MANOMETRIC ANALYSIS OF GAS MIXTURES

I. THE DETERMINATION, BY SIMPLE ABSORPTION, OF CARBON DIOXIDE, OXYGEN, AND NITROGEN IN MIXTURES OF THESE GASES

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APPLICABILITY OF MANOMETRIC APPARATUS TO ANALYSIS OF GAS MIXTURES

In the original description of the manometric blood gas apparatus by Van Slyke and Neill (1924) it was pointed out that the apparatus could be used for air analyses. Details for adaptation of the apparatus to the different gas mixtures encountered in biological analyses were not, however, perfected at that time. Such details are now available.

The constituents of a gas mixture can be successively removed by absorption or combustion, and the amounts so removed estimated by the decrease in gas pressure registered on the manometer.

The absorption, in the cases of CO₂ and O₂, can be carried out by admitting the necessary solutions to the chamber itself, so that transfer of the gas to other vessels for absorption is avoided. Such transfer can, however, readily be accomplished to modified Hempel pipettes when desirable.

Another procedure, especially adapted to estimation of a gas forming only a minute proportion of a mixture, is based on isolation of such a gas by absorbing it in the chamber of the apparatus with suitable reagents, such as alkali for CO₂, or reduced blood for CO. The unabsorbed gases are then ejected, and the absorbed gas is set free from solution and measured, as in blood gas determinations.

Analysis by combustion is carried out as easily as with ordinary volumetric apparatus. The manometric apparatus has an ad-
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... advantage in analysis of highly explosive mixtures, which in other methods are ordinarily diluted with inert gas to reduce their explosibility. Here such dilution and its resultant loss of accuracy are unnecessary, because the explosibility can be decreased merely by putting the mixture under reduced pressure during ignition.

In convenience, analysis of gas mixtures by the manometric apparatus is not inferior to methods of equal accuracy by the usual procedures with gas burettes and absorption bulbs. When the absorbing solution can be admitted into the chamber of the manometric apparatus, making gas transfer unnecessary, the manometric procedure is likely to be the more convenient.

In the maximum accuracy attainable, when simple absorption procedures are used to remove the gases determined, the manometric technique is inferior to the more refined types of volumetric methods. A 0.1 mm. division on the 500 mm. length of manometer ordinarily employed corresponds to 0.0002 of the gas measured, and marks the limit of manometric accuracy in this type of analysis. Volumetric gas burettes, on the other hand, for special purposes can be made with relatively large volumes and with small bores at the points where measurements are made, so that a 0.1 mm. division corresponds to 0.0001 of the gas measured, as in the ordinary 10 cc. Haldane apparatus, or to a still smaller fraction if it is desired. For many purposes, however, the accuracy of 0.0002 suffices, and the convenience of the manometric procedure then may make it the one of choice.

Furthermore, the manometric technique is not limited to simple absorption procedures. The isolation method with the manometric apparatus makes possible a great extension of its refinement, and permits determination, without unusual precautions, of minute proportions of gases, with an accuracy such as can be attained with volumetric methods only by extreme precautions and use of special apparatus. Thus CO₂ in atmospheric air can easily be determined manometrically by the isolation method with a precision approaching 0.0003 of a volume per cent of the air, and small amounts of carbon monoxide to 0.001 volume per cent.

The manometric method also has an advantage for determining small amounts of inert gas admixed with great amounts of other gases capable of removal by absorption. In such a case the sample can be measured by its pressure at 50 cc. volume, and the
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residual unabsorbed gas by its pressure at 0.5 cc. volume, so that its pressure is multiplied 100-fold. Thus 1 volume per cent of nitrogen present as impurity in oxygen can be determined with an accuracy approaching 0.001 volume per cent.

In all the methods outlined in the present series of papers, the manometric apparatus described by Van Slyke and Neil (1924) and Van Slyke (1926-27) is used without alteration. The chamber could be modified, so that readings could be taken with the gas at other volumes than the 0.5, 2, and 50 cc. provided by the original chamber, but such modifications have as yet not been found necessary. The same apparatus, used for determination of the blood gases and various other substances by methods previously published in this Journal, can also be used without alteration for the gas analyses described in this and the succeeding papers.

Methods A and B described in this paper for determination of O₂, CO₂, and N₂ in air by simple absorption are capable of being carried out with errors not exceeding 0.1 volume per cent, and usually within 0.05 volume per cent. When greater accuracy is required, the isolation method is used for CO₂ (Van Slyke, Sendroy, and Liu, 1932) and the combustion method for O₂ (Van Slyke and Hanke, 1932), as described in accompanying papers of this series. Method C, described in this paper for small amounts of N₂ or other inert gas present in oxygen or carbon dioxide, is of the highly accurate type mentioned above.

GENERAL POINTS OF TECHNIQUE FOR APPLICATION OF MANOMETRIC APPARATUS TO ANALYSES OF GAS MIXTURES

Extension of Manometer Scale for Low \( p_0 \) Readings—The zero readings with the mercury in the chamber at the 50 cc. mark fall in the low part of the manometer tube opposite the bottom of the chamber. Most of the closed tube manometers made for the Van Slyke-Neill apparatus before 1931 have scales which fail by 10 or 20 mm. to extend so low, since none of the methods used prior to this time involved zero readings with more than 2 cc. of gas space in the chamber. It is, however, not difficult to improvise an extension of the scale to make possible zero readings at the lower point. On transparent paper a ladder of parallel lines 1 mm. apart is made with black India ink. Each line is made long enough to extend half way around the manometer tube, except that
every fifth line is made a little longer to facilitate counting the distances. The strip of paper with the lines is cut of sufficient width to extend two-thirds of the way around the manometer tube. It is then pasted onto the tube in such a way that the open third is towards the observer's eye, and the uppermost mark on the paper covers the zero mark on the glass scale. If such a scale extension is used, a convenient way to employ it in connection with the scale already present is to add 100 mm. to each reading made on the latter, and consider the zero point to be the point on the extrapolated scale 100 mm. lower than the original zero of the glass scale.

Temperature Control and Corrections

Control—In so far as atmospheric conditions are concerned, the manometric apparatus with the closed manometer is independent of changes in barometric pressure, because the manometer and chamber of the apparatus form a closed system. Temperature changes, however, occurring in the manometric apparatus in the course of an analysis, cannot be automatically compensated by a device like the thermobarometer. The manometric apparatus is therefore used under conditions to minimize temperature changes during the short time required for an analysis. If the temperature registered by the thermometer in the water jacket of the chamber of the apparatus differs from that registered by a thermometer in the air of the room at the same level, the water jacket is warmed or cooled by wrapping it for a minute or longer in a towel wet with hot or cold water. The chamber is then shaken and the temperature on its thermometer noted. It is desirable to bring it within 0.2° or 0.3° of the room temperature. During an analysis the room temperature is kept as constant as possible.

Corrections—If significant temperature changes do occur during an analysis, corrections for them must be applied. The corrections are estimated from the following considerations.

The procedure in most of the analyses is to measure the sample by its pressure, $P_s$, as described below for "Measurement of sample," then to remove the gas determined, and finally to measure the pressure, $P_R$, of the residual gas. The constituent gas determined is measured by the difference, $P_s - P_R$. 
$P_s$ of the sample is measured as the difference between two manometer readings, $p_0$ taken with the manometer chamber empty, and $p_1$ taken after admission of the sample. These two readings are taken within such a short time interval that there is ordinarily no significant temperature change between them. Similarly $P_R$ is measured as the difference between two quickly succeeding manometer readings, one before and one after the residual gases have been ejected from the chamber.

Between the observations of $P_s$ and $P_R$, however, a period of several minutes may elapse during which the constituent gas determined is in process of removal by absorption or combustion, so that temperature changes of 0.2° or 0.3° may occur between the $P_s$ and $P_R$ measurements. For comparison with $P_s$ in the calculation of results, $P_R$ must in such a case be corrected, in order to obtain the value it would have at the temperature of the sample measurement. For this purpose the observed value of $P_R$ is multiplied by the factor $\frac{T_s}{T_R}$, where $T_s$ represents the absolute temperature (centigrade +273°) observed in the water jacket of the chamber at the time of the sample measurement, and $T_R$ is the absolute temperature of the final $P_R$ measurement. The correction amounts to about 1 part per 3000 for 0.1° temperature change.

(1) \[ P_R \text{ corrected to } T_s = P_R \text{ observed } \times \frac{T_s}{T_R} \]

The following values of the factor $\frac{T_s}{T_R}$ are used for the conditions encountered and are convenient to have at hand. When $T_s$ is less than $T_R$, the factor $\frac{T_s}{T_R}$ has the value 0.9997 for 0.1° difference between $T_s$ and $T_R$, 0.9993 for 0.2°, 0.9990 for 0.3°, and 0.9986 for 0.4°. When $T_s$ exceeds $T_R$ the values of the factor are 1.0003 for 0.1° difference, 1.0007 for 0.2°, 1.0010 for 0.3°, and 1.0014 for 0.4°.

In the analyses described in this paper, $P_R$ is represented by the pressure, $P_{N_2}$, of the residual nitrogen left after absorption of the CO₂ and O₂.
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The above correction is the only one that need ordinarily concern the analyst who uses the methods described in this series of papers. The precautions outlined under "Control" are usually sufficient, as stated above, to prevent significant temperature changes in the interval between the two successive manometer readings involved in the measurement of any one gas portion.

Technique of Manometer Readings

Before every manometer reading in these gas analyses, the mercury meniscus in the chamber is lowered below either the 2 or the 50 cc. mark, and is then brought slowly up to the mark by admitting mercury from the leveling bulb while the latter rests level with the bottom of the chamber. While the mercury in the chamber is rising to the mark it is observed with a magnifying glass (a good reading glass serves well), and the cock from the leveling bulb is closed just as the top of the curved mercury meniscus reaches the mark. With practice one can bring the mercury in the chamber thus to the same level with a constancy of 0.1 mm. It is essential that the mercury surface should always be brought to the mark in the same manner from below upwards, and never from above downwards, because the manometer readings obtained after these two different approaches differ, slightly but measurably. After the mercury is at the mark in the chamber the reading on the manometer is taken. If there is any doubt concerning the accuracy of the placing of the mercury meniscus in the chamber, the mercury is lowered and brought up to the mark again, and the reading is repeated. In such duplicate observations the readings on the manometer (also with the help of a lens) should differ by not more than 0.1 mm.

Preparation of Manometric Chamber to Receive Gas Sample

The manometric chamber is washed, if necessary, to free it from interfering solutions used in preceding analyses. Then all the water present is removed except the invisible film adherent to the walls. To remove excess water the mercury in the chamber is lowered to the bottom, and then is permitted to rise slowly to the top. The water which collects on the surface is expelled, and about 2 cc. of mercury are driven up into the cup above the chamber. The chamber is then evacuated and the mercury lowered to
the 50 cc. mark. If more water then collects on the mercury surface than will form a slight ring about the edge, the above procedure is repeated to finish the removal of the water. The repetition will not be necessary unless during the first removal the mercury was allowed at some point to rise too rapidly to permit the water to detach itself completely from the glass walls ahead of the ascending mercury.

Fig. 1. Admission of gas sample into manometric chamber

The zero reading, \( p_0 \), of the apparatus, with the chamber free of gas and visible water, is now taken, as described above under "Technique of manometer readings," with the mercury meniscus at either the 2 or the 50 cc. mark, whichever is to be used in the analysis.

The tip of the capillary from the sample container is inserted into mercury in the cup of the chamber, as shown in Fig. 1. Any satisfactory container with a 3-way cock may be used, such as the familiar Barcroft tube, or the modified Hempel pipette of Van Slyke and Hiller (1928). The connecting capillary should be
narrowed at the tip, which is fitted with a rubber ring. Such a ring is made by cutting a section about 10 mm. long from a soft rubber tube of about 1 mm. bore with walls 2 mm. thick. The bottom of the ring is beveled slightly by grinding on an emery wheel or with sandpaper, so that it will fit the curvature of the bottom of the cup when pressed into the latter as shown in Fig. 1.

The manometric leveling bulb is first placed in the ring above the chamber, and mercury is forced up through the connecting capillary and 3-way cock of the sample container, displacing the air in its capillary, as shown in Fig. 1. During this operation the capillary is pressed into the bottom of the cup with one hand, so that the rubber ring makes a tight seal under the mercury, while the cocks are turned with the other hand.

Admission of Sample Regulated by Volume

For most gas analyses one takes a sample sufficient to give 450 to 550 mm. of pressure at either 2 or 50 cc. volume, according to whether a micro or macro analysis is to be made. Such a sample is of about 1.5 or 35 cc. volume at atmospheric pressure. Its admission can be regulated with sufficient accuracy as a rule by the following procedure.

The gas container and manometric chamber are arranged as shown in Fig. 1, and the leveling bulb of the chamber is placed about level with the bottom of the chamber. The cock connecting leveling bulb and chamber is left open, so that the contents of the chamber are under slight negative pressure. Gas from the sample container is then admitted to the chamber until the volume in the latter is approximately 1.5 or 35 cc. The volume can, with slight practice, be estimated with sufficient accuracy from the height of the mercury surface in the chamber above the 2 or 50 cc. mark.

Another procedure, which can be used also for samples of size not easily estimated from the marks on the chamber, is to admit the gas sample first to a container which holds at atmospheric pressure approximately the desired amount. From the container the sample is transferred to the manometric chamber by the technique shown in Fig. 9 of Van Slyke and Neill (1924). The water there shown in the container is here replaced by gas.
Admission of Sample Regulated by Pressure

For admission of samples intermediate between the 1 to 1.5 and the 30 to 35 cc. sizes the following procedure can be used. It requires somewhat more skill than admission regulated by volume, but has the advantage that it obviates the use of a special container for preliminary approximate measurement of the sample.

The apparatus is prepared and the $p_0$ reading taken as described above. The sample container is then permitted to hang in position, with its cock closed and the tip of its capillary outlet immersed in the mercury of the cup of the chamber. The capillary of the gas container is filled with mercury as in Fig. 1. The mercury in the chamber is then lowered till it is about 10 mm. above the 50 cc. mark. The cock between leveling bulb and chamber is then closed, and the leveling bulb is rested in the medium position, level with the bottom of the evacuated chamber. The tip of the capillary from the sample container is then pressed into the bottom of the cup, as shown in Fig. 1, and the cock of the container is turned to connect container and chamber. Then the cock at the top of the chamber is slightly opened, just long enough to admit enough gas to depress the mercury level in the chamber a little below the 50 cc. mark. The mercury in the manometer rises 20 to 40 mm. The cock leading to the manometric leveling bulb is now opened to admit enough mercury to the chamber to make the meniscus rise again about 10 mm. above the 50 cc. mark; then enough gas is again let in to force the mercury a little below the mark. This is repeated one, two, or three times, until the mercury in the manometer has risen to about the desired final level. During this procedure one holds the capillary tube of the sample container in position with the left hand, while with the right hand one alternately opens the cock at the top of the chamber to admit gas, then the cock from the leveling bulb to admit mercury. The procedure is in fact simple, and the admission of the entire sample by alternate turns of the two cocks requires less than a minute. Before the last admission of gas, the amount of mercury admitted is regulated from previous experience so that the subsequent admission of enough gas to press the mercury down to the mark will raise the mercury column in the manometer to the desired height; e.g., the amount of mercury admitted before the last portion of
gas may need to be only enough to raise the meniscus 5 mm., instead of 10 or 15, above the 50 cc. mark in the chamber.

**Measurement of Sample**

After the sample has been admitted by either of the above procedures, the sample container is removed and the bore of the cock at the top of the chamber is filled with mercury from the cup (this cock is gas-tight only when both bores are filled with mercury). The mercury meniscus is then lowered below either the 2 cc. or the 50 cc. mark, and is brought back to the mark as above directed. The manometer reading \( p_1 \) is then taken, and the temperature of the chamber is read on the thermometer in the water jacket. The size of the gas sample is indicated by the pressure \( P_s \), which the gas exerts at the chosen volume, either 2 or 50 cc.

(2) \[ P_s = p_1 - p_0 \]

The volume, \( V_s \), of the gas sample, reduced to 0°, 760 mm., can be calculated from \( P_s \) by the formula:

(3) \[ V_s = a \times \frac{P_s}{760} \times \frac{1}{1 + 0.00384t} \]

Here \( a \) is the volume (50 or 2 cc., as a rule) of the gas sample when its pressure, \( P_s \), is measured, and \( t \) is the temperature centigrade. The formula is similar to the familiar one

\[ V_{0^\circ, 760} = V_{r, B - W \text{ mm.}} \times \frac{B - W}{760 (1 + 0.00367t)} \]

In Equation 3, \( a \) represents the observed volume at which the gas is measured under \( P_s \), instead of \( B - W \), mm. of pressure. The coefficient 0.00384 for \( t \), instead of the usual 0.00367, is employed in order to correct for expansion of mercury in the manometer with temperature, as explained on p. 540 of Van Slyke and Neill’s paper (1924).

In calculating the results of analyses described in this paper only pressure figures are used, so that transformation of the sample measurement into terms of volume is not necessary. Equation 3 is given, however, as it is sometimes desirable to measure a gas
by pressure in the apparatus, and then to calculate the volume under standard conditions for other purposes.

METHOD A. DETERMINATION OF OXYGEN AND CARBON DIOXIDE IN AIR

The gas sample is measured by the pressure it exerts at 50 cc. volume, and the diminutions of pressure noted after successive absorption of CO₂ in the chamber with sodium hydroxide, and of oxygen with hyposulfite, are used to calculate these gases. For CO₂, when it forms less than 10 per cent of the gas analyzed, this method is less accurate than the isolation procedure described in the second paper of this series (Van Slyke, Sendroy, and Liu, 1932), and for O₂ the precision is less than in the method based on combustion with H₂ given in Paper IV (Van Slyke and Hanke, 1932). The determinations by simple absorption are, however, most convenient and rapid, and are reliable within limits which are sufficiently precise for many purposes.

Gas samples are taken of 30 to 35 cc. volume, giving a pressure at 50 cc. of about 500 mm. of mercury. The manometer readings are reproducible to 0.2 mm., corresponding to 0.04 volume per cent of the sample. If errors of this size, but opposite in direction, were made before and after absorption of either gas, the resultant error in the analysis would be the sum, or 0.08 per cent of an atmosphere. However, by performing check readings for each observation of the manometer, it is possible to keep the usual error within ±0.05 volume per cent (see Table I).

Reagents

1 N Sodium Hydroxide—The solution need not be freed of air for this analysis.

30 Per Cent Sodium Hyposulfite in 2 N Potassium Hydroxide—15 gm. of the hyposulfite, Na₂S₂O₄, are stirred up with 50 cc. of 2 N potassium hydroxide solution and filtered quickly through cotton into a 100 cc. flask, containing enough paraffin oil to make a layer 1 or 2 cm. thick.

Fieser’s anthrahydroquinone-β-sulfonate catalyst, which has proved its convenience in blood oxygen determinations (Van Slyke, 1927), is here left out of the hyposulfite solution, because the intensely red color of the catalyst would prevent reading the
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Mercury meniscus when the solution is in the chamber. The analysis could be accomplished in 1 minute less time with the sulfonate catalyst present, but it appears usually to be preferable to use the water-clear solution of hyposulfite without the catalyst.

For Methods A and B the solution is used without freeing it of dissolved air, because the oxygen is absorbed with the system at nearly atmospheric pressure. For Method C, however, the solution is freed of air as described on p. 535 of Van Slyke and Neill (1924). The air-free solution is kept over mercury and out of contact with air. A layer of oil would not protect it from absorption of sufficient atmospheric nitrogen to affect the results of analyses by Method C.

**Measurement of Sample**

The sample of 30 to 35 cc. is admitted into the apparatus as described above on p. 516, and \( P_S \) is measured as described on p. 518 for “Measurement of sample.”

\[ P_S = P_1 - P_0 \]

**Absorption of CO₂**

1 cc. of 1 N sodium hydroxide is measured accurately into the chamber from a stop-cock pipette in the manner shown in Fig. 3, p. 125, of a previous paper (Van Slyke, 1927). During the admission of the alkali the manometric leveling bulb is at the medium level, with the mercury surface in the bulb at about the height of the 50 cc. mark on the chamber. The cock between leveling bulb and chamber is left open, so that the contents of the chamber are under slightly negative pressure, and the chamber is about one-third full of mercury. After the alkali is admitted the chamber is shaken for 2 minutes so that the alkali will absorb the CO₂ from the gas sample. On account of the weight of mercury in the chamber the shaking is somewhat slower than in most analyses with this apparatus. During the shaking, the cock between the chamber and its leveling bulb is left open. The 10 or 15 cc. of mercury in the chamber and the alkali solution over the mercury are thrown about in such a way that thorough contact between gas and liquid is obtained, and CO₂ absorption is completed in 2 minutes. It is usually, in fact, finished during the 1st minute.
After absorption is finished the manometer reading \( p_2 \) is taken with the meniscus of the mercury (not of the water solution) at the 50 cc. mark in the chamber.

**Absorption of Oxygen with Hyposulfite**

After the \( p_2 \) reading has been taken the cock between the leveling bulb and the chamber is opened and 3.00 cc. of hyposulfite solution, accurately measured from a calibrated stop-cock pipette, are run into the chamber in the same manner in which the 1 cc. of sodium hydroxide was added. The absorption of oxygen is accomplished by shaking the chamber in the same manner as for CO\(_2\) absorption, except that for oxygen 3 minutes instead of 2 are taken.

After the absorption is completed the meniscus of the mercury is again brought to the 50 cc. mark and \( p_3 \) is read.

The gas is then ejected from the top of the chamber without loss of any of the solution (Van Slyke, 1926–27, p. 240) and \( p_4 \) is read with the 4 cc. of solution, but with no gas, in the chamber, and with the mercury meniscus again at the 50 cc. mark. The analysis is now complete.

**Calculation**

All quantities of gas measured are calculated in terms of the pressure exerted with the gas at 50 cc. volume and at the temperature of the \( P_S \) measurement. The sample is calculated as:

\[
P_S = p_1 - p_0
\]

The pressure of O\(_2\) + N\(_2\) is measured at 49 cc. volume. To calculate it for 50 cc. volume, therefore, it is necessary to multiply the observed pressure by \( \frac{50}{49} \), or 0.98.

\[
P_{O_2 + N_2} = 0.98 \left( p_2 - [p_0 + c] \right)
\]

The significance of the \( c \) correction will be discussed below.

The pressure of the CO\(_2\) is calculated by subtracting the pressure of the O\(_2\) + N\(_2\) from that of the total sample.

\[
P_{CO_2} = P_S - P_{O_2 + N_2}
\]
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The pressure of the N₂ at 46 cc. volume is measured as $p_2 - p_4$. At 50 cc. therefore one calculates:

(6) $P_{\text{N}_2} = 0.92 \ (p_2 - p_4)$

The oxygen is calculated by subtracting the N₂ from the O₂ + N₂.

(7) $P_{\text{O}_2} = P_{\text{O}_2 + \text{N}_2} - P_{\text{N}_2}$

The final results are calculated from the above data as follows:

(8) Per cent CO₂ = \[ \frac{100 \ P_{\text{CO}_2}}{P_S} \]

(9) Per cent O₂ = \[ \frac{100 \ P_{\text{O}_2}}{P_S} \]

(10) Per cent N₂ = \[ \frac{100 \ P_{\text{N}_2}}{P_S} \]

Remarks on Calculation

As shown above, one must multiply the observed O₂ + N₂ and N₂ pressures by 0.98 and 0.92, respectively, in order to calculate the pressures at 50 cc. volume from those at 49 and 46 cc. In practice, the simplest way to make this calculation is to subtract 0.02 and 0.08 of their values from the observed pressures, $p_2 - [p_0 + c]$, and $p_2 - p_4$.

Example of Calculation—The data are from an analysis of laboratory air. $c = 1.4$ mm. for the chamber used.

<table>
<thead>
<tr>
<th>mm.</th>
<th>mm.</th>
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<tbody>
<tr>
<td>$p_1 = 551.4$</td>
<td>$p_2 = 561.8$</td>
</tr>
<tr>
<td>$p_0 = 88.0$</td>
<td>$p_0 + c = 89.4$</td>
</tr>
<tr>
<td>$P_S = 463.4$</td>
<td>$P_{\text{O}_2 + \text{N}_2}$ at 49 cc. = 472.4</td>
</tr>
<tr>
<td>[ 0.02 \text{ of same} = 9.4 ]</td>
<td>[ P_{\text{O}_2 + \text{N}_2}$ at 50 cc. = 463.0</td>
</tr>
</tbody>
</table>
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\[ p_2 = 487.0 \]
\[ p_4 = 89.0 \]

\[ P_{N_2}, \text{at} 46 \text{ cc.} = 398.0 \]
\[ 0.08 \text{ of same} = 31.8 \]

\[ P_{N_2}, \text{at} 50 \text{ cc.} = 366.2 \]

\[ \text{Per cent CO}_2 = 100 \times \frac{463.4 - 463.0}{463.4} = 0.09 \]

\[ \text{Per cent O}_2 = 100 \times \frac{463.0 - 366.2}{463.4} = 20.89 \]

\[ \text{Per cent N}_2 = 100 \times \frac{366.2}{463.4} = 79.02 \]

**Determining the c Correction**

After the CO\(_2\) has been absorbed the pressure exerted by the residual O\(_2\) + N\(_2\) at 49 cc. volume would be inexactly calculated as \( p_2 - p_n \). The manometer reading without any gas present, but with the 1 cc. of NaOH solution in the chamber, would be slightly higher than the \( p_0 \) observed at the beginning of the analysis, with neither gas nor solution in the chamber. The weight of the short column of solution in the chamber presses on the mercury there, and in consequence raises the height of the mercury column in the manometer tube required to balance the meniscus in the chamber at the 50 cc. mark. The c correction required for this effect varies somewhat with the shape of the bottom of the chamber and the consequent height of the column of 1 cc. of solution. The value of c is, however, usually in the neighborhood of 1.5 mm.

The c correction is determined as follows: The \( p_0 \) point is determined, with the chamber free of both gas and visible amounts of water, as described on p. 515. Then 1 cc. of 1 N sodium hydroxide is admitted, as described for absorption of CO\(_2\), the chamber is evacuated till the mercury falls to the 50 cc. mark, and the air is extracted from the solution by shaking the latter 1 minute. The extracted small bubble of gas is ejected from the top of the chamber without loss of solution. The chamber is again
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Evacuated and the mercury meniscus is brought to the 50 cc. mark. The manometer is again read. This reading is \( p_0 + c \).

The difference between it and the \( p_0 \) reading is the \( c \) correction. To determine \( c \) within 0.1 mm. one makes several check readings of \( p_0 \) with the chamber empty and also several of \( p_0 + c \), with the 1 cc. of solution in the chamber. Once determined, the \( c \) correction serves for all analyses in which the same chamber is used.

Temperature Correction

If, during the interval between the \( P_S \) and the \( P_{O_2 + N_2} \) or \( P_{N_2} \) measurement, changes exceeding 0.1° from the temperature of the \( P_S \) measurement are noted in the thermometer of the water jacket, the value of \( P_{O_2 + N_2} \) or \( P_{N_2} \) is calculated by Equation 10 or 11 instead of by Equation 4 or 6.

\[
\begin{align*}
\text{(11)} & \quad \text{Corrected } P_{O_2 + N_2} = 0.98 (p_2 - [p_0 + c]) + 1.3 \left( t_0 - t_2 \right) \times \frac{T_4}{T_2} \\
\text{(12)} & \quad \text{Corrected } P_{N_2} = 0.92 (p_4 - p_0) \times \frac{T_2}{T_4}
\end{align*}
\]

\( T_0, T_2, \) and \( T_4 \) = values of absolute temperature at the readings \( p_0, p_2, \) and \( p_4 \); \( t_0 \) and \( t_2 \) = temperature in degrees centigrade at readings \( p_0 \) and \( p_2 \). The values of the ratio, \( T_0 : T_2 \), or \( T_0 : T_4 \), for ordinary temperature changes are given below Equation 1 on p. 513.

In Equation 11 the term, \( 1.3 (t_0 - t_2) \), serves to correct for the vapor pressure change, of about 1.3 mm. per 1°, caused by the temperature change, \( t_0 - t_2 \). Equation 11 covers the temperature correction in an exceptional case, where an intermediate operation (absorption of CO₂) may allow time for a change of temperature between the two readings (\( p_0 \) and \( p_2 \)) on which a single gas measurement (\( P_{O_2 + N_2} \)) depends.

Necessity for Accuracy in Measurement of Volumes of Alkali and Hyposulfite Solutions Added

The accuracy with which the volumes 49 and 46 cc. are defined, at which the pressures of residual gases are measured after absorption of CO₂ and O₂ respectively, is determined by the accuracy
with which the 1 and 3 cc. portions of alkali and hyposulfite solution, respectively, are measured into the chamber. An error of 0.01 cc. in the measurement of either solution would cause an error of 1 part in 5000 in the volume of gas space at which the pressure is measured. With calibrated stop-cock pipettes, however, it is simple to make the deliveries of solution into the chamber with errors less than 0.01 cc.

**TABLE I**

**Manometric Analysis of Gas Mixtures for Carbon Dioxide, Oxygen, and Nitrogen by Simple Absorption**

Pressure measurements at 50 cc. volume

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Manometric analysis by Method A with approximately 35 cc. samples</th>
<th>Haldane analysis, with approximately 10 cc. samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>O₂</td>
</tr>
<tr>
<td></td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td>1</td>
<td>5.59</td>
<td>19.68</td>
</tr>
<tr>
<td></td>
<td>5.53</td>
<td>19.75</td>
</tr>
<tr>
<td></td>
<td>5.49</td>
<td>19.70</td>
</tr>
<tr>
<td></td>
<td>5.39</td>
<td>19.66</td>
</tr>
<tr>
<td></td>
<td>5.61</td>
<td>19.74</td>
</tr>
<tr>
<td>2</td>
<td>10.36</td>
<td>10.45</td>
</tr>
<tr>
<td></td>
<td>19.46</td>
<td>73.88</td>
</tr>
<tr>
<td></td>
<td>6.70</td>
<td>6.71</td>
</tr>
<tr>
<td>3</td>
<td>6.66</td>
<td>19.38</td>
</tr>
<tr>
<td></td>
<td>73.82</td>
<td>6.70</td>
</tr>
<tr>
<td></td>
<td>4.01</td>
<td>6.00</td>
</tr>
<tr>
<td>4</td>
<td>3.98</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>3.88</td>
<td>19.96</td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td>70.07</td>
</tr>
</tbody>
</table>

Similar accuracy in the calibration of the exact total gas volume held above the 50 cc. mark is not necessary. Any error in this calibration will have so nearly a proportional effect on pressure measurements at 49 and 46 cc., that an error of 0.1 cc. in the 50 cc. calibration is required to affect oxygen results by 1 part in 5000.

Table I shows results obtained with the technique outlined above
I. Manometric CO₂ and O₂ by Absorption

compared with those yielded by the standard Haldane (1912) method for air analysis.

METHOD B. NITROGEN IN AIR, OR IN MIXTURES OF CO₂, O₂, AND N₂ WITH OVER 10 PER CENT OF N₂

In some cases, as in the lung volume determinations by the nitrogen dilution method used by Lundsgaard and Van Slyke

| TABLE II |

**Determination of Nitrogen in Atmospheric Air and in Air Diluted with Oxygen. Simple Absorption of Carbon Dioxide and Oxygen by Method B**

Pressure measurements at 50 cc. volume

| Sample No. | p₀, Chamber empty | p₁, Sample in chamber | Temperature at pₛ, mm. | pₛ, Na₂S₂O₄ in chamber | Temperature at pₛ, mm. | Calculations |
|------------|-------------------|-----------------------|------------------------|------------------------|------------------------|----------------
|            | mm.               | mm.                  | °C.                    | mm.                    | °C.                    | pₛ = p₁ - p₀ |
| 1          | 89.5              | 609.7                | 26.5                   | 526.0                  | 26.7                   | 520.2        |
| 2          | 90.6              | 617.2                | 27.2                   | 533.1                  | 27.4                   | 526.6        |
| 3          | 88.6              | 617.2                | 26.4                   | 532.6                  | 26.6                   | 528.4        |
| 4          | 87.0              | 624.0                | 24.5                   | 538.4                  | 24.7                   | 537.0        |
| 5          | 85.7              | 617.0                | 25.0                   | 531.6                  | 25.2                   | 531.3        |
| 6          | 85.4              | 487.8                | 25.0                   | 239.7                  | 25.2                   | 402.4        |
| 7          | 85.4              | 488.4                | 25.2                   | 240.0                  | 25.4                   | 403.0        |
| 8          | 84.4              | 497.8                | 24.0                   | 205.2                  | 24.2                   | 413.4        |
| 9          | 84.6              | 494.3                | 24.6                   | 204.4                  | 24.9                   | 409.7        |
| 10         | 85.7              | 496.8                | 24.9                   | 233.0                  | 25.1                   | 411.1        |
| 11         | 85.2              | 487.5                | 25.0                   | 229.8                  | 25.2                   | 402.3        |
| 12         | 84.3              | 498.8                | 24.1                   | 201.4                  | 24.3                   | 414.5        |
| 13         | 84.0              | 486.9                | 23.7                   | 197.9                  | 24.0                   | 402.9        |

**Per cent N₂ = 100 * Pₛ / pₛ**

*Atmospheric air. Nitrogen content = 79.04 per cent.*

(1918), the nitrogen content of the air is the only figure desired. In this case the analysis is simplified by absorbing the CO₂ and O₂ together by the alkaline hyposulfite.

The sample is measured as in the preceding analysis.

**Pₛ = p₁ - p₀**
Then 3 cc. of the hyposulfite solution are introduced into the chamber, as above described, and the O₂ and CO₂ are absorbed together by 3 minutes shaking. Reading \( p_2 \) is taken with the mercury meniscus at the 50 cc. mark. The gases are then ejected without loss of solution and reading \( p_3 \) is taken.

All readings being taken with the \textit{mercury} meniscus in the chamber at the 50 cc. mark, the calculations resemble those of the preceding analysis.

\[
P_{N_2} = 0.94 (p_2 - p_1)
\]

Per cent \( N_2 \) = \( 100 \times \frac{P_{N_2}}{P_S} \)

Per cent \((CO_2 + O_2)\) = 100 - per cent \( N_2 \)

Table II indicates the results for \( N_2 \) obtained by the above method. Samples 1 to 5 were those of atmospheric air, which should contain 79.04 per cent of \( N_2 \). Samples 6 to 9 were mixtures of respired air and oxygen analyzed in the course of lung volume determinations.

**METHOD C. SMALL AMOUNTS OF \( N_2 \) OR OTHER INERT GAS PRESENT AS IMPURITY IN \( O_2 \) OR \( CO_2 \)**

In case one wishes to determine traces of \( N_2 \) as impurity in \( CO_2 \) or \( O_2 \), the unabsorbed \( N_2 \) is measured by its pressure at 2 or 0.5 cc. volume. In such analyses it is necessary to use \textit{gas-free} hyposulfite solution \textit{kept over mercury}, because when the oxygen has been absorbed the contents of the chamber are under a high vacuum, and dissolved \( N_2 \) present in the hyposulfite solution would escape into the gas phase in sufficient amount to affect the results. \( P_S \) is measured as \( p_1 - p_0 \), in the manner described above. Then the \( O_2 \) and \( CO_2 \) are absorbed with \textit{air-free} hyposulfite, and \( p_2 \) is read with the unabsorbed gas (\textit{solution meniscus}) at either 2 or 0.5 cc. volume. The gas is then ejected without loss of solution and \( p_3 \) is read, with the chamber free of gas and the solution meniscus at the same mark as for the \( p_2 \) reading.

\[
P_{N_2} = p_s - p_1
\]
Per cent $N_2 = 100 \times \frac{c}{A} \times \frac{P_{N_2}}{P_S}$

$a$ is the small volume, 0.5 or 2 cc., at which $P_{N_2}$ is measured, and $A$ is the total chamber volume, 50 cc. in the usual chamber, at which $P_S$ is measured. For chambers of the ordinary dimensions,

TABLE III

<table>
<thead>
<tr>
<th>Tank No.</th>
<th>Observations</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P_0$</td>
<td>$P_1$</td>
</tr>
<tr>
<td></td>
<td>mm.</td>
<td>mm.</td>
</tr>
<tr>
<td>1</td>
<td>75.6</td>
<td>479.8</td>
</tr>
<tr>
<td>2</td>
<td>76.9</td>
<td>307.4</td>
</tr>
<tr>
<td>3</td>
<td>77.6</td>
<td>485.8</td>
</tr>
<tr>
<td></td>
<td>78.4</td>
<td>482.8</td>
</tr>
<tr>
<td></td>
<td>89.1</td>
<td>487.0</td>
</tr>
<tr>
<td></td>
<td>89.7</td>
<td>485.7</td>
</tr>
</tbody>
</table>

with $A = 50$ cc. and $a = 0.5$ or 2 cc., the calculations simplify to the following.

$$\text{Per cent } N_2 = \frac{P_{N_2}}{P_S} \text{ when } a = 0.5 \text{ cc. or}$$

$$\text{Per cent } N_2 = \frac{4 \times P_{N_2}}{P_S} \text{ when } a = 2 \text{ cc.}$$

1 If, on checking the calibration of $c$ with water, $a'$ the actual volume is found to be different from the supposed gas volume (0.5 or 2 cc.), the observed pressure $P_{N_2}$ must here be corrected by multiplication by $\frac{a'}{a}$. 
The gas thus calculated as "N₂" may be N₂, H₂, or any other gas which does not combine with alkali or hyposulfite.

Table III indicates the results obtained when the contents of three tanks of commercial oxygen gas were thus analyzed for inert impurities.

SUMMARY

Methods are described for the determination of carbon dioxide, oxygen, and nitrogen in gas mixtures by simple absorption in the manometric apparatus originally designed by Van Slyke and Neill for blood gases.

The gas sample and the nitrogen are measured by the pressures they exert at defined volumes. Carbon dioxide and oxygen are measured by successively absorbing them with alkali and hyposulfite solution, respectively, in the chamber of the manometric apparatus, and noting the resultant decreases in pressure.

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MANOMETRIC ANALYSIS OF GAS MIXTURES: I. THE DETERMINATION, BY SIMPLE ABSORPTION, OF CARBON DIOXIDE, OXYGEN, AND NITROGEN IN MIXTURES OF THESE GASES
Donald D. Van Slyke and Julius Sendroy, Jr.


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