ORSAT ANALYSIS

Determination of Hydrogen and Paraffin Hydrocarbons

In the residual gas there still remains hydrogen, paraffins, and nitrogen. The combustible gases will be fractionally oxidized to water and carbon dioxide by passing over heated copper oxide. The remainder is nitrogen.

Combustion of Hydrogen

The combustion tube, filled with nitrogen, is heated to 270-290°C. and the gas is passed back and forth over the heated copper oxide by raising and lowering the leveling bulb until no further contraction results. After allowing to cool, the resulting water vapor is condensed as liquid water. The volume contraction which results is equal to the hydrogen content. In the selective combustion, it is necessary to pay attention to the correct working temperature. With respect to this, a temperature of 290°C. in the interior of the tube is appropriate. However, the gas may be passed too rapidly over the copper oxide, so that the liberated heat of combustion may produce a local sharp temperature rise, and thereby a combustion of paraffins can take place. For the first pass, the velocity should not be permitted to exceed 20 ml./min. After the combustion of hydrogen, it is necessary to determine whether any CO_2 has been formed by passing the gas through caustic potash. The resulting CO_2 is then brought into the calculations according to the nature of the gases under investigation. It follows that if the preceding absorption of CO was incomplete, then the resulting CO_2 formed at 300°C. can be ascribed wholly or in part to the CO. Accordingly this amount should be added to the CO figure. At this temperature, it is also possible appreciably to attack the higher hydrocarbons, C_3H_8, C_4H_{10}, etc., the combustion of which results in increase in volume. On occasion, it is necessary to calculate the true hydrogen contraction through the CO_2 determination.

Combustion of Paraffin Hydrocarbons

The combustion of paraffin hydrocarbons takes place over copper oxide at a temperature above 700°C. For the quantitative combustion of methane, a bright red heat and repeated passes of the gas are necessary. The gas is passed directly into KOH in order to remove the resultant CO_2. Combustion is complete when an additional pass results in no further contraction. After cooling, one has in the difference in volume, a direct measure of methane (or paraffin hydrocarbons). The residue is nitrogen.

Determination of "C Number"

      In order to ascertain the composition of a mixture of 2 paraffins having different numbers of carbon atoms in the molecule, as might be required for the calculation of average molecular weight, it is necessary to determine the "carbon number" ("n value"). For the determination of "carbon number", the CO_2 formed during combustion must be measured. The gas is repeatedly passed over the copper oxide until a constant reading is obtained (or the change in volume is constant). The gas is then passed into the KOH reagent. The difference between the reading before and after is the volume of CO_2 produced. The difference between the volume after hydrogen combustion and the second (red heat) combustion is the amount of saturated hydrocarbons. The volume of CO_2 divided by the volume of saturated hydrocarbons, gives, then, the "C value". This "C value" determination will influence the concurrent and successive following reactions. It is necessary to establish the optimum conditions with pure gases. It is especially important to pay attention that during the combustion, absorption of CO_2 due to dirty capillaries and the like is avoided.

(Accurate) Nitrogen Determination

      For the accurate determination of nitrogen, 400-500 mls. of the gas sample should be burned directly. The gas is passed over the red hot copper oxide directly into the KOH and back into the measuring burette, repeating until the volume is constant. The nitrogen volume found divided by the volume of gas used and multiplied by 100 gives the nitrogen content in %.

Example of Calculations for the Accurate Determination of Nitrogen

      Unit of Measurement: ml., Results reported in Volume Percent,

rounded off to 2 decimal places. If the volume of gas measured for combustion is denoted by V and the volume of nitrogen found by N_2, then it follows that the amount of nitrogen in Vol. % can be calculated by means of the following formula:

$$x = \frac{N_2 \cdot 100}{V} \tag{1}$$

If the analysis of a sample which originally contained no oxygen indicates the presence of this element, then it is a proof that, during the sampling or during storage, air leaked into the sample gas holder. The corresponding true volume of nitrogen is

$$VN_2 = VN_2^1 - VN_2^L \tag{2}$$

in which VN_2^1 is the volume of nitrogen observed after combustion, and VN_2^L is the volume of nitrogen obtained from the air. The corresponding true gas volume used in the combustion is

$$V = V_1 - V_L \tag{3}$$

in which V_1 = volume of the measuring burette, i.e., the gas volume together with air measured out for combustion, and V_L = volume of air equivalent to the amount of oxygen. The corrected quantity of nitrogen contained in the sample is calculated in volume percent according to the following equation:

$$x = \frac{(VN_2^1 - VN_2^L) \; 100}{V_1 - V_L} \tag{4}$$

i.e., the amount of nitrogen in the sample in volume percent is found by subtracting the nitrogen equivalent to the air present from the total nitrogen, multiplying by 100 and dividing by the measured gas volume corrected by subtracting the volume of air corresponding to the oxygen found.

Since V_L and VN_2^L are unknown quantities, it is necessary to calculate them from the amount of oxygen found. For technical purposes it is usually assumed that air contains about 21% oxygen and 79% nitrogen.

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Translator's Note: Two pages on detailed analysis of air and evaluation of numerical constants in equation (4) have been omitted. The explicit equation is given as

$$x = \frac{\left[VN_2^1 - (0.0376 V_{1}O_2)\right] \; 100}{V_1 \; (1 - 0.0476 \; O_2)} \tag{7}$$

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Example of Application

(a) Nitrogen in an oxygen-free sample. Measured gas volume = V_1 = 470.2 ml. After combustion, the volume of nitrogen found is 48.3 ml.

The required volume of nitrogen in the gas mixture is obtained using Equation (1).

$$x = \frac{N_2^1 \cdot 100}{V_1} = \frac{48.3 \cdot 100}{470.2} = 10.27\%$$

(b) Assuming that the sample contains 0.8% O_2, then Equation 7 comes into use.

$$x = \frac{\left[VN_2^1 - 0.0376 \cdot V_1 \cdot O_2\right] \cdot 100}{V_1(1 - 0.0476 \cdot O_2)} = \frac{(48.3 - 0.0376 \cdot 470.2 \cdot 0.8) \cdot 100}{470.2 \; (1 - 0.0476 \cdot 0.8)}$$

$$= 7.55\%$$

The same result will be obtained when the equation for the burette with 470.2 ml.* is employed. The constants 17.69 and 22.39 can be rounded off to 17.7 and 22.4, respectively. These changes have but little influence on the first two decimal places of the results.

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* Specific equations for 3 fixed sample volumes (V_1) were derived in omitted section.

$$x_{470.2} = \frac{\left[V\overset{1}{N}2 - 17.7O_2\right] \cdot 100}{470.2 - 22.4 \cdot O_2} = \frac{\left[48.3 - 17.7 \cdot 0.8\right] \cdot 100}{470.2 - 22.4 \cdot 0.8} = 7.55\%$$

Sources of Error

It is especially important to pay attention that the temperature remain constant for all readings on gases introduced into the measuring burette during the course of analysis. It is expedient to cool the burette and also the combustion tube with running water.

Constant drainage of the confining fluid should be secured in order to make all observations under exactly identical conditions. In practice, for the initial measurement of the gas and after absorption, the level is immediately noted, while on the other hand, after the hydrogen combustion, we find that the confining liquid is allowed to drain completely during the cooling, thus the true contraction is exaggerated. In the CO absorption in β-naphthol, standardization of the level causes a delay, thus a similar error can again occur. It is also important to pay attention that the liquid in the capillaries of the pipettes is brought to the same level before and after the analysis.

It is especially important to take care that the absorbent solutions are not permitted to reach the horizontal capillary (bridge). As an example, the gas in the CO_2 determination may be drawn back and forth through the KOH solution with great speed so that a small drop of alkali may very easily be drawn into the capillary. Therewith exists the possibility that during the combustion of the hydrocarbons the CO_2 formed may be partially absorbed in the capillary and the "C number" determination give an erroneous value. The resulting carbonate can easily be drawn into the measuring burette and come into contact with the confining water or on the introduction of acid confining liquid into the capillary would decompose with evolution of CO_2 and so give another cause for error.

Leaks in connecting tubings or stopcocks are frequent sources of errors in analysis. Before using an Orsat apparatus, it should be tried out and tested for leaks. This may be done very simply as follows: fill the burette with water up to the upper capillary, then the exit stopcock is closed and the leveling bulb is placed as low as possible. Leaks may then be detected by dropping of the water in the burette.

Incomplete gas absorption may be traced to insufficient contact between gas and absorbent and this likewise may produce error.

It is also a possibility that saturation of the gases with vapors of the absorption reagents may be noticed during manipulation. For example SO_3, etc., In these cases the absorption must be followed with an after treatment of the gas with alkali (SO_3) or acid (NH_3).