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Manometer Report III: Manometric Calibrations of Primary CO_2 Reference Gases During 1974

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Manometer Report III:

Manometric Calibrations of Primary CO_2 Reference Gases During 1974

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Preface

Absolute calibration of the carbon dioxide reference gas system has been an important concern since the inception of the CO_2 Project at Scripps Institution of Oceanography in 1957. In 1959 and again in 1961, C. D. Keeling made calibrations of reference gases with a specially constructed precision constant-volume manometric system located in Room 2317 Ritter Hall. During both years the internal volume-ratios of the manometer were also determined.

The calibrations of 1959 were the basis for establishing a provisional manometric mole fraction scale defined to be linear with the response of the Applied Physics infrared analyzer installed in Room 2317, and the scale was made to agree very nearly with the true mole fraction at 312 ppm (parts per million), which was approximately the concentration of atmospheric CO_2 in 1959, referred to dry air. The original data have not been previously reported, but will be documented in Manometric Report V, in preparation. All published data up to 1975 have been expressed using the 1959 linear scale. In 1968 C. S. Wong made a gravimetric calibration of the Applied Physics infrared analyzer reported in his thesis. The gravimetric data were fit to infrared data with a quadratic relationship. In 1969-70, P. R. Guenther made an extended set of reference gas calibrations on the constant volume manometric system, reported in Manometric Report I. In

1972 he made a second gravimetric calibration similar to Wong's, not yet set down in a report. Later in 1972, he ran another set of manometric reference gas calibrations and carried out another internal volume ratio calibration, reported in Manometer Report II.

After all the work cited above there still remained a 1% (3 ppm) spread in absolute calibration among the methods. In January, 1974, P. R. Guenther began another set of calibrations using the constant volume manometric system. During the same period J. A. Adams worked on an independent volumetric calibration as part of a concurrent effort to reduce the uncertainty in the absolute calibration.

The following report summarizes the manometric calibration of reference gases carried out between January and October, 1974. Internal volume ratio calibrations of the manometric system carried out in 1974 are reported in Manometer Report IV. The work of Adams is reported in Volumetric Report I.

I. Introduction

The reference gas calibrations made in 1974 had a threefold purpose. The first goal was to redetermine the concentration of reference gases previously analyzed in 1970 and 1972. These gases contained CO_2 in a carrier gas of pure nitrogen. The second goal was to extend the range of the infrared analyzer calibration curve by analyzing new reference gases of lower and higher CO_2 concentration. The third goal was to determine the effect of oxygen as a carrier gas on the response of the Applied Physics infrared analyzer by analyzing gas mixtures containing oxygen as well as nitrogen. To accomplish the first two goals, twenty-five determinations of eleven different CO_2 in nitrogen references gases, ranging in CO_2 concentration from about 200 ppm to about 470 ppm, were made. To accomplish the third goal eleven determinations of five different compressed natural air gases and fourteen determinations of seven different synthetic CO_2 in oxygen and nitrogen reference gases were made.

II. Experimental Procedures

The general procedure, although basically as described in Manometer Report I, will be reviewed here to emphasize specific features developed and followed in 1974. A problem with jumping mercury, which has from time to time plagued the manometric work, will also be discussed. Finally, methods of analyzing oxygen-containing reference gases for oxygen content and compressed air reference gases

for nitrous oxide content will be discussed.

A. Manometric Analysis of Carbon Dioxide in Nitrogen Containing Reference Gases

Summary. Reference gases containing CO_2 were analyzed with a constant volume manometric system as described below. First, a five-liter glass manometric chamber is filled with a sample of reference gas vented from a steel cylinder in which it is permanently stored. The gas sample is dried by passage through a dry ice trap prior to being admitted to the manometer. The sample is confined and its pressure and temperature are measured in a 5000 cc chamber. The CO_2 which the sample contains is then quantitatively separated from carrier gas and the pressure and temperature of this CO_2 sample measured in a 4 cc manometric chamber. The pressure and temperature data and the precise volume ratio of the (nominally) 4 cc and five-liter chambers are used, along with appropriate expressions for the nonideality of the gases and for the density of mercury, to calculate the CO_2 mixing ratio in the sample.

A description of the manometric system and procedure follows.

1. Description of Constant Volume Manometric System

The constant volume manometric system is located in Room 2317, Ritter Hall at the Scripps Institution of Oceanography. It was constructed in 1958 from an original design by C. D. Keeling shown in Figure 1.

The manometric system itself is principally of glass. It is enclosed in a wooden insulated cabinet with double glass-windowed

doors. The cabinet rests on a mounting platform of alternating cork and brick to isolate the system from vibration. The glass system is connected by a glass vacuum manifold and additional glass tubing to an associated vacuum line. The temperature within the box is stabilized by five air circulating fans. The fan motors are mounted outside the box on independent ceiling supports to avoid heating the cabinet air or producing vibration within the cabinet. The speed of the fans can be continuously varied to allow optimum circulating conditions to be established and maintained. Seven thermometers are mounted permanently at different points within the cabinet to monitor air temperature and possible gradients near the manometric system. A precision screw cathetometer is mounted in front of the glass doors of the cabinet to measure the heights of mercury in the manometric system. A bank of fluorescent lights provides broadly diffuse lighting of the columns. The entire laboratory room is temperature controlled to within 0.3° C.

The manometric system proper consists of three independent constant volume manometers. Each manometer consists of vertical columns containing mercury. These are connected with U-shaped capillary tubes to suppress surges of mercury. An additional capillary tube connects the U-shaped capillary tubes to a mercury reservoir. One column of each manometer is normally kept evacuated while another column contains the sample gas. The pressure of sample gas is measured as the difference in heights of mercury in the two columns after correcting

for meniscus effects. The volume of the sample at the time of making the pressure measurement is determined by the mercury surface being positioned so as to be just barely in contact with a flattened glass pointer attached to the manometer column tube. Mercury levels are controlled via the mercury reservoir which is connected in tandem with two ballast chambers to which nitrogen gas can be admitted at any pressure between zero and one atmosphere. The inner ballast chamber is connected to the outer by a control valve such that the pressure within the mercury reservoir can be varied either rapidly or slowly by bleeding nitrogen gas between the ballast chambers at a predetermined initial differential pressure. It is thus possible to raise or lower the mercury in the sample column at any rate desirable.

Two of the manometers are almost duplicates of each other. Each of these has one sample column and one vacuum column. Each sample column contains a series of five sample volume cut-off cavities or chambers, of approximately 1, 4, 16, 64 and 250 cc capacity, respectively. Each chamber includes the volume of all smaller chambers. The third manometer contains three independent sample columns and one vacuum column. Each sample column has two sample volume cut-off chambers of 1000 and 5000 cc capacity. Each of the two smaller manometers and the larger manometer has an independent mercury level control system consisting of its own mercury reservoir, two ballast chambers and auxiliary connecting and regulating valves and cocks.

Each of the five sample chambers of the small manometers is

defined by the mercury level in the sample column brought to an appropriate glass pointer mounted within the sample column. When the mercury column is set at the lowest pointer in the column, the full volume of nominally 250 cc is above the mercury level. This volume includes a part of the column cut off by a 4 mm hollow plug stopcock through which the sample gas is admitted to the manometer. This cock introduces an error related to how it has been greased. The relative error is small because the volume is large compared to the volume occupied by grease. When the mercury column is raised to the next highest pointer which defines a volume of nominally 64 cc, the stopcock and entrance tube are no longer in contact with the sample volume. This volume is now defined only by a close ended glass tube and the mercury surface. This and succeeding sample volumes can thus be determined as accurately as the mercury can be reproducibly reset at the proper pointer. The 1 cc chamber has never been used because equally good results have been obtained using the 4 cc chamber. For reference gas analyses and most other work with samples having CO_2 concentrations close to that of air, the 4 cc chamber is used.

The inside diameter of the glass tube where the 4 cc pointer is mounted is smaller (8mm) than that of the glass tube of the vacuum arm of the small manometer (19 mm). Thus a significant correction must be applied to the measured mercury column heights to compensate for the meniscus depression in the smaller tube.

The pointers for the 16, 64 and 250 cc chambers, on the other hand, are all located where the glass tube of the sample column is approximately equal to that of the vacuum column. The meniscus correction is correspondingly small.

In each large manometer sample column only one pointer is present. It defines a volume of nominally 1000 cc. A volume of 5000 cc can also be obtained by opening a 6 mm hollow plug stopcock to connect the column to an auxiliary cylindrical flask with a volume of nominally 4000 cc. This flask is removable to allow absolute determination of its volume. In routine work only the sample column mounted nearest the small manometer is used.

In total, there are eight columns in the manometric system: a sample column and a vacuum column for each of the two small manometers, and a vacuum column and three sample columns for the large manometer. Only one of the small manometers has so far been placed in use. Numbered from the left in the cabinet the columns are arranged as follows: (1) duplicate (unused) small manometer vacuum column; (2) small manometer vacuum column; (3) duplicate (unused) small manometer sample column; (4) small manometer sample column; (5), (6), (7), large manometer sample columns; (8) large manometer vacuum column. Each of the sample columns terminates at the top with a three way stopcock through which sample gas can be introduced from a separate line or through which evacuation can be made via a common connection to an associated vacuum line. A vacuum manifold also connects all of the

columns including the three vacuum columns. Thus gases can be transferred between any pair of columns within the manometric system or any or all of the columns can be equalized in pressure for special purposes.

An auxiliary vacuum line, mounted on a rack near the manometer cabinet, is available for preparation and disposal of gases used in the manometric procedures. This line is equipped with a ring manifold with two mercury diffusion pumps and associated liquid nitrogen traps. Evacuation of the vacuum line to less than 1 millitorr pressure can be accomplished using either or both mercury diffusion pumps.

In routine calibration of reference gases the appropriate gas is piped from its steel storage cylinder into the line through a thimble trap cooled to dry ice temperature and thence into the left most 5000 cc chamber of the large manometer (column 5). After determination of the sample's pressure and temperature, the CO_2 is quantitatively separated from the sample by pumping the entire reference gas mixture from the 5000 cc chamber via connecting tubing through a spherical trap cooled with liquid nitrogen in the auxiliary vacuum line. After the entire sample has been pumped through and the CO_2 frozen down in the trap, the CO_2 is freed of water by repeated sublimations at dry ice temperature using a series of tandem U-traps. Pressure in various portions of the vacuum line is measured with simple mercury manometers and four Pirani tube vacuum gauges installed near the U-traps. The latter also measure the vacuum quality and any residual non-condensable gas during sublimations.

The cathetometer used to measure the mercury column heights consists of a telescope mounted on a 1 mm pitch screw. The instrument was made by Fred Henson and Company of Pasadena in 1956 from a design of the Chemical Engineering Department of the California Institute of Technology. Height measurements from the cathetometer are made by aligning a crosshair in the telescope with images of the mercury surface in the sample and vacuum columns. The telescope moves up and down on the screw both by motor control and manual control. The height of the crosshair is registered on a counter and 360° dial to a readibility of .002 mm with a stated precision of .005 mm. To promote a reproducible position of the mercury meniscus image in the telescope field, a meniscus reader is set behind each pointer just outside each glass column within the manometer cabinet. Movable meniscus viewing cards behind the vacuum columns allow identical optical viewing of the sample and vacuum mercury columns. Each meniscus card consists of a scale one mm in length with divisions of .050 mm set in a white field below a black field. Each card is positioned so that the black field begins 0.80 mm above the meniscus image.

2. Filling the Five Liter Chamber with Reference Gas

A cylinder containing reference gas to be analyzed is placed in position for infrared analysis in Room 2317 Ritter Hall. Gas is flowed through the APC nondispersive infrared gas analyzer via a dry ice trap until a low noise steady trace is obtained on the analyzer chart recorder. The gas flow is then switched to allow passage through a loop of copper

tubing to the auxiliary vacuum line and thence back to the analyzer until a trace, identical in level to that for direct flow, is obtained. The five-liter manometric chamber, previously evacuated, is then filled with gas through a dry ice thimble trap to remove any residual water vapor from the gas. The flow rate for filling is not allowed to exceed about 0.5ℓ/min., equivalent to a rate of increase in pressure of 10 sec/cm of mercury. Pressure in the copper reference gas line is kept above ambient to avoid possible contamination from room air by leaks. Filling the five-liter chamber takes about eight minutes under these conditions. The maximum pressure obtainable is about 650 mm Hg. Actual pressures obtained in the reported work were never less than 620 mm, and were usually about 630 mm. The sample is confined in Sample Chamber No. 1 of the large manometer by closing the stopcock at the top of Column No. 5. The gas is afterwards again flowed through the analyzer via the manometric loop and finally flowed again directly to the analyzer to ascertain that the concentration in the loop still agrees with that of direct flow. The chart traces for these manometric fillings are saved.

3. Measurement of Reference Gas Sample in the Large Manometer

The air circulating fans in the manometric system cabinet are turned on at least one hour prior to measurement of the pressure and temperature of the sample. As will be shown below, temperature gradients within the manometric system cabinet are routinely within allowable limits.

After the cabinet temperature has stabilized, the mercury levels

in the large manometer are raised slowly until the level in the sample column is about 0.300 mm below the pointer. This level is close enough to insure reproducible results and a closer approach to the pointer is usually not attempted. The mercury levels in the sample column and in the vacuum column are now measured with the cathetometer to ±.002 mm. Before measuring the vacuum column height, the moveable meniscus viewing card is set. The average of two determinations of the sample column height, one before and one after a determination of the vacuum column height, is routinely accepted as the height of the mercury in the sample column. Routinely, each determination of mercury height is based on the average of two independent settings of the cathetometer crosshair.

Temperature readings of thermometer number 6112, located near the small manometer, are taken before the manometric measurement begins, immediately after the first sample column measurement, and immediately after the final sample column measurement. An average of the last two uncorrected readings of this thermometer is adopted as the temperature of the measurement. The two individual temperatures usually differ by no more than 0.02°C. Finally, the remaining six thermometers are read at the end of the measurement to determine temperature gradients within the cabinet.

4. Separation of CO_2 from Carrier Gas and Transfer into the 4 cc Chamber

Quantitative separation of the CO_2 from the five-liter reference gas sample is accomplished by slowly pumping the gas from the five-liter chamber through the spherical trap of the auxiliary line, the trap being cooled to liquid nitrogen temperature. The pressure of the

gas entering the trap during this separation is held between 0.7 and 1.0 cm/Hg by gradually opening a stopcock. No attempt has been made to determine the maximum permissible rate of separation, but it is probably considerably higher than 1.0 cm pressure because short-lived surges of pressure up to 1.5 cm have occurred occasionally without any detectable lowering in the amount of CO_2 recovered. After the pressure in the five-liter volume has fallen to below 2.0 cm, pumping is continued with the regulating stopcock wide open until the pressure of gas in the lines is less than 1 millitorr as registered on a Pirani gauge. The total time for separation of CO_2 from the reference gas sample is about forty-five minutes.

The CO_2 is next subjected to a series of four or more vacuum sublimations ending with transfer into the small manometer sample chamber. The first transfer is to U-trap U-4 and is accomplished by warming the spherical trap to room temperature while U-4 is kept at liquid nitrogen temperature. After the spherical trap is fully thawed, the transfer line is pumped to remove noncondensable gas possibly trapped in the frozen CO_2. For the first three runs of 1974 the second transfer was a sublimation at dry ice temperature to trap U-3 (i. e. liquid nitrogen on U-3, dry ice on U-4). This was followed by a similar transfer to trap U-1. In later runs, the second transfer was directly from U-4 to U-1. The sample is then transferred to trap U-R-4 and finally into the small manometer sample chamber with the cup around a portion of the sample chamber cooled to liquid nitrogen temperature. Transfer times for these sublimations are generally

two minutes. This is approximately twice the time for the monitoring vacuum gauge to return to a reading of less than 1 millitorr. The sample is confined in the sample chamber above the 64 cc pointer by raising the mercury column well past the entrance tube. The manometer cup is then thawed and the mercury column is raised to its maximum height to sweep off mercury adhering to the glass near the liquid nitrogen cup. Finally, the mercury column is lowered to about one cm below the 4 cc pointer.

After the extracted CO_2 sample is thus confined within the sample chamber, the contents of the traps used in the separation and sublimations are checked for additional CO_2 by thawing and then reading the pressure of the contents on the appropriate vacuum gauges. These checks routinely indicated that the samples had been quantitatively transferred into the small manometer. Also, no evidence of condensable gas has ever been found in liquid nitrogen trap D1 downstream from the spherical trap.

5. Measurement of CO_2 Gas Sample

After the air circulating fans have been on for at least one hour with the doors on the manometric system cabinet closed, the pressure of the sample contained in the 4 cc chamber is determined by gradually raising the mercury column until it makes contact with the pointer. On a run where no difficulties occur, the mercury column is raised to within .010 to .020 mm below the pointer with no detectable bulging of the mercury surface. A determination of the height of mercury in the sample column is made followed by a reading of thermometer No. 6112 and a determination of the mercury height on the vacuum column. The moveable

meniscus viewing card is repositioned before each measurement. After redetermining the sample column mercury height, the mercury is raised until contact with the pointer occurs. Another determination of the mercury height in the sample column in contact is made, compensating for the slight bulge always present in the mercury meniscus under these conditions by setting the crosshair at the estimated smooth surface which the mercury would exhibit if the pointer were not proximate. A second vacuum column mercury height determination is then made followed by another temperature reading on thermometer 6112. The two vacuum column readings are usually .050 to .100 mm apart. Averages of the sample column height determinations before and after contact, the two associated vacuum column height determinations and the two temperature readings are recorded. Again, the uncorrected readings of thermometer 6112 are almost always within .02°C of each other.

Excellent runs as described above are not always obtainable. Rather often the mercury meniscus makes contact before the cathetometer is returned from making the first vacuum column measurement. Usually the second vacuum column measurement under these conditions is close to the first (within .020 to .030 mm). Averages are taken in the same way in these cases and usually agree well with runs where no difficulties have occurred. The ability of the operator to approach the pointer closely without premature contact with the pointer is strongly dependent on whether a "jumping mercury" condition exists as discussed below.

Without exception during 1974, two or more independent approaches to the 4 cc pointer were made for each reference gas determination. No

reruns involving transfer of CO_2 back to the extraction line were made as in the 1969-1970 measurements reported in Manometer Report I, because that work had shown that an essentially negligible amount of CO_2 is lost in the transfers of CO_2 into the 4 cc chamber.

6. Saving of CO_2 Gas Sample

Prior to 1 March, 1974, samples were routinely pumped away after completion of the CO_2 gas pressure measurements. After that date beginning with Run No. 1 on tank 35441, at least one of the CO_2 gas samples for each reference gas analyzed was transferred to a sample tube and saved for possible mass spectrographic analysis at a future date. Some of these samples were later used for N_2O analyses as discussed below.

B. Meniscus Corrections

Corrections to compensate for the influence of different glass tube cross sections and for the nonlevel swing of the cathetometer were determined before, during and after the 1974 set of measurements. They are referred to as meniscus corrections although in a strict sense this term applies to the former effect alone.

Determinations of the meniscus correction for the mercury level at the 4 cc pointer in the small manometer sample chamber are made as follows. The chambers above the vacuum and sample columns of the small manometer are both evacuated to less than 1 millitorr pressure while connected to each other via the manifold in the manometric system. Both chambers are then isolated by closing the stopcocks at the top of the respective columns. The mercury is raised to a level just below the 4 cc pointer in the sample column. Care is taken that the mercury is far enough below the pointer

so that the surface does not noticeably bulge toward the pointer. In 1974, this level varied from .080 mm to .330 mm below the pointer. The mercury level is stabilized from drift caused by leakage in the mercury reservoir control system by closing the stopcock above the mercury reservoir. Finally, the heights of mercury in the two columns are measured with the cathetometer. The standard procedure adopted is to make ten measurements of each column, alternating columns with each measurement.

The meniscus correction for the large manometer is almost entirely a correction for the nonlevel swing of the cathetometer since both sample and vacuum columns have the same diameter. The correction is made in basically the same way as for the small manometer. However, with a 1 millitorr vacuum above the columns, the minimum mercury level turns out to be slightly above the large manometer pointer. Therefore, a small amount of dried nitrogen gas corresponding to a pressure of about 2 cm of mercury is routinely admitted to both the vacuum and sample chambers of the large manometer. The two chambers remain connected to each other throughout the determination via the connecting manifold in the manometric system. In 1974, determinations of the correction were made as described above with the mercury level stabilized about 0.300 mm below the large manometer pointer.

C. The Jumping Mercury Problem

Occasionally during the 1974 calibrations, close approach to

the 4 cc pointer was difficult or impossible because the mercury jumped into contact with the pointer from a comparatively great distance below. This problem had been severe during the 1972 calibrations. It also occurred in January, 1970, but was otherwise rarely present in 1969 and 1970.

During periods when the mercury is jumping, approach to the pointer can sometimes be made no closer than .050 mm. From a calculation of the volume subtended in the 4 cc chamber by a height of .050 mm, it can be determined that the jumping effect can cause errors of about one part per thousand or 0.3 ppm, thus a significant error. In contrast, the routine error resulting from a subtended volume .010 mm distance from the pointer is only .06 ppm.

Two different explanations for the mercury jumping problem have been proposed. In 1972, when the mercury was jumping more often than not, the problem seemed related to external vibrations which moved the surface of the mercury. Measurements were made with the air circulating fans turned off. Even the vacuum pumps and air conditioner in the laboratory were checked as sources of vibration. Better approach was possible after normal working hours, as though foot and vehicle traffic in and near the building, use of the elevator and other daily activities contributed to the vibration. In 1974, however, the jumping appeared more like an electrostatic effect that came and went sometimes within a short period of time independent of vibrations. In fact, excellent approaches were often achieved with noticeable vibration on the mercury surface. Also, difficulties in

approach seemed to correlate with the ambient humidity. During a number of clear dry days in January 1974, with the relative humidity in the lab 40% or less, the jumping problem was very severe. On foggy or cloudy days when the relative humidity exceeded 60%, the problem tended to disappear. These two contrasting situations often occurred on adjacent days. In retrospect, the severity of the problem in 1972 may be explained as due to the measurements having been made during October and November under prevailing dry weather conditions. It is possible that once the conditions for jumping are present, vibration accentuates the problem. This would help to explain the correlation with vibration observed previously.

Efforts were made in 1974 to solve the jumping problem. A pan of water was sometimes kept in the bottom of the manometric system cabinet to increase the humidity. This had, at best, only a slight effect, perhaps because the cabinet is by no means airtight, and the water was at room temperature. A better method, not yet tried, would be to heat the water slightly. Another approach was to paint the outer glass surface of the small manometer sample chamber with water, hoping to promote dissipation of static charges on the glass surface. Results were inconclusive. One maneuver that seemed to make a difference was to drastically lower the mercury and slowly approach the pointer. Perhaps this movement of the mercury and expansion of the gas served to dissipate static charges. This procedure of lowering the mercury has been adopted as a standard procedure between adjacent duplicate measurements at the 4 cc pointer beginning on 8 March, 1974. In 1972,

the opposite approach was tried without success: the mercury was raised over the pointer to sweep static charges off the pointer. In conclusion, no definite solution has yet been found to the problem.

D. Oxygen Analyses of CO_2 in Nitrogen and Oxygen Reference Gases

One of the major aims of the 1974 reference gas calibrations was to establish how different carrier gases affect the response of the Applied Physics Analyzer. To accomplish this aim, both synthetic oxygen plus nitrogen containing reference gases and compressed air were analyzed in the manometer from 20 March to 5 April, 1974. The synthetic mixtures were supplied by Liquid Carbonic Corporation. Mixtures with oxygen concentrations between 20% and 60% were prepared. Since the accuracy of the commercial estimates of oxygen concentrations was not high, the oxygen concentration of each mixture was analyzed directly. Several methods were attempted, all with the equipment and advice of Dr. G. Kooyman and E. Sinnett of Dr. E. Hemmingsen's group in the Physiological Research Laboratory. The help of these scientists is gratefully acknowledged.

The first method involved an oxygen electrode system housed in a "Blood Micro" analyzer. In principle, this system can measure to a precision of 0.1% at all oxygen concentrations from 0 to 100%. A large drift in the system, probably due to electrode problems, could not be eliminated, however, and the method was abandoned after several days.

The second method was a volumetric procedure using a chemical oxygen absorber in a commercial instrument called the "Thomas-Van Slyke

Manometric Gas Analyzer." Results were inconsistent and inaccurate (e.g. analyses of one compressed air yielded two results of 20.6% oxygen and 20.4% oxygen instead of 20.9% oxygen).

The third method used a mass spectrometer located in the Pulmonary Department at the San Diego Veterans' Hospital. This instrument had been well cared for and seemed reliable, but suffered from the disadvantage that calibration with 100% oxygen and compressed air yield a sensitivity of only about 1% oxygen. The instrument is capable of higher precision when calibrated near the concentration of the unknowns (e.g. by making calibrating mixtures with Wosthoff mixing pumps). All the measurements were made in about one half hour by injecting samples brought to the instrument in large syringes. Contamination may have occurred, and indeed some duplicate samples yielded different concentrations.

The fourth and best method involved a Beckman paramagnetic oxygen analyzer, capable of both high sensitivity and accuracy. The PRL instrument suffered only from the restriction that the maximum measurable concentration was about 23% oxygen. Settings on the instrument are made by balancing a dumbbell-shaped indicator light on a line by adjusting a 10-turn potentiometer. All the gases except the 40% and 60% oxygen gases were analyzed on this instrument on 4 and 5 April, 1974.

The first set of determinations was made using the procedure outlined in the instrument instructions and discussed with Dr. G. Kooyman. To calibrate, the instrument was first set on the range of 19-21%. The zero was set with nitrogen gas from a commercial cylinder, and the span

calibration was made with room or outside air taken at 20.95%. Several lower calibrating points were made by lowering the pressure of the air in the instrument with a water manometer. Samples were taken from inside the room, outside the building, and directly from cylinders of gas. They were drawn into a large syringe and injected without delay into the oxygen analyzer at a slow rate of flow. Contamination problems were minimal. Analyses of three compressed air cylinders run as checks, all came within 0.1% to 20.95%. Check runs of outside air were also highly reproducible. Some drift was observed during calibration as the procedure was somewhat lengthy.

The major source of imprecision in the above method was in reading the pressure on the water manometer. Therefore a different, simpler method of calibration was used for the second set of determinations. Here the instrument was set on the 0-21% range. The zero was set with tank nitrogen and the span was set using outside air at atmospheric pressure. This two-point calibration was found to be adequate in view of the nearly linear instrument response. In fact, the sensitivity of the instrument seemed just as good as when using the 19 to 21% range. The analyses, which took much less time than before, agree closely with the first set.

A few oxygen determinations of CO_2 in nitrogen reference gases were also made on the paramagnetic analyzer on 28 May 74 to determine whether some suspicious cylinders had appreciable oxygen content.

On 21 February, 1975, another set of oxygen determinations on all the available long-term CO_2 in nitrogen standards was made. The

standard gases were compared in the paramagnetic analyzer to pure nitrogen from a cylinder. Problems were encountered on this day with drift and lack of reproducibility. It was obvious that the instrument could compare the reference pure nitrogen gas and the unknown standard gases to no better than 0.1% oxygen.

E. Nitrous Oxide Determinations on Compressed Air Reference Gases

The manometric method for analyzing CO_2 in reference gases, because it involves freezing out CO_2 from noncondensable carrier gas using liquid nitrogen, does not distinguish between CO_2 and any other component of air that will also freeze out at liquid nitrogen temperature after passing through a trap at dry ice temperature. Nitrous oxide, N_2O, as far as we know is the only normal component of air that fits this criterion. It usually has a concentration in air of about 0.3 ppm. The compressed air reference gases, as well as a few other gases, were analyzed for N_2O content by R. Cutler of Dr. H. Craig's group. The determinations were made from 11 March to 14 March 1974.

The method employed by Cutler used a gas chromatograph to determine the molar ratio of N_2O to CO_2. A two-liter sample of air provides the proper amount of gas for the calibration of the instrument. Cutler normally separates the CO_2 and N_2O from the sample gas and then injects the liquid nitrogen condensate, after removal of any residual water, into the chromatograph. To save time in the present experiments, he was usually given in the sample tubes liquid nitrogen condensates previously separated from reference gases. As a check, he also separated the CO_2 and N_2O from a 2-liter sample of compressed air on his system.

The usual procedure in the CO_2 laboratory in 2317 Ritter Hall was first to fill a two-liter flask with dried reference gas. Then the CO_2 and N_2O were separated from the carrier gas as in the normal manometric procedure, and the liquid nitrogen condensate transferred into a sample tube. In a few cases, liquid nitrogen condensates from five-liter samples of reference gases already in sample tubes were split approximately in two. The following procedure was used: (1) the whole sample was first transferred from the sample tube to trap U-2 on the isotope rack using liquid nitrogen sublimation; (2) the sample was expanded into U-1; (3) the cock between U-2 and U-1 was closed; (4) the contents of each trap were separately transferred to sample tubes.

A single determination of the N_2O to CO_2 ratio was made for each of four of the compressed air reference gases. These analyses were made on liquid nitrogen condensates prepared in the CO_2 laboratory from two-liter samples of the gases. Determination of the N_2O to CO_2 ratio was made on three liquid nitrogen condensates from one of the compressed air gases. Two of these condensates were prepared in the CO_2 laboratory, the first from a two-liter sample of gas and the second by splitting, as discussed above. The third condensate was prepared by R. Cutler from a two-liter sample of gas. The N_2O to CO_2 ratio found for the last sample differed slightly from that found for the first two.

Determinations of the N_2O to CO_2 ratios were also made for comparison on the two high-oxygen content synthetic reference gases. Analyses were made on the liquid N_2 condensates prepared on the

associated vacuum line from five-liter samples of the gases.

F. Other Gas Analyses

One of the CO_2 in nitrogen reference gases, contained in cylinder No. 2424, fell nearly 2 ppm off the calibration curve defined by the rest of the gases. To check for the possible presence of other gases which may cause a carrier gas effect on the infrared analyzer, R. Weiss and J. Slater in H. Craig's group analyzed the gas mixture for argon and nitrogen on their gas chromatographic system on 1 October 1974. Subsequently a mass spectrum of the gas was run by H. G. Staley at Gulf General Atomic Laboratory on 4 October 1974. The results are reported in section III.F below.

The synthetic CO_2 in nitrogen and oxygen reference gas contained in cylinder No. 35389 was suspected of containing argon because it alone among the synthetic mixtures had an atmospheric oxygen content indistinguishable from natural air and a carrier gas effect similar to that of compressed air. J. Slater and R. Weiss determined the argon and nitrogen concentrations of this gas on 8 November 1974, but the results showed very little argon and no appreciable amounts of any other gases, as reported below.

III. Calculations and Summary of Data

This section will discuss the procedure followed to calculate the CO_2 mole fraction for reference gases analyzed on the constant volume manometric system and will discuss the 1974 results. The determinations of oxygen and nitrous oxide and other gases will also be discussed.

The direct observations for reference gases made during 1974 are listed in Table 1 in chronological order. For each measurement the vacuum column height, sample column height, meniscus correction, temperature and date of measurement are recorded. A measurement of total gas is indicated by specifying a volume of 5000 cc. A CO_2 gas measurement is indicated by specifying a volume of 4 cc.

A. Calculation of Reference Gas CO_2 Mole Fractions from Manometric Data

The equation of state used to calculate the amount, n, in moles of either CO_2 or the carrier gas is expressed in the implicit form:

$$PV = nRT \left(1 + \frac{n}{V} B(T) + ...\right) \tag{1}$$

where P, V, and T are the measured pressure, volume, and absolute temperature, N is the moles of the gas, R is the gas constant, and B(T) is the temperature dependent second virial coefficient in the expansion of the compressibility factor PV in the powers of the density 1/V. Higher order terms in 1/V are neglected. Equation (1), when solved for n, reads:

$$n = - \frac{V}{2B(T)} \left(1 - \sqrt{1 + \frac{4PB(T)}{RT}}\right) \tag{2}$$

where we choose by experience the positive root of the equation in n^2. The equation of state for reference gas is treated as if it were 100% carrier gas because the effect of the very small concentration of CO_2 on the virial coefficient is negligible. The mole fraction of CO_2 in dry gas is then given by:

$$\frac{n_1}{n_2}\ (\text{in ppm}) = \frac{10^6 V_1 B_2(T_2)}{V_2 B_1(T_1)} \left\{ \frac{1 - \sqrt{1 + \frac{4P_1 B_1(T_1)}{RT_1}}}{1 - \sqrt{1 + \frac{4P_2 B_2(T_2)}{RT_2}}} \right\}$$

where specifically:

(1) Subscripts 1 and 2 refer to the measurement of CO_2 in the 4 cc chamber in the small manometer and of total gas in the 5000 cc chamber in the large manometer of the manometric system, respectively.

(2) V_2/V_1 is the 5000 cc/4 cc volume ratio determined separately as reported in Manometer Report IV as 1320.6.

(3) P and T are expressed in dynes cm^{-2} and °K, respectively.

(4) B(T) is the value of the second virial coefficient for the gas at temperature T, in cm^3/mol.

(5) R is the gas constant, taken as 8.31436×10^7 ergs $mol^{-1}{}^\circ K^{-1}$.

The pressure P is calculated from the difference between two measured heights of mercury by the equation:

$$P = \Delta h \cdot \rho_{Hg}\ (T) \cdot g$$

where:

Δh is the observed mercury height difference in cm

$\rho_{Hg}(T)$ is the density of mercury at temperature T in g/cm^3 (g/ml ÷ 1.000027)

g is the acceleration of gravity at 32°52'N taken to be 979.558 cm sec^{-2}

Values for the second virial coefficients are interpolated from tables of Sengers, Klein, and Gallagher (1971), who made a compendium of all known determinations. Their numbers are reproduced in Table 2. For CO_2 in nitrogen reference gases, the nitrogen virial coefficient is used for the 5000 cc chamber calculations; and for compressed air gases the virial coefficient for CO_2-free dry air is used. For the CO_2 in nitrogen and oxygen gases a linear combination of the oxygen and nitrogen virial coefficients is used, according to the proportions of each gas in the mixture. The temperature dependence is obtained by Lagrangian interpolation of tabular values at five degree intervals for CO_2 and twenty degree intervals for nitrogen, oxygen and air. In practice the calculation of moles, n, is insensitive enough to the value of the virial coefficient so that any reasonable interpolation method would work. Indeed, the ideal gas law applied to all of the gases would predict a mixing ratio only 0.5 ppm in error. If the CO_2 virial is varied by 10% an error of only .06 ppm occurs in the determination of a typical reference gas. A 10% variation in the nitrogen virial produces a still smaller and entirely negligible effect. According to Sengers et al (1971), discrepancies between data from different sources for CO_2 virial coefficients are not more than several cm^3/mol in a total virial of about 120 cm^3/mol. For the nitrogen virials discrepancies are not over 25%.

Initially the results were calculated using a Wang programmable calculator and a linear interpolation for the virials. J. A. Adams

subsequently wrote a Fortran computer program using a quadratic interpolation. Results of the two methods agree to within a few hundredths of one ppm. A printout of the Fortran program is included in the appendix.

Table 3 presents all the reference gas determinations of 1974, organized by type of carrier gas and by ascending CO_2 concentration. The standard deviation of an individual measurement is given by:

$$\sigma = \sqrt{\frac{\Sigma d_i^2}{N_a - N_f}} \qquad (5)$$

where:

d_i = deviation of individual run from the mean for that reference gas

N_a = total number of determinations

N_f = total number of reference gases

For the 50 determinations of all 23 gas mixtures analyzed in 1974 σ is calculated to be 0.08 ppm. As in the case of determinations made in 1970 and 1972, the reference gas with the worst scatter in the results is that contained in cylinder No. 2399. No explanation for this scatter has been established. For the five compressed air gases alone σ is .07 ppm, and for the five synthetic gases with approximately 20% oxygen content, .08 ppm, and for the eleven CO_2 in nitrogen gases, .09 ppm.

B. Meniscus Corrections

Table 4 lists the meniscus corrections determined during the 1974 calibrations. Corrections at both the large manometer pointer and the

4 cc pointer of the small manometer were made on three occasions: before, during and after the reference gas calibrations of January to May 1974. The average applied corrections, weighted by the number of determinations, were added to the differences between the vacuum and sample column heights for all the data from January through May. A single set of 10 determinations of the meniscus corrections made in October, 1974 was applied to the reference gas data obtained during that month.

Some difficulty was encountered in establishing the meniscus correction for the 4 cc pointer. The determinations on 2 January and 22 February were both made with the mercury less than 0.10 mm below the pointer. In both cases the mercury was not bulging toward the pointer, and the corrections are in close agreement. When the mercury was set at 0.10 mm below the pointer on 31 May 1974, the mercury was noticeably bulging toward the pointer and the meniscus correction found was substantially smaller. Another set of determinations was run with the mercury about 0.18 mm below the pointer. This was far enough away from the pointer so that the mercury didn't bulge. These determinations were in much better agreement with the first two determinations. It seems reasonable to conclude that the determination under conditions when the mercury meniscus was not bulging was more representative of the true effect. This set of values was therefore used with the first two determinations to calculate the average used to correct the reference gas pressure measurements. Similarly, the determination on 17 Oct. 1974 had to be made

at the even greater distance below the pointer of about .33 mm before a nonbulging situation was obtained.

The discrepancy noted for the 31 May determinations suggests that the meniscus correction decreases in absolute amount as the pointer is approached and the mercury begins to bulge. This is the expected effect if the bulge is a result of the mercury meniscus in the sample column being raised by attraction to the pointer. The effect is, however, contrary to the relationship found in 1970 and reported in Manometer Report I.

No further attempts were made to investigate the dependence of the meniscus correction upon the distance from the mercury to the pointer.

The three large manometer meniscus corrections for the period 2 Jan. 1974 to 31 May 1974 show slightly more scatter than the determinations accepted for the small manometer. Since the large manometer correction is much less critical to the overall computation, the weighted average of these determinations is precise enough, and was used for all measurements in 1974 except those made in October.

To illustrate the error which a false meniscus correction might introduce, results were calculated using the extreme values of the determined corrections for both a low (~200 ppm) and a high CO_2 content (~475 ppm) reference gas. A -0.111 mm to -0.068 mm change in the large manometer correction causes a 0.01 ppm difference in CO_2 mole fraction for the low gas and a 0.03 ppm difference for the high gas. If the small manometer correction is changed from -0.341 mm to -0.296 mm

a 0.05 ppm difference occurs for both gases. The combined extreme error is thus 0.08 ppm. This error takes into account the bulging mercury determinations for the small manometer. In addition it should be realized that there is no way to be certain that corrections determined under vacuum or near-vacuum conditions are exactly applicable to pressure conditions when a gas sample is present in the sample column. Since the 4 cc chamber in the small manometer is confined by mercury above the gas entrance tube the only way to determine the meniscus correction is with a vacuum above both the sample and vacuum column.

C. Temperature Gradients in the Manometric System Cabinet

During the large manometer measurements, all seven of the thermometers in the manometric system cabinet were read to keep a record of the temperature gradients within the cabinet. Table 5 summarizes the cabinet thermometer readings corrected according to the thermometer calibrations done by Elliot Atlas in 1968. The maximum correction found then was 0.03°C. The temperatures shown in Table 5 for thermometer No. 6112, except for one run with bad temperature instability due to a malfunctioning air conditioner, have been found always to be within .04°C of the temperature recorded for the run and most often within .02°C.

As noted above, the average uncorrected reading of thermometer No. 6112 is recorded as the temperature of the determination. At the end of Table 5 the average deviation of each thermometer from thermometer No. 6112 is shown. The average gradient is of the order of .02°C

difference between thermometers. It can be concluded that the systematic error introduced by the temperature gradients in the cabinet is not likely to exceed about .05 ppm in the results.

For all of the 1974 determinations, only three of the five air circulating fans were operated because one outer fan burned out a bearing early in the preparatory work. The other outer fan was also not run to preserve balance.

Figure 2 shows the placement of the thermometers in the manometric system cabinet in relation to the various columns.

D. Oxygen Determinations

Table 6 presents all the oxygen analyses made on reference gases. The first set reports the analyses made on the mass spectrometer and the second set, those on the paramagnetic oxygen analyzer. As discussed above in section II, D, the mass spectrometer method claimed an accuracy of only 1% in oxygen content. Agreement with the paramagnetic method is, however, in all cases within 0.2% for those gases analyzed by both methods. Problems were encountered with the nominally 40% and 60% oxygen gases. Duplicate measurements of each of these gases differed considerably from each other. Two analyses of the 60% gas yielded 57.9% and 37.4% oxygen. The latter analysis was evidently contaminated and was thrown out. The two results for the 40% gas, agreeing within ± 1% have been averaged. The scatter in the results for these high oxygen gases probably reflects leakage of ambient air into the syringes containing the samples while they were being transported to the Veterans' Hospital for analysis. The mass spectrometer

data have been accepted only because no other method of analysis was available. The results, which were not used for the calculation of the average carrier gas effect, nevertheless support an effect which is linear with oxygen concentration taking into account the more accurate data on gases with about 20% oxygen.

The precision of the data from the paramagnetic analyzer falls within the expected 0.1% in oxygen concentration. For gases with oxygen concentrations near the calibrating standard of atmospheric air this method is quite accurate. For gases near zero percent oxygen the accuracy depends more critically upon the linearity of the instrument, which according to G. Kooyman is very good, and upon the absence of oxygen in the zero gas, nitrogen from a commercial cylinder. According to the manufacturer's specifications the nitrogen gas should contain less than .01% oxygen. A number of CO_2 in nitrogen reference gases were analyzed for oxygen content. No significant difference from the oxygen content of the reference nitrogen was found except for cylinder 7350, a cylinder with a notorious history of drift. Even for this gas, the oxygen content was found to be on the borderline of measureability, 0.1% oxygen.

E. Nitrous Oxide Determinations

Table 7 presents the analyses of N_2O content in compressed air reference gases. The method has more than adequate accuracy for correcting the apparent CO_2 concentrations for N_2O content in the extracted condensate. The sum of the concentrations of CO_2 and N_2O is given by the manometric analysis, whereas the gas chromatograph

yields values for the N_2O to CO_2 molar ratio. Simultaneous solution of two equations in two unknowns yields the individual CO_2 and N_2O concentrations.

All of the compressed air gases were found to have N_2O concentrations within .01 ppm of .29 ppm N_2O. This is the normal atmospheric concentration according to R. Weiss (private communication).

The two high oxygen content reference gases were also analyzed. These were found to have less than .01 ppm N_2O content. No other gases were tested for N_2O.

F. Other Gas determinations

By gas chromatographic analysis the reference gas in cylinder No. 2424 was found to contain 1.06% argon and 96.4% nitrogen, leaving several percent unaccounted for. Mass spectrometric analysis revealed the following components and concentrations (in mole percent):

N_2: 98%; H_2: 1.2%; Ar: 1.1%; O_2: .11%; CO_2: .053% and a trace of water vapor. The analysis was done on a gas sample dried by passage through a trap at dry ice temperature. This reference gas was prepared very early in the history of the CO_2 Project, about 1956, probably by burning oxygen from air with excess hydrogen. It may also contain N_2O although this has not yet been checked.

On the basis of the gas analysis results for cylinder No. 2424 this mixture is omitted from further consideration in the calibration of the reference gas system. The observed carrier gas discrepancy for this gas has not been successfully explained. Theory predicts

that hydrogen gas causes a carrier gas effect opposite in sign to the anomaly actually observed.

The CO_2 in nitrogen and oxygen mixture in cylinder No. 35389 also was analyzed for argon and nitrogen gas on the gas chromatograph because its carrier gas effect was somewhat different from the rest of the synthetic oxygen-containing gases. Analysis showed .053% argon and 79.25% nitrogen. These concentrations combined with the measured oxygen concentration of 20.9% indicate that no substantial amounts of unknown carrier gases are present.

G. Infrared Index Values for Reference Gases

Table 8 summarizes the index values determined on the Applied Physics Infrared Analyzer No. 55 for the manometric reference gases analyzed in 1974. These index values are related linearly to the instrument response. The index scale is that established in 1956 and used in Scripps reference gas reports from the beginning of the project until now. All of the infrared analyzer index determinations for each gas are listed in the appendix in order of cylinder number copied from Table 9 of Reference Gas Report 26. The 1959 manometrically determined scale, J, used in published results and referred to below as the "infrared adjusted index," is related to the 1956 index, I, by the linear relationship:

$$J = 1.2186\ (I - 311.51) + 311.51 \qquad (6)$$

where I and J are expressed in parts per million CO_2.

Part I of Table 8 summarizes the CO_2 in nitrogen reference gas data. The weighted average index value based on all calibrations

of the gas is shown on the left side of the table, along with the dates of the first and last runs, through Report 26. These values are not altogether satisfactory for manometric comparison because they are based on routine determinations of analyzer sensitivity made over only a narrow range of CO_2 index near atmospheric air, i.e. between about 315 and 340 ppm, and often over such long periods of time that drift in the index value cannot be ruled out.

To reduce the chance that drift could influence the evaluation of index values for the manometric reference gases, the index values of these were determined exhaustively over a relatively short time period by repeated comparison with the most recent of the routinely used primary and span gases. The results of these special infrared analyses were then adjusted to cancel insofar as possible the extrapolation errors arising from the narrow range of the initial calibrating tanks. This adjustment is discussed in a separate report (in preparation). After this adjustment, which has no influence on the mean value for any gas, the standard deviation for a 10-comparison run was found to be 0.17 ppm. The lowest and highest gas mixtures, cylinder Nos. 2408 and 35316, were run twice (10 comparisons per run) on each of the sixteen special calibration days between 23 May 1974 and 10 September 1974. Six other mixtures were run once on every other day of operation, or eight times. When the results of these 16 days were examined it became evident that calibrations of more than 8 gases were needed to decide whether a three or four parameter equation best represented the data. Two additional

reference gases (cylinder Nos. 1540 and 39239) were then added to the system. These were run twice each on each of eight calibration days between 10 October and 4 November 1974. Four of the original set of CO_2 in nitrogen reference gases were rerun on each of these days as well.

Table 8 also lists the weighted average index obtained from special calibration days. It can be seen that the averages of all runs actually agree well with these special runs, the largest difference being only .21 ppm.

Parts II and III of Table 8 list the average index values obtained for the compressed air and CO_2 in nitrogen and oxygen reference gases. The possibility of drift in these analyses was investigated and found to be insignificant.

IV. Conclusions: Establishing an Analyzer Calibration Curve

The results reported above will now be used to establish a new Applied Physics Analyzer calibration curve for reference gases consisting of CO_2 in nitrogen and a correction for that calibration to be applied to reference gases also containing oxygen and argon.

A. Calibration Curve for CO_2 in Nitrogen

Table 9 summarizes the manometric and infrared analyzer data of Tables 3 and 8 for reference gases containing CO_2 in nitrogen. The 1956 index values of Table 8 have been replaced by adjusted index values based on the 1959 manometric calibration according to equation (6). Various functions were tested for goodness of fit by R. Bacastow in order to find the best relationship between the manometric and

infrared data. The best three-parameter relationship, based on a chi-square criterion, was found to be a Gauss equation of the form:

$$J = g_{N_2}(x) - C_1 - C_2(1 - \text{Gauss } [C_3\sqrt{X}])$$

where: J = infrared adjusted index value; X = 1974 manometric mole fraction x 10^6 and

$$\text{Gauss } (u) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{u} e^{-1/2\ t^2} dt$$

It was found that the analyses for cylinder No. 2424 fell well off any curve defined by the other ten reference gases. As discussed earlier, the results for this gas were eliminated from further consideration.

It was found that the departures in the experimental points of the 10 point fit to the Gauss function were still suggestive of a systematic residual larger than the expected random experimental error. Rather than resort to a four parameter equation with an arbitrary fourth coefficient and still to reduce the deviations of the experimental data from the curve in the region of air CO_2 mole fraction where a possible systematic bias was particularly objectable, a new Gauss fit was made over the upper eight data points by eliminating from the fit the results for cylinders Nos. 2408 and 3753. The coefficients of best fit were found to have the values:

$$C_1 = 1305.666$$
$$C_2 = 3374.024$$
$$C_3 = .03060376$$

Figure 3 is a plot of the data points for CO_2 in nitrogen using the Gauss function. The position of the anomalous gas 2424 is shown by a +. The two lowest gases, not included in the fit, are represented by x's.

Since a fit of an empirical four parameter cubic equation of X in powers of J over all 10 points agreed within .02 ppm (almost surely by accident) with the 8 point Gauss fit between 300 and 400 ppm, this fit was afterwards adopted to furnish an equation over the full range of calculation. This equation takes the form:

$$X = f_{N_2}(J) = C_1 + C_2J + C_3J^2 + C_4J^3$$

The coefficients of best fit were found to have the values:

$$C_1 = 76.582$$
$$C_2 = 0.58491$$
$$C_3 = 3.1151 \times 10^{-4}$$
$$C_4 = 7.3225 \times 10^{-7}$$

B. Carrier Gas Effect

Table 10 summarizes the data of Tables 3 and 8 for compressed air reference gases and CO_2 in nitrogen and oxygen reference gases. As in the case of Table 9, the 1956 index values of Table 8 have been adjusted according to the 1959 manometric calibration using equation (6). These manometric and infrared analyzer data furnish the basis for determining the influence of oxygen and argon as carrier gases on the calibration established above for CO_2 in nitrogen gas. Also shown are the results for two high oxygen concentration gas mixtures. As

shown by the near constancy of the correction term listed in column 7 of Parts II and III for CO_2 in nitrogen and oxygen mixtures, the carrier gas effect is nearly linear with oxygen concentration.

The basic assumption underlying the treatment of the data of Table 10 is that the presence of a second carrier gas in fixed proportion to nitrogen alters the infrared analyzer response to a constant degree, i.e. the carrier gas effect can be expressed by multiplying the infrared index values by a constant factor. Results of the volumetric calibrations reported by J. A. Adams in Volumetric Report I with pure oxygen and argon as carrier gases over a range of CO_2 mole fraction from 200 to 450 ppm support the validity of this assumption. Column number 5, labeled Virtual Infrared Adjusted Index, is an index value calculated from 1974 manometric data using the 10 point cubic equation valid for gases containing CO_2 in nitrogen. It represents the best available estimate of the index value of the gas if the gas contained no other carrier gas except nitrogen. The carrier gas factors listed in Column 6 express for each reference gas the difference between the measured and virtual index values divided by the measured index and normalized to normal atmospheric oxygen concentration. The compressed air gas results are <u>not</u> normalized. This normalization assumes a carrier gas effect linear with oxygen concentration as supported by the data for high oxygen concentration gases. Column 7 lists, by way of illustration, the additive corrections, in manometric concentration units, corresponding to the factors of Column 6, applied to an infrared adjusted index (J_{obs}) of 320 ppm. The values of Column 7 are

obtained by the relation:

$$\text{additive correction} = f_{N_2}(J_{corr}) - f_{N_2}(J_{obs})$$

where:

$$J_{corr} = (1 + \text{carrier gas factor})\, J_{obs}$$

and where:

$f_{N_2}(J)$ is as defined by equation (8)

The difference between the results for compressed air and for CO_2 in nitrogen and 20.9 percent oxygen is found to be 0.21 ppm. This is attributable to the pressure broadening effect of argon present in the compressed air as discussed below.

Table 11 compares the results just discussed for the carrier gas effect with independent results obtained by J. A. Adams using a volumetric method, and pure nitrogen, oxygen, and argon as carrier gases. The volumetric data involving the three separate pure carrier gases were first separately fit by the Gauss relation of the form of equation 7. The coefficients found are as follows:

	Nitrogen	Oxygen	Argon
C_1 =	1306.025	1423.987	1240.516
C_2 =	3363.277	3538.291	3181.161
C_3 =	.03042650	.02665229	.02970056

The following relation for air was then calculated assuming a linear carrier gas effect for a gas mixture containing 0.934% argon and 20.946% oxygen:

$$Jair = g_{air}(x) = .78120\ g_{N_2}(x) + .20946\ g_{O_2}(x) + .00934\ g_A(x) \qquad (10)$$

The carrier gas effect is expressed in Table 11 as an additive correction equivalent to the corrections listed in column 7 of Table 10.

The good agreement between the two methods suggest that no serious systematic errors affect the results. The volumetric calibration is a synthetic method in which gas mixtures are made with known absolute concentration and then analyzed in the infrared analyzer. The manometric method, on the other hand, is an analytic method where gases of known infrared index value are separated and analyzed on the manometer. Thus the two methods are to a considerable extent independent.

The final results for the carrier gas effect, as summarized in Tables 10 and 11, indicate that normal air concentrations as determined on the Applied Physics Infrared Analyzer using reference gases consisting of CO_2 in nitrogen should be corrected by adding approximately 4.0 ppm to the CO_2 in nitrogen manometric mole fraction obtained from the measured index value by equation (8). More generally, the following relation which combines equation (8) and the carrier gas factor should be used to compute CO_2 mole fractions in dry air:

$$X = \sum_{n=0}^{3} C_n (J')^n$$

where:

$J' = 1.01201 \cdot J$

J = adjusted infrared index, in ppm

X = CO_2 mole fraction, in ppm

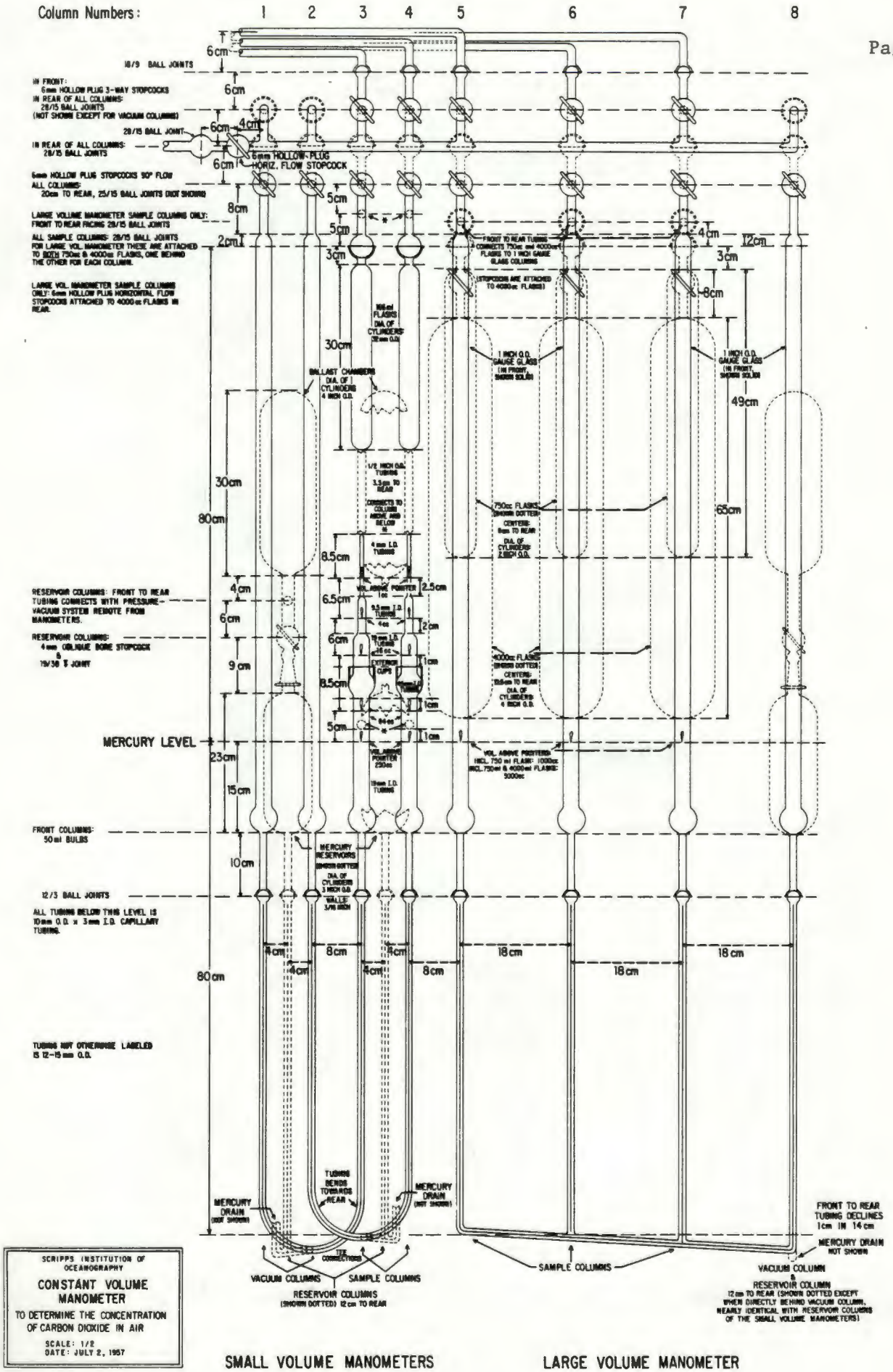
$C_0 = 76.582$

$C_1 = 0.58491$

$C_2 = 3.1151 \times 10^{-4}$

$C_3 = 7.3225 \times 10^{-7}$

Figure 1a. Construction drawing of Constant Volume Manometric System. Scale of this reproduction with respect to the actual apparatus is about 1:8.7.



SCRIPPS INSTITUTION OF OCEANOGRAPHY

CONSTANT VOLUME MANOMETER

TO DETERMINE THE CONCENTRATION OF CARBON DIOXIDE IN AIR

SCALE: 1/2
DATE: JULY 2, 1957

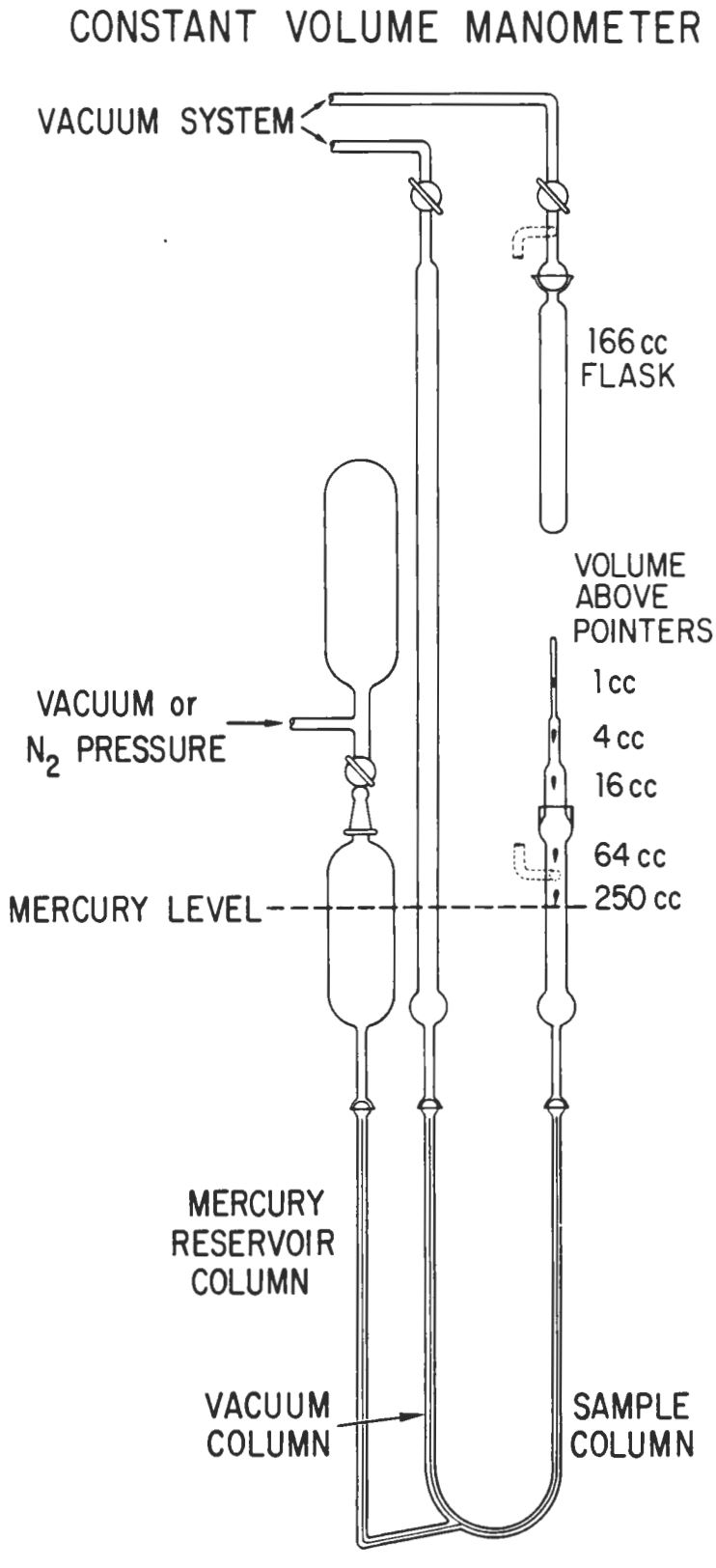


Figure 1b. Simplified schematic of small volume manometer.

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
6078- 1	CO2 IN N2	16 JAN 74	5000	806.112	173.226	18.05	-0.096
		17 JAN 74	4	630.310	370.613	18.12	-0.346
		18 JAN 74	4	630.018	370.616	17.78	-0.346
6078- 2	CO2 IN N2	17 JAN 74	5000	808.666	173.278	18.17	-0.096
		18 JAN 74	4	633.028	370.615	19.97	-0.346
		21 JAN 74	4	633.696	370.604	20.63	-0.346
35435- 1	COMPRESSED AIR	21 JAN 74	5000	803.574	173.248	20.48	-0.096
		21 JAN 74	4	648.730	370.629	20.35	-0.346
		22 JAN 74	4	648.808	370.594	20.53	-0.346
35435- 2	COMPRESSED AIR	22 JAN 74	5000	803.725	173.275	20.66	-0.096
		23 JAN 74	4	648.762	370.582	20.52	-0.346
		23 JAN 74	4	648.838	370.590	20.56	-0.346
2399- 1	CO2 IN N2	23 JAN 74	5000	807.787	173.234	20.58	-0.096
		24 JAN 74	4	642.001	370.607	20.70	-0.346
		24 JAN 74	4	641.622	370.544	20.56	-0.346
		25 JAN 74	4	641.968	370.584	20.70	-0.346
2399- 2	CO2 IN N2	24 JAN 74	5000	807.650	173.232	20.67	-0.096
		28 JAN 74	4	641.952	370.641	20.51	-0.346
		28 JAN 74	4	642.088	370.603	20.66	-0.346
2399- 3	CO2 IN N2	28 JAN 74	5000	801.884	173.293	20.58	-0.096
		29 JAN 74	4	639.336	370.654	20.39	-0.346
		30 JAN 74	4	639.482	370.636	20.55	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
10069- 1	CO2 IN N2	30 JAN 74	5000	808.097	173.326	20.80	-0.096
		30 JAN 74	4	668.694	370.628	20.94	-0.346
		31 JAN 74	4	668.442	370.654	20.74	-0.346
10069- 2	CO2 IN N2	30 JAN 74	5000	799.587	173.198	20.94	-0.096
		1 FEB 74	4	663.690	370.674	20.12	-0.346
		1 FEB 74	4	663.540	370.634	20.03	-0.346
2424- 1	CO2 IN N2	1 FEB 74	5000	799.548	173.217	20.08	-0.096
		1 FEB 74	4	694.926	370.648	20.22	-0.346
		4 FEB 74	4	695.554	370.672	20.58	-0.346
		5 FEB 74	4	695.071	370.660	20.30	-0.346
2424- 2	CO2 IN N2	5 FEB 74	5000	800.724	173.258	20.31	-0.096
		5 FEB 74	4	695.576	370.660	20.47	-0.346
		6 FEB 74	4	695.941	370.684	20.83	-0.346
7366- 1	CO2 IN N2	6 FEB 74	5000	818.852	173.252	20.81	-0.096
		6 FEB 74	4	606.055	370.629	20.15	-0.346
		7 FEB 74	4	606.245	370.658	20.50	-0.346
		7 FEB 74	4	606.380	370.622	20.46	-0.346
7366- 2	CO2 IN N2	7 FEB 74	5000	813.325	173.333	20.54	-0.096
		8 FEB 74	4	604.208	370.661	20.13	-0.346
		8 FEB 74	4	604.116	370.648	19.94	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
3753- 1	CO2 IN N2	8 FEB 74	5000	812.929	173.306	20.05	-0.096
		8 FEB 74	4	578.580	370.658	20.11	-0.346
		11 FEB 74	4	579.294	370.636	21.07	-0.346
3753- 2	CO2 IN N2	11 FEB 74	5000	824.325	173.280	20.99	-0.096
		12 FEB 74	4	582.288	370.660	21.08	-0.346
		13 FEB 74	4	582.150	370.656	20.92	-0.346
35452- 1	SYNTHETIC AIR	12 FEB 74	5000	799.477	173.418	21.11	-0.096
		13 FEB 74	5000	798.985	173.243	20.99	-0.096
		13 FEB 74	4	637.822	370.630	20.67	-0.346
		13 FEB 74	4	637.689	370.612	20.62	-0.346
35452- 2	SYNTHETIC AIR	13 FEB 74	5000	802.350	173.350	20.64	-0.096
		14 FEB 74	4	639.234	370.666	20.30	-0.346
		14 FEB 74	4	639.229	370.645	20.27	-0.346
		14 FEB 74	4	639.196	370.652	20.20	-0.346
6078- 3	CO2 IN N2	14 FEB 74	5000	800.465	173.242	20.24	-0.096
		20 FEB 74	4	627.881	370.593	20.19	-0.346
		21 FEB 74	4	627.693	370.595	19.99	-0.346
35434- 1	SYNTHETIC AIR	25 FEB 74	5000	805.011	173.240	20.83	-0.096
		25 FEB 74	4	640.876	370.573	20.97	-0.346
		25 FEB 74	4	640.912	370.570	20.99	-0.346
		26 FEB 74	4	640.212	370.622	20.27	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
35434- 2	SYNTHETIC AIR	26 FEB 74	5000	801.586	173.274	20.36	-0.096
		26 FEB 74	4	639.810	370.593	20.99	-0.346
		27 FEB 74	4	639.709	370.624	20.87	-0.346
35389- 1	SYNTHETIC AIR	27 FEB 74	5000	803.450	173.274	20.86	-0.096
		27 FEB 74	4	649.209	370.607	20.65	-0.346
		27 FEB 74	4	649.449	370.584	20.77	-0.346
35389- 2	SYNTHETIC AIR	27 FEB 74	5000	803.218	173.300	20.72	-0.096
		28 FEB 74	4	648.837	370.622	20.15	-0.346
		28 FEB 74	4	649.021	370.595	20.20	-0.346
35441- 1	SYNTHETIC AIR	28 FEB 74	5000	801.108	173.278	20.14	-0.096
		28 FEB 74	4	646.485	370.577	20.92	-0.346
		1 MAR 74	4	645.232	370.616	19.64	-0.346
35441- 2	SYNTHETIC AIR	1 MAR 74	5000	803.402	173.218	19.74	-0.096
		1 MAR 74	4	647.291	370.603	20.16	-0.346
		1 MAR 74	4	647.306	370.610	20.20	-0.346
35442- 1	SYNTHETIC AIR	4 MAR 74	5000	813.978	173.276	20.60	-0.096
		4 MAR 74	4	647.417	370.592	20.89	-0.346
		5 MAR 74	4	647.324	370.620	20.65	-0.346
35442- 2	SYNTHETIC AIR	5 MAR 74	5000	800.229	173.332	20.70	-0.096
		5 MAR 74	4	641.505	370.601	21.01	-0.346
		7 MAR 74	4	640.722	370.625	20.11	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
35435- 3	COMPRESSED AIR	5 MAR 74	5000	803.052	173.280	21.00	-0.096
		7 MAR 74	4	648.074	370.620	20.57	-0.346
		7 MAR 74	4	648.027	370.587	20.49	-0.346
2399- 4	CO2 IN N2	7 MAR 74	5000	795.051	173.212	20.63	-0.096
		8 MAR 74	4	636.706	370.580	20.76	-0.346
		8 MAR 74	4	636.866	370.586	20.84	-0.346
35405- 1	COMPRESSED AIR	9 APR 74	5000	797.619	173.284	20.36	-0.096
		9 APR 74	4	648.984	370.643	20.75	-0.346
		10 APR 74	4	649.046	370.650	20.86	-0.346
44726- 1	SYNTHETIC AIR	10 APR 74	5000	801.326	173.243	20.85	-0.096
		10 APR 74	4	627.215	370.644	20.79	-0.346
		10 APR 74	4	627.325	370.612	20.80	-0.346
35405- 2	COMPRESSED AIR	10 APR 74	5000	807.931	173.256	20.79	-0.096
		11 APR 74	4	653.406	370.648	21.02	-0.346
		11 APR 74	4	653.436	370.607	21.03	-0.346
44695- 1	SYNTHETIC AIR	11 APR 74	5000	802.820	173.263	21.03	-0.096
		12 APR 74	4	662.720	370.636	20.70	-0.346
		12 APR 74	4	663.005	370.631	20.95	-0.346
44726- 2	SYNTHETIC AIR	12 APR 74	5000	801.111	173.240	20.95	-0.096
		12 APR 74	4	627.333	370.614	21.05	-0.346
		12 APR 74	4	627.322	370.618	21.04	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
44695- 2	SYNTHETIC AIR	15 APR 74	5000	803.283	173.256	20.96	-0.096
		15 APR 74	4	663.100	370.624	20.98	-0.346
		15 APR 74	4	663.245	370.632	20.96	-0.346
35378- 1	COMPRESSED AIR	6 MAY 74	5000	800.343	173.254	20.65	-0.096
		7 MAY 74	4	665.224	370.644	20.76	-0.346
		7 MAY 74	4	665.161	370.608	20.65	-0.346
35378- 2	COMPRESSED AIR	7 MAY 74	5000	800.246	173.278	20.72	-0.096
		8 MAY 74	4	665.419	370.642	20.95	-0.346
		8 MAY 74	4	665.409	370.616	20.96	-0.346
35401- 2	COMPRESSED AIR	9 MAY 74	5000	805.116	173.232	20.48	-0.096
		10 MAY 74	4	665.067	370.653	20.33	-0.346
		10 MAY 74	4	664.922	370.630	20.23	-0.346
34770- 1	COMPRESSED AIR	10 MAY 74	5000	797.885	173.261	20.27	-0.096
		10 MAY 74	4	649.649	370.630	20.08	-0.346
		10 MAY 74	4	649.455	370.601	19.75	-0.346
34770- 2	COMPRESSED AIR	14 MAY 74	5000	799.107	173.238	20.70	-0.096
		15 MAY 74	4	650.481	370.632	20.59	-0.346
		15 MAY 74	4	650.509	370.600	20.65	-0.346
35401- 3	COMPRESSED AIR	15 MAY 74	5000	798.520	173.284	20.61	-0.096
		15 MAY 74	4	662.242	370.602	20.80	-0.346
		15 MAY 74	4	662.328	370.570	20.79	-0.346

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
2408- 1	CO2 IN N2	21 MAY 74	5000	799.513	173.319	20.28	-0.096
		22 MAY 74	4	533.715	370.644	20.36	-0.346
		22 MAY 74	4	533.662	370.620	20.43	-0.346
2408- 2	CO2 IN N2	22 MAY 74	5000	809.296	173.247	20.42	-0.096
		22 MAY 74	4	536.086	370.620	20.25	-0.346
		22 MAY 74	4	536.005	370.602	20.17	-0.346
35316- 1	CO2 IN N2	22 MAY 74	5000	795.825	173.264	20.22	-0.096
		23 MAY 74	4	758.428	370.624	19.92	-0.346
		23 MAY 74	4	757.934	370.581	19.63	-0.346
35316- 2	CO2 IN N2	23 MAY 74	5000	796.412	173.266	19.81	-0.096
		23 MAY 74	4	758.398	370.618	19.31	-0.346
		23 MAY 74	4	758.636	370.592	19.46	-0.346
35299- 1	CO2 IN N2	23 MAY 74	5000	799.722	173.256	19.43	-0.096
		24 MAY 74	4	714.074	370.621	19.77	-0.346
		24 MAY 74	4	714.054	370.582	19.86	-0.346
35299- 2	CO2 IN N2	24 MAY 74	5000	800.763	173.193	19.80	-0.096
		24 MAY 74	4	714.184	370.606	19.94	-0.346
		24 MAY 74	4	714.235	370.584	19.90	-0.346
39239- 1	CO2 IN N2	14 OCT 74	5000	815.255	173.596	20.23	-0.142
		14 OCT 74	4	652.583	371.044	20.06	-0.391
		14 OCT 74	4	652.609	371.039	19.96	-0.391
		15 OCT 74	4	652.628	371.068	19.89	-0.391

TABLE 1. MANOMETRIC REFERENCE GAS CALIBRATIONS - EXPERIMENTAL DATA

CYLINDER NO. -RUN NO.	REF. GAS TYPE	DATE	VOLUME CC	VAC. COL. HEIGHT, MM	SAMPLE COL. HEIGHT, MM	TEMP. DEG. C	MENIS. CORR., MM
1540- 1	CO2 IN N2	15 OCT 74	5000	800.690	173.708	19.89	-0.142
		15 OCT 74	4	685.812	371.067	19.89	-0.391
		15 OCT 74	4	685.739	371.066	19.82	-0.391
39239- 2	CO2 IN N2	16 OCT 74	5000	800.907	173.639	20.00	-0.142
		16 OCT 74	4	646.394	371.068	19.76	-0.391
		16 OCT 74	4	646.288	371.020	19.76	-0.391
1540- 2	CO2 IN N2	16 OCT 74	5000	799.969	173.625	19.77	-0.142
		17 OCT 74	4	685.224	371.029	19.47	-0.391
		17 OCT 74	4	685.436	371.032	19.66	-0.391

Table 2. Second Virial Coefficients (B) for Selected Gases, in cm^3/mole

Temp/Gas	CO_2	N_2	O_2	CO-free Dry Air	Argon
260°K		-13.8	-25.6	-16.9	-25.3
280°K		- 8.9	-20.2	-11.9	-20.1
285°K	-136.2				
290°K	-131.1				
295°K	-126.2				
300°K		- 4.7	-15.7	- 7.7	-15.7

Source: "Pressure-Volume-Temperature Relationships of Gases, Virial Coefficients"; J.M.H. Levelt Sengers, Max Klein, John S. Gallagher; Heat Division, National Bureau of Standards (1971).

Table 3. Summary of 1974

Manometric Reference Gas Calibrations

I. CO_2 in Nitrogen Reference Gases

Cylinder No.	Run No.	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
2408	1	196.93	196.89	196.90	2
		196.85			
	2	196.91	196.90		
		196.89			
3753	1	246.03	246.04	246.02	2
		246.05			
	2	246.00	246.00		
		245.99			
7366	1	276.82	276.79	276.80	2
		276.66			
		276.90			
	2	276.76	276.80		
		276.85			
6078	1	310.78	310.80	310.82	3
		310.81			
	2	310.84	310.88		
		310.91			
	3	310.79	310.79		
		310.79			
2399	1	323.90	323.82	324.05	4
		323.68			
		323.89			
	2	324.19	324.21		
		324.23			
	3	324.06	324.06		
		324.07			
	4	324.08	324.12		
		324.17			
39239	1	332.64	332.77	332.78	2
		332.80			
		332.87			
	2	332.83	332.80		
		332.76			
10069	1	355.69	355.65	355.60	2
		355.61			
	2	355.55	355.54		
		355.53			
1540	1	380.50	380.50	380.56	2
		380.51			
	2	380.63	380.62		
		380.62			

Table 3. Summary of 1974

Manometric Reference Gas Calibrations

I. CO_2 in Nitrogen Reference Gases (continued)

Cylinder No.	Run No.	Individual Determinations (ppm)	Run Average (ppm)	Overall Average (ppm)	No. of Runs
2424	1	392.30	392.39	392.34	2
		392.52			
		392.34			
	2	392.33	392.28		
		392.23			
35299	1	415.19	415.13	415.06	2
		415.07			
	2	414.91	414.98		
		415.05			
35316	1	473.03	473.00	472.97	2
		472.98			
	2	472.91	472.94		
		472.97			

Table 3. Summary of 1974

Manometric Reference Gas Calibrations

II. Compressed Air Reference Gases

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

Table 3. Summary of 1974

Manometric Reference Gas Calibrations

III. CO_2 in Nitrogen and Oxygen Reference Gases

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

Table 4. Meniscus Corrections

	Date	Approx. Distance from Mercury to Pointer (mm)	Pointer Reading (mm)	No. of Det'ns	Average Sample Column Height (mm)	Average Vacuum Column Height (mm)	Applied Correction (mm)	Comments
4 cc Pointer in Small Manometer (Col. #4 [sample] vs. Col. #2 [vacuum])								
(1)	2 JAN 74	.09	370.613	10	370.527	370.868	-0.341	Hg not bulging toward pointer.
(2)	22 FEB 74	.08	370.596	5	370.515	370.859	-0.344	Hg not bulging toward pointer.
(3)	31 MAY 74	.10	370.644	10	370.542	370.838	-0.296	Hg bulging toward pointer - jumped into contact once.
(4)	31 MAY 74	.18	370.642	10	370.457	370.808	-0.351	Hg not bulging toward pointer.
			Weighted (by Det'ns) average of 1, 2, 4 (nonbulging Hg)				-0.346	
(5)	17 OCT 74	.33	371.074	10	370.744	371.135	-0.391	Hg not bulging toward pointer.
Pointer in Large Manometer (Col. #5 [sample] vs. Col. #8 [vacuum])								
(1)	2 JAN 74	.34	173.395	10	173.060	173.171	-0.111	Hg not bulging toward pointer.
(2)	22 FEB 74	.30	173.434	5	173.136	173.257	-0.121	Hg not bulging toward pointer.
(3)	31 MAY 74	.24	173.440	10	173.202	173.270	-0.068	Hg not bulging toward pointer.
				Weighted (by Det'ns) average of 1, 2, 3			-0.096	
(4)	17 OCT 74	.20	173.876	10	173.674	173.816	-0.142	Hg not bulging toward pointer.

Table 5. Readings of Thermometers in Manometric System Cabinet

1974 Run Number	Date	Corrected Deviations of Thermometers from No. 6112 in °C						
		6114	6113	6111	6112	6115	6117	6116
6078-1	16 JAN 74	+.04	-.01	.00	18.05	-.01	-.06	+.01
6078-2	17 JAN 74	+.05	+.01	.00	18.18	-.01	-.04	+.03
35435-1	21 JAN 74	+.02	-.03	+.02	20.46	+.01	-.05	+.02
35435-2	22 JAN 74	+.01	-.01	+.01	20.68	.00	-.01	+.02
2399-1	23 JAN 74	+.01	-.01	+.01	20.60	-.01	-.01	+.02
2399-2	24 JAN 74	+.02	-.02	+.01	20.65	+.02	-.02	+.04
2399-3	28 JAN 74	.00	.00	+.01	20.61	-.01	-.02	+.02
10069-1	30 JAN 74	+.02	-.01	+.01	20.80	+.01	-.04	+.03
10069-2	30 JAN 74	+.01	-.03	.00	20.93	+.01	.00	+.04
2424-1	1 FEB 74	+.01	-.02	+.01	20.08	.00	-.04	+.03
2424-2	5 FEB 74	-.02	-.04	+.01	20.31	-.01	-.02	.00
7366-1	6 FEB 74	+.01	-.01	+.01	20.82	+.01	-.02	+.02
7366-2	7 FEB 74	.00	.00	+.01	20.57	-.02	-.03	+.01
3753-1	8 FEB 74	+.03	-.02	+.01	20.05	.00	-.02	+.04
3753-2	11 FEB 74	+.01	.00	+.01	21.00	+.01	+.01	+.03
35452-1	12 FEB 74	-.02	-.04	.00	21.13	.00	-.02	.00
35452-1a	13 FEB 74	-.01	-.02	+.01	21.01	.00	-.05	.00
35452-2	13 FEB 74	+.02	-.02	+.01	20.66	+.01	.00	+.05
6078-3	14 FEB 74	+.03	.00	+.02	20.24	+.01	-.01	+.05
35434-1	25 FEB 74	-.02	-.02	+.01	20.85	.00	-.01	.00
35434-2	26 FEB 74	+.02	+.01	+.01	20.40	-.01	-.01	+.04
35389-1	27 FEB 74	+.01	-.02	.00	20.88	+.01	-.02	+.02
35389-2	27 FEB 74	.00	-.01	.00	20.75	.00	-.01	+.02
35441-1	28 FEB 74	+.01	-.02	+.01	20.16	.00	-.02	+.03
35441-2	1 MAR 74	.00	-.01	+.01	19.78	.00	+.01	+.05
35442-1	4 MAR 74	+.01	-.01	+.01	20.61	.00	+.02	+.04
35442-2	5 MAR 74	-.03	-.02	+.01	20.72	.00	-.01	.00
35435-3	5 MAR 74	+.02	.00	+.01	21.01	+.01	+.01	+.04
2399-4	7 MAR 74	+.02	-.01	+.01	20.65	.00	+.01	+.04
35405-1	9 APR 74	+.03	.00	+.02	20.37	-.01	-.03	+.02
44726-1	10 APR 74	+.01	-.01	+.01	20.86	+.01	+.01	+.04
35405-2	10 APR 74	+.01	-.01	+.01	20.80	+.01	.00	+.04
44695-1	11 APR 74	+.01	-.02	.00	21.04	+.01	-.02	+.03
44726-2	12 APR 74	+.01	-.02	.00	20.97	.00	-.01	+.02
44695-2	15 APR 74	+.01	-.01	+.01	20.98	+.01	-.02	+.03

Table 5. Readings of Thermometers in Manometric System Cabinet

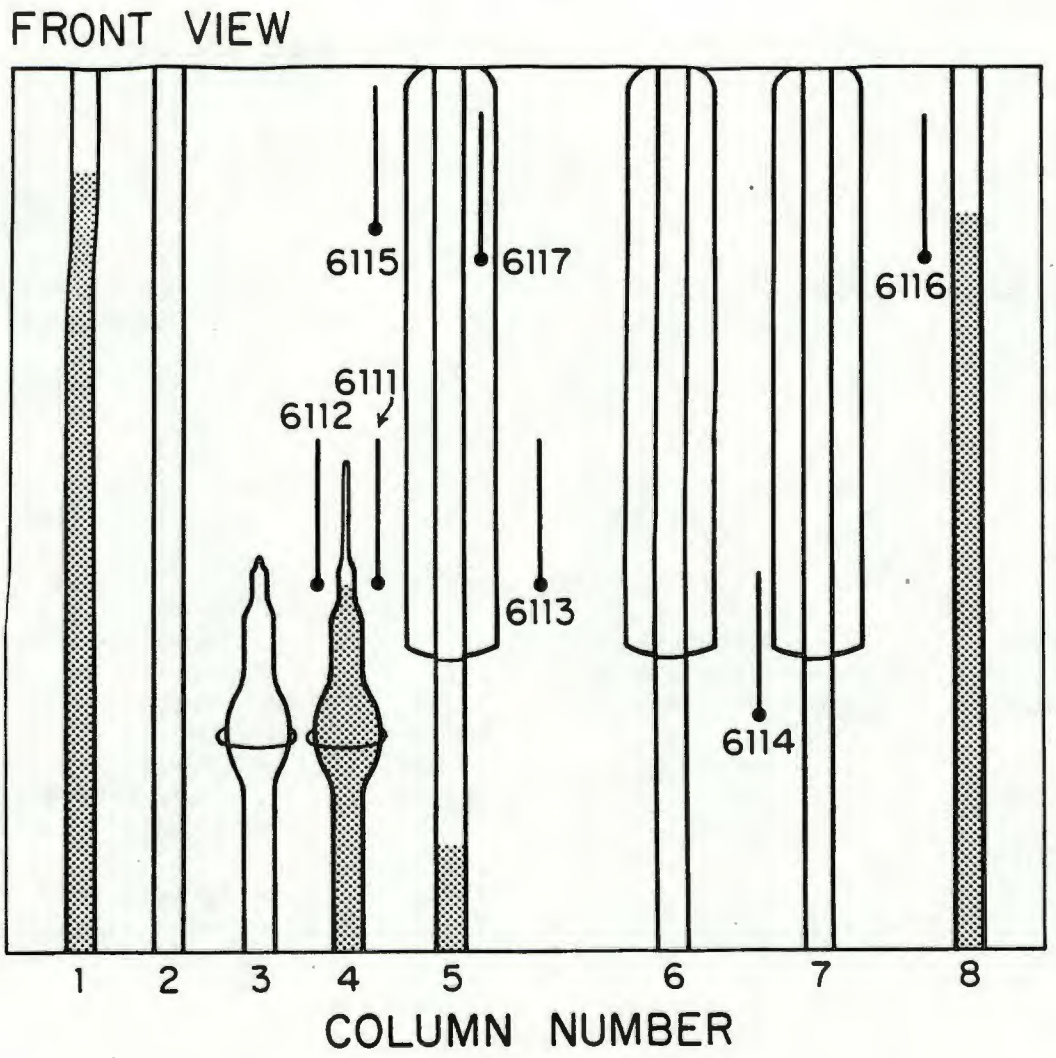
1974 Run Number	Date	Corrected Deviations of Thermometers from No. 6112 in °C						
		6114	6113	6111	6112	6115	6117	6116
35378-1	6 MAY 74	.00	-.04	+.01	20.66	+.01	-.02	+.02
35378-2	7 MAY 74	+.01	-.03	+.01	20.71	+.02	.00	+.03
35401-1	8 MAY 74	+.01	-.02	+.01	20.97	.00	-.01	+.01
35401-2	9 MAY 74	+.02	-.02	+.01	20.49	.00	-.01	+.02
34770-1	10 MAY 74	-.02	-.04	.00	20.28	.00	+.02	+.04
34770-2	14 MAY 74	+.01	-.02	+.01	20.70	+.01	-.03	+.02
35401-3	15 MAY 74	.00	-.03	+.01	20.63	-.01	-.01	+.01
2408-1	21 MAY 74	+.01	-.03	+.01	20.29	-.01	-.05	+.02
2408-2	22 MAY 74	.00	-.03	+.01	20.42	.00	-.01	+.02
35316-1	22 MAY 74	.00	-.03	+.01	20.22	-.01	-.02	+.03
35316-2	23 MAY 74	+.02	-.02	+.01	19.84	-.02	-.03	+.03
35299-1	23 MAY 74	+.02	.00	+.01	19.50	-.04	-.05	+.02
35299-2	24 MAY 74	+.03	-.02	+.01	19.78	+.01	+.01	+.06
Average Deviation from #6112		+.01	-.02	+.01		.00	-.02	+.03
σ of Deviation		$.01_6$	$.01_3$	$.00_5$		$.01_1$	$.01_9$	$.01_4$

Notes: (1) Temperatures are observed thermometer readings plus the following corrections determined by Elliot Atlas in September, 1968 (Manometer Calibrations Book II, part 3, page 29):

#6114	-0.03°C	#6115	+0.03°C
#6113	+0.02°C	#6117	-0.03°C
#6111	0.00°C	#6116	-0.03°C
#6112	+0.01°C		

(2) 3 of 5 cabinet fans on (Mid and Intermediate fans) at 40 volts.

Figure 2. Placement of Thermometers in Manometric System Cabinet



Front to Rear Placement:

6111, 6112: Close to front beside Col. No. 4 at 4cc pointer

6114, 6117: About halfway to rear

6113, 6115: Close to rear beside Col. No. 5

6116: Between 6113 and 6114 beside large manometer control ballast (not pictured)

Table 6. Oxygen Analyses on Selected Reference Gases

Reference Gas Cylinder No.	Carrier Gas	Indiv. Analyses (%)	Av. O_2 (%)	Method
35435	Compressed Air	20.9	20.9	Mass Spectrometer+
35389	Nitrogen-Oxygen	20.9	20.9	Mass Spectrometer
		20.9		
35434	Nitrogen-Oxygen	18.9	18.9	Mass Spectrometer
		18.9		
		18.9		
35452	Nitrogen-Oxygen	18.9	18.9	Mass Spectrometer
35441	"40% O_2"Nitrogen-Oxygen	42.5	41.5	Mass Spectrometer
		40.4		
35442	"60% O_2"Nitrogen-Oxygen	57.9	57.9	Mass Spectrometer
		(2nd Sample Contaminated)		
35378	Compressed Air	21.02	21.02	Beckman Paramagnetic Analyzer++
35405	Compressed Air	20.91	20.91	Beckman Paramagnetic Analyzer
35435	Compressed Air	20.88	20.86	Beckman Paramagnetic Analyzer
		20.84		
35389	Nitrogen-Oxygen	20.94	20.94	Beckman Paramagnetic Analyzer
35434	Nitrogen-Oxygen	18.82	18.82	Beckman Paramagnetic Analyzer
35452	Nitrogen-Oxygen	18.76	18.76	Beckman Paramagnetic Analyzer
		18.76		
44695	Nitrogen-Oxygen	21.66	21.66	Beckman Paramagnetic Analyzer
44726	Nitrogen-Oxygen	22.36	22.36	Beckman Paramagnetic Analyzer

Remarks:

+Method good to ±1% in O_2.

++Method good to ±0.1% in O_2 or better.

Table 7. Analyses of Compressed Air Reference Gases from S.I.O. Diving Locker for N_2O Content

Gas Cylinder Number	Manometric Mole Fraction (ppm)	No. of Manometric Det'ns	$\frac{[N_2O]}{[CO_2]} \times 10^3$	No. of N_2O Det'ns	CO_2 Mole Fraction (ppm)	N_2O Mole Fraction (ppm)
34770	338.84	2	0.8566	1	338.55	0.2900
35378	355.93	2	0.8288	1	355.64	0.2948
35401	353.26	2	0.8477	1	352.96	0.2992
35405	337.28	2	0.8638	1	336.99	0.2911
35435	334.40	3	0.8746*	2	334.11	0.2922
35435	334.40	3	0.8614**	1	334.11	0.2878**
35441***	332.04	2	0.0055	1	332.04	0.0018
35442***	327.02	2	0.0104	1	327.02	0.0034

Unless noted, extractions of CO_2 and N_2O from compressed air cylinders done by P.R.G. in 2317 R.H.

Manometric mole fractions determined on constant volume manometric system in 2317 R.H. by P.R. Guenther.
$[N_2O]/[CO_2]$ determined on gas chromatograph by R. Cutler.

*average of two (.8748 and .8743).
**extraction done by R. Cutler.
***CO_2 in nitrogen and oxygen reference gases run for comparison.

Table 8. Infrared Analyzer Index Values - Summary

Gas Cylinder No.	All Calibrations: Date of 1st Run	All Calibrations: Date of Last Run	All Calibrations: Total Number of Comparisons	All Calibrations: Weighted Average Index (ppm)	Special Manometric Reference Gas Calibrations: Date of 1st Run	Special Manometric Reference Gas Calibrations: Date of Last Run	Special Manometric Reference Gas Calibrations: Total Number of Comparisons	Special Manometric Reference Gas Calibrations: Weighted Average Index (ppm)
I. CO_2 in N_2 Reference Gases								
2408	22 MAY 74	10 SEP 74	321	204.29	23 MAY 74	10 SEP 74	321	204.27
3753	10 JUN 66	9 SEP 74	291	253.99	23 MAY 74	9 SEP 74	80	253.91
7366	2 JUL 68	9 SEP 74	288	282.21	23 MAY 74	9 SEP 74	80	282.00
6078	17 JUL 69	4 NOV 74	459	311.42	23 MAY 74	4 NOV 74	159	311.23
2399	12 SEP 68	4 NOV 74	439	322.12	24 MAY 74	4 NOV 74	161	321.95
39239	21 FEB 73	4 NOV 74	287	329.01	10 OCT 74	4 NOV 74	157	329.00
10069	13 JUN 69	4 NOV 74	433	346.73	24 MAY 74	4 NOV 74	167	346.76
1540	19 JAN 73	4 NOV 74	294	365.21	10 OCT 74	4 NOV 74	168	365.27
2424	11 MAR 60	18 NOV 74	322	372.62				
35299	28 MAR 74	4 NOV 74	218	389.48	24 MAY 74	4 NOV 74	167	389.50
35316	28 MAR 74	10 SEP 74	369	427.24	23 MAY 74	10 SEP 74	317	427.25
II. Compressed Air Reference Gases								
35435	7 DEC 72	13 NOV 74	272	326.86				
35405	11 OCT 73	13 MAY 74	87	329.03				
34770	6 JUL 73	13 NOV 74	224	330.26				
35401	11 OCT 73	13 NOV 74	192	341.26				
35378	11 DEC 73	13 NOV 74	162	343.31				
III. CO_2 in Nitrogen and Oxygen Reference Gases								
44726	4 APR 74	5 JUN 74	53	307.28				
35442	20 APR 73	5 NOV 74	127	315.53				
35452	29 NOV 73	13 NOV 74	193	319.20				
35434	29 NOV 73	13 NOV 74	197	319.28				
35441	20 APR 73	5 NOV 74	131	322.54				
35389	30 JAN 73	13 NOV 74	222	327.79				
44695	4 APR 74	5 JUN 74	51	340.57				

Table 9. Summarized Data for CO_2 in Nitrogen Reference Gases

Reference Gas Cylinder No.	Average 1974 Manometric Mole Fraction (ppm)	Average Adjusted Index Value (Special Tank Days) (ppm)
2408	196.90	180.83
3753	246.02	241.32
7366	276.80	275.55
6078	310.82	311.17
2399	324.05	324.23
39239	332.78	332.82
10069	355.60	354.47
1540	380.56	377.02
2424	392.34	385.98
35299	415.06	406.55
35316	472.97	452.55

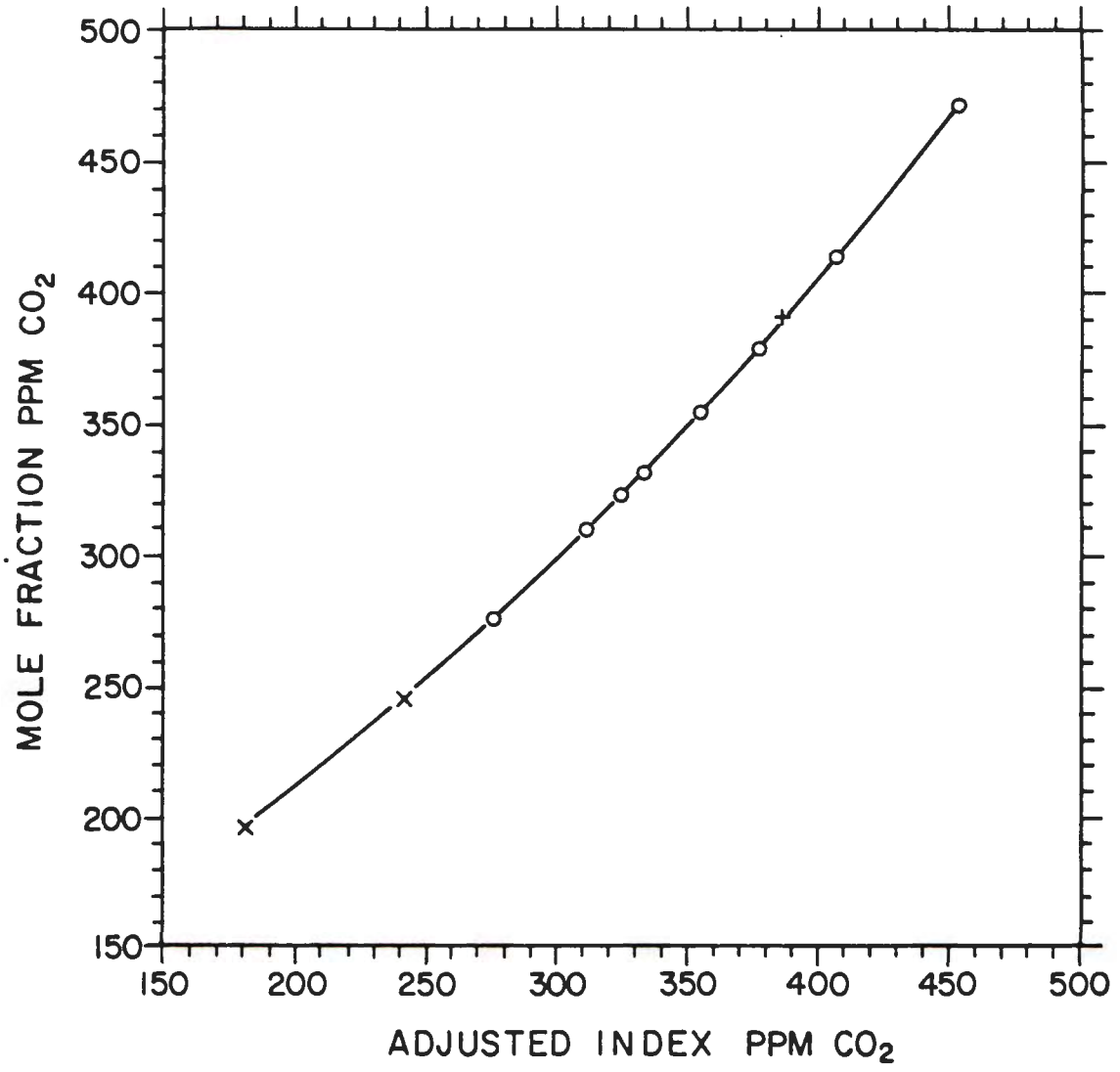


Figure 3. Calibration curve for CO_2 in N_2 reference gases. Plots the measured manometric mole fractions of the ten calibration gases versus their adjusted indices. Fit made to upper eight points only. Position of anomalous gas 2424 shown by +.

Table 10. Summary of 1974 Manometric Calibrations of Oxygen-Containing Reference Gases

1	2	3	4	5	6	7
Gas Cylinder Number	Measured Infrared Adjusted Index (ppm)	Measured Manometric Mole Fraction (ppm)	O_2 Conc. by Analysis (%)	Virtual Infrared Adjusted Index[1] (ppm)	Multiplicative Factor[2]	Additive Correction[3] at 320 ppm (ppm)
I. Compressed Air Reference Gases						
35435	330.22	334.11[4]	20.9	334.13	.011840	3.84
35405	332.86	336.99[4]	20.9	336.90	.012137	3.94
34770	334.36	338.55[4]	——	338.39	.012053	3.91
35401	347.76	352.96[4]	——	351.96	.012077	3.92
35378	350.26	355.64[4]	21.0	354.44	.011934	3.87
				Average of 5	.012008	3.90
				σ	.000120	.04
II. CO_2 in Nitrogen and Oxygen Reference Gases (~20% O_2)						
44726	306.36	309.57	22.4	309.92	.010866	3.53
35452	320.88	323.86	18.8	324.16	.011389	3.70
35434	320.98	323.91	18.8	324.21	.011212	3.64
35389	331.35	335.36	20.9	335.33	.012038	3.91
44695	346.92	351.92	21.7	350.99	.011324	3.68
				Average of 5	.011366	3.69
				σ	.000426	.14
III. High O_2 Concentration Reference Gases						
35442	316.41	327.02	58.0	327.25	.012372	4.01
35441	324.95	332.04	41.0	332.13	.011288	3.66

Notes:

1. Infrared Index if gas were CO_2 in N_2, from inverting:

$$X = 76.582 + .58491J + 3.1151 \times 10^{-4}J^2 + 7.3225 \times 10^{-7}J^3$$

where X = 1974 Manometric Concentration and J is Adjusted Index

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

where I is Index.

2. Carrier Gas "Constant Factor" $\equiv \frac{\text{Col \#5} - \text{Col \#2}}{\text{Col \#2}} \times \frac{20.946}{O_2\%}$

3. Carrier gas additive correction in manometric mole fraction units for Measured Index = 320 ppm.

4. Corrected for analyzed N_2O concentration (0.29 - 0.30 ppm)

Table 11. Carrier Gas Effects on AP55 CO_2 Analyses - Summary

Adjusted Index (ppm)	Method	79.1% N_2 20.9% O_2 (ppm)	99.07% N_2 0.93% Argon (ppm)	Air+ (ppm)
310	Volumetric	3.44	.24	3.68*
310	Manometric	3.50	.20**	3.70
320	Volumetric	3.63	.25	3.88*
320	Manometric	3.68	.21**	3.89
330	Volumetric	3.82	.26	4.08*
330	Manometric	3.87	.23**	4.10

+Add corrections to air CO_2 concentrations obtained from AP55 analyzer with CO_2 in N_2 standard gases.

*Sum of determined values for oxygen and argon.

**Difference of determined values for air and CO_2 in 20.9% O_2 and 79.1% N_2.