it could possibly have collected in the large plenum with the CO_2, remained condensed on the dry ice in the large plenum while the CO_2 filled the manifold and plenums, and evaporated after all CO_2 ice was gone, but remained in the large plenum because of slow diffusion through CO_2 at 1 atmosphere

pressure in a long, narrow tube. This water vapor would have been removed in the dry ice-covered U-traps used by Guenther in transferring the CO_2 from the plenum to the 4 cc chamber. The result would have been less gas in the 4 cc chamber than calculated and a consequent lower pressure reading on the gas in the 4 cc chamber than should have been obtained, resulting in an erroneously large volume.

This was consistent with a finding that the samples contained residual water vapor by the following test. The CO_2 was transferred from the large plenum to a U-trap at liquid nitrogen temperature with a dry ice trap on the plenum. After transfer, the manifold to which the plenum was attached was closed to the U-trap and the dry ice removed from the plenum. The pressure in the manifold then rose from less than 1 millitorr to 7 or 8 millitorr. The manifold volume was estimated to be about 200 times the plenum volume. There-fore, the previous water vapor pressure in the plenum was evidently about 1.5 mm, or 2 parts per thousand, an unacceptable contamination. This phenomenon was not noted when the small plenum was attached to the manifold. To eliminate water vapor from the CO_2 samples, four alterations were made in the procedure for filling the CO_2 plenum:

(1) A glass flask consisting of a closed 20 mm diameter tube 10 cm long with an attached glass stopcock was placed on the vacuum line next to stopcock S8 (see Figure 1). CO_2 could be distilled back and fourth between flask and U-trap U2 as many times as necessary to remove

residual water. A liquid N_2 bath was placed on the flask, the flask stopcock opened, stopcock S8 closed, and liquid N_2 on the trap U2 replaced with dry ice. After about 1 1/2 hours, the flask stopcock was closed, the dry ice taken off trap U2, stopcock S8 opened, and a heat gun played on trap U2 to warm it up and drive off adsorbed water. Then a liquid N_2 bath was place on U-trap U2, stopcock S8 closed, a dry ice trap placed on the flask, and the flask stopcock opened. This transfer took about 1 hour. Then stopcock S7 was closed, stopcock S8 opened, the dry ice taken off the flask and a heat gun played on the flask. Stopcock S7 was then opened from U-trap U2 to stopcock S8. This process was repeated twice.

(2) A large vial was put onto the plenum manifold initially to trap the CO_2. This vial consisted of a closed 12 mm tube 20 cm long with attached glass stopcock (see Figure 1). The CO_2 was then sublimed into this vial from the line, and from the vial into the volume-calibrated plenums and connecting manifold. Any water in the vial thus tended to remain there and not enter the calibrated plenum, just as previously the water remained in the large plenum.

(3) CO_2 gas was introduced directly from a cylinder of commercial grade CO_2 gas purchased from the Matheson Company, Inc., 99.5% pure, rather than derived from a Na_2CO_3 solution. This eliminated liquid water from the vacuum system (see Figure 1). By setting the CO_2 flow from the cylinder such that the pressure, registered on Pirani-gauge

G2 was 0.5 mm, sufficient CO_2 for the experiment was frozen in about 10 minutes into the liquid N_2 concentric spherical trap. Then stop-cocks S3 and S4 were closed and the process described above for Na_2CO_3-derived CO_2 was repeated, with the additional glass vessels and procedures described above in items (1) and (2) of this section.

(4) The bulb trap immersed in the dry ice slurry between stopcocks S3 and S4 was replaced with a simple thimble trap filled with glass wool. This removed a greater proportion of the water vapor from the CO_2 stream than the spherical trap.

These modifications in the procedure seemed to remove all water from the CO_2, as no further evidence came to light of water vapor in the CO_2 transferred into the 4 cc chamber of the manometer. Also, no further discrepancies between 4 cc manometer chamber volume determinations measured by CO_2 from different plenums were found.

The initial calibrations of the 4 cc chamber were not included in Manometer Report IV. Further measurements, after eliminating the water vapor problem, are reported in Manometer Report IV.

Water in the CO_2 plenums may explain some of the scatter in the points about the calibration curves for each carrier gas, (figure 3, Table 6).

D. Calibration of the Wall Barometer in 2328 Ritter Hall

On 15 June 1976 the wall barometer from which pressures were obtained in the foregoing experiments was calibrated with the cathetometer and columns No. 2 and 4 in the manometer in 2317

Ritter Hall. (For definition of column numbers, see Manometer Report I)
Atmospheric pressure was introduced to column No. 4 in the manometer,
with column No. 2 connected to the vacuum pump. The doors to the
laboratory rooms were opened to the hall in insure pressure equilibration.
A pair of readings was taken by Mr. Peter Guenther on the level of
mercury on column No. 4 (low level), followed by a pair of readings on
column No. 2 (high level, vacuum), followed by readings on column No. 4,
then No. 2, then No. 4. The pairs of readings were averaged together, and
differences were calculated for each set of adjacent readings on columns
No. 2 and No. 4. Temperatures of the case were read during readings of
column No. 4.

While readings were being taken on the mercury level in
column No. 4, the pressure was taken in 2328 on the wall barometer by
Adams, along with the temperature of the mercury column from a
thermometer attached to the barometer. The column heights read in 2328
were normalized to the temperature of the manometer case by multiplying
the wall barometer column height by the ratio of mercury density at
temperature of 2328 to mercury density at manometer case temperature.
This resulted in average pressures of 762.40 mm by the cathetometer, and
762.42 mm by the wall barometer. These values were well within experimental
error of each other, since the wall barometer is readable to only 0.1 mm.

Table 13 lists the data obtained in this experiment.   Table 13

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index

CO_2-N_2 MIXTURES

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
4297	3755	35.9						
		35.9						
				C-8	-82.0	-67.70	250.19	236.79
				C-8	-82.1	-67.78	250.11	236.69
				C-7	-46.2	-38.14	279.75	272.81
				C-7	-46.4	-38.31	279.58	272.60
				C-10	-10.7	-8.83	309.06	308.52
				C-10	-10.8	-8.92	308.97	308.41
				C-5	10.1	8.34	326.23	329.45
				C-5	10.1	8.34	326.23	329.45
				C-3	26.8	22.13	340.02	346.25
				C-3	26.8	22.13	340.02	346.25
				C-9	65.6	54.16	372.05	385.28
				C-9	65.6	54.16	372.05	385.28
4297	3755	35.9						
		36.0						
	Average of four	35.925	29.66					

16 May 74
Rpt 25

Recorder Scale Factor = 0.82561 ppm/scale division

Primary Index Value = 317.89 ppm

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-N_2 MIXTURES				
4297	3755	29.5						
		29.4						
				C-11	84.9	85.72	403.61	423.74
				C-11	84.7	85.52	403.41	423.50
				C-8	-67.1	-67.75	250.14	236.72
				C-8	-67.1	-67.75	250.14	236.72
				C-7	-37.7	-38.07	279.82	272.89
				C-7	-37.8	-38.17	279.72	272.77
				C-10	-8.8	-8.89	309.00	308.45
				C-10	-8.8	-8.89	309.00	308.45
				C-5	8.1	-8.18	326.07	329.25
				C-5	8.2	-8.28	326.17	329.37
				C-3	21.8	22.01	339.90	346.11
				C-3	21.7	21.91	339.80	345.98
				C-9	53.7	54.22	372.11	385.36
				C-9	53.7	54.22	372.11	385.36
				C-11	84.7	85.52	403.41	423.50
				C-11	84.7	85.52	403.41	423.50
4297	3755	29.2						
		29.4						
Average of four		29.375	29.66					

16 May 74

Recorder Scale Factor = 1.00970 ppm/scale division

Primary Index Value = 317.89 ppm

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	Number High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-N_2 MIXTURES				
6078*	10069*	34.7						
		34.8						
				C-8	-60.4	-61.62	249.61	236.08
				C-8	-60.6	-61.83	249.40	235.82
				C-7	-31.2	-31.83	279.40	272.38
				C-7	-31.2	-31.83	279.40	272.38
				C-10	-2.3	-2.35	308.88	308.31
				C-10	-2.2	-2.24	308.99	308.44
				C-5	14.7	15.00	326.23	329.45
				C-5	14.7	15.00	326.23	329.45
				C-3	28.2	28.77	340.00	346.23
				C-3	28.2	28.77	340.00	346.23
				C-9	59.9	61.11	372.34	385.64
				C-9	59.8	61.01	372.24	385.52
				C-11	90.7	92.54	403.77	423.94
				C-11	90.8	92.64	403.87	424.06
6078*	10069*	35.0						
		34.8						
	Average of four	34.825	35.53					

21 May 74

Recorder Scale Factor = 1.02024 ppm/scale division

Primary Index Value = 311.23 ppm

*Manometric Reference Gases

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-Ar MIXTURES				
4297	3755	26.1						
		25.9						
				C-8	−74.8	−85.00	232.89	215.70
				C-8	−74.8	−85.00	232.89	215.70
				C-7	−50.2	−57.05	260.84	249.76
				C-7	−50.2	−57.05	260.84	249.76
				C-10	−26.4	−30.00	287.89	282.73
				C-10	−26.4	−30.00	287.89	282.73
				C-5	−12.8	−14.55	303.34	301.55
				C-5	−12.8	−14.55	303.34	301.55
				C-3	−1.3	−1.48	316.41	317.48
				C-3	−1.3	−1.48	316.41	317.48
				C-9	25.7	29.21	347.10	354.88
				C-9	25.7	29.21	347.10	354.88
				C-11	50.9	57,84	375.73	389.77
				C-11	50.9	57.84	375.73	389.77
4297	3755	26.2						
		26.2						
	Average of four	26.10	29.66					

31 May 74

Recorder Scale Factor = 1.13640 ppm/scale division

Primary Index Value = 317.89 ppm

TABLE 1.   Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-Ar MIXTURES				
4297	3755	26.2						
		26.2						
				C-8	-74.8	-84.68	233.21	216.09
				C-8	-74.8	-84.68	233.21	216.09
				C-7	-50.2	-56.83	261.06	250.03
				C-7	-50.2	-56.83	261.06	250.03
				C-10	-26.5	-30.00	287.89	282.73
				C-10	-26.6	-30.11	287.78	282.59
				C-5	-12.7	-14.38	303.51	301.76
				C-5	-12.7	-14.38	303.51	301.76
				C-3	-1.4	-1.58	316.31	317.36
				C-3	-1.4	-1.58	316.31	317.36
				C-9	25.8	29.21	347.10	354.88
				C-9	25.7	29.09	346.98	354.73
				C-11	50.9	57.62	375.51	389.50
				C-11	50.9	57.62	375.51	389.50
4297	3755	26.2						
		26.2						
	Average of four	26.20	29.66					

31 May 74

Recorder Scale Factor = 1.13206 ppm/scale division

Primary Index Value = 317.89 ppm

TABLE I. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2–O_2 MIXTURES				
4297	3755	22.9						
		22.8						
				35316*	84.1	109.16	427.05	452.31
				35316*	84.2	109.29	427.18	452.47
				2408†	−87.0	−112.93	204.98	181.69
				2408†	−87.1	−113.06	204.83	181.51
				C−8	−60.2	−78.14	239.75	224.06
				C−8	−60.1	−78.01	239.88	224.22
				C−7	−38.1	−49.45	268.44	259.02
				C−7	−38.1	−49.45	268.44	259.02
				C−10	−16.6	−21.55	296.34	293.02
				C−10	−16.6	−21.55	296.34	293.02
				C−5	−4.0	−5.19	312.70	312.96
				C−5	−4.1	−5.32	312.57	312.80

10 June 74

*High-CO_2 manometric CO_2-N_2 compressed gas cylinder

†Low-CO_2 manometric CO_2-N_2 compressed gas cylinder

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-O_2 MIXTURES				
				C-3	6.1	7.92	325.81	328.94
				C-3	6.1	7.92	325.81	328.94
				C-9	29.8	38.68	356.57	366.42
				C-9	29.8	38.68	356.57	366.42
				C-11	53.3	69.18	387.07	403.57
				C-11	53.3	69.18	387.07	403.57
				35316*	83.8	108.77	426.66	451.83
				35316*	83.8	108.77	426.66	451.83
				2408†	-87.2	-113.19	204.70	181.35
				2408†	-87.3	-113.32	204.57	181.19
4297	3755	22.9						
		22.8						
	Average of four	22.85	29.66					

(10 June 74 cont'd)

Recorder Scale Factor = 1.29803 ppm/scale division

Primary Index Value = 317.89 ppm

*High-CO_2 manometric CO_2-N_2 compressed gas cylinder

†Low-CO_2 manometric CO_2-N_2 compressed gas cylinder

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	Cylinder Number High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-O_2 MIXTURES				
4297	3755	22.9						
		22.8						
				35316*	84.1	108.93	426.82	452.07
				35316*	84.0	108.80	426.69	451.87
				2408†	-87.1	-112.81	205.08	181.81
				2408†	-87.2	-112.94	204.95	181.66
				C-8	-60.1	-77.84	240.05	224.43
				C-8	-60.3	-78.10	239.79	224.11
				C-7	-38.3	-49.61	268.28	258.83
				C-7	-38.3	-49.61	268.28	258.83
				C-10	-16.7	-21.63	296.26	292.93
				C-10	-16.8	-21.76	296.13	292.77
				C-5	-4.2	-5.44	312.45	312.66
				C-5	-4.2	-5.44	312.45	312.66

*High-CO_2 manometric CO_2-N_2 compressed gas cylinder

†Low-CO_2 manometric CO_2-N_2 compressed gas cylinder

TABLE 1. Index and Adjusted Index Values for Volumetric Gas Samples

Cylinder Number Primary	High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask Number	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index
				CO_2-O_2 MIXTURES				
				C-3	6.1	7.90	325.79	328.91
				C-3	6.0	7.77	325.66	328.75
				C-9	29.8	38.60	356.49	366.32
				C-9	29.8	38.60	356.49	366.32
				C-11	53.2	68.90	386.79	403.25
				C-11	53.2	68.90	386.79	403.25
				35316*	83.9	108.67	426.56	451.71
				35316*	83.9	108.67	426.56	451.71
				2408†	-87.1	-112.81	205.08	181.81
				2408†	-87.2	-112.94	204.95	181.66
4297	3755	23.2						
		22.7						
	Average of four	22.90	29.66					

(10 June 74 Cont'd)

Recorder Scale Factor = 1.29520 ppm/scale division

Primary Index Value = 317.89 ppm

35316 was the High-CO_2 manometric standard.

2408 was the Low-CO_2 manometric standard.

*High-CO_2 manometric CO_2-N_2 compressed gas cylinder

†Low-CO_2 manometric CO_2-N_2 compressed gas cylinder

TABLE 2. Summary of Index and Adjusted Index Values for Volumetric Gas Samples

CO_2-N_2 MIXTURES

Flask No.	Index Values	Adjusted Index Values	Average Index	Average Adjusted Index
C-8	250.19	236.79		
	250.11	236.69		
	250.14	236.72		
	250.14	236.72		
	249.61*	236.08*		
	249.40*	235.82*	250.14	236.72
C-7	279.75	272.81		
	279.58	272.60		
	279.82	272.89		
	279.72	272.77		
	279.40*	272.38*		
	279.40*	272.38*	279.72	272.77
C-10	309.06	308.52		
	308.97	308.41		
	309.00	308.45		
	309.00	308.45		
	308.88*	308.31*		
	308.99*	308.44*	309.01	308.46
C-5	326.23	329.45		
	326.23	329.45		
	326.07	329.25		
	326.17	329.37		
	326.23*	329.45*		
	326.23*	329.45*	326.18	329.39
C-3	340.02	346.25		
	340.02	346.25		
	339.90	346.11		
	339.80	345.98		
	340.00*	346.23*		
	340.00*	346.23*	339.94	346.15

*Referred to values based on comparison with Manometric Standards – not used in average.

TABLE 2. Summary of Index and Adjusted
Index Values for Volumetric Gas Samples

CO_2-N_2 MIXTURES

Flask No.	Index Values	Adjusted Index Values	Average Index	Average Adjusted Index
C-9	372.05	385.28		
	372.05	385.28		
	372.11	385.36		
	372.11	385.36		
	372.34*	385.64*		
	372.24*	385.52*	372.08	385.32
C-11	403.61	423.74		
	403.41	423.50		
	403.41	423.50		
	403.41	423.50		
	403.77*	423.94*		
	403.87*	424.06*	403.46	423.56

*Referred to Manometric Standards - not used in average.

TABLE 2. Summary of Index and Adjusted
Index Values for Volumetric Gas Samples

CO_2-Ar MIXTURES

Flask No.	Index Values	Adjusted Index Values	Average Index	Average Adjusted Index
C-8	232.89	215.70		
	232.89	215.70		
	233.21	216.09		
	233.21	216.09	233.05	215.90
C-7	260.84	249.76		
	260.84	249.76		
	261.06	250.03		
	261.06	250.03	260.95	249.90
C-10	287.89	282.73		
	287.89	282.73		
	287.89	282.73		
	287.78	282.59	287.86	282.70
C-5	303.34	301.55		
	303.34	301.55		
	303.51	301.76		
	303.51	301.76	303.42	301.65
C-3	316.41	317.48		
	316.41	317.48		
	316.31	317.36		
	316.31	317.36	316.36	317.42
C-9	347.10	354.88		
	347.10	354.88		
	347.10	354.88		
	346.98	354.73	347.07	354.84
C-11	375.73	389.77		
	375.73	389.77		
	375.51	389.50		
	375.51	389.50	375.62	389.63

TABLE 2. Summary of Index and Adjusted
Index Values for Volumetric Gas Samples

CO_2-O_2 MIXTURES

Flask No.	Index Values	Adjusted Index Values	Average Index	Average Adjusted Index
C-8	239.75	224.06		
	239.88	224.22		
	240.05	224.43		
	239.79	224.11	239.87	224.21
C-7	268.44	259.02		
	268.44	259.02		
	268.28	258.83		
	268.28	258.83	268.36	258.93
C-10	296.34	293.02		
	296.34	293.02		
	296.26	292.93		
	296.13	292.77	296.27	292.94
C-5	312.70	312.96		
	312.57	312.80		
	312.45	312.66		
	312.45	312.66	312.54	312.77
C-3	325.81	328.94		
	325.81	328.94		
	325.79	328.91		
	325.66	328.75	325.77	328.89
C-9	356.57	366.42		
	356.57	366.42		
	356.49	366.32		
	356.49	366.32	356.53	366.37
C-11	387.07	403.57		
	387.07	403.57		
	386.79	403.25		
	386.79	403.25	386.93	403.42

TABLE 3. Gas State Data

CO_2

Plenum No.	Volume cc
P-1	1.2978
P-2	1.4619
P-3	1.6360
P-4	1.7457
P-5	1.8359
P-6	2.0367
P-7	2.2733

Gas Mixtures

Date	Flask No.	Volume cc	Barometer Reading mm	Barometer Temp. °C	Gas Temp. °C
CO_2N_2 Mixtures					
	Plenums	Variable	761.8	20.7	20.72
14 MAY 74	C-8	5389.1	761.8	20.2	20.74
14 MAY 74	C-7	5350.2	762.7	20.0	20.74
14 MAY 74	C-10	5329.8	762.1	20.6	20.73
14 MAY 74	C-5	5320.2	762.3	20.6	20.73
14 MAY 74	C-3	5315.0	762.1	20.1	20.75
14 MAY 74	C-9	5237.2	762.8	20.5	20.76
14 MAY 74	C-11	5224.1	762.0	20.2	20.74
CO_2-Ar Mixtures					
	Plenums	Variable	763.2	21.8	20.74
28 MAY 74	C-8	5389.1	763.9	19.7	20.76
28 MAY 74	C-7	5350.2	763.1	20.7	20.77
28 MAY 74	C-10	5329.8	764.1	20.3	20.77
28 MAY 74	C-5	5320.2	764.1	19.7	20.76
28 MAY 74	C-3	5315.0	763.7	20.6	20.76
28 MAY 74	C-9	5237.2	764.0	20.5	20.77
28 MAY 74	C-11	5224.1	763.4	20.6	20.78
CO_2O_2 Mixtures					
	Plenums	Variable	760.0	20.7	20.75
6 JUN 74	C-8	5389.1	758.5	20.3	20.75
6 JUN 74	C-7	5350.2	758.5	20.3	20.74
6 JUN 74	C-10	5329.8	758.3	20.9	20.76
6 JUN 74	C-5	5320.2	757.8	20.4	20.76
6 JUN 74	C-3	5315.0	757.9	20.6	20.76
6 JUN 74	C-9	5237.2	757.9	20.3	20.75
6 JUN 74	C-11	5224.1	758.0	20.8	20.76

TABLE 4. Gas Pressure Calculations

Flask No.	Barometer Temperature °C	Hg Density g/ml	Hg Density g/cc	Hg Column Height mm	Pressure Dynes/cm^2
CO_2-N_2 Mixtures					
Plenums	20.7	13.5445	13.5441	761.8	$1.01070:10^6$
C-8	20.2	13.5457	13.5453	761.8	$1.01079:10^6$
C-7	20.0	13.5462	13.5458	762.7	$1.01202 \cdot 10^6$
C-10	20.6	13.5448	13.5444	762.1	$1.01112:10^6$
C-5	20.6	13.5448	13.5444	762.3	$1.01138:10^6$
C-3	20.1	13.5460	13.5456	762.1	$1.01121:10^6$
C-9	20.5	13.5450	13.5446	762.8	$1.01206:10^6$
C-11	20.2	13.5457	13.5453	762.0	$1.01106 \cdot 10^6$
CO_2-Ar Mixtures					
Plenums	21.8	13.5418	13.5414	763.2	$1.01236 \cdot 10^6$
C-8	19.7	13.5470	13.5466	763.9	$1.01367 \cdot 10^6$
C-7	20.7	13.5445	13.5441	763.1	$1.01243 \cdot 10^6$
C-10	20.3	13.5455	13.5451	764.1	$1.01383 \cdot 10^6$
C-5	19.7	13.5470	13.5466	764.1	$1.01394 \cdot 10^6$
C-3	20.6	13.5448	13.5444	763.7	$1.01324 \cdot 10^6$
C-9	20.5	13.5450	13.5446	764.0	$1.01366 \cdot 10^6$
C-11	20.6	13.5448	13.5444	763.4	$1.01284 \cdot 10^6$

Local acceleration of gravity = 979.558 cm/sec^2

1g/cc = 1g/ml ÷ 1.000027

TABLE 4. Gas Pressure Calculations

Flask No.	Barometer Temperature °C	Hg Density g/ml	Hg Density g/cc	Hg Column Height mm	Pressure Dynes/cm^2
CO_2-O_2 Mixtures					
Plenums	20.7	13.5445	13.5441	760.0	$1.00831 \cdot 10^6$
C-8	20.3	13.5455	13.5451	758.5	$1.00639 \cdot 10^6$
C-7	20.3	13.5455	13.5451	758.5	$1.00639 \cdot 10^6$
C-10	20.9	13.5440	13.5436	758.3	$1.00602 \cdot 10^6$
C-5	20.4	13.5452	13.5448	757.8	$1.00545 \cdot 10^6$
C-3	20.6	13.5448	13.5444	757.9	$1.00555 \cdot 10^6$
C-9	20.3	13.5455	13.5451	757.9	$1.00560 \cdot 10^6$
C-11	20.8	13.5443	13.5439	758.0	$1.00564 \cdot 10^6$

Local acceleration of gravity = 979.558 cm/sec^2

1g/cc = 1g/ml ÷ 1.000027

TABLE -5. <u>Volumetric</u> CO_2 <u>Concentrations</u>

Flask No.	CO_2 Volume cc	CO_2 Temp. °C	CO_2 Pressure Dynes/cm^2	CO_2 Density Virial cm^3/mole	Total Gas Volume cc	Total Gas Temp. °C	Total Gas Pressure Dynes/cm^2	Total Gas Density Vir. cc/mole	Gas Constant erg/°mole	Volumetric CO_2 Concentrat ppm
CO_2-N_2 Mixtures										
C-8	1.2978	20.72	$1.01070 \cdot 10^6$	-127.3	5389.1	20.74	$1.01079 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	242.04
C-7	1.4619	20.72	$1.01070 \cdot 10^6$	-127.3	5350.20	20.74	$1.01202 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	274.29
C-10	1.6360	20.72	$1.01070 \cdot 10^6$	-127.3	5329.8	20.73	$1.01112 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	308.39
C-5	1.7457	20.72	$1.01070 \cdot 10^6$	-127.3	5320.2	20.73	$1.01138 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	329.58
C-3	1.8359	20.72	$1.01070 \cdot 10^6$	-127.3	5315.0	20.75	$1.01121 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	347.03
C-9	2.0367	20.72	$1.01070 \cdot 10^6$	-127.3	5237.2	20.76	$1.01206 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	390.39
C-11	2.2733	20.72	$1.01070 \cdot 10^6$	-127.3	5224.1	20.74	$1.01106 \cdot 10^6$	-5.9	$8.31436 \cdot 10^7$	437.24
CO_2-Ar Mixtures										
C-8	1.2978	20.74	$1.01236 \cdot 10^6$	-127.3	5389.1	20.76	$1.01367 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	241.63
C-7	1.4619	20.74	$1.01236 \cdot 10^6$	-127.3	5350.2	20.77	$1.01243 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	274.51
C-10	1.6360	20.74	$1.01236 \cdot 10^6$	-127.3	5329.8	20.77	$1.01383 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	307.96
C-5	1.7457	20.74	$1.01236 \cdot 10^6$	-127.3	5320.2	20.76	$1.01394 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	329.15
C-3	1.8359	20.74	$1.01236 \cdot 10^6$	-127.3	5315.0	20.76	$1.01324 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	346.73
C-9	2.0367	20.74	$1.01236 \cdot 10^6$	-127.3	5237.2	20.77	$1.01366 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	390.23
C-11	2.2733	20.74	$1.01236 \cdot 10^6$	-127.3	5224.1	20.78	$1.01284 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	437.02
CO_2-O_2 Mixtures										
C-8	1.2978	20.75	$1.00831 \cdot 10^6$	-127.3	5389.1	20.75	$1.00639 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	242.39
C-7	1.4619	20.75	$1.00831 \cdot 10^6$	-127.3	5350.2	20.74	$1.00639 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	275.01
C-10	1.6360	20.75	$1.00831 \cdot 10^6$	-127.3	5329.8	20.76	$1.00602 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	309.08
C-5	1.7457	20.75	$1.00831 \cdot 10^6$	-127.3	5320.2	20.76	$1.00545 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	330.59
C-3	1.8359	20.75	$1.00831 \cdot 10^6$	-127.3	5315.0	20.76	$1.00555 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	347.98
C-9	2.0367	20.75	$1.00831 \cdot 10^6$	-127.3	5237.2	20.75	$1.00560 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	391.74
C-11	2.2733	20.75	$1.00831 \cdot 10^6$	-127.3	5224.1	20.76	$1.00564 \cdot 10^6$	-17.0	$8.31436 \cdot 10^7$	438.34

TABLE 6. Index Values, Adjusted Index Values, and Volumetric CO₂

CO_2-N_2 Mixtures

Concentrations of Calibrated Gas Mixtures

N_2 !

(Mixtures prepared 15 May 1974)

Flask Number	Plenum Number	Index (Flask Tanks) (ppm)	Adjusted Index (Flask Tanks) (ppm)	Volumetric (ppm) '74 Mano. Equation		Vd - Equa.	Index (Manometric Tanks) (ppm)	Adjusted Index (Manometric Tanks) (ppm) 74 Mano		Vd - Equa.
C-8	P-1	250.14	236.72	*242.21*	242.04	−.17	249.50	*241.54* 235.94		+.50
C-7	P-2	279.72	272.77	*274.17*	274.29	+.12	279.40	*273.81* 272.38		+.48
C-10	P-3	309.01	308.46	*308.13*	308.39	+.26	308.94	*308.05* 308.38		+.34
C-5	P-4	326.18	329.39	*329.21*	329.58	+.37	326.23	*329.27* 329.45		+.31
C-3	P-5	339.94	346.15	*346.74*	347.03	+.29	340.00	*346.83* 346.23		+.20
C-9	P-6	372.08	385.32	*390.10*	390.39	+.29	372.29	*390.40* 385.58		−.01
C-11	P-7	403.46	423.56	*435.85*	437.24	+1.39	403.82	*436.40* 424.00		+.84

TABLE 6. Index Values, Adjusted Index Values, and Volumetric CO_2 Concentrations of Calibrated Gas Mixtures

Ar¹

Flask Number	Plenum Number	Index (ppm)	Adjusted Index (ppm)	Volumetric (ppm)
C-8	P-1	233.05	215.90	241.63
C-7	P-2	260.95	249.90	274.51
C-10	P-3	287.86	282.70	307.96
C-5	P-4	303.42	301.65	329.15*
C-3	P-5	316.36	317.42	346.73
C-9	P-6	347.07	354.84	390.23
C-11	P-7	375.62	389.63	437.02

* jiggled Hg manometer bulb during equilibration; may have lost some CO_2

TABLE 6. Index Values, Adjusted Index Values, and Volumetric CO_2 Concentrations of Calibrated Gas Mixtures CO_2-N_2 Mixtures

Flask Number	Plenum Number	Index (ppm)	Adjusted Index (ppm)	Volumetric (ppm)
C-8	P-1	239.87	224.21	242.39
C-7	P-2	268.36	258.93	275.01
C-10	P-3	296.27	292.94	309.08
C-5	P-4	312.54	312.77	330.59
C-3	P-5	325.77	328.89	347.98
C-9	P-6	356.53	366.37	391.74
C-11	P-7	386.93	403.42	438.34

TABLE 7. <u>Cubic</u> <u>Coefficients</u> <u>for</u> <u>Volumetric</u>

<u>vs</u>. <u>1959</u> <u>Adjusted</u> <u>Index</u> <u>Plots</u>

Carrier Gas	A_0	A_1	A_2	A_3
N_2	39.706	0.93795	$-8.0035 \cdot 10^{-4}$	$1.8923 \cdot 10^{-6}$
Ar	12.580	1.3202	$-1.9615 \cdot 10^{-13}$	$3.5101 \cdot 10^{-6}$
O_2	75.027	0.62527	$3.6272 \cdot 10^{-4}$	$7.9242 \cdot 10^{-7}$

TABLE 8. Comparison of Infrared Analyzer* Response to
CO_2-N_2, CO_2-Ar, and CO_2-O_2 Mixtures

Volumetric	J_{N_2}	J_{Ar}	J_{O_2}	$\dfrac{J_{N_2}-J_{Ar}}{J_{N_2}}$	$\dfrac{J_{N_2}-J_{O_2}}{J_{N_2}}$	$\dfrac{J_{N_2}-J_{O_2}}{J_{O_2}}$
240	234.45	214.34	221.57	0.0858	0.0549	.058131
260	256.98	234.95	243.26	0.0857	0.0534	.056400
280	278.80	255.12	264.04	0.0849	0.0559	.055901
300	299.84	274.72	283.99	0.0858	0.0529	.055812
320	320.10	293.66	303.16	0.0826	0.0529	.055898
340	339.56	311.87	321.61	0.0815	0.0529	.055813
360	358.24	329.34	339.39	0.0807	0.0526	.055541
380	376.16	346.05	356.55	0.0800	0.0521	.054999
400	393.37	362.04	373.13	0.0796	0.0514	.054244
420	409.88	377.31	389.17	0.0795	0.0505	.053216
440	425.75	391.92	404.70	0.0806	0.0494	.052014
				Aver.=0.0824	0.0526	.055268
				σ =0.0026	0.0018	.001638

*APC Analyzer in 2317 Ritter Hall.

TABLE 9. Carrier Gas Effects on APC Analyzer CO_2 Analyses

20.94690

1959 Adjusted Index (ppm)	Method	Error Caused by 0.93% O_2 (ppm)	Error Caused by 0.93% Ar (ppm)	Air Correction† (ppm)
310	Volumetric	3.44	0.24	3.69*
310	Manometric	3.50	0.20**	3.70
320	Volumetric	3.62	0.25	3.88*
320	Manometric	3.68	0.21**	3.89
330	Volumetric	3.81	0.26	4.08*
330	Manometric	3.87	0.23**	4.10
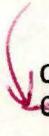
* sum of determined values of O_2 and Ar

** difference between values for air and artificial air

† to be added to CO_2 mole fractions obtained from APC analyzer for air samples measured against CO_2-N_2 standards.

TABLE 10. Index Values for CO_2-N_2-N_2O and CO_2-N_2-H_2O Mixtures

Tank Number Primary	Tank Number High Span	Scale Difference Between Reference Gases	Index Difference Between Reference Gases	Flask No.	Scale Difference Between Sample and Primary	Index Difference Between Sample and Primary	Sample Index	Sample Adjusted Index	Flask Average Adjusted Index
4297	4288	19.5							
		19.3							
					H_2O-CO_2-N_2 Mixtures				
					Without dry ice trap				
				C-5	17.9	23.05	340.95	347.39	347.39
				C-7	37.6	48.41	366.31	378.29	378.29
				C-8	37.4	48.15	366.05	377.97	377.97
				C-3	18.4	23.69	341.59	348.17	348.17
					With dry ice trap				
				C-3	−0.1	−0.13	317.77	319.14	319.14
				C-5	−0.6	−0.77	317.13	318.36	318.36
				C-7	19.0	24.46	342.36	349.10	349.10
				C-8	19.0	24.46	342.36	349.10	349.10
					N_2O-CO_2-N_2 Mixtures				
				C-9	5.7	7.34	325.24	328.24	
				C-9	5.8	7.47	325.37	328.40	328.32
				C-10	7.3	9.40	327.30	330.75	
4297	4288	19.3		C-10	7.4	9.53	327.43	330.91	330.83
		19.2		C-11	29.2	37.59	355.49	365.10	
	Average of four	19.325	24.88	C-11	29.3	37.72	355.62	365.26	365.18

Recorder scale factor = 1.28745 ppm/scale division
Primary index value = 317.89 ppm

TABLE 11. N_2O Effect on Infrared Analyzer*

Flask No.	Adjusted Index of CO_2-N_2O-N_2	Apparent CO_2/(CO_2+N_2+N_2O) Mole Ratio (ppm)	N_2O Pressure (mm Hg)	Total Pressure (mm Hg)	N_2O/(N_2O+N_2+CO_2) Mole Ratio (ppm) (Pressure Ratio)	Adjusted Index of CO_2/ N_2 Mixtures	CO_2/N_2 Mole Ratio (ppm)	Actual CO_2/ (N_2+N_2O+CO_2) Mole Ratio (ppm) Corrected for N_2O Dilution	Apparent CO_2 ppm Seen by Analyzer as Result of N_2O	Response Ratio (ppm N_2O/ ppm CO_2)
C-9	328.32	328.35	5.1	761.7	6696	318.40	318.29	316.16	12.19	550
C-10	330.82	330.93	9.3	761.8	12208	318.40	318.29	314.40	16.53	740
C-11	365.18	367.65	18.1	761.9	23756	349.90	350.97	342.63	25.02	950

*APC Analyzer in Room 2314 Ritter Hall

TABLE 12. Water Effect on Infrared Analyzer*

Flask No.	Temp. H_2O °C	H_2O Pressure (mm Hg)	Total Pressure (mm Hg)	$H_2O/H_2O+CO_2+N_2$ Mole Ratio (ppm) (Pressure Ratio)	Adjusted Index Without Dry Ice Trap	Apparent $(N_2+CO_2+H_2O)$ Mole Ratio (ppm)	Adjusted Index With Dry Ice Trap	$CO_2/(N_2+CO_2)$ Mole Ratio (ppm)	Actual $CO_2/(CO_2+N_2+H_2O)$ Mole Ratio (ppm) Corrected for H_2O Dilution	Apparent CO_2 ppm Seen By Analyzer As Result of H_2O	Response Ratio (ppm H_2O/ ppm CO_2)
C-3	22.0	19.827	761.5	26037	348.17	349.12	319.14	319.04	310.73	38.39	680
C-5	21.9	19.709	761.5	25882	347.39	348.29	318.36	318.25	310.01	38.28	680
C-7	22.1	19.951	761.6	26196	378.29	382.43	349.10	350.11	340.94	41.49	630
C-8	22.0	19.827	761.6	26037	377.97	382.06	349.10	350.11	.341.00	41.06	630

*APC Analyzer in Room 2314 Ritter Hall

TABLE 13. Calibration of Wall Barometer

	Cathetometer Readings (mm)		Column Height	Temp. °C	Barometer Column Height (mm)	Temp. °C
	Atmosphere	Vacuum				
	110.260				762.1	20.5
	110.262					
Average	110.261			22.04		
		872.694				
		872.698				
Average		872.696	762.435			
	110.304				762.2	20.5
	110.310					
Average	110.307		762.389	22.07		
		872.728				
		872.740				
Average		872.734	762.427			
	110.360				762.2	20.5
	110.388					
Average	110.374		762.360	22.09		

Average column height = 762.40 mm
temp. = 22.07°C
density of Hg = 13.5411 g/ml

Average column height = 762.2 mm
temp. = 20.5°C
density of Hg = 13.5450 g/ml

Densities obtained from Handbook of Chemistry and Physics 43rd Ed.,
p. 2157, Chemical Rubber Publishing Co., 1962

To normalize to manometer temperature: Barometer column height = 762.2 mm $\cdot \frac{13.5450}{13.5411}$ = 762.42 mm

VOLUMETRIC REPORT I
APPENDIX A

J. Alexander Adams
Carbon Dioxide Project
Scripps Institution of Oceanography
La Jolla, California 92093

August 27, 1975

I. Introduction

During January, February, and March 1974, seven five-liter glass flasks, one four-liter manometer flask, and seven glass plenums with volumes from 1 1/4 to 2 1/4 cc had their volumes calibrated. The overall technique in the case of the large flasks was to evacuate the volume to be measured, weigh the flask, fill it with distilled water from which dissolved air had been removed, and weigh again. The difference in the weights, assumed to be the weight of water, was divided by the known density to give the volume. Flasks C-8 and C-11 had this procedure repeated five times; C-3- C-5, C-7, C-9, and C-10 had it done twice. Three runs were made on manometer flask no. 2.

The same technique was used on the plenums, numbered P-1 through P-7, except that mercury was used instead of water. Each was filled and weighed five times.

The large flasks were weighed on a Mettler P-11N single-pan balance, serial no. 474434 in room 0256 Ritter Hall. (This room is part of Professor Harmon Craig's laboratory.) The plenums were weighed on a Seederer-Kohlbusch two-pan 5 kilogram analytical balance, register no. 6971 in 2328 Ritter Hall, using class S rhodium plated brass weights.

Water densities were obtained from the Handbook of Chemistry and Physics, 43rd edition, page 2155, Chemical Rubber Publishing Co., 1962.

Mercury densities were from the same source, page 2157.

Values at non-integer temperatures were obtained by linear interpolation between listed densities. The mass per cc was obtained by dividing the mass per ml by 1.000027 (Handbook of Chemistry and Physics, 43rd edition, pages 2157 and 3197).

II. Experimental Procedure

A. Large Glass Flask Calibrations

The procedure for the large flask calibrations was done with with apparatus shown in Figure 1 by the techniques described below.
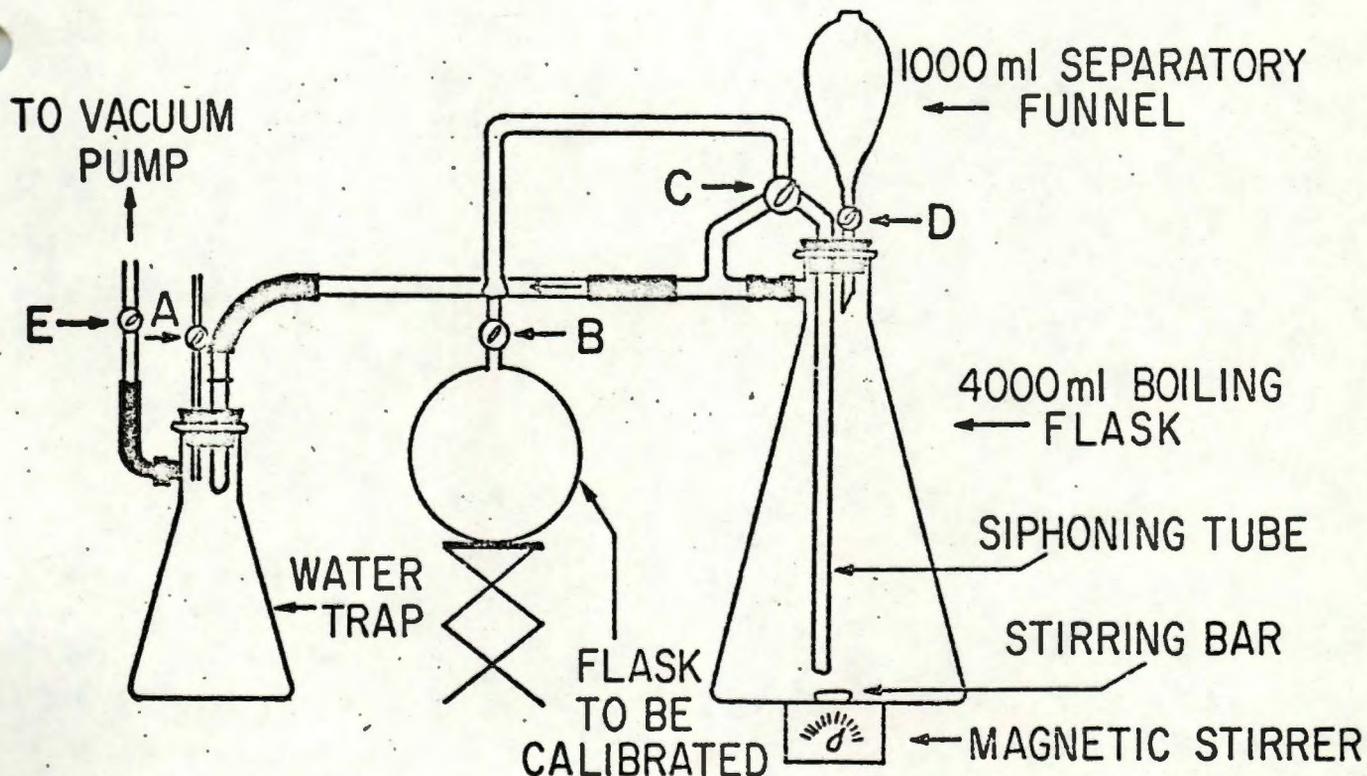
Figure 1. Apparatus to Fill Large Glass Flasks with Water

Stopcock "C" is a 120° glass stopcock with the following positions:

POSITION 1   POSITION 2   POSITION 3

Stopcock "A" is an oblique bore glass vacuum stopcock to let air into the system; stopcock "B" is a hollow plug glass vacuum stopcock attached to the flask; stopcock "D" is a standard straight bore separatory funnel glass stopcock; stopcock "E" is a "T" three-way glass vacuum stopcock.

The apparatus was assembled with the stopcocks greased with Apiezon "N" lubricant. Liquid nitrogen was placed on both of two cold traps adjacent to the vacuum pump (not shown in Figure 1). Just enough liquid nitrogen was placed around the water trap to touch its bottom. A higher level of refrigerant was avoided to reduce tendency of the trap to plug up with ice.

Initially the flask to be calibrated was evacuated on another vacuum line and installed in the filling apparatus. With the filling system at ambient pressure stopcock "A" was closed and stopcock "E" was slowly opened to evacuate the system. Stopcock "C" was set in position 1. After evacuation was completed, the separatory funnel was filled with de-ionized water from the tap in 2328 Ritter Hall and the magnetic stirrer started.

Stopcock "D" was opened slightly and water admitted to the 4000 ml boiling flask. The separatory funnel was filled with additional water if necessary to complete the filling of the boiling flask.

When the boiling flask was filled to near the top, stopcock "D" was closed and the water boiled for five to ten minutes under vacuum. If the top of the water trap got too cold, the water coming into the trap froze in the end of the inlet tube from the boiling flask and plugged it. To unplug it, stopcock "E" was closed, stopcock "A" was slowly opened to the air, and the water trap heated with a heat gun until the ice plug fell off. Then stopcock "A" was closed, stopcock "E" slowly opened, and the operation continued.

After five to ten minutes had elapsed without interference of any plug of ice, stopcock "C" was turned to position 2 for about thirty seconds to evacuate the siphoning tube, and the magentic stirrer was turned off. Stopcock "C" was then turned to position 3.

Stopcock "E" was closed and stopcock "A" was slowly opened to air. The water was thus forced up the siphoning tube and filled the tube running from the 4000 ml boiling flask to the flask to be calibrated.

Stopcock "B" was opened slightly and water admitted to the flask to be calibrated until the water level in the 4000 ml boiling flask was close to the bottom of the siphoning tube. Then stopcock "B" was closed.

To prepare additional degassed water, stopcock "A" was closed and stopcock "E" slowly opened. After about one minute of evacuation, stopcock "C" was turned to position 1. The magnetic stirrer was turned on and stopcock "D" was opened slightly to refill the 4000 ml boiling flask. Then stopcock "D" was closed and the water boiled under vacuum for five to ten minutes. The magnetic stirrer was then turned off and the previous procedure used to complete filling of the flask to be calibrated.

After filling, the water in the flask to be calibrated was slightly heated with a heat gun with the system still open to the vacuum pump via stopcock "E". Bubbles were jarred loose from the bottom half of the flask by tapping. The water was warmed to about 2° above ambient temperature and boiled for ten minutes under vacuum. Then stopcock "E" was closed, stopcock "A" slowly opened to let air pressure into the system and force water into the flask.

After boiling, an air bubble at 1 atm pressure and about 10 cc volume always remained in stopcock "B". To remove it the following procedure was used:

Stopcock "A" was closed and stopcock "E" was slowly opened to pull the bubble out through the vacuum pump. Stopcock "B" was closed and stopcock "C" turned to position 2 for about thirty seconds, then to position 3 to remove any air still in the system. Stopcock "E" was closed, stopcock "A" slowly opened and stopcock "B" opened slightly to admit water into the volume formerly occupied by the air bubble. Stopcock "B" was opened fully when water had ceased to flow. If any small residual bubble remained in the stopcock "B", then stopcock "A" was

closed, stopcock "E" slowly opened, and after about thirty seconds the procedure was repeated.

Up to a dozen 1 mm diameter bubbles at atmospheric pressure were allowed to remain, as they would later be absorbed into the water, which was greatly undersaturated with respect to dissolved air at 1 atmosphere pressure.

The flask to be calibrated was carefully removed from the line, leaving stopcock "B" open. A glass tube with a 14/35 female ground glass fitting on one end was placed over a corresponding male fitting above stopcock "B" and filled with distilled water. Then the flask stood overnight to reach temperature equilibrium and allow absorption of air bubbles in the water.

Before weighing, stopcock "B" was closed, the tube removed from the flask neck above stopcock "B", and the water removed from the inside of the flask neck. Grease and water were cleaned from the flasks exterior with trichloroethylene and the ambient temperature was recorded. The flask was then weighed.

The small amount of dissolved air still in the water probably could not affect the calibration results significantly because water saturated with air at 1 atmosphere pressure has a density lower than that of pure water by about 3 parts in 10^6 (International Critical Tables, Vol. 3, Page 26). Since the water in the flask was greatly undersaturated, any error in density owing to dissolved air was negligible.

B. Calibration of Plenums

The design of a plenum is shown in Figure 2.

14/35 GG MALE FITTING

HOLLOW STOPCOCK PLUG

BARE HOLE IN
STOPCOCK PLUG

PLENUM VOLUME
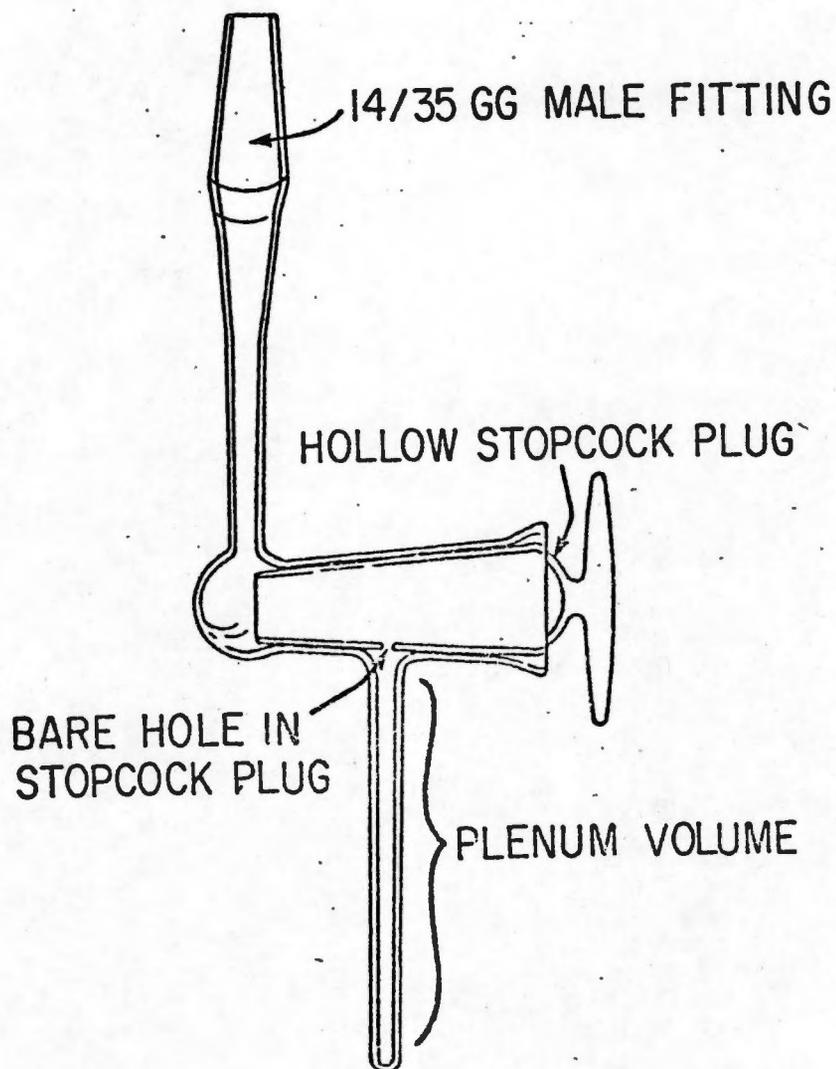
Figure 2. CO_2 Plenum

With the plenum chamber previously evacuated, mercury was

injected into the hollow plug of the stopcock with a syringe attached

to a teflon spaghetti tube which was small enough to pass through the neck above the stopcock into the plug. The bore of the hollow plug was about 2/3 filled with mercury, and the stopcock was turned so that the bore hole was below the surface of the murcury, but not open to the plenum chamber. The air was removed from the space in the stopcock above the mercury in order to dislodge and remove any air bubbles trapped in the bore under the mercury. Air pressure was restored over the mercury, and the stopcock was opened slightly to admit the mercury into the plenum chamber slowly. When the plenum had been filled, the stopcock was opened fully to the chamber and again the air was evacuated from above the mercury to remove any further trapped air bubbles. After thirty minutes of temperature equilibration, the stopcock was closed and excess mercury poured out of the stopcock plug bore. Ambient temperature was recorded. The inside of the stopcock was then rinsed with nitric acid followed by distilled water and the plenum attached to a vacuum line and evacuated to dry out the water still remaining inside the stopcock. The plenum was removed and its exterior cleaned with trichloroethylene. The plenum was then weighed. The air bubble problem was less serious than in the case of the large flasks, since air does not dissolve appreciably in mercury.

C. Preparation for Recalibration

The water was removed from the large flasks by removing the stopcock plugs and draining. The stopcocks were then cleaned of

grease and regreased. The flasks were evacuated to dry out all residual water. To remove mercury from the plenums, the stopcocks were opened, the plenums turned nearly upside down so that the mercury fell into the end of the stopcock plug near the handle, and the air removed from the stopcock plug. The mercury fell from the plenum chamber into the stopcock plug, whence it was poured out. The stopcock plug was removed, all surfaces cleaned of grease, and a teflon spaghetti tube pushed in so that its end was at the closed end of the plenum chamber. Through this tube the plenums were rinsed with nitric acid followed by water, all injected by a syringe attached to the tube. The aqueous liquids were shaken out of the plenum chambers. The plenum stopcocks were then air-dried and regreased. The plenum chambers were evacuated to dry.

III. Calculations and Results

Nine weighings were made on each evacuated flask and nine more on each after filling with water, except that in the first filling of flask C-8, six weighings each were made on the evacuated and full flask. Each plenum was weighed three times evacuated and three times filled with mercury. Mean weights and volumes were then computed. The standard deviation for the weights of water or mercury was computed as the square root of sum of squares of standard deviations of weights empty and full.

A universal standard deviation for a single plenum weighing or large flask weighing was calculated by the formula

$$\sigma_{universal} = \left(\frac{\sum\limits_{i}^{N} \sum\limits_{j}^{M_i} (X_{ij} - \overline{X}_i)^2}{\sum\limits_{i}^{N} M_i - N} \right)^{1/2}$$

where X_{ij} was the jth weight measurement for the ith full or empty

vessel; $\overline{X}_i$ was the average weight for the ith vessel; M_i was the

number of weighings made on the ith vessel; and N was the number of

vessels. The σ for weight of water or mercury was $\sigma_{universal} \cdot \sqrt{2}$,

since these weights were differences between two measured weights. The

$\sigma_{universal}$ for volumes due to weighing uncertainty was $\sigma_{universal}$

for weights divided by liquid densities -- 1.0g/cc for water and

13.54g/cc for mercury.

Tables 1 and 2 list the results of the flask calibrations;

Table 3 and 4 list the results of the plenum calibrations. Table 5

lists the standard deviations, and standard deviations of the means.

The $\sigma_{universal}$ for volume measurements from individual fillings

of flasks and plenums was calculated by the above formula, where X_{ij}

was the jth volume measurement of the ith vessel; X_i was the average

volume for the vessel; M_i was the number of volume measurements made

on the ith vessel; and N was the number of vessels. This was assumed

to be $\sigma_{universal}$ (total) for the volumes.

This $\sigma_{universal}$ for volume measurements was partitioned into

uncertainty due to weighing and uncertainty due to filling changes.

If it was assumed that $\sigma^2_{universal}$ (weighings) + $\sigma^2_{universal}$ (fillings) =

$\sigma^2_{universal}$ (total), and $\sigma_{universal}$ (weighings) and $\sigma_{universal}$ (total)

were already available then $\sigma_{universal}$ (fillings) could be calculated.

Standard deviations of the mean values were the $\sigma_{universal}$'s divided by the square root of number of measurements made for each mean. Relative uncertainty was absolute uncertainty divided by the value of the measurement (a "standard" volume for flasks and plenums is indicated in Table 5).

In June of 1976 the Mettler P11N single-pan balance used in the above experiment was calibrated using Class S rhodium-plated brass weights. Two 1-kg weights and one 2-kg weight were used. In addition a glass bottle of mercury, weighed on the Seederer-Kohlbusch two-pan balance at 2826.8 g, was used. These weights were weighed on the P11N. The readings obtained from the P11N are listed in Table 6. Weighings were done for 1 kg, 2 kg, 2.8268   Table 6 kg, and 6.8268 kg. In general, it can be noted that "true" readings were obtained if the weights were quickly placed on the pan. If they were held so they gradually settled on the pan (over a period of 2-3 seconds) the scale reading was from 1/2 to 2 grams low. The difference seemed to be independent of weight on the pan. Sometimes tapping the side of the balance caused the pan to settle further so that a truer reading was obtained. However, this did not cause concern as far as the volume calibrations were concerned for two reasons: (1) The volumes were based on differences between full and empty weights. Errors caused by "settling" the weights onto the pan would tend to cancel out. (2) σ for the volume was 0.64 cc,

so this error could arguably be called statistical, since 3σ is about 2 cc.

Apparently, however, the balance tends to bind at an erroneously low weight reading if the pan is pushed down too slowly by the weights.

TABLE 1. Flask Weights

Flask No. C-8, Filling No. 1

Evacuated Flask			Full Flask		
8 Jan 74	Wt. No.	Wt.(g)	9 Jan 74	Wt. No.	Wt.(g)
	1	782.4		1	6162.4
	2	782.1		2	6162.4
	3	782.0		3	6162.2
	4	782.2		4	6162.3
	5	782.3		5	6162.6
	6	782.1		6	6162.3
	Average = 782.2			Average = 6162.4	

Wt. Water = 5380.2 g

Flask No. C-8, Filling No. 2

Evacuated Flask			Full Flask		
9 Jan 74	Wt. No.	Wt.(g)	10 Jan 74	Wt. No.	Wt.(g)
	1	780.5		1	6161.9
	2	780.6		2	6161.9
	3	779.3		3	6161.2
	4	780.6		4	6162.1
	5	780.6		5	6162.0
	6	781.0		6	6162.1
	7	781.0		7	6162.7
	8	780.3		8	6161.8
	9	779.8		9	6162.1
	Average = 780.4			Average = 6162.0	

Wt. Water = 5381.6 g

TABLE 1. Flask Weights

Flask No. C-8, Filling No. 3

Evacuated Flask			Full Flask		
10 Jan 74 Wt. No.	Wt.(g)		11 Jan 74 Wt. No.		Wt.(g)
1	779.2		1		6163.6
2	780.5		2		6162.7
3	781.4		3		6162.6
4	779.8		4		6162.4
5	780.0		5		6162.0
6	780.5		6		6162.6
7	780.5		7		6162.1
8	780.8		8		6162.7
9	780.9		9		6162.8
Average = 780.4			Average = 6162.6		

Wt. Water = 5382.2 g

Flask No. C-8, Filling No. 4

Evacuated Flask			Full Flask		
11 Jan 74 Wt. No.	Wt.(g)		14 Jan 74 Wt. No.		Wt.(g)
1	779.6		1		6162.0
2	780.1		2		6162.1
3	780.5		3		6162.7
4	780.7		4		6162.3
5	780.4		5		6162.6
6	778.9		6		6162.2
7	780.5		7		6162.0
8	780.5		8		6162.0
9	780.9		9		6162.5
Average = 780.2			Average = 6162.3		

Wt. Water = 5382.1 g

TABLE 1. Flask Weights

	Flask No. C-8, Filling No. 5						Flask No. C-11, Filling No. 1				
	Evacuated Flask			Full Flask			Evacuated Flask			Full Flask	
14 Jan 74	Wt. No.	Wt.(g)	15 Jan 74	Wt. No.	Wt.(g)	17 Jan 74	Wt. No.	Wt.(g)	18 Jan 74	Wt. No.	Wt.(g)
	1	780.1		1	6160.5		1	991.6		1	6206.3
	2	781.5		2	6161.1		2	991.4		2	6207.0
	3	780.8		3	6160.5		3	991.4		3	6206.3
	4	780.8		4	6160.2		4	991.8		4	6206.5
	5	779.6		5	6160.7		5	991.0		5	6206.3
	6	781.3		6	6161.0		6	990.4		6	6206.5
	7	780.2		7	6160.4		7	991.6		7	6206.6
	8	781.4		8	6160.4		8	991.3		8	6206.6
	9	781.9		9	6160.8		9	991.4		9	6207.0
	Average = 780.8			Average = 6160.6			Average = 991.3			Average = 6206.6	

Wt. Water = 5379.8 g

Wt. Water = 5215.3 g

TABLE 1. Flask Weights

Flask No. C-11, Filling No. 2

18 Jan 74 Wt. No.	Wt.(g)	21 Jan 74 Wt. No.	Wt.(g)
	Evacuated Flask		**Full Flask**
1	992.2	1	6207.5
2	991.1	2	6208.5
3	991.3	3	6208.3
4	991.8	4	6208.3
5	990.8	5	6208.8
6	991.5	6	6209.1
7	991.6	7	6209.0
8	991.3	8	6209.0
9	991.1	9	6209.3
Average = 991.4		Average = 6208.6	

Wt. Water = 5217.2 g

Flask No. C-11, Filling No. 3

21 Jan 74 Wt. No.	Wt.(g)	22 Jan 74 Wt. No.	Wt.(g)
	Evacuated Flask		**Full Flask**
1	991.6	1	6208.4
2	992.1	2	6209.4
3	991.9	3	6208.6
4	991.7	4	6207.2
5	992.3	5	6209.5
6	992.6	6	6209.5
7	992.1	7	6207.7
8	991.9	8	6209.8
9	991.3	9	6209.1
Average = 991.9		Average = 6208.8	

Wt. Water = 5216.9 g

TABLE 1. Flask Weights

Flask No. C-11, Filling No. 4

Evacuated Flask			Full Flask		
22 Jan 74	Wt. No.	Wt.(g)	23 Jan 74 Wt. No.		Wt.(g)
	1	991.1		1	6205.7
	2	991.5		2	6205.9
	3	991.6		3	6205.8
	4	991.3		4	6205.3
	5	991.8		5	6205.3
	6	992.2		6	6205.3
	7	991.1		7	6205.3
	8	992.7		8	6205.4
	9	991.8		9	6205.3
	Average = 991.7			Average = 6205.5	

Wt. Water = 5213.8 g

Flask No. C-11, Filling No. 5

Evacuated Flask			Full Flask		
23 Jan 74	Wt. No.	Wt.(g)	24 Jan 74 Wt. No.		Wt.(g)
	1	990.7		1	6205.0
	2	991.2		2	6204.6
	3	991.9		3	6205.0
	4	991.5		4	6204.6
	5	991.3		5	6204.2
	6	991.7		6	6204.9
	7	990.6		7	6205.2
	8	991.4		8	6205.2
	9	991.8		9	6204.7
	Average = 991.3			Average = 6204.8	

Wt. Water = 5213.5 g

TABLE 1. Flask Weights

Flask No. C-11, Filling No. 6						Flask No. C-3, Filling No. 1					
Evacuated Flask			Full Flask			Evacuated Flask			Full Flask		
24 Jan 74	Wt. No.	Wt.(g)	25 Jan 74	Wt. No.	Wt.(g)	28 Jan 74	Wt. No.	Wt.(g)	29 Jan 74	Wt. No.	Wt.(g)
	1	991.2		1	6205.8		1	905.9		1	6211.3
	2	992.0		2	6205.9		2	907.2		2	6211.3
	3	992.1		3	6205.8		3	906.8		3	6210.7
	4	992.1		4	6205.8		4	906.6		4	6210.9
	5	992.4		5	6206.1		5	907.1		5	6211.4
	6	992.2		6	6205.9		6	906.0		6	6210.6
	7	991.7		7	6205.7		7	907.0		7	6211.3
	8	991.9		8	6205.7		8	906.4		8	6211.3
	9	991.6		9	6206.0		9	906.4		9	6210.9
	Average = 991.9			Average = 6205.9			Average = 906.6			Average = 6211.1	

Wt. Water = 5214.0 g

Wt. Water = 5304.5 g

TABLE 1. Flask Weights

Flask No. C-3, Filling No. 2

Evacuated Flask			Full Flask		
29 Jan 74	Wt. No.	Wt.(g)	30 Jan 74	Wt. No.	Wt.(g)
	1	907.2		1	6211.3
	2	907.7		2	6211.1
	3	906.8		3	6210.9
	4	907.2		4	6211.6
	5	906.2		5	6210.7
	6	907.5		6	6211.0
	7	907.3		7	6210.5
	8	907.0		8	6211.3
	9	908.3		9	6211.3
	Average =	907.2		Average =	6211.1

Wt. Water = 5303.9 g

Flask No. C-5, Filling No. 1

Evacuated Flask			Full Flask		
28 Jan 74	Wt. No.	Wt.(g)	29 Jan 74	Wt. No.	Wt.(g)
	1	882.1		1	6190.5
	2	880.4		2	6190.8
	3	881.3		3	6190.7
	4	881.5		4	6190.3
	5	880.7		5	6190.8
	6	881.2		6	6191.3
	7	881.1		7	6191.1
	8	880.5		8	6191.1
	9	881.3		9	6190.9
	Average =	881.1		Average =	6190.8

Wt. Water = 5309.7 g

TABLE 1. Flask Weights

Flask No. C-5, Filling No. 2

Evacuated Flask			Full Flask		
29 Jan 74	Wt. No.	Wt.(g)	30 Jan 74	Wt. No.	Wt.(g)
	1	881.8		1	6190.3
	2	881.4		2	6190.6
	3	881.3		3	6190.3
	4	881.7		4	6190.9
	5	880.8		5	6190.6
	6	881.3		6	6190.9
	7	881.9		7	6190.2
	8	882.0		8	6190.0
	9	881.7		9	6190.9
Average = 881.5			Average = 6190.5		

Wt. Water = 5309.0 g

Flask No. C-7, Filling No. 1

Evacuated Flask			Full Flask		
28 Jan 74	Wt. No.	Wt.(g)	29 Jan 74	Wt. No.	Wt.(g)
	1	897.7		1	6236.7
	2	897.3		2	6236.8
	3	898.4		3	6236.9
	4	897.9		4	6236.9
	5	898.2		5	6236.9
	6	897.8		6	6236.6
	7	897.0		7	6236.4
	8	897.6		8	6236.8
	9	897.2		9	6237.1
Average = 897.7			Average = 6236.8		

Wt. Water = 5339.1 g

TABLE 1. Flask Weights

Flask No. C-7, Filling No. 2

	Evacuated Flask			Full Flask	
29 Jan 74	Wt. No.	Wt.(g)	30 Jan 74	Wt. No.	Wt.(g)
	1	896.9		1	6236.9
	2	897.8		2	6236.7
	3	897.5		3	6236.3
	4	897.8		4	6237.0
	5	897.2		5	6237.3
	6	897.3		6	6237.1
	7	897.7		7	6237.0
	8	897.5		8	6236.8
	9	896.9		9	6237.3
	Average =	897.4		Average =	6236.9

Wt. Water = 5339.5 g

Flask No. C-9, Filling No. 1

	Evacuated Flask			Full Flask	
30 Jan 74	Wt. No.	Wt.(g)	31 Jan 74	Wt. No.	Wt.(g)
	1	999.9		1	6227.5
	2	1000.4		2	6227.5
	3	999.8		3	6227.3
	4	1000.0		4	6227.5
	5	1001.7		5	6227.6
	6	999.9		6	6227.9
	7	1000.2		7	6227.3
	8	1000.9		8	6227.1
	9	1000.7		9	6227.4
	Average =	1000.4		Average =	6227.5

Wt. Water = 5227.1 g

TABLE 1. Flask Weights

Flask No. C-9, Filling No. 2						Flask No. C-10, Filling No. 1					
Evacuated Flask			**Full Flask**			**Evacuated Flask**			**Full Flask**		
31 Jan 74	Wt. No.	Wt.(g)	1 Feb 74	Wt. No.	Wt.(g)	30 Jan 74	Wt. No.	Wt.(g)	31 Jan 74	Wt. No.	Wt.(g)
	1	1000.6		1	6226.9		1	900.0		1	6218.8
	2	1001.3		2	6227.3		2	900.5		2	6218.9
	3	999.8		3	6226.7		3	900.3		3	6219.1
	4	1001.9		4	6227.1		4	901.0		4	6219.2
	5	1000.6		5	6226.4		5	899.7		5	6219.4
	6	1000.5		6	6227.1		6	899.5		6	6219.2
	7	1002.0		7	6227.2		7	900.2		7	6218.9
	8	1000.1		8	6227.1		8	899.5		8	6219.3
	9	1000.2		9	6226.0		9	900.5		9	6219.1
	Average =	1000.8		Average =	6226.9		Average =	900.1		Average =	6219.1

$= 0.8$

$= 0.5$

Wt. Water = 5226.1 g

Wt. Water = 5319.0 g

TABLE 1. Flask Weights

Flask No. C-10, Filling No. 2

Evacuated Flask			Full Flask		
31 Jan 74	Wt. No.	Wt.(g)	1 Feb 74	Wt. No.	Wt.(g)
	1	900.1		1	6218.9
	2	900.0		2	6219.1
	3	899.4		3	6219.0
	4	900.2		4	6219.3
	5	900.4		5	6218.1
	6	900.8		6	6219.2
	7	900.0		7	6219.4
	8	899.3		8	6219.5
	9	900.2		9	6219.3
	Average =	900.0		Average =	6219.1

Wt. Water = 5319.1 g

Manometer Flask No. 2, Filling No. 1

Evacuated Flask			Full Flask		
28 Mar 74	Wt. No.	Wt.(g)	29 Mar 74	Wt. No.	Wt.(g)
	1	1120.3		1	5057.7
	2	1121.7		2	5059.3
	3	1121.0		3	5059.0
	4	1121.3		4	5058.9
	5	1121.3		5	5059.0
	6	1121.5		6	5058.6
	7	1121.1		7	5058.8
	8	1121.4		8	5059.5
	9	1121.4		9	5059.0
	Average =	1121.2		Average =	5058.9

Wt. Water = 3937.7 g

TABLE 1. Flask Weights

Manometer Flask No. 2, Filling No. 2

Evacuated Flask			Full Flask		
29 Mar 74	Wt. No.	Wt.(g)	1 Apr 74	Wt. No.	Wt.(g)
	1	1121.0		1	5059.5
	2	1119.9		2	5059.2
	3	1121.2		3	5059.3
	4	1120.8		4	5058.9
	5	1120.8		5	5059.2
	6	1121.0		6	5058.9
	7	1121.1		7	5059.0
	8	1121.0		8	5059.5
	9	1120.6		9	5058.7
Average =		1120.8	Average =		5059.1

0.4   0.3

Wt. Water = 3938.3 g

$\sigma = 0.5$ g

Manometer Flask No. 2, Filling No. 3

Evacuated Flask			Full Flask		
1 Apr 74	Wt. No.	Wt.(g)	2 Apr 74	Wt. No.	Wt.(g)
	1	1121.0		1	5058.3
	2	1121.2		2	5059.4
	3	1120.9		3	5059.5
	4	1120.8		4	5059.3
	5	1120.7		5	5059.2
	6	1120.8		6	5059.3
	7	1119.9		7	5059.6
	8	1121.3		8	5059.8
	9	1120.9		9	5059.5
Average =		1120.8	Average =		5059.3

Wt. Water = 3938.5 g

$\sigma = 0.$ g

TABLE 2.   Flask Volumes

Date	Book No.	Page No.	Wt. of Water (g)	σ(g)[†]	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
			Flask No. C-3				
29 Jan 74	1	134	5304.5	0.64	21.0	0.997992	5315.2
30 Jan 74	1	135	5303.9	0.64	21.2	0.997948	5314.8
						Average volume = 5315.0 cc	
			Flask No. C-5				
29 Jan 74	1	136	5309.7	0.64	21.0	0.997992	5320.4
30 Jan 74	1	137	5309.0	0.64	21.2	0.997948	5319.9
						Average volume = 5320.2 cc	
			Flask No. C-7				
29 Jan 74	1	138	5339.1	0.64	21.0	0.997992	5349.8
30 Jan 74	1	139	5339.5	0.64	21.2	0.997948	5350.5
						Average volume = 5350.2 cc	

[†] $\sigma_{universal}$ for Mettler P-11 balance given.

TABLE 2. Flask Volumes

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)$[†]	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
Flask No. C-8							
9 Jan 74	1	121	5380.2	0.64	18.5	0.998501	5388.3
10 Jan 74	1	122	5381.6	0.64	18.8	0.998444	5390.0
11 Jan 74	1	123	5382.2	0.64	17.3	0.998722	5389.1
14 Jan 74	1	124	5382.1	0.64	18.1	0.998576	5389.8
15 Jan 74	1	125	5379.8	0.64	19.1	0.998385	5388.5

Average volume = 5389.1 cc

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)$	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
Flask No. C-11							
17 Jan 74	1	127	5215.3	0.64	21.0	0.997992	5225.8
18 Jan 74	1	128	5217.2	0.64	17.9	0.998613	5224.4
22 Jan 74	1	129	5216.9	0.64	16.3	0.998893	5222.7
23 Jan 74	1	130	5213.8	0.64	20.3	0.998141	5223.5
24 Jan 74	1	131	5213.5	0.64	21.2	0.997948	5224.2
25 Jan 74	1	132	5214.0	0.64	20.5	0.998099	5223.9

Average volume = 5224.1 cc

* Handbook of Chemistry and Physics, 43rd Edition, page 2155, Chemical Rubber Publishing Co., 1962.

† $\sigma_{universal}$ for Mettler P-11 balance given.

TABLE 2. Flask Volumes

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)^{\dagger}$	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)

Flask No. C-9

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)$	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
31 Jan 74	1	140	5227.1	0.64	21.1	0.997970	5237.7
1 Feb 74	1	141	5226.1	0.64	21.0	0.997992	5236.6

Average volume = 5237.2 cc

Flask No. C-10

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)$	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
31 Jan 74	1	142	5319.0	0.64	21.1	0.997970	5329.8
1 Feb 74	1	143	5319.1	0.64	21.0	0.997992	5329.8

Average volume = 5329.8 cc

Manometer Flask #2

Date	Book No.	Page No.	Wt. of Water (g)	$\sigma(g)$	Water temp. (°C)	Density of Water (g/cc)	Computed Flask Volume (cc)
29 Mar 74	2	31	3937.7	0.64	22.1	0.997747	3946.6
1 Apr 74	2	32	3938.3	0.64	21.9	0.997792	3947.0
2 Apr 74	2	33	3938.5	0.64	21.8	0.997815	3947.1

Average volume = 3946.9 cc

$\sigma_{universal}$ of balance (based on 426 weighings, 48 averages) = 0.45 g.

$\sigma_{universal}$ of weights of water (differences between empty and full flasks) = $0.45\sqrt{2}$ g = 0.64 g.

$\sigma_{universal}$ of volume due to weighings = 0.64 cc

$\sigma_{universal}$ of individual volume determinations = (based on 24 fillings, 8 averages) = 0.74 cc

$\sigma_{universal}$ of volume due to repetitive fillings with water = 0.37 cc

$\dagger$ $\sigma_{universal}$ for Mettler P-11 balance given.

TABLE 3. Plenum Weights
Plenum No. P-1

	Evacuated Plenum			Full Plenum				Evacuated Plenum			Full Plenum		
	Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)
		Filling No. 1							Filling No. 4				
28 Feb 74	1	52.407	1 Mar 74	1		69.984	11 Mar 74	1	52.419	11 Mar 74		1	69.998
	2	52.408		2		69.983		2	52.418	2		2	69.998
	3	52.406		3		69.983		3	52.418			3	69.999
	Average = 52.407		Average = 69.983					Average = 52.418				Average = 69.998	
	Wt. Mercury = 17.573 g*							Wt. Mercury = 17.577 g*					
		Filling No. 2							Filling No. 5				
4 Mar 74	1	52.408	5 Mar 74	1		69.985	13 Mar 74	1	52.415	13 Mar 74		1	69.996
	2	52.409		2		69.985		2	52.415	4		2	69.994
	3	52.409		3		69.985		3	52.416			3	69.996
	Average = 52.409		Average = 69.985					Average = 52.415				Average = 69.995	
	Wt. Mercury = 17.573 g*							Wt. Mercury = 17.577 g*					
		Filling No. 3											
6 Mar 74	1	52.401	8 Mar 74	1		69.980							
	2	52.400		2		69.981							
	3	52.400		3		69.980							
	Average = 52.400		Average = 69.980										
	Wt. Mercury = 17.577 g*												

* Buoyancy correction for weights = -0.003 g added to weight of mercury.

TABLE 3. Plenum Weights
Plenum No. P-2

	Evacuated Plenum				Full Plenum				Evacuated Plenum			Full Plenum	
		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)			Wt. No.	Wt.(g)	Wt. No.	Wt.(g)
			Filling No. 1									**Filling No. 4**	
28 Feb 74		1	52.442	28 Feb 74 *1 Mar*		1	72.244	11 Mar 74		1	52.439	12 Mar 74	1 72.243
		2	52.442			2	72.244			2	52.438		2 72.242
		3	52.442			3	72.244			3	52.439		3 72.242
	Average = 52.442				Average = 72.244				Average = 52.439			Average = 72.242	
			Wt. Mercury = 19.799 g*									Wt. Mercury = 19.800 g*	
			Filling No.2									**Filling No. 5**	
4 Mar 74		1	52.443	4 Mar 74 *5*		1	72.242	13 Mar 74		1	52.442	14 Mar 74	1 72.239
		2	52.444			2	72.243			2	52.442		2 72.239
		3	52.443			3	72.241			3	52.441		3 72.238
	Average = 52.443				Average = 72.242				Average = 52.442			Average = 72.239	
			Wt. Mercury = 19.796 g*									Wt. Mercury = 19.794 g*	
			Filling No. 3										
7 Mar 74		1	52.439	8 Mar 74		1	72.240						
		2	52.438			2	72.240						
		3	52.438			3	72.240						
	Average = 52.438				Average = 72.240								
			Wt. Mercury = 19.799 g*										

*Buoyancy correction for weights = −0.003 g added to weight of mercury

TABLE 3. Plenum Weights
Plenum No. P-3

		Evacuated Plenum		Full Plenum				Evacuated Plenum			Full Plenum	
	Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No.	Wt.(g)
			Filling No. 1							**Filling No. 4**		
28 Feb 74	1	54.090	1 Mar 74	1	76.248	11 Mar 74		1	54.089	12 Mar 74	1	76.247
	2	54.090		2	76.248			2	54.089		2	76.247
	3	54.090		3	76.248			3	54.089		3	76.246
	Average =	54.090		Average =	76.248			Average =	54.089		Average =	76.247
		Wt. Mercury = 22.155 g*							Wt. Mercury = 22.155 g*			
			Filling No. 2							**Filling No. 5**		
4 Mar 74	1	54.088	5 Mar 74	1	76.249	13 Mar 74		1	54.092	14 Mar 74	1	76.247
	2	54.090		2	76.246			2	54.091		2	76.248
	3	54.090		3	76.249			3	54.091		3	76.247
				4	76.248							
	Average =	54.089		Average =	76.248			Average =	54.091		Average =	76.247
		Wt. Mercury = 22.156 g*							Wt. Mercury = 22.153 g*			
			Filling No. 3									
7 Mar 74	1	54.087	8 Mar 74	1	76.245							
	2	54.087		2	76.245							
	3	54.087		3	76.245							
	Average =	54.087		Average =	76.245							
		Wt. Mercury = 22.155 g*										

* Buoyancy correction for weights = -0.003 g added to weight of mercury.

TABLE 3. Plenum Weights
Plenum No. P-4

	Evacuated Plenum			Full Plenum				Evacuated Plenum			Full Plenum	
	Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No.	Wt.(g)
			Filling No. 1							**Filling No. 4**		
25 Feb 74	1	57.529	26 Feb 74	1	81.179		7 Mar 74	1	57.521	8 Mar 74	1	81.167
	2	57.530		2	81.180			2	57.521		2	81.169
	3	57.530		3	81.178			3	57.520		3	81.167
	Average = 57.530			Average = 81.179				Average = 57.521			Average = 81.168	
	Wt. Mercury = 23.646 g*							Wt. Mercury = 23.644 g*				
			Filling No. 2							**Filling No. 5**		
1 Mar 74	1	57.526	1 Mar 74	1	81.168		11 Mar 74	1	57.519	12 Mar 74	1	81.169
	2	57.525		2	81.168			2	57.519		2	81.167
	3	57.525		3	81.168			3	57.520		3	81.167
	Average = 57.525			Average = 81.168				Average = 57.519			Average = 81.168	
	Wt. Mercury = 23.640 g*							Wt. Mercury = 23.646 g*				
			Filling No. 3									
4 Mar 74	1	57.521	5 Mar 74	1	81.162							
	2	57.521		2	81.160							
	3	57.521		3	81.161							
	Average = 57.521			Average = 81.161								
	Wt. Mercury = 23.637 g*											

* Buoyancy correction for weights = -0.003 g added to weight of mercury.

TABLE 3. Plenum Weights
Plenum No. P-5

Evacuated Plenum			Full Plenum				Evacuated Plenum			Full Plenum		
	Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No.	Wt.(g)
		Filling No. 1								**Filling No. 4**		
6 Mar 74	1	77.592	8 Mar 74	1	102.458		14 Mar 74	1	77.588	14 Mar 74	1	102.453
	2	77.592		2	102.456			2	77.588		2	102.454
	3	77.592		3	102.456			3	77.588		3	102.454
	Average =	77.592		Average =	102.457			Average =	77.588		Average =	102.454
		Wt. Mercury = 24.861 g*							Wt. Mercury = 24.862 g*			
		Filling No. 2								**Filling No. 5**		
11 Mar 74	1	77.589	12 Mar 74	1	102.459		15 Mar 74	1	77.590	15 Mar 74	1	102.455
	2	77.589		2	102.460			2	77.591		2	102.456
	3	77.589		3	102.459			3	77.592		3	102.457
	Average =	77.589		Average =	102.459			Average =	77.591		Average =	102.456
		Wt. Mercury = 24.866 g*							Wt. Mercury = 24.861 g*			
		Filling No. 3										
13 Mar 74	1	77.597	14 Mar 74	1	102.463							
	2	77.596		2	102.464							
	3	77.595		3	102.463							
	Average =	77.596		Average =	102.463							
		Wt. Mercury = 24.863 g*										

* Buoyancy correction for weights = -0.004 g added to weight of mercury.

TABLE 3. Plenum Weights
Plenum No. P-6

	Evacuated Plenum		Full Plenum				Evacuated Plenum		Full Plenum		
	Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No. Wt.(g)

Filling No. 1

28 Feb 74	1	58.649	1 Mar 74	1	86.239	11 Mar 74	1	58.645	12 Mar 74	1	86.231
	2	58.650		2	86.238		2	58.644		2	86.231
	3	58.650		3	86.238		3	58.644		3	86.233

Average = 58.650   Average = 86.238   Average = 58.644   Average = 86.232

Wt. Mercury = 27.584 g*   Wt. Mercury = 27.584 g*

Filling No. 2   **Filling No. 5**

4 Mar 74	1	58.652	5 Mar 74	1	86.233	13 Mar 74	1	58.644	14 Mar 74	1	86.227
	2	58.651		2	86.232		2	58.643		2	.86.225
	3	58.650		3	86.232		3	58.643		3	86.226

Average = 58.651   Average = 86.232   Average = 58.643   Average = 86.226

Wt. Mercury = 27.577 g*   Wt. Mercury = 27.579 g*

Filling No. 3

7 Mar 74	1	58.643	8 Mar 74	1	86.230
	2	58.642		2	86.232
	3	58.644		3	86.232

Average = 58.643   Average = 86.231

Wt. Mercury = 27.584 g*

* Buoyancy correction for weights = -0.004 g added to weight of mercury.

TABLE 3. Plenum Weights
Plenum No. P-7

Evacuated Plenum			Full Plenum				Evacuated Plenum			Full Plenum		
	Wt. No.	Wt.(g)		Wt. No.	Wt.(g)			Wt. No.	Wt.(g)		Wt. No.	Wt.(g)
		Filling No. 1								Filling No. 4		
28 Feb 74	1	57.838	1 Mar 74	1	88.630		11 Mar 74	1	57.830	12 Mar 74	1	88.622
	2	57.838		2	88.630			2	57.830		2	88.622
	3	57.838		3	88.631			3	57.830		3	88.622
	Average = 57.838			Average = 88.630				Average = 57.830			Average = 88.622	
		Wt. Mercury = 30.787 g*								Wt. Mercury = 30.787 g*		
		Filling No. 2								Filling No. 5		
28 Feb 74	1	57.837	5 Mar 74	1	88.624		13 Mar 74	1	57.834	14 Mar 74	1	88.623
	2	57.835		2	88.623			2	57.835		2	88.623
	3	57.835		3	88.623			3	57.834		3	88.623
	Average = 57.836			Average = 88.623				Average = 57.834			Average = 88.623	
		Wt. Mercury = 30.782 g*								Wt. Mercury = 30.784 g*		
		Filling No. 3										
7 Mar 74	1	57.832	8 Mar 74	1	88.624							
	2	57.831		2	88.623							
	3	57.832		3	88.624							
	Average = 57.832			Average = 88.624								
		Wt. Mercury = 30.787 g*										

* Buoyancy correction for weights = -0.005 g added to weight of mercury.

TABLE 4. Plenum Volumes

Date	Book No.	Page No.	Wt. of Hg (g)	σ(g)[+]	Hg temp. (°C)	Density of Hg[*] (g/ml)	Density of Hg^{+} (g/cc)	Plenum Volume (cc)
					Plenum No. P-1			
1 Mar 74	1	146	17.573	.001	21.2	13.5433	13.5429	1.2976
5 Mar 74	1	147	17.573	.001	21.9	13.5416	13.5412	1.2977
6 Mar 74	1	148	17.577	.001	21.1	13.5436	13.5432	1.2978
11 Mar 74	1	149	17.577	.001	20.9	13.5440	13.5436	1.2978
13 Mar 74	1	150	17.577	.001	22.0	13.5413	13.5409	1.2981

17.5754   1/8000
$S_i = .0022$

Average volume = 1.2978 cc

σ_{mean} = .00008 S_i 1/7250 .0002

Date	Book No.	Page No.	Wt. of Hg (g)	σ(g)[+]	Hg temp. (°C)	Density of Hg[*] (g/ml)	Density of Hg^{+} (g/cc)	Plenum Volume (cc)
					Plenum No. P-2			
1 Mar 74	2	2	19.799	.001	21.2	13.5433	13.5429	1.4619
5 Mar 74	2	3	19.796	.001	21.9	13.5416	13.5412	1.4619
7 Mar 74	2	3	19.799	.001	21.1	13.5436	13.5432	1.4619
11 Mar 74	2	4	19.800	.001	20.9	13.5440	13.5436	1.4619
13 Mar 74	2	4	19.794	.001	22.0	13.5413	13.5409	1.4618

19.7976   1/7900
$S_i = .0025$

Average volume = 1.4619 cc

σ_{mean} = .0000 $S_i = $ 1/36 500 .00004

[*]Obtained from linear interpolation of tabulated densities (Handbook of Chemistry and Physics, 43rd Edition, page 2157, Chemical Rubber Publishing Co., 1962).

[+]Equal to density in g/ml ÷ 1.000027.

[+]$\sigma_{universal}$ for solution balance given.

TABLE 4. Plenum Volumes

Date	Book No.	Page No.	Wt. of Hg (g) σ(g)[†]	Hg temp. (°C)	Density of Hg (g/)	Density of Hg (g/cc)	Plenum Volume (cc)
				Plenum No. P-3			
1 Mar ~~28 Feb~~ 74	2	7	22.155 .001	21.2	13.5433	13.5429	1.6359
5 ~~4~~ Mar 74	2	8	22.156 .001	21.9	13.5416	13.5412	1.6362
8 Mar 74	2	8	22.155 .001	21.1	13.5436	13.5432	1.6359
12 Mar 74	2	9	22.155 .001	20.9	13.5440	13.5436	1.6358
1*4* ~~3~~ Mar 74	2	9	22.153 .001	22.0	13.5413	13.5409	1.6360

22.1548 $1/20,000$
$s_i = .0011$

Average volume = 1.6360 cc
$\sigma_{mean} = .00007$ $s_c = 1/10400$ $.0002$

				Plenum No. P-4			
26 Feb 74	2	11	23.646 .001	20.2	13.5457	13.5453	1.7457
1 Mar 74	2	11	23.640 .001	21.2	13.5433	13.5429	1.7456
5 ~~4~~ Mar 74	2	12	23.637 .001	21.9	13.5416	13.5412	1.7456
8 Mar 74	2	12	23.644 .001	21.1	13.5436	13.5432	1.7458
12 Mar 74	2	13	23.646 .001	20.9	13.5440	13.5436	1.7459

23.6426 $1/5900$
$s_i = .0040$

Average volume = 1.7457 cc
$\sigma_{mean} = .00006$ $s_c = 1/13,000$

$.0001$

[*]Obtained from linear interpolation of tabulated densities (Handbook of Chemistry and Physics, 43rd Edition, page 2157, Chemical Rubber Publishing Co., 1962).

[+]Equal to density in g/ml ÷ 1.000027.

[†]$\sigma_{universal}$ for solution balance given.

TABLE 4. Plenum Volumes

Date	Book No.	Page No.	Wt. of Hg (g)	σ(g)‡	Hg temp. (°C)	Density of Hg* (g/ml)	Density of Hg+ (g/cc)	Plenum Volume (cc)
					Plenum No. P-5			
8 Mar 74	2	17	24.861	.001	21.1	13.5436	13.5432	1.8357
12 Mar 74	2	18	24.866	.001	20.9	13.5440	13.5436	1.8360
14 Mar 74	2	18	24.863	.001	22.0	13.5413	13.5409	1.8361
14 Mar 74	2	19	24.862	.001	21.6	13.5423	13.5419	1.8359
15 Mar 74	2	19	24.861	.001	21.9	13.5416	13.5412	1.8360

$24.8626 \quad 1/11,800$

$x = .0021$

Average volume = 1.8359 cc

$\sigma_{mean} = .00007 \qquad s_i = 1/11,700$

.0002

Date	Book No.	Page No.	Wt. of Hg (g)	σ(g)‡	Hg temp. (°C)	Density of Hg* (g/ml)	Density of Hg+ (g/cc)	Plenum Volume (cc)
					Plenum No. P-6			
1 Mar 74	2	21	27.584	.001	21.1	13.5433	13.5429	2.0368
5 Mar 74	2	22	27.577	.001	21.9	13.5416	13.5412	2.0365
8 Mar 74	2	22	27.584	.001	21.1	13.5436	13.5432	2.0367
12 Mar 74	2	23	27.584	.001	20.9	13.5440	13.5436	2.0367
14 Mar 74	2	23	27.579	.001	22.0	13.5413	13.5409	2.0367

$27.5816 \quad 1/8100$

$s_i = .0034$

Average volume = 2.0367 cc

$\sigma_{mean} = .00005 \qquad 1/18200$

.0001

*Obtained from linear interpolation of tabulated densities (Handbook of Chemistry and Physics, 43 Edition, page 2157, Chemical Rubber Publishing Co., 1962).

+Equal to density in g/ml ÷ 1.000027.

‡$\sigma_{universal}$ for solution balance given.

TABLE 4. Plenum Volumes

Date	Book No.	Page No.	Wt. of Hg (g)	$\sigma(g)$[†]	Hg temp. (°C)	Density of Hg[*] (g/ml)	Density of Hg^{+} (g/cc)	Plenum Volume (cc)
					Plenum No. P-7			
~~28~~ Mar 74	2	26	30.787	.001	21.2	13.5433	13.5429	2.2733
5 Mar 74	2	27	30.782	.001	21.9	13.5416	13.5412	2.2732
8 Mar 74	2	27	30.787	.001	21.1	13.5436	13.5432	2.2732
12 Mar 74	2	28	30.787	.001	20.9	13.5440	13.5436	2.2732
14 Mar 74	2	28	30.784	.001	22.0	13.5413	13.5409	2.2734

(handwritten next to 28 Mar: "1 Mar ~~Feb.~~")

(handwritten below table: 30785.4 1/13400 ; $s_i = .0023$)

Average volume = 2.2733 cc

(handwritten: $\sigma_{mean} = .00004$; $s_i^- = 1/25400$; .00009)

$\sigma_{universal}$ of balance (based on 261 weighings, 87 averages) = 0.73 mg.

$\sigma_{universal}$ of weights of Hg (difference between empty and full plenums) = 0.73 $\sqrt{2}$ mg = 1.0324 mg.

$\sigma_{universal}$ of individual vial volume determinations $\cong \dfrac{1.0324}{13.54} \cdot 10^{-3}$ cc = 0.000076 cc.

$\sigma_{universal}$ of individual volume determination (based on 35 fillings, 7 averages) = .000135 cc.

$\sigma_{universal}$ of volume due to repetitive fillings with mercury = .000112 cc.

[*]Obtained from linear interpolation of tabulated densities (Handbook of Chemistry and Physics, 43rd Edition, page 2157, Chemical Rubber Publishing Co., 1962).

[+]Equal to density of g/ml ÷ 1.000027.

[†]$\sigma_{universal}$ for solution balance given.

TABLE 5. Uncertainties in Weight and Volume Measurements

Vessel Type	$\sigma_{universal}$ Individual Weighings	$\sigma_{universal}$ Weights of Liquid	$\sigma_{universal}$ Volume due to Weighings	Uncertainty in Mean Volume due to Weighings	Relative[+] Uncertainty in Mean Volume due to Weighings
Flask	0.45g	0.64g	0.64cc	0.21cc*	$4.0 \cdot 10^{-5}$
Plenum	0.73mg	1.03mg	$0.76 \cdot 10^{-4}$cc	$0.44 \cdot 10^{-4}$cc[†]	$2.2 \cdot 10^{-5}$

* For flasks weighed nine times.

† All plenums were weighed three times.

+ Flask volume was taken as 5300 cc and plenum volume was taken as 2 cc for relative error calculations.

TABLE 5. Uncertainties in Weight and Volume Measurements

Vessel Type	$\sigma_{universal}$ Volume due to Filling	Uncertainty in Mean Volume due to Filling	Relative[†] Uncertainty in Mean Volume due to Filling	$\sigma_{universal}$ Volume Total	Uncertainty in Mean Volume Total	Relative[†] Uncertainty in Mean Volume Total
Flask	0.37cc	0.26cc**	$5.0 \cdot 10^{-5}$	0.74cc	0.52cc**	$1.0 \cdot 10^{-4}$
Plenum	$1.12 \cdot 10^{-4}$cc	$0.50 \cdot 10^{-4}$cc[†]	$2.5 \cdot 10^{-5}$	$1.35 \cdot 10^{-4}$cc	$0.60 \cdot 10^{-4}$cc[††]	$3.0 \cdot 10^{-5}$

[†] All plenums were weighed three times.

** For flasks filled twice during volume calibration.

[††] All plenums were filled five times during volume calibration.

[†] Flask volume was taken as 5300 cc and plenum volume was taken as 2 cc for relative error calculations.

TABLE 6. Calibration of Mettler P11N

Single-Pan Analytical Balance

1 Kg Wt.		2 Kg Wt.		2826.8 g Bottle Hg		2826.8 g (Wts. + Bottle Hg)	
Wt. No.	Wt.(g)	Wt. No.	Wt.(g)	Wt. No.	Wt.(g)	Wt. No.	Wt.(g)
1	999.8	1	2000.1	1	.2827.1	1	6827.2
2	998.5*	2	2000.1	2	2827.0	2	6827.0
3	1000.0	3	2000.1	3	2826.9	3	6827.1
4	998.9*	4	1998.2*	4	2827.0*	4	6826.7*
5	1000.2	5	1997.0 (1999.3)*5		2825.5*	5	6826.1 (6827.0)*
6	998.1*	6	1998.9*		2824.6 (2826.2)*6		6824.7 (6826.3)*

* Settled slowly onto the pan.

Numbers in parentheses were obtained by tapping the side of the balance while the weights were still on the pan.