

~~For use in the lab~~

BURRELL
MANUAL
FOR
GAS ANALYSTS

SEVENTH EDITION

Orsat apparatus

BURRELL
MANUAL
FOR
GAS ANALYSTS

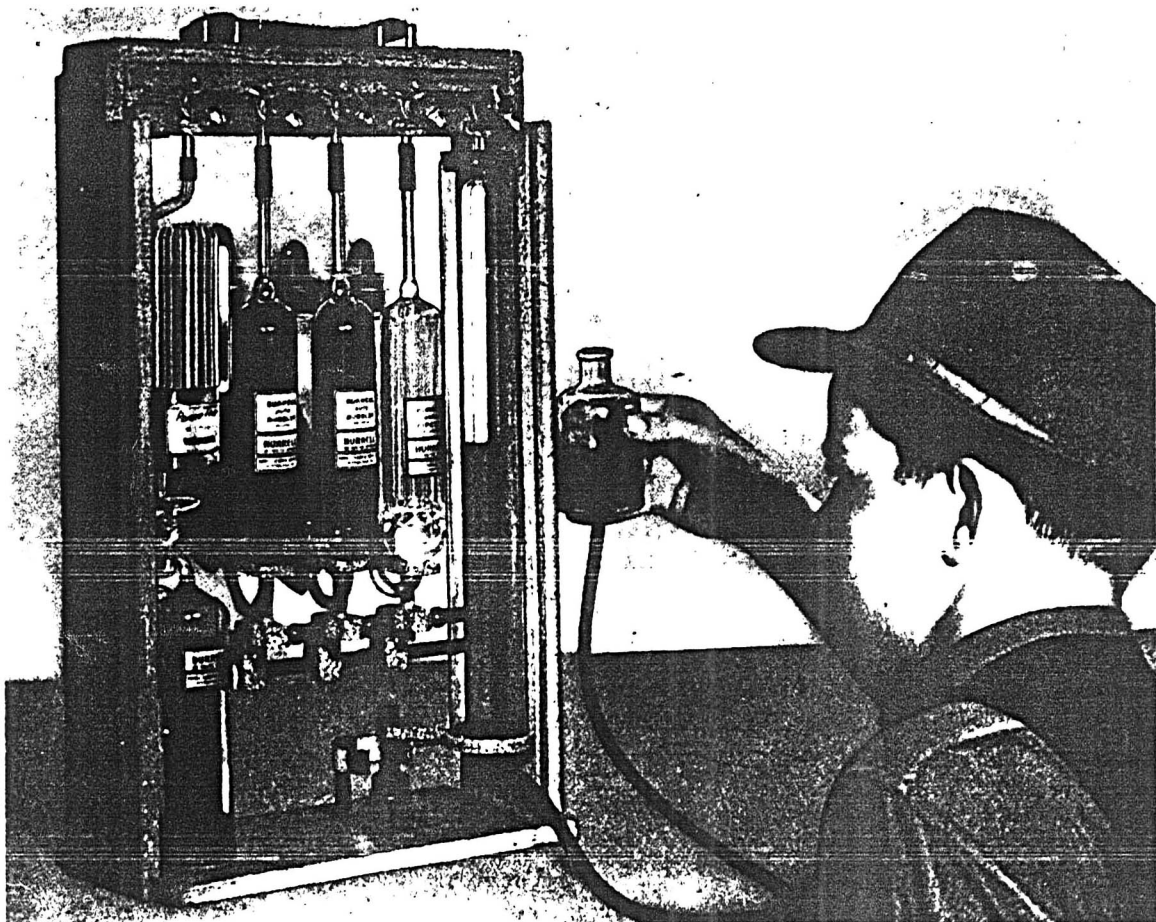
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G A S A N A L Y S I S

The industrial gas analyst is principally concerned with the analysis of gaseous fuels and products of combustion thereof by the volumetric method involving oxidation or selective absorption in liquid reagents of the various components.

Other methods of gas analysis include fractional adsorption, absorption and subsequent titration, gravimetric determinations, fractional distillation, fractional adsorption, thermal conductivity measurements, colorimetric methods, and those depending upon other optical or physical properties.

The Burrell Manual for Gas Analysts on the following pages is devoted to the volumetric method. It attempts to describe technique and apparatus in sufficient detail to provide the inexperienced analyst with adequate working knowledge. For additional technical information on gas analysis-a bibliography is shown on page 43.



CHAPTER 1

CHARACTERISTICS OF SOME
COMMERCIAL GASES

NATURAL GAS

Natural gas is composed principally of paraffin hydrocarbons with small amounts of nitrogen and carbon dioxide. Methane is almost always the predominating hydrocarbon with considerable ethane and smaller amounts of propane, butane, pentane, and higher homologs. Carbon dioxide is present as a major component in some natural gases but normally occurs in quantities under 1 per cent.

Propane is usually scrubbed from the gas to make so-called liquefied petroleum gas. Likewise, butanes and higher are removed to produce natural gasoline for blending and alkalation purposes.

The usual analysis of natural gas includes the determination of carbon dioxide, oxygen, hydrocarbons, and nitrogen. The hydrocarbons are usually reported as methane and ethane or total paraffins, but a further separation of the hydrocarbons can be made by absorbing the propane and higher in lusorbent before the oxidation of the residual gas. For the purposes of heating value calculations a b.t.u. value of 2519 is assigned to the propane and higher fraction.

Hydrogen sulfide, if present, should be removed before the sample is drawn into the burette (see "Coke Oven Gas") and must, therefore, be determined in a separate sample by other methods. The Tutwiler Apparatus (see page 41) is sufficiently accurate for practical purposes.

Suggested Apparatus for Analysis

Laboratory Utility Models LP
Portable Junior Models 510 and 610

PRODUCER GAS

This gas is produced by the partial combustion of coal or coke and the decomposition of water by forcing air and steam through hot coke. The reaction products, comprising a high per cent of nitrogen, plus carbon dioxide, carbon monoxide, hydrogen and small amounts of methane, and illuminants, vary with the type of fuel. The presence of significant amounts of oxygen usually indicates air contamination of the sample. Hydrogen sulfide is a possible component but must be determined in a separate sample by other methods.

Suggested Apparatus for Analysis

Laboratory Precision Models D and VD
Laboratory Bureau of Mines Model VL
Portable Senior Models 310 and 410

BLAST FURNACE GAS

In the reduction of iron ore, coke is fired in contact with the charged ore and limestone mixture by means of a blast of preheated air. The gaseous product is largely nitrogen plus carbon dioxide and carbon monoxide. A little hydrogen is usually present and sometimes traces of methane. Oxygen is not a normal component.

Suggested Apparatus for Analysis

Laboratory Precision Models D and VD
Laboratory Bureau of Mines Model VL
Portable Senior Models 310 and 410

COAL GAS

When coal contained in refractory retorts is destructively distilled in the absence of oxygen, the composition of the gaseous product varies with the type of coal, retort, temperature, and other details of the process. The usual analysis is made for carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen.

Coal gas and coke oven gas are made in essentially the same manner, except that in the latter case the charge size is larger and the manufacturing process is adjusted to increase the by-product yield and to produce metallurgical quality coke.

Suggested Apparatus for Analysis

Laboratory Premier Model VB
Laboratory DeLuxe Models J and VJ
Portable Master Models 111 and 211

COKE OVEN GAS

Coke oven gas is produced from the distillation of coal in the production of metallurgical coke. The raw coke oven gas also carries ammonia, benzene and its homologs, carbon bisulfide, hydrogen sulfide, and hydrocyanic acid. In the scrubbing process to which the raw gas is subjected, the ammonia, carbon bisulfide, most of the benzene homologs and part of the hydrogen sulfide are removed, leaving carbon dioxide, illuminants, carbon monoxide, hydrogen, methane, ethane, nitrogen, and small amounts of hydrogen sulfide as the significant components for analysis.

Hydrogen sulfide is highly soluble in water, will react with mercury, and will be absorbed in the potassium hydroxide solution along with carbon dioxide. Therefore, before a sample is taken into the burette, this component is removed by passing the gas sample through a solution prepared in the following way:

Dissolve 2½ grams of arsenious acid in 15 ml. of hydrochloric acid and add to a solution containing 20 grams of sodium chloride dissolved in 210 ml. of water.

Suggested Apparatus for Analysis

Laboratory Premier Model VB
 Laboratory De Luxe Models J and VJ
 Portable Master Models 111 and 211

BLUE OR WATER GAS

Blue or water gas is produced by a cyclic process. Air is passed through a bed of ignited coal or coke until the temperature is sufficiently high. The air supply is then shut off and steam substituted. Ordinarily only the gases evolved when the steam is introduced are collected and it is obvious the products of combustion will vary with the cycle and kind of fuel. The process produces a gas of low b.t.u. value. Usually, the analysis is made for carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen.

Suggested Apparatus for Analysis

Laboratory Precision Models D and VD
 Laboratory Bureau of Mines Model VL
 Portable Senior Models 310 and 410

CARBURETTED WATER GAS

The b.t.u. value of water gas is commonly increased by fortifying the gas with products of the thermal decomposition of oil. This process called carburetting increases the hydrocarbons and decreases the hydrogen and carbon monoxide.

Suggested Apparatus for Analysis

Laboratory De Luxe Models J and VJ
 Laboratory Precision Models D and VD
 Laboratory Bureau of Mines Model VL
 Portable Master Models 111 and 211

CYLINDER GASES

Compressed cylinder oxygen is either produced by the fractional distillation of oxygen from liquid air or by the electrolytic decomposition of water.

Oxygen produced from liquid air may contain 1 per cent or less of nitrogen as an impurity, and electrolytic oxygen may contain small amounts of hydrogen.

Cylinder hydrogen is usually produced by the electrolytic process and may contain small amounts of oxygen as an impurity.

Suggested Apparatus for Analysis

Cylinder Oxygen from Liquid Air
 Portable Purity Tester Model VG
Cylinder Oxygen—Electrolytic
 Portable Purity Tester Model VO
Cylinder Hydrogen
 Portable Purity Tester Model VE
 Portable Purity Tester Model VO
Cylinder Oxygen and Hydrogen
 Portable Purity Tester Model VP

MINE GASES

The air in coal mines under normal operating conditions is principally composed of carbon dioxide, oxygen, methane, and nitrogen.

Methane is the component of paramount interest as its explosive properties present an ever-present hazard. The inflammable limits of methane in air are from 5.3 to 14 per cent by volume. Atmospheres containing methane within this range but with the oxygen content diminished to 12 per cent or less are non-inflammable.

Mine air may be contaminated with carbon monoxide and hydrogen produced by blasting operations, mine fires, and explosions. The conduct of recovery operations during mine fires and after mine explosions is governed largely by the composition of the mine atmosphere in the affected areas as determined by gas analysis.

In the case of metal mines with sulfide ores, sulfur dioxide may be a constituent of the mine atmosphere. In some cases the atmosphere of metal mines contain high concentrations of carbon dioxide and nitrogen.

Suggested Apparatus for Analysis

Laboratory Haldane Model VC
 Portable Junior Models 510 and 610

FLUE GAS

A knowledge of the components of the flue or stack gas is essential in establishing firing conditions that will yield the most heat with the least fuel consumption. The gas analyzer is, therefore, a tool

TABLE 1
Fuel Gases
 Typical Composition in Per Cent by Volume

Kind of Gas	Carbon Dioxide	Illuminants	Oxygen	Carbon Monoxide	Hydrogen	Methane	Ethane	Nitrogen
Natural	0 to 1					75 to 96	4 to 20	0 to 8
Producer	4 to 8		0 to 0.6	22 to 28	10 to 18	0.5 to 3		50 to 60
Blast Furnace	8 to 15			25 to 30	1 to 3			58 to 60
Coal	1 to 3	2 to 7	0 to 0.8	7 to 11	46 to 55	24 to 34		2 to 11
Coke Oven	1 to 3	3 to 4	0.2 to 0.8	5 to 7	45 to 58	28 to 34		3 to 8
Blue or Water	3 to 6		0.5 to 1	36 to 43	47 to 51	0.5 to 2		1 to 8
Carburetted Water	1 to 4	7 to 13	0.5 to 1	30 to 35	34 to 41	10 to 16		2 to 8
Reformed Natural	1 to 2		Trace	12 to 25	45 to 50	20 to 35		1 to 4
Oil	1 to 5	2 to 4	0 to 0.5	7 to 13	48 to 60	25 to 27		2 to 4

of major importance in the control of combustion, whether in the large steam plant or in adjusting the burners in small household oil and gas fired units.

Waste gases will vary in composition with the type of fuel and the furnace and may include carbon dioxide, oxygen, carbon monoxide, hydrogen, water vapor, hydrocarbons, sulfur compounds and dust.

Usually, the analysis will include the determination of carbon dioxide, oxygen, and carbon monoxide. Depending upon the type of fuel, the carbon dioxide is normally between 8-14 per cent, oxygen 8-12 per cent and the carbon monoxide $\frac{1}{2}$ per cent or under.

Apparatus with three absorption pipettes for car-

bon dioxide, oxygen, and carbon monoxide are popular flue gas models.

Since the advent of the Burrell Catalytic Method for combustible components such as hydrogen and hydrocarbons, apparatus equipped with a catalytic unit is finding increasing use for the complete analysis of flue gases.

At times only one component, carbon dioxide, is determined in a single pipette model, or two components with the two-pipette models.

Suggested Apparatus for Analysis
 Portable Junior Models 510 and 610
 Portable Flue Gas Models
 Industro Model B

TABLE 2

*Composition of Typical Controlled Atmospheres

No.	Description	N ₂	CO	CO ₂	H ₂	CH ₄	O ₂
1	Completely Burned Fuel	89.0	0.5	10.0	0.5	0.0	0.0
2	Partially Cracked Fuel (self-propelled)	69.0	10.0	5.0	15.0	1.0	0.0
3	Completely Reacted Fuel (auxiliary heat needed)	41.7	19.0	0.0	38.0	1.3	0.0
4	No. 1 (above) Scrubbed of CO ₂ and H ₂ O	98.0	1.0	0.0	1.0	0.0	0.0
5	No. 2 (above) Scrubbed of CO ₂ and H ₂ O	72.0	11.0	0.0	16.0	1.0	0.0
6	Dissociated Ammonia	25.0	0.0	0.0	75.0	0.0	0.0
7	No. 6 (above) Completely Burned	99.0	0.0	0.0	1.0	0.0	0.0
8	No. 6 (above) Partially Burned	80.0	0.0	0.0	20.0	0.0	0.0

*C. E. Peck, Westinghouse Electric & Manufacturing Company, Metal Progress, June, 1942.

FURNACE ATMOSPHERES

Controlled atmospheres are modern tools of the chemist and metallurgist in achieving various effects in the treatment of metals, ceramics, finishes, and other materials.

Such atmospheres are produced by mixing commercial gases, partial and complete combustion of gaseous fuels, dissociation of ammonia, combustion of carbon in atmospheric air, cracking, or by any other method which will produce a gas of the required composition. Components of furnace atmospheres may include carbon dioxide, oxygen, carbon monoxide, hydrogen, hydrocarbons, nitrogen, water vapor, and sulfur dioxide.

Gas analysis by manual methods offers the means whereby the percentage composition of such mixtures may be established. Partial analysis including only the more readily determined components such as carbon dioxide, oxygen, and carbon monoxide serves in some instances; but complete analysis including also hydrogen and hydrocarbons, is now possible without the complexities that formerly attended the determination of combustible components in the hands of the average analyst.

Apparatus with three absorption pipettes and a catalytic assembly permit the determination of carbon dioxide, oxygen, and carbon monoxide by absorption; and hydrogen and hydrocarbons by catalytic oxidation. This method for the combustible components removes the uncertainties and the time-

consuming routine of the former slow combustion method.

Suggested Apparatus for Analysis
 Laboratory Precision Models D and VD
 Portable Junior Models 510 and 610
 Portable Flue Gas Models
 Industro Model C

LIQUEFIED PETROLEUM GASES

Commercial grades of liquefied petroleum gases are either propane or butane fractionated from natural or refinery gas.

If obtained from natural gas, propane contains small amounts of ethane and butane; but if obtained from refinery gas, substantial amounts of propene and butenes are also present.

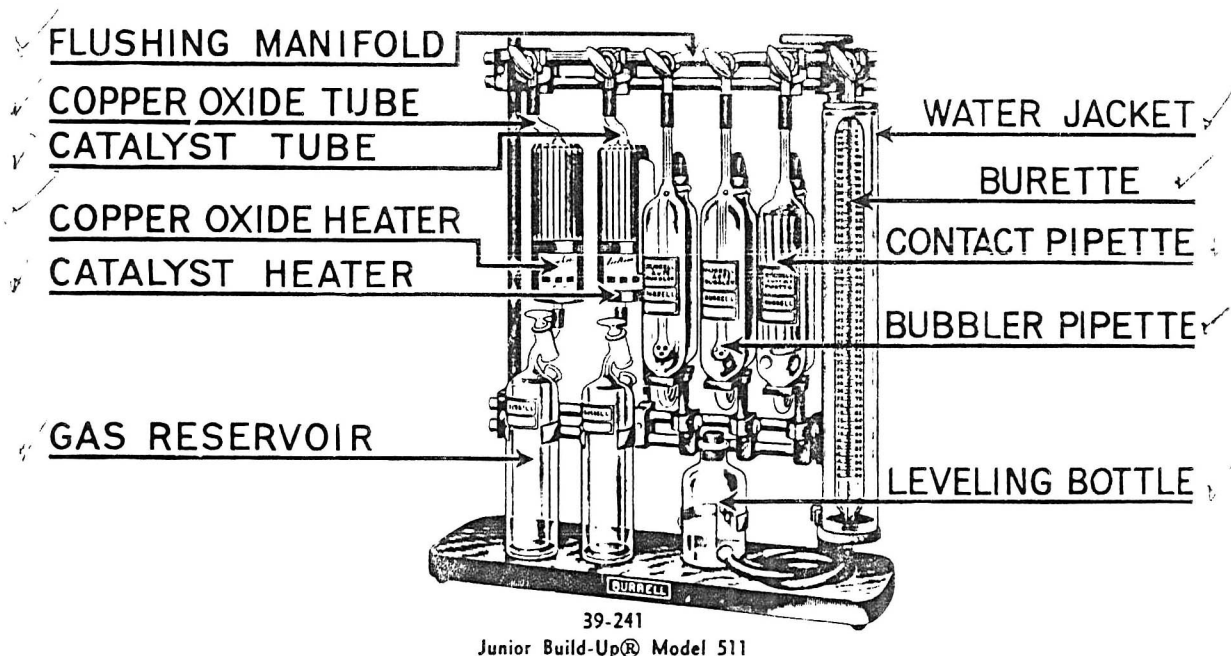
Butane from natural gas is a mixture of normal and isobutanes with small amounts of propane and pentanes. Refinery butane is predominantly butanes and butenes with a little propane and propene.

OTHER GASES

Mixtures may contain, in addition to those previously listed, such ingredients as dust, tar vapor, hydrogen sulfide, cyanogen, hydrocyanic acid, ammonia, water vapor, and sulfur dioxide.

More often than not these are not present in interfering amounts, but if so must be determined in separate samples other than those taken for volumetric gas analysis. In some instances they must be removed from the sample before analysis, as with hydrogen sulfide.

CHAPTER II
PRINCIPLES OF GAS ANALYSIS



In the analysis of a gaseous mixture by absorption and oxidation methods, the components of the mixture are determined by a systematic measurement of changes in gas volume. These volume changes are effected by the successive removal of certain components from the mixture by treatment with suitable liquid absorbing reagents and by subjecting the combustible components to oxidation.

Certain liquids are specific as shown in Table 3 for the chemical absorption of certain gases from a mixture. Other gases for which there are no suitable selective absorption reagents are oxidized. The products of oxidation are measured and the data utilized in calculations which yield the volume of gas burned. In the latter category are hydrogen and hydrocarbons.

The essentials of a gas analysis apparatus are:

1. Burette—a graduated glass tube for measuring gas volumes.
2. Absorption Pipettes—the vessels containing the selective absorption reagents.
3. Oxidation Assemblies—for the oxidation of combustible components.
4. Manifold—a closed path for the gas between the burette, the pipettes, and oxidation assemblies.

ABSORPTION

Starting with a measured volume of the gas mixture in the burette and proceeding in a prescribed manner, the mixture is passed by way of the interconnecting manifold into one absorption pipette

after the other in the proper order with volume reading being taken before and after each treatment. The difference in volume due to absorption represents the amount of the particular component present in the mixture, and the results are expressed in per cent by volume.

OXIDATION

Other components occurring with frequency in gas mixtures include hydrogen and hydrocarbons. Oxidation methods are applied to these because of the absence of suitable absorbing reagents. Carbon monoxide can be determined by oxidation as well as by absorption and is included in the discussion of the combustible group.

Assuming the presence of hydrocarbons, hydrogen, and carbon monoxide, the procedure is to first subject the residual gas after absorption to fractional oxidation over copper oxide. Hydrogen is oxidized to water and carbon monoxide to carbon dioxide. Hydrocarbons remain unaffected and are subjected to catalytic oxidation or slow combustion with added oxygen.

Oxidation over copper oxide is used only for hydrogen and carbon monoxide, but all four gases can be oxidized catalytically or by slow combustion. However, only certain combinations when oxidized catalytically or by slow combustion will yield the necessary data for calculating the volume percentages. Therefore, when more combustibles are present than can be handled catalytically or by slow combustion, the copper oxide method must be called upon to effect complete separation.

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TABLE 3
Recommended Reagents and Pipettes

Gas	Symbol	†Absorbing Reagent	Pipette
Carbon dioxide	CO ₂	Disorbent [Ⓐ]	Burrell Contact /
•Illuminants	Ill	Lusorbent [Ⓐ]	Burrell Auto-Bubbler [Ⓐ]
•Illuminants	Ill	Fuming Sulfuric Acid	Burrell Auto-Bubbler
Oxygen	O ₂	Oxsorbent [Ⓓ]	Burrell Auto-Bubbler
Oxygen	O ₂	Alkaline Pyrogallol	Burrell Contact /
Carbon Monoxide	CO	Cosorbent [Ⓓ]	Burrell Auto-Bubbler
Carbon Monoxide	CO	Cuprous Chloride	Burrell Auto-Bubbler
Total Olefins	—	Sorbent—A [Ⓐ]	Burrell Contact
Isobutene	C ₄ H ₈	Sorbent—B [Ⓐ]	Burrell Contact
Propene and Butenes	—	Sorbent—C [Ⓐ]	Burrell Contact
Acetylene	C ₂ H ₂	Sorbent—D [Ⓐ]	Burrell Contact

*Illuminants include olefins such as ethylene, propene and butene; acetylenes; and aromatic hydro-carbons such as benzene and its homologs.

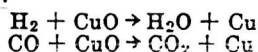
†See page 12.

Combinations which may be determined at the same time catalytically or by slow combustion are as follows:

- Methane and ethane
- Methane and hydrogen
- Carbon monoxide and hydrogen
- Carbon monoxide and methane
- Carbon monoxide, hydrogen and methane

OXIDATION OF HYDROGEN AND CARBON MONOXIDE OVER COPPER OXIDE

Fractional oxidation, whereby some of the components of a gas mixture are oxidized and others unaffected, is applied to the determination of hydrogen and carbon monoxide. Hydrogen and carbon monoxide may be determined separately or together by copper oxide oxidation. If the combination of combustible components present prevents the use of the catalytic oxidation or slow combustion method for hydrogen, then copper oxide oxidation is recommended for both hydrogen and carbon monoxide. Of the several methods which include the use of palladium asbestos, palladium sponge or copper oxide, the latter is most commonly used. Copper oxide contained in a glass tube and heated to 290-300° C. by means of an electric furnace gives up its oxygen, converting the hydrogen to water and the carbon monoxide to carbon dioxide. The reactions are as follows:



The presence of hydrogen will cause a contraction in volume of the sample which is theoretically equal to the amount of hydrogen present.

The carbon dioxide formed by the oxidation of carbon monoxide is determined by absorption in potassium hydroxide solution. Theoretically, the amount of carbon dioxide formed is equal to the amount of carbon monoxide in the sample, but a significant error will occur if the sample contains more than 30 per cent carbon monoxide (see page 12).

The temperature of the copper oxide should not be less than 275° C. as the reaction will be too slow, or above 300° C. else hydrocarbons may be oxidized.

When hydrogen is absent or when it can be deter-

mined by catalytic oxidation or by slow combustion, carbon monoxide may be determined by absorption. The absorption method for carbon monoxide is faster than copper oxide combustion, but if a variety of gas mixtures are to be handled, it is desirable to have the apparatus equipped for both methods.

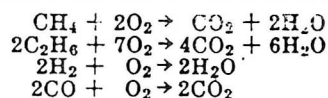
The copper oxide may be partially reoxidized in the tube by periodically passing oxygen through the tube at the temperature of the heater. Complete reoxidation requires a temperature higher than is attained by the heater.

CATALYTIC OXIDATION

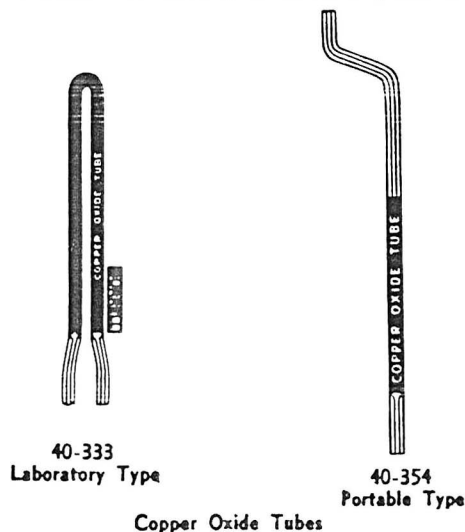
Hydrocarbons as well as hydrogen and carbon monoxide may be determined by oxidation over a catalyst in the presence of oxygen.

The method is employed chiefly for methane and its homologs, and hydrogen—infrequently for carbon monoxide.

The reactions involved are as follows:



The paraffin hydrocarbons are usually limited to methane and ethane. These usually predominate and are ordinarily calculated in terms of methane only, methane and ethane, or as total paraffins.



ⒹTrademark Registered—U.S. Patent Office.

ⒶTrademark.

Three factors which may be measured (see Table 4) and which result from the oxidation of combustible components are:

- r = Contraction in volume
- s = Carbon dioxide produced
- t = Oxygen consumed

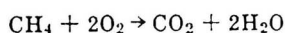
The contraction in volume is measured directly and is the difference in volume of the sample before and after oxidation. The quantity of carbon dioxide produced is determined by passing the sample into potassium hydroxide solution after oxidation. The oxygen consumed is the difference between the amount of oxygen in the sample before and after oxidation.

If the values of r, s, and t are known, the following components may be determined singly or in certain combinations as described in this chapter.

- y = carbon monoxide (CO)
- z = hydrogen (H₂)
- w = methane (CH₄)
- x = ethane (C₂H₆)
- v = propane (C₃H₈)
- u = butane (C₄H₁₀)

If the mixture contains only one combustible component and the identity of this component is known, only one of the above data (r, s, or t) is required as a basis for calculating the volume percentage.

For example, assume the component is methane, then the reaction due to oxidation is



One volume of methane requires two volumes of oxygen producing one volume of carbon dioxide. Therefore, the contraction in volume due to oxidation is two volumes. The water vapor condenses and is of negligible volume. The volume of methane in the sample is equal to the amount of carbon dioxide produced, or one-half the amount of the contraction. Both of these factors are usually used in the calculation and the formula thus becomes

$$w = \frac{r + s}{3}$$

$$\text{CH}_4 = \frac{(\text{Contraction} + \text{CO}_2 \text{ Produced})}{3}$$

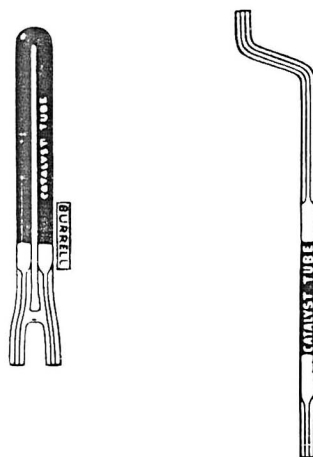
If the mixture contains two combustibles of known identity, two of the data are needed, the contrac-

TABLE 4

Volume per Volume Changes Produced by Catalytic Oxidation

One Volume of Gas Burned	Volume*		
	Contraction (r)	Carbon Dioxide Produced (s)	Oxygen Consumed (t)
Methane (CH ₄)	2.0	1.0	2.0
Ethane (C ₂ H ₆)	2.5	2.0	3.5
Carbon Monoxide (CO)	0.5	1.0	0.5
Hydrogen (H ₂)	1.5	0.0	0.5

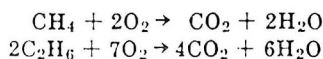
*The term "volume" means any unit of volume as cubic centimeter, cubic inch, etc. Formulas developed from the oxidation calculations are given on pages 34 to 36.



40-337 Laboratory Type
40-358 Portable Type
Catalyst Tubes

tion in volume and the amount of carbon dioxide produced.

Considering methane and ethane as the combustibles, the reactions are



Two volumes of ethane and seven volumes of oxygen produce four volumes of carbon dioxide — a contraction of five volumes.

One volume of methane and two volumes of oxygen produce one volume of carbon dioxide — a contraction of two volumes.

$$r = 2.5x + 2w$$

$$\text{Total contraction} = 2.5 (\text{Vol. of C}_2\text{H}_6) + 2 (\text{Vol. of CH}_4)$$

$$s = 2x + w$$

$$\text{CO}_2 \text{ produced} = 2 (\text{Vol. of C}_2\text{H}_6) + (\text{Vol. of CH}_4)$$

Solving these equations

$$w = \frac{s - 2x}{1}$$

$$\text{CH}_4 = \text{CO}_2 \text{ produced} - 2 (\text{Volume of C}_2\text{H}_6)$$

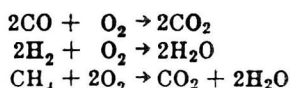
$$x = \frac{4s - 2r}{3}$$

$$\text{C}_2\text{H}_6 = \frac{4 (\text{CO}_2 \text{ produced}) - 2 (\text{Contraction})}{3}$$

When three components are burned at the same time, all three of the data are required including the amount of oxygen consumed. Usually, this so-called triple oxidation is employed only when hydrogen, carbon monoxide, and methane are present. More often than not, in such a case hydrogen and carbon monoxide are determined by oxidation over copper oxide, and methane separately by catalytic oxidation or by slow combustion.

The triple oxidation is limited to combinations which do not include three components of a homologous series; for instance, a combination of hydrogen, methane, and ethane could not be separated since hydrogen is considered the first member of the paraffin series.

Assuming carbon monoxide, hydrogen, and methane as the combustibles, the reactions are



$$\begin{aligned} r &= 0.5y + 1.5z + 2w \\ \text{Total Contraction} &= 0.5\text{CO} + 1.5\text{H}_2 + 2\text{CH}_4 \end{aligned}$$

$$\begin{aligned} s &= y + w \\ \text{Carbon dioxide produced} &= \text{CO} + \text{CH}_4 \end{aligned}$$

$$\begin{aligned} t &= 0.5y + 0.5z + 2w \\ \text{Oxygen consumed} &= 0.5\text{CO} + 0.5\text{H}_2 + 2\text{CH}_4 \end{aligned}$$

By solving these equations

$$z = \frac{r}{H_2} = \frac{\text{Contraction in volume} - \text{oxygen consumed}}{t}$$

$$w = \frac{s}{\text{CH}_4} = \frac{\text{CO}_2 \text{ produced} - \text{volume-carbon monoxide}}{y}$$

$$y = \frac{r}{3} + \frac{4s}{3} - t$$

$$\text{CO} = \frac{\text{Contraction} + 4 (\text{CO}_2 \text{ produced})}{3} - \text{oxygen consumed}$$

SLOW COMBUSTION

The combustion of methane, ethane, carbon monoxide, and hydrogen by slow combustion differs from catalytic oxidation only in the apparatus required and in the operating technique. Until the advent of the Burrell Catalytic Method, slow combustion over a hot platinum wire was generally used.

Briefly, the slow combustion method requires that the sample shall be slowly passed from the burette over a hot platinum ignition wire located inside the slow combustion pipette close to the point where the gas enters. An excess of oxygen should be contained in the pipette. The gas mixes with the oxygen as it enters the pipette and the mixture burns at contact with the hot wire.

The reactions and calculations attending slow combustion are the same as for catalytic oxidation.

COMBUSTION ANALYSIS BY THE EXPLOSION METHOD

The fastest method of burning gases is by explosion. The gas mixture containing the combustible components is purposely made explosive by the addition of oxygen, and is exploded in the pipette by jumping an electric spark between platinum electrodes. This method is convenient for hydrogen, or for hydrogen and small percentages of hydrocarbons, but it is not recommended for mixtures containing principally hydrocarbons, nor for carbon monoxide. The chemical reactions involved are the same as those attending catalytic oxidation or slow combustion.

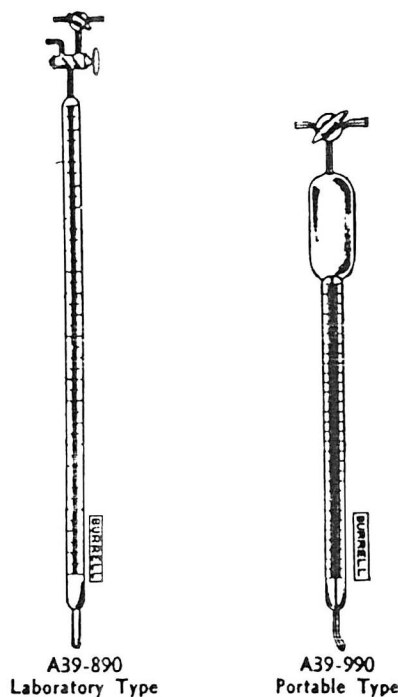
NITROGEN

Nitrogen (N₂), an inert gas not possible to separate by ordinary means, is determined by difference. The sum of the percentages of all other components is subtracted from 100 to get the percentage of nitrogen.

MEASUREMENT OF GAS VOLUMES WITH THE BURETTE

Essentially, the burette is a graduated glass tube, the upper end of which communicates with the manifold, and thence with the various pipettes. The lower end of the burette is usually fitted with a length of rubber tubing, the other end of which is attached to the leveling bulb or bottle. A confining liquid, such as mercury or aqueous salt solution, occupies the leveling bulb, rubber tubing, and that portion of the burette which is not filled with the gas sample. Thus, the leveling bulb, connecting tubing, and the burette form a U in one side of which the gas sample is held at a pressure dependent upon the relative positions of the confining liquid in the burette and leveling bulb.

Burettes designed for aqueous salt solution as the confining liquid usually have a blue glass line lengthwise in the rear. The liquid magnifies the blue line below the meniscus and the reading is made where the magnified and unmagnified lines meet (see Fig. 1).



A39-890 Laboratory Type A39-990 Portable Type

Gas Burettes

When mercury is used as the confining liquid, the reading is made at the top of the rounded meniscus (see Fig. 2).

Volume measurements in gas analysis are commonly made at constant pressure, usually atmospheric, eliminating the necessity for corrections. The burette is surrounded by a water jacket which serves to maintain the gas sample at constant temperature so that temperature corrections are also unnecessary. Usually, the temperature of the water in the jacket will not change significantly during the course of an analysis. The temperature of the gas sample should be as close as possible to that of the water before the sample is brought into the burette. For example, in sampling flue gas directly into the apparatus, provision should be made, if necessary, for cooling the gas.

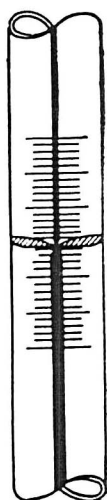


Fig. 1—Meniscus of Aqueous Salt Solution

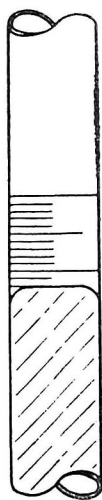


Fig. 2—Meniscus of Mercury

With aqueous salt solution as the confining liquid, atmospheric pressure is established in the burette by holding the leveling bottle alongside the burette at such a height that the solution in the burette and leveling bottle are at same level (see Fig. 3).

With mercury, a device called a compensator is employed to insure that all readings are made at the same pressure. This consists of a manometer, or U-tube, one leg of which is connected to the burette and the other end terminating in a closed end glass tube of about the same volume as the burette and enclosed in the water jacket beside the burette (see Fig. 4). A stopcock opening to the atmosphere is located in one leg of the compensator manometer. The manometer ordinarily contains mercury, although more sensitivity may be obtained with a mixture of half water and half glycerine.

By means of this device, the measurement of gas volume in the burette is made by balancing the pressure of the gas in the burette against the pressure

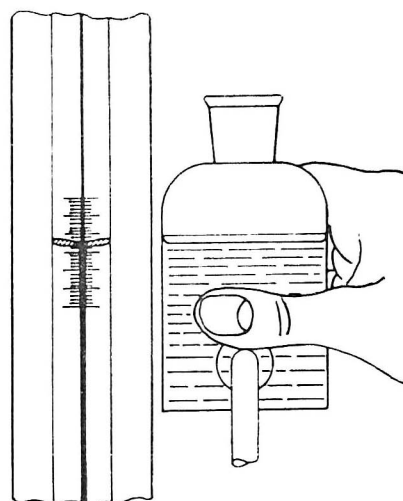


Fig. 3—Establishing Atmospheric Pressure using Aqueous Salt Solution

of the gas in the closed tube, or in other words, against a fixed volume of gas saturated with water vapor and for practical purposes at a constant temperature. Any change in the temperature of the water jacket will affect the gas in the burette and in the closed tube equally, thus compensating for any changes in temperature.

The balancing or compensating operation is performed before making each reading of gas volume in the burette. This is accomplished by first adjusting the leveling bulb so that the mercury levels in the bulb and burette are about equal, then turning the stopcock at the top of the burette so that the burette communicates with the U-tube of the compensator manometer. The height of the liquid in the compensator manometer is then adjusted by raising or lowering the leveling bulb slightly until the liquid in one leg of the U-tube coincides with a fixed reference mark.

The final close adjustment may be made by manipulating the leveling ring screw to raise or lower the bulb slightly.

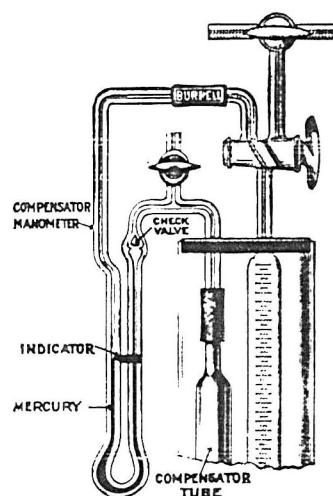


Fig. 4—Compensator Assembly

$$\frac{C}{5} = \frac{F-32}{9}$$

CORRECTION OF GAS VOLUMES TO STANDARD CONDITIONS

In ordinary analysis where the results are reported in per cent by volume only relative values are sought, and if temperature, pressure, and water vapor content of the gas are held constant during an analysis, the results obtained are comparable to the results of any other gas analysis made under similarly controlled conditions, and corrections to standard conditions of temperature and pressure are not necessary for purposes of comparison.

However, the volume of a gas varies with temperature, pressure, and water vapor content. Therefore, if it is desired to calculate certain properties of the gas sample, b.t.u. per cubic foot for example, it is necessary to correlate this with some definite condition of temperature, pressure, and water vapor content. The usual commercial standard conditions are saturated gas at 60° F. and 30 inches mercury pressure.

In calculating the density of a gas mixture, the conditions need not be referred to, but if the weight of a unit volume (as pound per cubic foot) is calculated, then the result must be correlated with conditions.

DEVIATION FROM THE GAS LAWS

The molecular volume of certain gases varies from that of certain other gases under the same conditions and thus these are not perfect gases, or it may be said that they deviate from the simple gas laws. To express this in concrete form: The weight of 22.4 liters of these gases at 0° C. and 760 mm. pressure does not equal the gram molecular weight of the gas.

Appreciable errors may arise from this source in the case of gas samples containing carbon dioxide, ethane, the higher paraffins, and other gases of large molecular weight. In precise analysis precautions against this should be taken. The variations are not significant in the case of the lighter gases.

As the partial pressure of gases in a mixture decreases, the gases more nearly conform in behavior to the gas laws, and in the usual oxidation analysis, dilution of the sample with air or oxygen largely eliminates the error due to deviation. Unless the volume of carbon dioxide after oxidation exceeds 30 per cent, it is usually not the practice to apply a correction in the calculation.

A full discussion of this subject may be found in U. S. Bureau of Mines Technical Paper 54, "Errors in Gas Analysis Due to Assuming that the Molecular Volumes of all Gases are Alike", by G. A. Burrell and F. M. Seibert (1913).

SOLUBILITY OF GASES IN THE CONFINING LIQUID

By confining liquid is meant the liquid (mercury, water or aqueous salt solution) used in the burette, reservoirs, slow combustion or explosion pipettes which serves as a seal to confine the gas sample to the apparatus and as a medium for moving the sample through the apparatus.

Gases are soluble in water to varying degrees depending on the particular gas, its partial pressure

in the gas mixture, the absolute pressure of the gas above the liquid, and the temperature of the liquid. Serious errors might be introduced into an analysis by loss of certain constituents through solubility if the confining liquid were pure water.

The solubility of some common gases in water is shown in Table 5.

It is quite obvious from this table that the gas sample should not be brought into contact with pure water. The use of mercury as the confining liquid eliminates this source of error and its use is a necessity for work of the greatest accuracy, but sodium sulfate solution is often more convenient and the results entirely satisfactory in point of accuracy for many types of analyses.

If mercury is impracticable as a confining liquid, the solubility of the various gases may be substantially reduced by using a water solution containing 20 per cent sodium sulfate by weight, and 5 per cent sulfuric acid by volume. A few drops of methyl orange will facilitate the observation of the solution in the apparatus, and also indicate any change from an acid to an alkaline condition.

To further reduce the error, the aqueous salt solution may be saturated with the gas by permitting the solution to stand in contact with the gas for a day. However, a rise in temperature from that at which the solution is saturated with gas will cause the release of gas and a drop in temperature may cause further solubility. Also, a solution saturated with gas will give off the gas if exposed to the air or another sample of different composition.

WATER VAPOR

Errors due to the pressure of water vapor when mercury is used as the confining liquid are avoided by saturating the original sample and subsequent fractions thereof, with water vapor in the burette

TABLE 5
Solubility of Gases in Water

Gas	Solubility*
Acetylene	1.03
Air	0.019
Ammonia	710.6
Benzene	0.21 (22°)
Butane	0.021
Carbon dioxide	0.878
Carbon monoxide	0.023
Chlorine	2.260
Ethane	0.047
Ethene	0.122
Hydrogen	0.018
Hydrogen sulfide	2.672
Methane	0.033
Nitrogen	0.016
Oxygen	0.031
Propene	0.221

*Ml. of gas (reduced to 0° C. and 760 mm. pressure) absorbed per ml. of water at 20° C., when partial pressure of the gas equals 760 mm.

before readings are made. Thus, the moisture content of the sample is not taken into account and results obtained are on a dry basis. Prior to the analysis, a few milliliters of water are drawn into the burette; the mercury lowered the full distance and then slowly raised; the bulk of the water is discharged leaving only a film on the burette wall. The presence of this film must be constantly checked because some absorbing solutions such as sulfuric acid, potassium hydroxide, and alkaline pyrogallol take moisture from the gas. If the film only partially covers the wall, the time required to effect saturation may reach 20 to 30 minutes, whereas with the complete film about two minutes suffices. Water may easily be added in the midst of an analysis by storing the gas in the pipette in use at the time and proceeding with the wetting as before.

ABSORBING REAGENTS

Both physical and chemical absorption are involved in the removal of components from gas mixtures through the use of liquid reagents. Also, reagents are not truly selective in that some will readily absorb more than one component. All of them will, under certain conditions, remove slight and at times significant amounts of components other than the one for which they are specific. Therefore, each reagent should be used in its proper sequence.

Di-Sorbent is the Burrell trade name for an accurate, fast, clear and full strength potassium hydroxide solution for absorbing carbon dioxide.

While Di-Sorbent is specific for carbon dioxide, it will, in addition, absorb hydrogen sulfide, sulfur dioxide and any other acid gases that may be present.

Lusorbent, an activated acid reagent, absorbs illuminants (unsaturated hydrocarbons and aromatics), but does not absorb paraffin hydrocarbons (such as butane and propane) in significant amounts if the total hydrocarbons are below twenty-five per cent of the mixture. If saturated compounds comprise over twenty-five per cent of the mixture, Lusorbent absorbs only about one-fourth the volume of such compounds as does fuming sulfuric acid.

Lusorbent is fast, accurate, has no vapor pressure and no corrosive action on rubber tubing.

It is not recommended when the concentration of carbon monoxide is above 6 per cent by volume.

Fuming Sulfuric Acid absorbs illuminants and will take up a little methane and ethane on prolonged contact. The higher paraffins are more soluble and advantage is sometimes taken of this fact in the absence of illuminants to separate propane and higher from methane and ethane in natural gas.

Bromine has been used occasionally for the absorption of illuminants, but is not generally recommended for use in gas absorption pipettes.

Oxorbent, a stabilized chromous chloride solution, is a superior reagent for oxygen under all conditions. It usually removes all the oxygen in two passes; is slightly acid; forms a stable compound with oxygen; is clean, accurate and fast to exhaustion. It is one of the strongest reducing agents known. Oxorbent will take up small amounts of carbon dioxide

Alkaline Pyrogallol is a strongly alkaline solution of pyrogallic acid and usually requires from four to six passes to completely eliminate oxygen. Recent improvements in the Burrell formula minimize the formation of carbon monoxide when high percentages of oxygen are present in the gas mixture.

Cosorbent for carbon monoxide is distinguished from cuprous chloride in that it reacts to form a stable compound. This stable compound ($\text{Cu}_2\text{SO}_4 \cdot 2\text{CO}$) is formed by the combination of carbon monoxide and cuprous sulfate. Cosorbent will absorb oxygen slowly and may also be used to determine illuminants. Cosorbent has no appreciable vapor pressure and it is, therefore, unnecessary to pass the gas sample into the potassium hydroxide pipette to remove vapors before reading the burette. Cosorbent in a single pipette will take up all of the carbon monoxide that is present, but some analysts prefer a pipette filled with cuprous chloride placed before the Cosorbent pipette to conserve the latter solution.

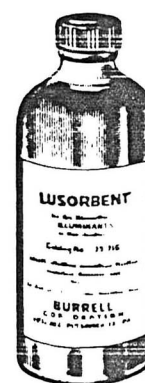
Acid Cuprous Chloride, for carbon monoxide, will also absorb oxygen. This reagent depends for its action upon the formation of a relatively unstable



A39-710
Oxorbent
for
Oxygen



A39-720
Cosorbent
for
Carbon
Monoxide



A39-715
Lusorbent
for
Illuminants

Gas Analysis Reagents

compound ($\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$) with carbon monoxide. Fresh solution will take up all of the carbon monoxide in the gas mixture, but after some absorption (evidence points to as little as 10 ml.) will give up carbon monoxide in contact with a gas containing small amounts. For this reason, two pipettes are recommended for this component; the first filled with cuprous chloride to remove the bulk of the carbon monoxide and the second filled with either Cosorbent or fresh cuprous chloride to remove the last traces.

Acid cuprous chloride will become oxidized and to prevent this action, copper wire or gauze should be kept in one of the barrels of the pipette.

Cuprous chloride has less absorption capacity than any of the other common reagents and, therefore, must be changed more frequently.

Sorbent-A, -B, -C, -D are specific reagents for the selective absorption of certain unsaturated hydrocarbon gases.

Sorbent-A is recommended for ethene, propene, butene, and pentenes. This reagent will not absorb aromatics, has a low solubility for paraffins and is preferable to Lusorbent when an appreciable amount of paraffins is present.

Sorbent-B will selectively absorb iso-butene and will take up 1-butene and 2-butene slowly. A contact pipette is a little faster than the bubbler type.

Sorbent-C is specific for propene, butenes and pentenes. Will absorb ethene slowly. Use in a contact or bubbler pipette. The former is a little faster.

Sorbent-D will absorb acetylene and higher members of the acetylene series. Best used in a contact pipette.

Mercury is recommended as the confining liquid for laboratory models equipped with a compensator manometer.

Burette Solution, an aqueous salt solution, is recommended as the confining liquid for all portable models and those laboratory models which do not have a compensator manometer.

Physical solubility of components in other than their specific reagents is illustrated by the fact that if certain components are absent from a mixture but the analyst nevertheless proceeds with a complete analysis, traces of these components may be indicated.

The capacity of the reagents to absorb foreign gases decreases as the solutions are exposed to contact with the gas mixture and, thereby, become more or less saturated. Before making a final analysis of a mixture varying significantly from the mixture previously analyzed, the analyst should make at least two preliminary analyses to bring the reagents into equilibrium with the new mixture.

Carbon dioxide, illuminants, and the higher paraffin hydrocarbons are more soluble than oxygen, carbon monoxide, hydrogen, nitrogen, methane, and ethane. However, contact that is prolonged beyond the necessary time should be avoided with any reagent.

SOURCES OF ERROR IN GAS ANALYSIS

Errors may be introduced by the reagents becoming exhausted. The operator by check analysis and by keeping a record of the amount of gas a reagent has absorbed, may avoid this possibility.

Incomplete absorption may also be caused by lack of sufficient contact between the gas and the reagent. This may be avoided by repeating the contact until constant consecutive readings are obtained.

Certain reagents like sulfuric acid and those strongly alkaline will dehydrate the gas sample, giving rise to appreciable contractions unless the sample is kept saturated in the burette by a water film (see page 12).

It is generally conceded that alkaline pyrogallol will evolve carbon monoxide under certain conditions. To avoid this the reagent must be properly prepared with a fairly high proportion of alkali and must not be used for removing high concentrations of oxygen such as in cylinder oxygen. Some investigators state that oxygen in excess of about 40 to 50 per cent may cause appreciable evolution of carbon monoxide. If the gas sample contains a high concentration of oxygen, it may be diluted with an amount of nitrogen sufficient to bring the oxygen content of the mixture to below 50 per cent.

Cuprous chloride is an offender in that an equilibrium is reached in the reaction beyond which carbon monoxide is given off. To avoid this possibility two pipettes should be used for this gas and reagent, especially if the percentage of carbon monoxide is substantial. The first pipette is used to remove the bulk of the gas and the second kept filled with fresh reagent to remove that which escapes the first. It is recommended that the second pipette be filled with Cosorbent.

Vapors from strongly acidic reagents may be carried along by the gas sample, and the sample should be passed into the caustic pipette several times to remove any such vapors prior to measuring the volume. Also, ammoniacal reagents may evolve ammonia gas necessitating passing the gas into acid or water for removal.

The solutions must not be permitted to pass into the main manifold header because absorption effects may occur to cause serious errors. Wash out the header periodically with acidulated water even though it has not been apparent that any solution has entered.

Keep stopcocks greased to avoid leaks and be sure that all rubber connections are sound.

Before making a final analysis of a gas that differs appreciably in composition from the gas previously analyzed, pass a sample through the solutions in the regular manner in order to bring the solutions into equilibrium with the new sample.

Other sources of error such as incomplete combustion, solubility of gases in water, and improper sampling, are discussed elsewhere in this book.

CHAPTER III

ASSEMBLING THE APPARATUS

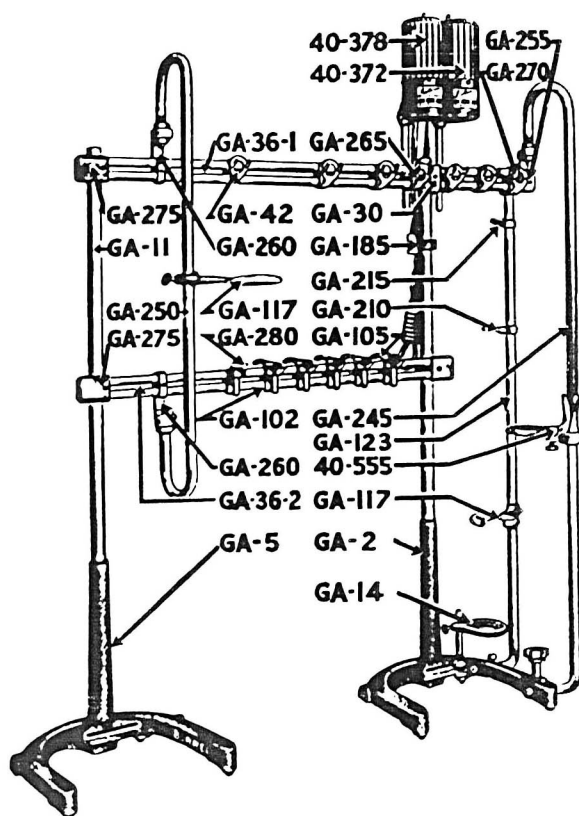


Fig. 5—Support Frame for Burrell Build-Up Laboratory Models*

SUPPORT FRAMES

Build-Up® Laboratory Models—The Build-Up frames for laboratory models are shipped in sections which can be assembled easily and quickly (see Fig. 5). In assembling the Build-Up laboratory models, be sure that all small pieces have been carefully unpacked and are ready for assembly. Depending upon the size of the apparatus, the frame will be mounted on either one or two bases. If one base is supplied it will be a GA-2, and if two bases are supplied, one will be a GA-2 and the other a GA-5.

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ⒶTrademark.

The two uprights, GA-11, are placed in their respective bases and set screws tightened. The upright fitting into the GA-2 usually carries the electrical outlet box for the heaters. The upright-to-crossbar clamps are mounted on the upright.

The paired crossrods are shipped with the pipette support clamps and manifold clamps attached. The shorter pair of crossrods support the pipette holders and form the lower portion of the frame. The long crossrods with manifold clamps are mounted at the top of the apparatus. The clamps for holding the leveling rod and sampling rod are on the upper pair of crossrods. Insert the leveling rod, GA-245, and sampling rod, GA-123, into the base, GA-2, and into the clamps GA-255 and GA-270 respectively. Mount the GA-260 clamps on the frame to the left of the manifold clamps and the pipette support clamps. The leveling rod, GA-250, is supported by the two GA-260 clamps.

Perma-Therm® catalytic and copper oxide heater assemblies are supported by the GA-265 clamp mounted on the upper crossrods. The copper oxide tube is mounted to the right and the catalyst tube is mounted to the left. Various clamps for holding leveling bottles, sampling bottles, etc., are mounted in their proper positions on the leveling rods.

The glassware is now mounted on the rack and it should not be necessary to make any changes in the holders or clamps inasmuch as the assembly was aligned before shipment was made.

Build-Up Portable Models—With the portable Build-Up models, the frame is shipped completely assembled. If Perma-Therm catalyst and copper oxide heaters are supplied, it will be necessary to mount these in their proper positions (see Fig. 6).

*For Build-Up Parts List See Page 42

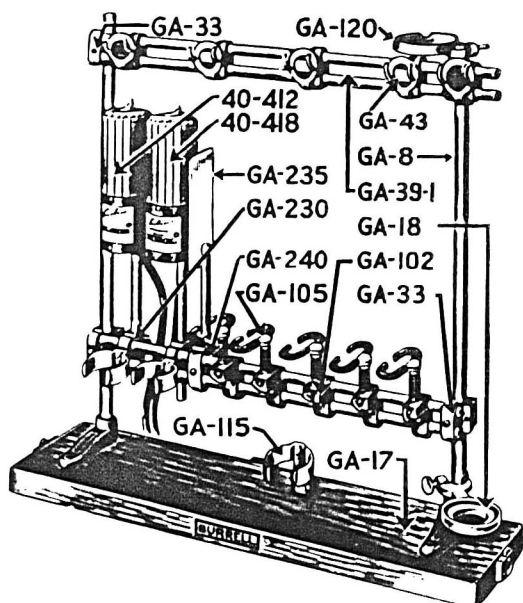


Fig. 6—Support Frame for Burrell Build-Up Portable Models*

Cabinet Models—The cabinets for laboratory and portable models are shipped completely assembled and it is only necessary to mount the electrical heaters in their proper position.

BURETTES

Burettes for laboratory apparatus are shipped disassembled from the water jacket and compensator. Burettes for portable apparatus are shipped assembled into their water jackets and do not carry compensators as standard equipment.

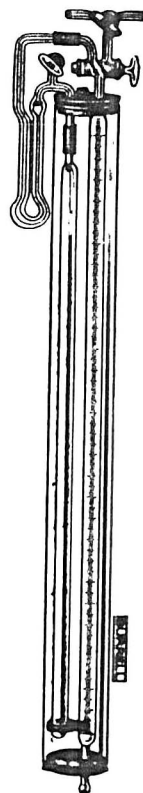
Mercury may be added to the compensator manometer before assembly or may be added directly from the burette after the apparatus has been assembled. In either case, it is wise to add a little dilute sulfuric acid to the mercury in the compensator manometer to help keep the mercury clean. If mercury is added to the compensator manometer prior to assembly, fill the manometer until the mercury reaches an inch or so into the capillary. If mercury is to be added from the burette, see page 20.

Slip the neck of the burette above the graduated barrel into the slit in the top rubber stopper and into the hole.

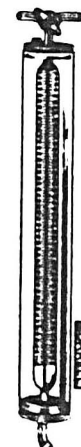
Pass the short vertical stem of the compensator

*For Build-Up Parts List See Page 42

manometer through the hole in the top stopper opposite the burette. Attach the compensator tube to the under side of the stem and the horizontal leg of the compensator to the right angled outlet of the first burette stopcock. Lower the assembly into the water jacket (see Fig. 7).



Laboratory Type



Portable Type

Burette Assemblies

Wet the bottom tubulature of the burette and also the hole in the bottom stopper. Pass the tubulature into the hole, shift the bottom stopper until the burette is straight and seat the stopper firmly.

Fill jacket with water, preferably distilled. The best method of doing this is to attach to a small funnel a piece of rubber tubing long enough to reach to the bottom of the jacket. Pass the tubing through the filling hole in the top stopper and add water through the funnel. This prevents the formation of small air bubbles which otherwise might collect on the burette and obscure the figures and graduation lines.

CHAPTER III

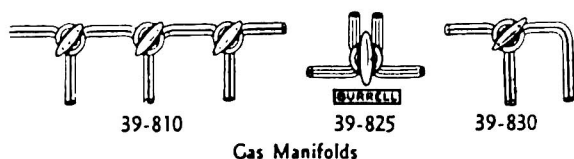
Laboratory models, Build-Up and Cabinet, have a rubber tubing clamp comprising a metal ball and a hand-operated screw mounted in the leg of the frame. Pass the heavy wall rubber tubing connecting the leveling bulb to the bottom tubulature of the burette through this clamp. Be sure that the metal ball remains in place.

MANIFOLDS

Depending upon the apparatus, the manifold may include several parts such as the main section which connects the pipettes, separate catalyst and copper oxide U-tube stopcocks, the burette stopcock, and the flushing end stopcock.

Wet the ends of the glass tubing and attach short pieces of heavy wall rubber tubing. These pieces should be at least $1\frac{1}{4}$ inches long.

Mount the manifold sections and complete the rubber tubing connections. The connections may be bound with fine cord at each end as a precaution against leakage, but with heavy-wall, well-fitted tubing this is usually not necessary.



Remove rubber bands and paper strips from all stopcocks. The paper strips are inserted to prevent the stopcock plugs from sticking during transit. Occasionally the strips will become so saturated with grease that they are difficult to see, although red paper is normally employed to increase visibility.

Manifold clamps on Build-Up apparatus are easily shifted. In the event that a manifold fits tightly in a cabinet model, cut or file the wood away until the manifold fits loosely.

ABSORPTION PIPETTES

Drop all of the pipette platforms the full distance, wet the ends of the pipette capillary tubes and insert the ends into the proper rubber tubing connections on the manifold until the glass meets. Raise the platforms and tighten in position.

The sequence of the pipettes is important. Those gases which are determined by absorption are dealt with in the following order;

- Carbon dioxide
- Illuminants
- Oxygen
- Carbon monoxide

MANUAL FOR GAS ANALYSTS

The first pipette, that is the one next to the burette, should be a Burrell contact type No. 40-130.

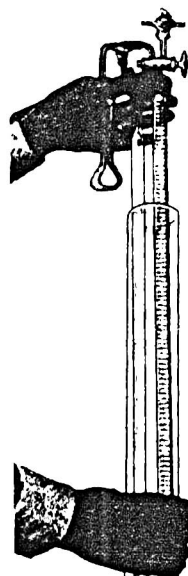
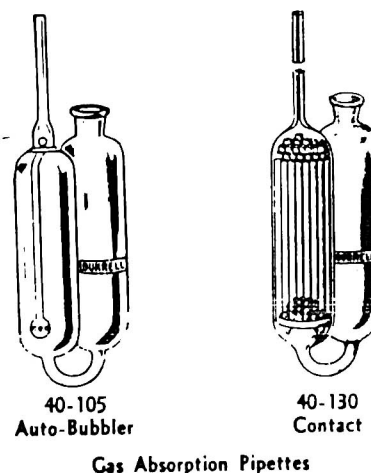


Fig. 7—Lowering Burette and Compensator into Water Jacket

The second should be a Burrell Auto-Bubbler No. 40-105; the third, a Burrell Auto-Bubbler Pipette No. 40-105 if Oxsorbent is used as the absorbing reagent, or a Burrell contact pipette No. 40-130 if alkaline pyrogallol is employed. The fourth pipette is a Burrell Auto-Bubbler No. 40-105. If the carbon monoxide content is substantial, two pipettes No. 40-105 are needed (see Page 12).



The order of the analysis should not change even though one or more of the above components are absent. For example, if illuminants are not present there is no need for having a pipette for this component, but carbon dioxide is still determined first, followed by oxygen and then carbon monoxide.

If the character of the gas mixture is such that

carbon monoxide may be determined in the copper oxide tube along with hydrogen, the need for absorption pipettes for carbon monoxide is eliminated .

Absorption pipettes ordinarily are equipped with rubber gas bags on the rear compartments to protect the reagents from contact with the atmosphere. Protection may also be provided as in the case of Premier Model VB by means of a manifold comprising rubber stoppers, glass T-tubes, and rubber tubing interconnecting the rear compartments to a single pipette filled with Di-Sorbent solution or to a single gas bag.

Due to the small amount of carbon dioxide present in normal atmospheric air, the gas bag may be omitted from the Di-Sorbent pipette, but all other reagents must be protected.

Replacement Glassware—Pipettes for replacement are usually shipped with capillary stems longer than necessary so that the analyst may cut them off to the exact length needed to match the rest of the assembly.

In cutting capillary glass tubing to length, file a small notch in the glass at the desired point, snap the glass between the fingers and then smooth the sharp edges with emery cloth.

COPPER OXIDE AND CATALYTIC ASSEMBLIES

Laboratory Models—The tubes are mounted between the burette and first absorption pipette and to the left of the burette, each tube using manifold U-tube stopcock No. 39-825. The copper oxide tube

is usually next to the burette. Tubes are shipped filled and ready for service.

Connect the tubes to the stopcocks before the stopcocks are assembled into the manifold. Wet the ends of the glass and also the rubber. Exercise care in applying pressure to the tubes.

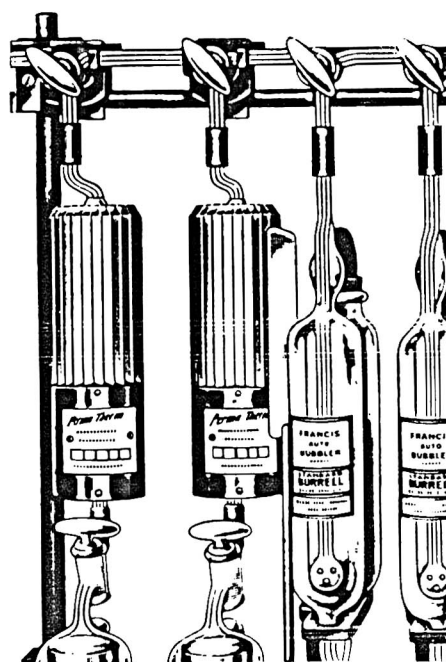
Perma-Therm heaters are specially designed electrical heaters to simplify oxidation procedures. They are hermetically sealed and pre-set at the correct operating temperature. No rheostats, thermometers or thermostats are required. Perma-Therm heaters quickly and automatically reach the proper temperature and remain constant throughout the analysis. A constant temperature is maintained by virtue of a boiling liquid.

Perma-Therm Catalytic and Copper Oxide Heaters may be used with all laboratory style catalyst and copper oxide tubes. The Perma-Therm Heaters are shipped in two parts—an electrical heating section and a finned temperature control section. The reduced section of the finned temperature control section fits into the top of the heating section. Care should be taken that the proper sections are assembled together. A name plate is attached to one fin of the temperature control section for identification. No temperature adjustments or thermometers are required.

The Perma-Therm heaters are mountel on rods and clamps on Build-Up laboratory apparatus and on slotted wood supports on Cabinet models. The laboratory heaters may be raised above the U-tubes for inspection or changing of the tubes.



Copper Oxide and Catalytic Assemblies
Laboratory Models



Copper Oxide and Catalytic Assemblies
Portable Models

All laboratory models except Premier VB, Haldane and U. S. Bureau of Mines VL take copper oxide tube No. 40-333 and catalyst tube 40-337 which are mounted in U-tube stopcocks No. 39-825.

Premier Model VB takes copper oxide tube No. 40-330 which is mounted on section B of manifold No. 39-860.

Bureau of Mines models take copper oxide tube No. 40-340.

Haldane Models take catalyst tube No. 40-336.

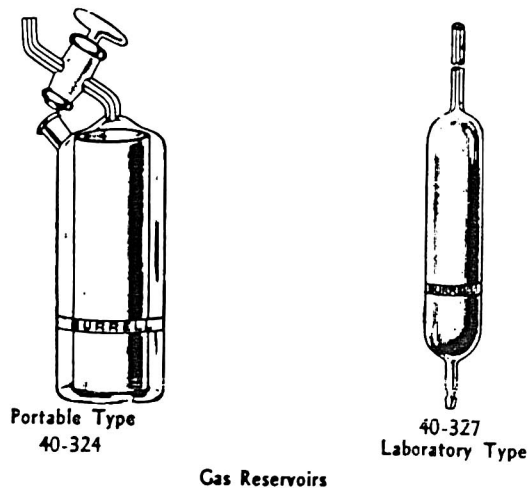
Portable Models—The vertical style of catalyst and copper oxide tubes No. 40-358 and No. 40-354, respectively, are used on portable models equipped with Perma-Therm heaters.

Former portable models using rheostat controlled catalyst and copper oxide heaters require No. 40-357 catalyst tubes and No. 40-353 copper oxide tubes.

The portable Perma-Therm heaters are made in two parts similar to the laboratory style except for size. Likewise, care should be taken to properly assemble the parts. No temperature adjustments or thermometers are required.

To install the tubes, remove the heater. Assemble the Perma-Therm and pass the tube down through the heater with bent end up. Replace the heater and connect the upper end of the tube to the manifold and the lower end to the reservoir.

Reservoirs—All laboratory models equipped with catalytic or copper oxide assembly except Premier



VB, Bureau of Mines VL, and Haldane VC have reservoir No. 40-327 connected to the left end manifold stopcock. The reservoir is connected at the bottom to a leveling bulb carried by a ring support on the left side rod. The reservoir for the Haldane VC is similar, but smaller in size.

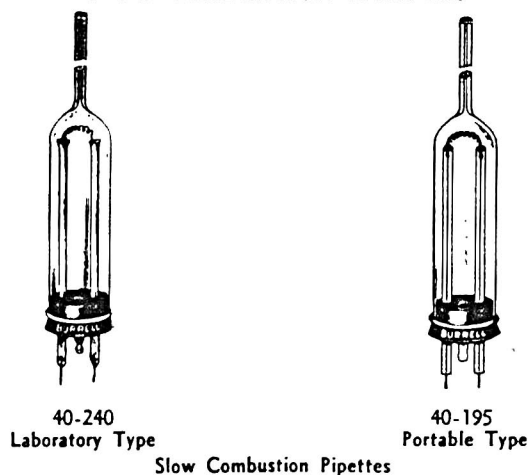
The laboratory type reservoir is normally filled with mercury and receives the gas sample as the gas

is passed from the burette through the catalyst or copper oxide tubes.

In the Premier and Bureau of Mines models, the slow combustion pipette serves as a reservoir for the copper oxide tube.

The Build-Up and Cabinet portable models employ reservoir No. 40-324 as a container for the gas sample as the sample is passed from the burette through the catalyst or copper oxide tube. The reservoir is mounted directly below and is connected to the tube. Aqueous salt solution is used as the confining liquid.

SLOW COMBUSTION PIPETTES



See that the bottom stopper is firmly seated and that the ignition coil is tightly fastened and in good contact. The coil should rise just above the shoulder of the Pyrex glass shell. If the coil has become mis-shapen, spread the loops out so that they do not touch. In winding new coils, use a mandrel not over 3/32 inch in diameter.

Pipettes Nos. 40-240 and 40-260 for mercury use a coil with its ends passing through small holes in the ends of the platinum posts and then wound around the posts terminating below the tops of the support tubes, dipping into the mercury to provide sure electrical contact.

The ends of the coil in pipette No. 40-195 for aqueous solution pass through small holes in the platinum support posts and are wound tightly around the posts.

Electrical connection is made in both types of pipettes to the wires which protrude from the lower ends of the support posts by means of the coiled clips on the ends of the wires from the control panel. The coiled clips are pushed over the wires and can be seated more firmly by bending the end of the coils slightly.

If the apparatus is supplied with a copper oxide tube the slow combustion pipette is usually mounted

BURRELL CORPORATION

ASSEMBLING APPARATUS

between the copper oxide tube and the first pipette. This arrangement provides a reservoir close at hand for the gas as it is passed through the copper oxide tube.

Connect the tubulature in the bottom of the pipette to a leveling bulb or bottle using heavy wall tubing for mercury and light wall for aqueous salt solution.

EXPLOSION PIPETTE

Usually placed at the end of the line of pipettes. Connect the wires from the explosion control box or panel to the platinum loops on the outside of the pipette near the top shoulder. Attach a leveling bulb or bottle to the bottom tubulature.

ELECTRIC HEATERS

The Perma-Therm catalyst and copper oxide heaters have heating elements of nickel chromium alloy and will automatically maintain the proper operating temperature for their respective units. Be sure that

they are properly assembled. After they are plugged into the proper electrical outlet, no further regulation is necessary.

Premier Model VB—All of the electrical equipment is mounted behind the panel board.

The circuit controlling the slow combustion pipette includes a small transformer, with a rheostat and a switch in the high voltage side. The leads from the low voltage side of the transformer are connected directly to the slow combustion pipette.

Electric heater No. 40-372 is used with the copper oxide tube.

The explosion pipette has a spark coil with a push button in the low voltage side of the coil.

Bureau of Mines Model VL—Electric Heater No. 40-372 is used with the copper oxide tube.

The slow combustion pipette circuit includes a small transformer with a rheostat and a switch connected in the high voltage side. The pipette is connected to the low voltage side of the transformer.

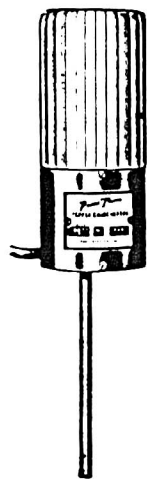
ELECTRICAL PARTS

The power requirements of a Burrell gas analysis apparatus are such that connection can be made to an ordinary lighting circuit. Standard equipment is available for either 115 or 230 volt current and with the models using heaters Nos. 40-372 to 40-438 the power supply may be either alternating or direct current.

Premier VB and Bureau of Mines VL, together with previous models equipped with a slow combustion pipette, have small transformers and in these instances 60-cycle alternating current, 115 or 230 volts, is necessary.

ELECTRIC CONTROL BOXES

Older models of Burrell gas analysis apparatus were equipped with boxes containing all of the electrical control equipment. These boxes are available to order.



40-372
40-378
Laboratory Types



40-412
40-418
Portable Types

Perma-Therm Copper Oxide and Catalytic Heaters

CHAPTER IV

PREPARING THE APPARATUS FOR USE

CONFINING LIQUIDS

Either mercury or aqueous salt solution (see page 11), is used to fill the burette, gas reservoir, explosion and slow combustion pipettes.

Sufficient liquid is poured into the respective leveling bulbs so that the vessels may be completely filled and liquid will remain in the bulbs.

THE COMPENSATOR MANOMETER

If the manometer was not filled prior to assembly, it is necessary to add mercury from the burette. Raise the burette leveling bottle until mercury has been forced from the burette into the compensator manometer. Turn the lower burette stopcock so that the burette communicates directly with the atmosphere and lower the burette leveling bottle. This action seals off the mercury in the compensator and draws air into the burette. Turn the lower burette stopcock so that it does not communicate with either the manometer or the manifold and raise the burette leveling bottle to put air under slight pressure. Open the burette stopcock slowly to the manometer again and push the mercury into the manometer using the air as a cushion. In the event that sufficient mercury has not been forced into the manometer, repeat this process until the mercury rises about an inch or so within the capillary legs of the manometers. A small amount of sulfuric acid may be added to the mercury in the manometer to help keep the meniscus clean.

Atmospheric pressure is established on each side of the mercury by opening the compensator manometer stopcock to the atmosphere and by removing the plug from the burette stopcock. The reference indicator on the leg of the manometer is adjusted

so that it is even with the mercury meniscus and then the stopcocks are closed. The air inside of the compensator tube is maintained in a saturated condition by introducing 2 or 3 ml of water into the compensator tube before assembly. The air responds to any changes in temperature of the jacket water the same as the gas in the burette, thus effecting no change in volume.

LUBRICATION OF STOPCOCKS

A well-ground stopcock if properly lubricated with the correct grease will not leak, wear, or stick.

The grease should be smooth with a body sufficiently viscous to prevent squeezing out; should resist the action of alkalis and acids; retain its lubricating properties over a considerable period and have little or no vapor pressure at working temperatures.

A great deal of annoyance caused by leaky or frozen stopcocks and the necessity for frequent regreasing can be eliminated through the use of a good grease prepared especially for gas analysis apparatus.

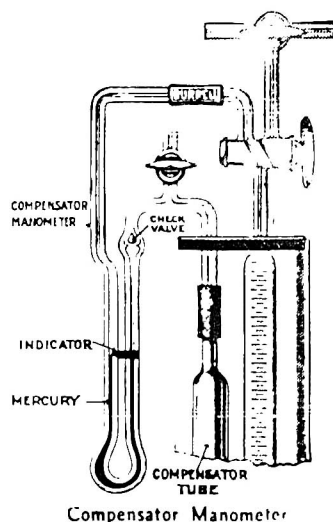
In view of the fact that the compounding and preparation of a suitable grease in the laboratory usually requires more time than is justified by the small consumption, it is more economical to purchase a stopcock grease especially prepared for gas analysis.

Loc-Lube is recommended and is available in two grades. Loc-Lube No. 1 is recommended when the gas sample will not be under excessive pressure at any time, such as is the case when aqueous salt solution is used as the confining liquid or if the temperature of the room is below normal.

Loc-Lube No. 2 is heavier than No. 1 and is recommended when mercury is used as the confining liquid or when the temperature is above normal.

Hy-Lube is recommended for lubricating the stopcocks when substantial quantities of hydrocarbon gases are present. This lubricant is especially prepared to have a low solubility of these hydrocarbon gases. When using this lubricant, care should be taken not to have excessive pressure within the apparatus.

To lubricate a stopcock, first wipe the plug and shell thoroughly with a clean cloth and then apply two horizontal streaks of just enough grease on opposite sides of the plug between the bore openings. Then insert the plug so that the bore openings coincide and firmly press into place, turning slightly until the grease film covers the surfaces entirely. Do not use an excess of grease.



Regrease at the first indication of thinning out or contamination.

If the apparatus is to stand idle for extended periods, the stopcocks may be cleaned and paper strips inserted between the plug and shell. However, if properly greased with the correct lubricant, idleness of several months or longer will not cause the stopcocks to stick.

FILLING THE PIPETTES

It is well to use all of the permissible solution capacity of the various pipettes to lengthen the time between refills.

Open the pipette to the atmosphere through the manifold. Remove rubber stopper and gas bag, then pour the solution into the rear compartment. Close manifold stopcock, inflate bag a little and replace stopper.

The first pipette is for the determination of carbon dioxide and is filled with Di-Sorbent solution; the second pipette is for illuminants and is filled with either Lusorbent or 15% fuming sulfuric acid; and the third pipette is for oxygen and is filled with either Oxsorbent or potassium pyrogallate solution.

Oxsorbent takes up oxygen very rapidly and it is, therefore, best to first fill the pipette with an oxygen free gas such as natural gas, or nitrogen and also partially fill the expansion bag with the same gas. Direct a stream of the gas upon the Oxsorbent as it is being poured into the pipette and immediately replace stopper and gas expansion bag. (See Fig. 9).

If carbon monoxide is to be determined by absorption, the fourth pipette is filled with either Cosorbent or cuprous chloride solution. If two pipettes are used, fill the first with cuprous chloride and the second preferably with Cosorbent, but both may be filled with cuprous chloride.

Next bring the liquid in each pipette up to the reference mark on the capillary stem. With flushing manifolds, a point about $\frac{1}{8}$ " below the stopcock or $\frac{1}{8}$ " below the rubber tubing connection may be selected as the mark. Open each pipette in turn to the burette and by carefully lowering the burette leveling bulb, bring the solution to the proper point.

If the rubber gas expansion bags are inflated a little at the outset, it will not be necessary to admit air to the rear chamber of the pipettes to permit drawing the solution up into the capillary.

RUBBER CONNECTIONS

At all points where there is a glass to glass contact such as pipettes to manifolds, the glass terminals should be butted firmly, one against the other to avoid excessive dead space.

Rubber tubing used at the joints should be about $\frac{3}{16}$ " or 5 mm. I. D., heavy wall, and about $1\frac{1}{4}$ " long. Emson transparent tubing No. 75-012 is convenient in that the flow of liquids may be followed, but this grade is not as durable as our black tubing No. 75-022.

Burrell white rubber tubing No. 75-032 $\frac{3}{16}$ " I. D., heavy wall, is recommended for the connections between the burette, gas reservoir, explosion pipette, slow combustion pipette and their leveling bottles when mercury is used. Burrell black rubber

tubing No. 75-022 in $\frac{3}{16}$ " size is suitable for these connections when aqueous salt solution is employed as the confining liquid.

Rubber tubing must make snug fit to prevent leaks at the joints and if necessary, should be wrapped with a rubber band or soft wire.

BALL AND SOCKET JOINTS

Ball and socket joints are much more convenient than rubber connections, are gastight and are particularly indicated when the gas mixture contains heavy hydrocarbons which are readily soluble in rubber.

Grease the ball lightly, distribute evenly by turning the ball in the socket and then clamp.

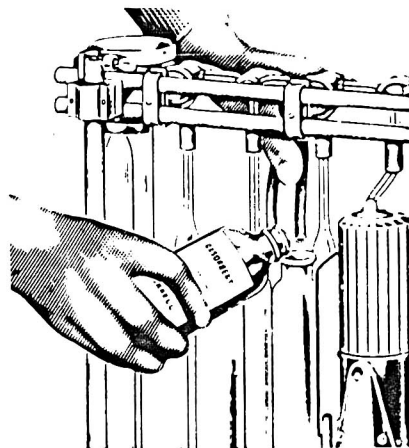


Fig. 9—Filling the Pipette with Oxsorbent

CALIBRATION OF COPPER OXIDE AND CATALYST TUBES

The volume of the catalyst and copper oxide tubes may be determined by filling the burette with a pure gas of such nature that it may be readily determined by absorption or oxidation, and passing this gas through the tube at the operating temperature. Two burettes full of gas should be passed through to insure that tube is completely filled with the calibrating gas. Cylinder carbon dioxide may be used for this purpose, or natural gas if it contains not over one per cent nitrogen.

After the tube is filled with the gas, the stopcocks communicating with the tubes are closed and the manifold and all connections are swept out with several portions of air. A final portion of air is passed through the catalyst or copper oxide tube, returned to the burette, and the volume of gas which was contained in the tube is determined by absorption or oxidation. This volume is used in connection with the correction referred to in Chapter VI, "Analytical Procedure" and Chapter VII, "Calculations".

TESTING THE APPARATUS FOR LEAKS

Level liquids in all pipettes at the proper points, and close pipette stopcocks.

Lower burette leveling bulb and draw in about 100 ml. of air and open the burette to the manifold. Turn the end stopcock on the manifold to seal (see Fig. 21) and raise burette leveling bulb sufficiently to place the air under about 8 inches pressure of mercury. With water as the confining liquid, raise the leveling bottle to the top of the support rod. A

leak in any stopcock or rubber connection is indicated by the liquid rising in the burette.

Drop gas reservoir, slow combustion and explosion leveling bulbs. Note whether the liquids drop in the vessel capillaries and also whether upon standing the liquid drops in any of the pipettes, indicating a leak in the rubber connections.

If a leak is indicated in a stopcock, clean and regrease the stopcock carefully, being sure that the paper strip is removed and the plug is seated firmly. If the leak is in the rubber connections, replace with smaller bore or heavier wall tubing, or bind each end of the sleeve tightly with wire or a rubber band.

ELECTRIC HEATERS

Be sure that the voltage of the power supply is the same as the voltage on the heater name plate. In the case of the Perma-Therm heaters, be sure that they are properly assembled. It is only necessary to plug in the Perma-Therm heaters—no regulation or thermometers are required. For most satisfactory operation, the voltage should not be excessively low and the apparatus should not be operated in a direct draft.

In the case of former models with rheostat controlled heaters, use the following procedure. Push heater switch to the No. 1 position. Before the temperature of the copper oxide heater reaches 290° C., switch to the No. 2 position and adjust rheostat until the temperature remains constant at some point between 290° C. and 300° C. When adjusting the catalyst heater, switch to No. 2 position before the temperature reaches 490° C., and then adjust the rheostat until the temperature remains constant at approximately 500° C.

CLEANING THE MANIFOLD

In manipulating the apparatus, the inexperienced operator is apt to pull solution from a pipette past the manifold stopcock and into the manifold. If this happens, the manifold must be immediately cleaned before the analysis is continued, otherwise the small amount of solution remaining in the manifold will have an absorption action on the gas sample and cause errors in the analysis.

Should this happen with a laboratory model equipped with a flushing manifold, connect a leveling bottle filled with water acidified with about 5% sulfuric acid to the left end of the manifold with about 6" of rubber tubing. The rubber tubing should be completely filled with the solution to eliminate air contamination of the sample. Draw the gas sample back into the burette and then open the end manifold stopcock permitting the solution to follow the sample through the manifold to the burette stopcock. With the sample completely in the burette, close the burette stopcock and open the end stopcock allowing the flushing liquid to flow through the manifold into a beaker at the opposite end.

Flush the manifold thoroughly and then return the flushing water to the burette stopcock. Open the burette stopcock to the manifold and force the water back to the left hand stopcock and proceed with the analysis.

With portable models equipped with flushing manifolds, the gas is stored in the pipette last used and the manifold thoroughly flushed out by raising the burette leveling bottle and permitting acidulated water from the burette to flush through the manifold and out through the opening at the left hand end of the manifold.

With the apparatus equipped with manifolds having the stopcocks in the vertical legs, the manifold should be removed from the apparatus and thoroughly flushed out with acidulated water.

CALIBRATION OF THE BURETTE

Gas analysis burettes of the better grade are accurately calibrated, and recalibration in the laboratory of use is ordinarily unnecessary. However, if the calibration is under suspicion or if the burette has been repaired so as to affect the calibration, proceed as follows:

Attach a 3-way T-stopcock to the bottom of the burette, preferably by sealing or by means of a piece of heavy wall tubing wired in place. (See Fig. 10). The stopcock should be so placed that one leg drawn out to a tip points down in line with the burette. The horizontal leg is attached to a leveling bulb with heavy wall rubber tubing. Thoroughly clean the burette with a saturated solution of potassium bichromate in sulfuric acid. Wash and dry.

Mount the burette in a water jacket with a thermometer through the top stopper. The water may be agitated and the temperature maintained uniform throughout by bubbling air through it at a slow rate by means of a glass capillary tube through the top stopper ending within about an inch of the bottom.

Starting at zero successive 1 ml. portions of mercury are run into a weighed glass vessel through the tip and weighed. The weights between 0 and 1 ml., 0 and 2 ml., 0 and 3 ml., etc., up to the capacity of the burette are calculated to a volume basis at the temperature of the calibration and the volumes obtained compared with the burette readings. If the volume determined by the calibration is greater than the burette reading, the correction is added to all readings in that range during the analysis and subtracted if less.

The burette should be calibrated using the liquid, mercury or aqueous salt solution, that will be employed in the analysis. With water the burette may be similarly checked, except that the water is measured and weighed in 5 ml. portions and is permitted to drain down the sides of the burette for five minutes prior to each reading.

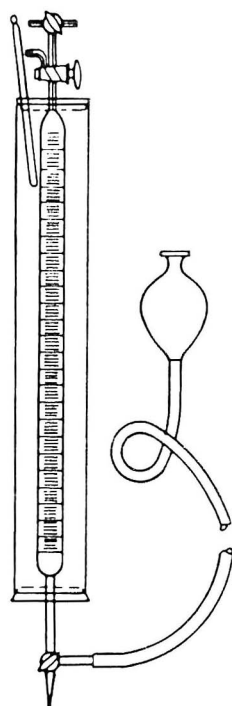


Fig. 10—Calibrating the Burette

CLEANING MERCURY

Coarse dirt may be removed from mercury by squeezing through chamois skin or by pouring into a glass funnel containing a filter paper with a pin hole in the apex of the cone; the mercury will trickle through the small hole, leaving the dirt behind.

An excellent method, especially if the mercury contains copper, zinc, or other easily oxidizable metals, is to spray the mercury through a 5% nitric acid solution. (See Fig. 11).

Seal a piece of capillary tubing, 2 to 3 mm. bore and about 10" long, to one end of a glass tube about 30" long and 1" diameter. Bend the capillary up along the large tube for four or five inches, and then down about an inch to form a gooseneck as shown in Fig. 11. Mount the tube vertically with the gooseneck at the bottom. Pour several inches of clean mercury into the tube and fill with 5% nitric acid solution. At the top mount a separatory funnel which has a piece of calico tied over the outlet. The cloth should not dip into the solution. If desired, a funnel with punctured filter paper may be mounted above the separatory funnel. The cloth will break the mercury into a fine spray, and the clean mercury will collect at the bottom of the tube and pass out through the gooseneck into the receiving vessel. Mercury so cleaned is usually satisfactory unless quite dirty at the outset, in which case a preliminary treatment may be given consisting of pouring an inch or so of 5% nitric acid solution on top of the mercury contained in a bottle and bubbling air through the mercury for eight or ten hours.

The mercury may be freed of acid by spraying through a similar column filled with water.



Fig. 11—Apparatus for Cleaning Mercury

If the mercury must be dry, such as is needed for a barometer, heat at about 125° C. under reduced pressure.

GENERAL NOTES ON CARE OF THE APPARATUS

Burettes which have become dirty inside can usually be cleaned with a solution prepared by pouring concentrated sulfuric acid over an excess of potassium bichromate and drawing off the liquid for use. If necessary, allow the solution to remain in the burette for several hours.

A stopcock remover is a handy tool. It will release frozen plugs in most instances.

Carbon tetrachloride will usually dissolve grease from capillaries, but all traces must be removed before the part is used else the sample will be contaminated.

If the solution is dropped below the joint when the apparatus is out of use, even one night, the rubber tubing connection to the fuming sulfuric acid pipette will last longer.

Wipe up spilled mercury or reagents.

SOLUTION CAPACITY OF PIPETTES

Burrell Auto-Bubbler Pipette No. 40-105.....	200 ml.
Burrell Auto-Bubbler Pipette No. 40-120.....	250 ml.
Burrell Contact Pipette No. 40-130.....	165 ml.
Burrell Contact Pipette No. 40-150.....	200 ml.
Burrell Contact Pipette No. 40-170.....	40 ml.
Burrell Contact Pipette No. 40-190.....	50 ml.

MERCURY REQUIRED

Catalytic Reservoir, laboratory type.....	5 lb.
Gas Measuring Burette, laboratory type, 100 ml.	5 lb.
Slow Combustion Pipette.....	7 lb.
Explosion Pipette.....	10 lb.

CHAPTER V

COLLECTION OF GAS SAMPLES

Correct sampling methods are no less important than careful workmanship in analyzing. In fact, sometimes it is more difficult to collect a truly representative gas sample than to make the analysis.

The principal factors to consider are the location of the sampling point, suitability of displacing liquids, types of sample containers, connections between the sampling tube and the sample container, and possible variations in composition of the gas through the cross-section of a flue or large pipe and variations due to cyclic operations or other factors.

DISPLACING LIQUIDS

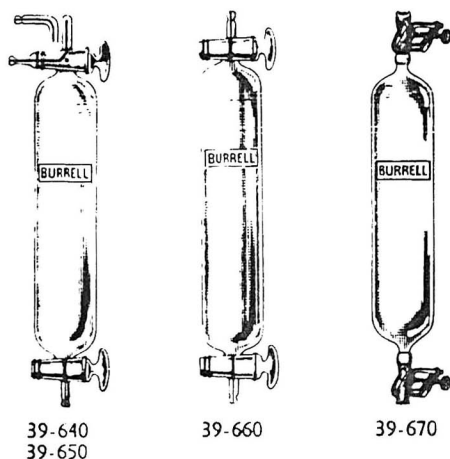
Water comes first to mind as the displacing liquid but should be avoided in most instances due to the solubility of gases in this medium. Aqueous salt solution (see page 11) is the most generally useful liquid, but mercury is the best. The latter is not always convenient or available in the quantity required and cannot, of course, be used in all types of metal containers or when the gas contains reactive components such as hydrogen sulfide.

SAMPLE CONTAINERS

If the gas is to be analyzed within a day, tubes with rubber tips and screw clamps similar to No. 39-670 are convenient. However, such a tube should not be used if the gas contains appreciable amounts of heavy hydrocarbons which are readily soluble in rubber.

Sampling tube No. 39-660 with stopcocks is more suitable if the gas is not to be analyzed for some time or if heavy hydrocarbons are present.

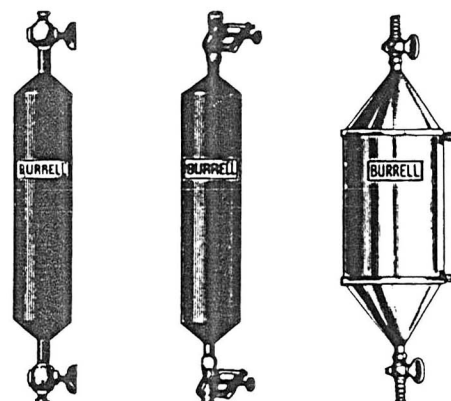
Sampling tubes Nos. 39-640 and 39-650 are equipped with a tail stopcock at one end. If the

39-640
39-650

39-660

39-670

Glass Containers



39-680

39-690

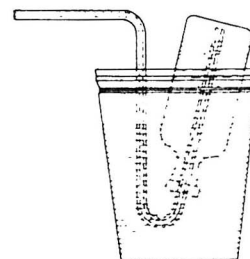
39-700

Metal Containers

gas to be sampled is under pressure the flow may be directed through the tail opening until the sampling connection is thoroughly flushed out, whereupon the stopcock is turned to admit the sample to the tube. If not under pressure the sampling lines may be cleared conveniently by drawing several portions of sample into the tube and discharging to the atmosphere through the tail opening. When connected to the gas apparatus, flushing liquid may be passed through the connections to the tail stopcock eliminating possibility of contamination due to any void space.

Copper and zinc tubes are sturdy, but the metal stopcocks are more apt to develop leaks than glass stopcocks. If the sample is to be retained for any length of time, the metal stopcocks should be dipped in paraffin. Metal containers are attacked by hydrogen sulfide and the copper and zinc types are not suitable for mercury. Steel tubes rust readily and the reaction with oxygen in the sample may be appreciable.

Glass bottles are sometimes useful. The sample may be collected by submerging a liquid filled bottle, neck down as shown in Fig. 12 and introducing the sample through the bent tube and then closing the neck with a cork or stopper while still submerged. The sample may likewise be withdrawn through a bent tube.

Fig. 12—Collecting Sample
in a Bottle

RUBBER CONNECTIONS AND SAMPLING LINES

Rubber tubing is convenient for sampling lines but is quite unsuitable for a gas containing heavy hydrocarbons. Carbon dioxide and hydrogen in significant amounts are also apt to be lost on prolonged contact.

For long sampling lines use small bore glass or suitable metal tubing with the ends closely butted where rubber connections are needed.

Where temperatures are high, porcelain, glass or fused silica sampling tubes may be inserted into the gas stream or container. Water cooled sample collectors as in Figure 13 are useful under some conditions.

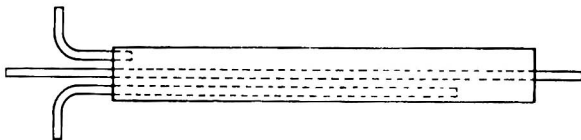


Fig. 13—Water-Cooled Sampling Tube

GRAB SAMPLES

A convenient and frequently used method of sampling is to fill the sample container with liquid

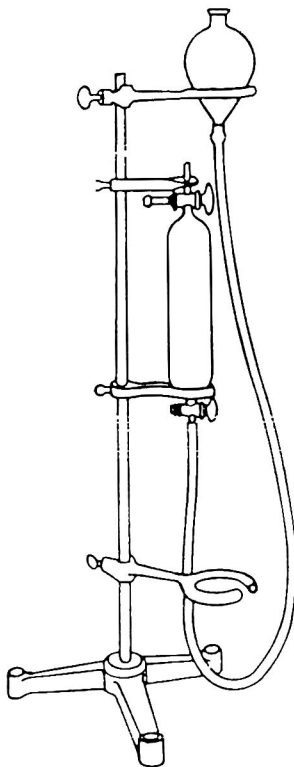


Fig. 14—Collecting Sample by Liquid Displacement

and to permit the discharging liquid to pull a gas sample into the container.

Figure 14 illustrates a good set-up for collecting small samples by liquid displacement. The tube and leveling bulb may be mounted for convenience on a small ring stand using a clamp for the tube and a split ring support for the bulb. When filled, the device may be taken directly to the gas apparatus and the sample discharged into the burette without disconnecting the tube from the leveling bulb.

GAS DISPLACEMENT

An excellent method of sampling is to flush the gas through the container until the original air or gas filler has all been displaced. This is easily accomplished if the gas is under pressure, but the flushing period must be sufficiently long to secure complete displacements. A volume of gas equal to 15 to 20 times the volume of the container should be permitted to flow before the container is sealed.

VACUUM SAMPLING

A method popular in mines or in sampling the atmosphere in large spaces is to break off the tip of an evacuated container like Figure 15 at the sampling point and then sealing the tip with wax for transportation to the gas analysis apparatus. A good wax for the purpose is made by mixing one part of Venice turpentine with two parts of beeswax. Similarly gas sampling tubes fitted with tight stopcocks may also be evacuated, but should be used immediately to avoid possibility of leakage.



Fig. 15—Evacuated Container (39-675)

DIRECT SAMPLING

At times, especially with portable gas apparatus, it is possible to place the apparatus close to the point of sampling, draw or force the sample directly into the burette and proceed at once with the analysis.

If the gas is under pressure, it is easy to permit a sufficient volume to flow through the sampling line to displace all of the air. If the sample must be pulled into the burette by lowering the burette liquid or forced into the burette by means of the rubber hand pump, a 100 ml. burette should be filled and discharged at least twice for every five feet of 1/4" I. D. sampling line to clear the line of air or residual gas.

CHAPTER V

MANUAL FOR GAS ANALYSTS

CONTINUOUS SAMPLING

A large sample or a sample collected over a long period of time may be gathered by the arrangement shown in Figure 16.

The upper bottle is filled with liquid to a tail or T stopcock in the connection to the sample source. The gas, if under pressure, is permitted to flush through the tail opening or the T stopcock side tube to clear the sampling line. Or, if not under pressure, the sample may be flushed through by means of a rubber hand pump.

The stopcock is then turned to permit the sample to pass into the bottle. The rate of sampling may be regulated by adjusting the screw clamp in the liquid discharge connection. This connection should dip below the surface in the liquid receiving vessel to prevent entrance of air if a negative pressure develops in the sampling system.

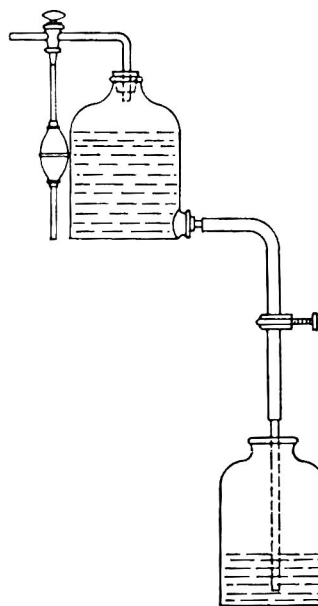


Fig. 16—Continuous Sampler

CHAPTER VI

ANALYTICAL PROCEDURE

ELECTRIC HEATERS

The first operation with an apparatus equipped with electric heaters is to stabilize the copper oxide and/or catalyst electric heaters at the proper temperatures.

Open the catalyst and/or copper oxide tubes to the atmosphere or burette (see Fig. 23). If the apparatus is equipped with Perma-Therm heaters, it is only necessary to plug in the heater. The proper temperature will be attained in 10-20 minutes. No temperature regulation or thermometers are required.

With our former models equipped with rheostat controlled heaters, use the following procedure. Throw the heater switches to the No. 1 position. Before the catalyst heater temperature reaches 490° C., throw the switch to the No. 2 position and adjust the rheostat until the temperature remains constant at 500° C. or a little above. With the copper oxide heater, throw the switch to the No. 2 position before the temperature reaches 290° C. and adjust rheostat to hold the temperature constant at a point between 290° and 300° C.

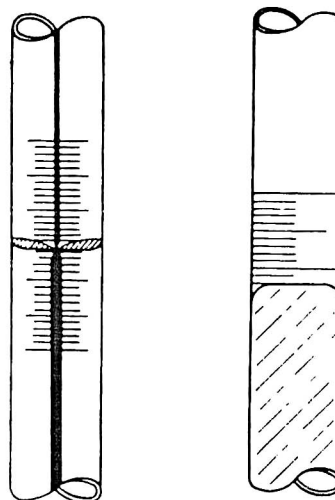
IMPORTANT

The temperature of the catalyst heater must be at least 500° C. for rapid and complete oxidation. Heaters must not vary over 5° C. during the entire analysis. Do not permit solutions or mercury to enter copper oxide or catalyst tubes.

FILLING CAPILLARIES WITH NITROGEN

The manifold, copper oxide and catalyst tubes should be filled with nitrogen before the analysis is started. To prepare the nitrogen, draw about 30 ml. of pure air into the burette and remove the oxygen by passing the air into the oxygen pipette until no further absorption takes place. The carbon dioxide need not be removed as normal air does not contain enough of this gas to be of significance in an ordinary analysis.

With the laboratory type apparatus, after the manifold and tubes have been swept out with nitrogen and before discharging the nitrogen from the burette, open the burette stopcock to the atmosphere momentarily. The nitrogen in the burette is now at atmospheric pressure. Then, open the burette to the manifold with the manifold stopcock at the end opposite the burette closed to the atmosphere. Open the U-tube stopcocks to the manifold with the electric heaters stabilized at their respective proper temperatures. Open burette stopcock to the atmosphere again and then back to the manifold to establish atmospheric pressure throughout the manifold and tubes. Next, turn the burette stopcock to the compensator and adjust indicator to the mercury level. The stopcock communicating with the closed end tube of the compensator should be open to the atmosphere while this adjustment is being made. After closing the compensator manometer stopcock, turn the burette stopcock away from the compensator and discharge the nitrogen from the burette.



Meniscus of Aqueous Salt Solution (left) and Mercury (right)

With portable types of apparatus having catalyst and/or copper oxide tubes, after sweeping the manifold and tubes with nitrogen open the oxidation tubes to the manifold. Establish the nitrogen therein at atmospheric pressure by leveling the confining liquid in the leveling bottle and burette. When level, close the oxidation tubes and manifold and discharge the nitrogen from the burette.

VOLUME OF SAMPLE

In general the best procedure is to take as large a sample as may be conveniently handled throughout the various stages of the analysis. The small unavoidable errors which are inherent to any analytical procedure will be of less magnitude with a large sample than with a small one.

When 100 ml. of sample can conveniently be used for analysis, the volume of each component determined is equal to the percentage of that component. The following paragraphs describe methods for obtaining exactly 100 ml. of sample for analysis.

When aqueous salt solution is used as the confining liquid, a little more than 100 ml. of sample is drawn into the burette. The burette stopcock is closed and the sample is allowed to stand for one minute to permit the confining liquid to drain down the sides of the burette. The leveling bottle is elevated above the confining liquid in the burette until the liquid level in the burette is exactly 100, thus placing the gas under a slight positive pressure. The connecting tubing is then pinched securely between the thumb and forefinger and the burette stopcock opened to the atmosphere momentarily, thus bringing the 100 ml. of gas in the burette to atmospheric pressure.

When aqueous salt solution is used as the confining liquid, the sample should be permitted to stand in the burette for one minute prior to each reading. This insures a uniform time for drainage down the sides of the burette.

It is more difficult to get an exact volume of 100 ml. of gas into a burette using mercury as the confining liquid. First, draw a little more than 100 ml. of sample into the burette, close the connecting rubber tubing with the clamp in the leg of the frame, and then raise the leveling bulb several inches. Open the rubber tubing clamp slowly, let the mercury rise to the 100 ml. mark and close the clamp again. Open burette stopcock to the atmosphere momentarily and permit excess gas to escape. Then lower the leveling bulb to the 100 ml. graduation and open burette stopcock to the compensator manometer. Adjust the mercury level in the burette to the 100 ml. mark and set the compensator indicator. Make all subsequent burette readings in the analysis at the same compensator pressure.

Since it is more difficult to get exactly 100 ml. of gas into the burette at atmospheric pressure using mercury as the confining liquid, the volume usually is brought as close to 100 ml. as possible. With approximately 100 ml. of gas in the burette, open the stopcock connecting to the compensator manometer which has previously been set at atmospheric pressure. The mercury in the manometer will usually rise or fall and is brought back to the indicator by raising or lowering the leveling bulb. Fine adjustments are easily made with the micrometer leveling bulb support. (See Fig. 17). The burette reading is taken and this volume is used as the initial volume in the calculation formula.

CARBON DIOXIDE BY ABSORPTION

Raise the burette leveling bulb slightly, thus putting the gas in the burette under slight pressure to avoid any possibility of pulling solution from the pipette into the manifold. Then turn the manifold stopcock to connect to the pipette (see Fig. 19) and continue raising burette leveling bulb until the confining liquid reaches the top of the burette and all the gas has been passed into the pipette. Lower the burette leveling bulb bringing the gas back into the burette. Repeat this three times. The last time the gas is returned to the burette, bring the level of the potassium hydroxide solution to the reference point on the capillary stem of the pipette. Close pipette stopcock (see Fig. 21) and read burette.

The gas should be passed twice more into the potassium hydroxide pipette as a check. If the reading is the same as before, all of the carbon dioxide has been removed and the operator may proceed with the analysis. If more than six passes

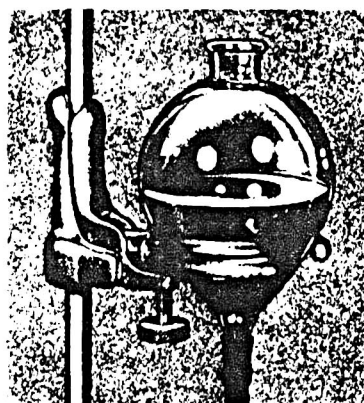


Fig. 17—Micrometer Leveling Bulb Support

are required to get complete absorption, the solution should be renewed. If the gas contains a high percentage of carbon dioxide, it is often advantageous to allow the gas to remain in the pipette for a minute to effect a more rapid absorption.

The volume after absorbing the carbon dioxide, subtracted from the initial volume of sample equals the volume of carbon dioxide in the sample.

$$\text{Per cent of carbon dioxide} = \frac{\text{ml. of carbon dioxide} \times 100}{\text{ml. of initial sample}}$$

ILLUMINANTS BY ABSORPTION

The gas sample is next passed four times into the Lusorbent pipette. (If fuming sulfuric acid is used the gas must be passed twice into the potassium hydroxide pipette to remove the sulfur trioxide). Return the gas to the burette, and read. Continue passing into Lusorbent pipette until check readings are obtained. Six passes should be sufficient to remove all of the illuminants.

The volume after absorption of illuminants subtracted from the volume after absorption of carbon dioxide equals the volume of illuminants in the sample.

$$\text{Per cent of illuminants} = \frac{\text{ml. of illuminants} \times 100}{\text{ml. of initial sample}}$$

OLEFINS AND ACETYLENE

Reagents as described on page 13 have been developed for the selective absorption of acetylene, iso-butene, propene and ethene.

The pipettes containing these reagents follow the carbon dioxide pipette, first Sorbent-D for acetylene, then Sorbent-B for iso-butene, next Sorbent-C for propene and other butenes and finally Sorbent-A for ethene. If only total olefins and acetylene are required, first determine acetylene in Sorbent-D after carbon dioxide followed by total olefins in Sorbent-A.

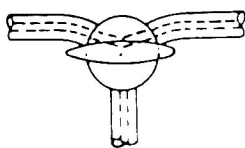


Fig. 18—Stopcock Open Across the Manifold

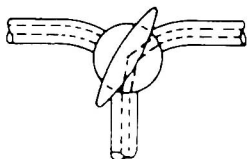


Fig. 19—Stopcock Connecting Pipette to Right Leg of Manifold

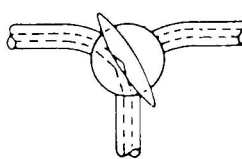


Fig. 20—Stopcock Connecting Pipette to Left Leg of Manifold

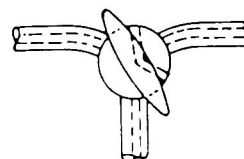


Fig. 21—Stopcock Closed

Pass the gas sample into the pipette five times and continue until a constant reading is obtained or until the rate of volume decrease becomes constant. Other gases present may be slightly soluble in the Sorbent reagents and for the best accuracy, determine the constant decrease per pass. The total volume of the next higher olefin absorbed may then be calculated by extrapolating the absorption to zero and adding to the next absorption.

With these determinations it is very important to condition the solutions before use, and the reagents should be replaced when approximately 1000 ml. of gas has been absorbed. When a high concentration of acetylene is present, the carbon dioxide should be absorbed in 5% potassium hydroxide rather than the stronger standard solution. The 5% solution may be prepared from our standard reagent by diluting with distilled water in the ratio of 85 ml. of water to 15 ml. of standard Di-Sorbent solution.

OXYGEN BY ABSORPTION

If Oxsorbent is used as the absorbing medium for oxygen, pass the gas twice into the pipette, and read the burette. Pass the gas once more to make sure that all oxygen has been removed and read again. The sample may pick up traces of acidic vapors from Oxsorbent and for close work pass the gas once through into the potassium hydroxide pipette before reading the burette.

If alkaline pyrogallol is used as the absorbing medium, pass the gas four times into the pyrogallol solution, permitting the gas to remain in the pipette a minute or so between passes. Continue this until constant readings are obtained. If more than twelve passes are required to remove the oxygen, replace with fresh solution.

The volume after absorption of oxygen subtracted from the volume after absorption of illuminants equals the volume of oxygen in the sample.

$$\text{Per cent of oxygen} = \frac{\text{ml. of oxygen} \times 100}{\text{ml. of initial sample}}$$

CARBON MONOXIDE BY ABSORPTION

Two absorption pipettes are recommended if carbon monoxide is present in substantial quantities. The first is filled with cuprous chloride and the second preferably with Cosorbent, but cuprous chloride may be used.

If cuprous chloride alone is used, the gas may be stripped of acid fumes in the potassium hydroxide pipette.

Pass the gas four times into the first pipette to remove the bulk of the carbon monoxide. If Cosorbent is used in the second pipette, remove acid fumes as described before and then pass twice into the second pipette. Cosorbent has no appreciable vapor pressure and the sample may be brought directly back to the burette for the reading.

If cuprous chloride is used in the second pipette, the solution must be kept fresh or the analysis will be subject to errors due to escape of carbon monoxide. After the cuprous chloride has absorbed about 10 ml. of carbon monoxide, it is apt to release some to the sample.

The volume after absorption of carbon monoxide subtracted from the volume after absorption of oxygen equals the volume of carbon monoxide in the sample.

$$\text{Per cent carbon monoxide} = \frac{\text{ml. of carbon monoxide} \times 100}{\text{ml. of initial sample}}$$

CARBON MONOXIDE AND HYDROGEN BY OXIDATION WITH COPPER OXIDE

If carbon monoxide is not determined by absorption, it may be determined together with hydrogen by oxidation over copper oxide.

If the confining liquid in the burette is aqueous salt solution, it is best to determine carbon monoxide by absorption because of the comparatively high solubility of carbon dioxide in water solutions.

The copper oxide tube heater should have been stabilized as described on page 27.

With the laboratory apparatus, close the tubing clamp at the base of the burette and raise burette leveling bulb to the top of the rod. Open the burette stopcock to allow passage through the copper oxide tube into the gas reservoir or the slow combustion pipette. Open tubing clamp just sufficiently to permit the gas to flow through the copper oxide tube at about 10 ml. per minute. At the same time, lower the gas reservoir or slow combustion pipette leveling bulb to keep the gas in the pipette as nearly as possible at atmospheric pressure in order to avoid leaks.

With portable apparatus using aqueous salt solution as the confining liquid, the leveling bottle is placed on the top platform and the flow of gas regulated by means of the burette stopcock.

When all the gas has passed through the copper oxide tube, draw the gas back into the burette by way of the copper oxide tube at the same rate. Four such double passes through the copper oxide tube generally suffice to completely oxidize the carbon monoxide and hydrogen, but if extremely high concentrations of these gases are present, additional passes may be necessary. In any event, continue the passes until two consecutive identical readings are obtained.

Draw the sample back into the burette through the copper oxide tube and read the burette.

Any contraction in volume observed is due to the oxidation of hydrogen to water, and the contraction is equal to the volume of hydrogen in the sample.

$$\text{Per cent hydrogen} = \frac{\text{ml. of contraction} \times 100}{\text{ml. of initial sample}}$$

Next, close the copper oxide tube and pass the gas into the potassium hydroxide pipette several times

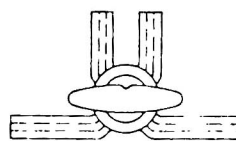


Fig. 22—U-Tube Stopcock Across the Manifold

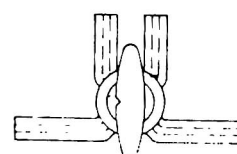


Fig. 23—U-Tube Stopcock Connecting Manifold to Catalyst or Copper Oxide Tube

to remove carbon dioxide; then, open the copper oxide tube and pass the gas through the tube to sweep out any carbon dioxide remaining. Again pass the gas into the potassium hydroxide pipette several times. This sweeping out process should be performed twice to insure complete removal of carbon dioxide. Return the gas to the burette and read the burette. Any contraction in volume observed is due to the removal of carbon dioxide which was formed by oxidation of carbon monoxide in the copper oxide tube.

The contraction in volume equals the volume of carbon monoxide in the sample.

$$\text{Per cent carbon monoxide} = \frac{\text{ml. of carbon monoxide} \times 100}{\text{ml. of initial sample}}$$

The heater temperature must not vary over 5° C. during the analysis.

At completion of the analysis, before permitting the heater to cool, open the copper oxide tube to the atmosphere through the manifold. With portable apparatus also close the reservoir cock.

HYDROCARBONS BY CATALYTIC OXIDATION OR SLOW COMBUSTION

The gas remaining in the burette at this stage of the analysis consists of hydrocarbons and nitrogen. The hydrocarbons may consist of methane, ethane, and higher homologs, but only two hydrocarbons can be calculated from the data obtained by combustion analysis, so the results of such analysis are usually reported as methane only, methane and ethane, or as total paraffins.

If the oxygen has been removed from the sample, air or oxygen must be added at this stage of the analysis to carry out the combustion. Oxygen is preferred as it permits burning a larger amount of sample.

Usually, the operator will find it necessary to take only a portion of the residual sample for catalytic or slow combustion because the volume of gas including the added oxygen at the end of the test will otherwise exceed the capacity of the burette. It is good practice to take a sample of a size such that after combustion the volume will be just slightly less than the capacity of the burette.

TABLE 6
Combustible Mixtures

Gas	Volume to oxidize 1 ml. of gas*	
	ml. of oxygen	ml. of air
Hydrogen	0.5	2.39
Carbon Monoxide	0.5	2.39
Methane	2.0	9.56
Ethane	3.5	16.72
Propane	5.0	23.89
Butane	6.5	31.06
Pentane	8.0	38.22

*Does not include 15 to 20 per cent excess oxygen required.

Oxygen must be present in an excess of at least 15 to 20 per cent. Insufficient oxygen may result in

the expansion of the sample due to the formation of hydrogen and carbon monoxide instead of carbon dioxide and water. If the size of the residue is sufficiently small, an even higher per cent of oxygen is recommended. The presence of an excess may be determined by testing the gas after the combustion in the oxygen pipette. Table 6 may be used as a basis in estimating the oxygen or air required for combustion. The amount of oxygen needed may be established by trial analysis or from a knowledge of the composition of the sample. If cylinder oxygen is to be used for the combustion it must be hydrogen free.

If the copper oxide tube has been previously used for the combustion of hydrogen and carbon monoxide, some of the sample containing hydrocarbons will have remained in the tube. The usual practice is to leave the copper oxide tube closed during catalytic oxidation or slow combustion and to apply a correction for the hydrocarbons left unburned. The application of this correction is explained on page 36.

The catalytic oxidation or slow combustion method may be used for the determination of any single combustible gas and of certain combinations of combustible gases. Care must be exercised in the combustion of gases having a lower limit of explosibility, as propane and butane for example. Such gases in high concentration are appreciably soluble in stopcock grease. It often is advisable to dilute the sample with air in order to reduce the partial pressure of these gases, and thus reduce their solubility in the grease.

Formulas for the calculation of the amounts of the components of certain gaseous mixtures from the combustion data are given in Chapter VII on "Calculations".

CATALYTIC OXIDATION

With the laboratory type apparatus, assuming the heater to be at the proper temperature, the first step in the catalytic oxidation is to store the measured amount of sample in the gas reservoir and then measure the required amount of oxygen in the burette. The oxygen is then passed into the gas reservoir and mixed with the sample. With laboratory apparatus employing mercury as the confining liquid, lower the reservoir leveling bulb as the gas enters in order to maintain atmospheric pressure throughout the system. Next, close the tubing clamp at the base of the burette and lower the burette leveling bulb to the bottom of the burette. Regulate the clamp so as to draw the sample back into the burette by way of the catalyst tube at not over 30 ml. per minute. After the first pass the gas is passed back and forth between burette and reservoir through the catalyst tube at a rate not exceeding 60 ml. per minute. With apparatus using mercury as the confining liquid maintain the level of the mercury in the leveling bulb of the gas reservoir at the same level as the mercury in the reservoir, thus maintaining atmospheric pressure during the passage of the gas. Three to four such passes should be sufficient. However, the gas should be passed until constant readings are obtained. A

burette reading is then taken to determine the contraction in volume due to oxidation. ("r" in calculations). The gas is then passed into the potassium hydroxide pipette several times to remove the carbon dioxide formed. After the removal of the carbon dioxide, pass the gas through the catalyst tube and into the potassium hydroxide pipette to remove any carbon dioxide remaining in the catalyst tube. The amount of gas absorbed represents the carbon dioxide formed and corresponds to "s" in the combustion calculations.

At completion of the analysis, before permitting the heater to cool, open the catalyst tube to the atmosphere through the manifold.

With the portable apparatus the gas is stored in the potassium hydroxide pipette, the oxygen measured in the burette and then mixed with the sample. The mixture ready for combustion is then drawn back into the burette, the leveling bottle raised to the top of the apparatus, and the gas allowed to flow through the catalyst tube into the reservoir at the rate of not over 30 ml. per minute. The rate of flow is regulated with the stopcock at the top of the burette. The gas is then drawn back into the burette at not over 60 ml. per minute, and this process repeated until constant readings are obtained. The reading is then taken to determine contraction in volume due to oxidation ("r" in calculations). The gas is then passed into the potassium hydroxide pipette several times to remove the carbon dioxide formed.

After the first removal of carbon dioxide, pass the residual gas from the burette through the catalyst tube and into the reservoir twice and then into the potassium hydroxide pipette to recover the carbon dioxide left in the tube. An amount of carbon dioxide of no significance may be left in the tube, but this amount can be further reduced by again sweeping out the tube after the second carbon dioxide absorption.

The final burette reading after sweeping out the tube is recorded. The contraction in volume due to the removal of carbon dioxide is designated by the letter "s" in calculations (see page 34).

At completion of the analysis, before permitting heater to cool, close reservoir cock and open catalyst tube to the atmosphere through the manifold.

IMPORTANT

The temperature of the catalyst heater must be at least 500° C. for rapid and complete oxidation. Heaters must not vary over 5° C. during the entire analysis. If oxidation is slow or incomplete the temperature of the heater is probably low. Check the thermometer. Do not permit solutions or mercury to enter copper oxide or catalyst tubes.

SLOW COMBUSTION

If the amount of combustible gas in the sample plus the oxygen added results in a mixture which is below the lower explosive limit, the mixture may be fed directly from the burette into the slow combustion pipette and burned.

If the amount of combustible in the sample is such that an explosive mixture would result from mixing the sample with the oxygen, the required amount

of the latter is measured and stored in the slow combustion pipette. The sample is then fed from the burette slowly into the slow combustion pipette so that the combustible gas burns as fast as it enters the combustion chamber, and the mixture in that pipette never reaches the explosive limits.

First, store the sample in the Di-Sorbent pipette. Then, carefully measure the correct amount of oxygen in the burette and pass the oxygen into the slow combustion pipette, lowering the pipette leveling bulb as the gas enters to maintain atmospheric pressure as nearly as possible.

Draw the required portion of sample back to the burette and measure carefully. Turn the air blast on the pipette and adjust the temperature of the filament to a bright yellow—almost white. Close tubing clamp and raise the burette leveling bulb to the highest point. Open burette to slow combustion pipette and open tubing clamp a little to permit the gas flow slowly into the pipette at not over 10 ml. per minute. The rate of gas flow must be regulated carefully, as too rapid flow into the combustion pipette may cause an explosion.

With portable apparatus using aqueous salt solution, place the burette leveling bottle on the top platform and regulate the gas flow with the burette stopcock.

Care must be exercised throughout this entire procedure to insure that the combustible gases and the oxygen do not become mixed accidentally, that the platinum spiral is at the correct temperature for complete combustion, and that the combustible gas is fed slowly and steadily from the burette into the combustion pipette.

If the combustibles are mostly paraffins and if burned properly, the filament will show an increase in temperature and a halo.

If the filament is too hot at the outset, the increase in temperature may cause the wire to fuse. If the burning is intermittent and minor explosions or puffs occur the rate of flow should be decreased. However, it is possible that the flow is being interrupted by globules of mercury or solution in the capillaries.

If it is apparent that the sample is not burning properly or if there is any question at all, turn off the current and discard the sample. Do not attempt to remedy the situation by increasing the temperature of the filament.

If the temperature of the filament is too low at the outset a part of the gas may go by without burning, mingle with the oxygen, and build up a mixture which will probably explode, but certainly will if the temperature of the filament is increased. Do not attempt to adjust the mercury level in the slow combustion pipette while the gas is first passing in. A decrease in pressure inside of the pipette may cause a sudden inrush of gas. Keep the gas flowing evenly and steadily.

With a flushing type of manifold, run the confining liquid from burette over to the pipette stopcock.

When all the gas has been fed into the combustion pipette, draw about 5 ml. back into the burette

TABLE 7
Limits of Inflammability of Gases and Vapors in Air

Name	Per Cent by Volume	
	Lower Limit	Upper Limit
Acetylene	2.5	80.0
Benzene	1.4	6.7
Isobutane	1.8	8.4
n-Butane	1.85	8.4
Butene	1.7*	9.0*
Carbon Monoxide	12.5	74.0
Ethane	3.2	12.5
Ethene	3.0	29.0
Hexane	1.2	6.9
Hydrogen	4.1	74.0
Hydrogen Sulfide	4.3*	45.5
Methane	5.3	14.0
Isopentane	1.3*	
n-Pentane	1.4	7.8
Propane	2.4	9.5
Propene	2.0*	11.1*
Toluene	1.3*	6.7*

Limits of Inflammability of Gases and Vapors, by H. F. Coward and G. W. Jones, U. S. Bureau of Mines. Bulletin 279.

*Values determined in closed apparatus.

and then pass back into the pipette slowly. Next, draw 10 or 15 ml. and finally a larger portion. This will clear the capillaries of combustible components without danger of an explosion. The gas is then brought slowly back to the burette leaving enough in the pipette to clear the filament and passed back and forth two or three times over the hot coil. Manipulate the pipette leveling bulb up and down so as to maintain the gas as nearly as possible at atmospheric pressure.

Finally, pass the gas back into the pipette, shut off the current and allow the pipette shell to cool to room temperature. Bring the gas back to the burette and measure carefully. The decrease in volume is referred to as contraction "r" in the combustion calculations. Then determine the amount of carbon dioxide formed ("s" in calculations) by passing the gas into the potassium hydroxide pipette.

When the combustibles in the sample exceed 5.0 per cent, a second burning and a second carbon dioxide absorption should be made to insure that all the combustible gas has been burned. The first and second contractions on burning, and the first and second contractions due to carbon dioxide formed are added and combustion calculations made from these totals. If necessary, also determine the oxygen remaining. When the combustion procedure has been successfully completed, the methane and ethane content of the sample are calculated from the contraction and the carbon dioxide formed.

Hydrogen burns at a lower temperature than methane. If the combustible is mostly hydrogen, the burning may not be perceptible. The filament need not be so hot with hydrogen as with paraffins or hydrocarbons.

COMBUSTIBLE COMPONENTS BY EXPLOSION

The explosion method for determining combustibles is more rapid and convenient than slow combustion, but has more disadvantages and errors than the other methods.

In this method, the sample is purposely made explosive by the addition of an air-oxygen mixture confined in the explosion pipette and ignited by means of an electric spark.

The method is convenient for hydrogen and for hydrogen with small percentages of hydrocarbons, but it is not recommended for carbon monoxide or for mixtures containing principally hydrocarbons.

The disadvantage for gases rich in hydrocarbons lies in the fact that so much oxygen is required to produce an explosive mixture that the sample is necessarily small in volume leading to multiplication of errors. Also, due to the narrow limits of inflammability, it is difficult to get the correct mixture for an adequate explosion. The method is unsatisfactory for carbon monoxide due to incomplete combustion.

Air as the source of oxygen is usually unsatisfactory because of the low oxygen content. If pure oxygen is used, oxides of nitrogen are apt to be formed by the explosion. The best plan is to use a mixture of approximately equal parts of air and pure oxygen.

The proportioning of the mixture for explosion is most important. If near the lower explosive limit, the flame-speed is slow and incomplete combustion may result. If near the upper limit, the oxygen content is inadequate for complete combustion. (For limits of inflammability, see Table 7). At the point of perfect combustion the high flame temperature may deposit carbon, cause the formation of appreciable quantities of oxides of nitrogen, and the violence of the explosion may shatter the pipette.

It has been determined that the best mixture seems to be about half-way between the lower explosive limit and the point of perfect combustion.

Table 8 is convenient in the preparation of explosive mixtures of hydrogen and methane using equal parts of air and oxygen.

If the combustible component is all methane, the mixture should contain 8 per cent methane and 92 per cent air-oxygen; if all hydrogen, 12 to 14 per cent hydrogen and 88 to 86 per cent air-oxygen; if one part methane and three parts hydrogen, 11

TABLE 8
Preparation of Explosive Mixtures

Ratio in Residual Sample		Per cent Methane and Hydrogen Mixture to be Exploded	Per cent Oxygen-Air Mixture
Methane	Hydrogen		
4	0	8	92
3	1	9	91
2	2	10	90
1	3	11	89
0	4	12-14	88-86

C. W. W. Grice & W. Payman, Fuel in Science and Practice, 1924, pp. 236-249.

per cent combustibles and 89 per cent air-oxygen, etc.

If the proportion of combustible present is too small to support an explosion with air-oxygen, a small amount of exciting gas, either hydrogen or electrolytic gas may be added.

Electrolytic gas is made by dissociating an electrolyte consisting of a 5 per cent solution of re-crystallized barium hydroxide in distilled water using platinum electrodes and direct current. Hydrogen may be conveniently prepared from pure zinc metal and sulfuric acid.

If electrolytic gas is used, the volume need not be measured as the gas disappears as a negligible amount of water in the explosion. Hydrogen must be measured in order that the resulting contraction may be corrected for the amount of hydrogen added

PROCEDURE IN THE USE OF THE EXPLOSION PIPETTE

If the total volume of the sample mixed with air-oxygen is 100 ml. or less, the auxiliary gas may be drawn directly into the burette and the volume of the mixture measured. Otherwise, the sample may be stored in the explosion pipette and the auxiliary gas measured in the burette and then added to the sample in the explosion pipette. If two or more explosions are required to burn all the gas, part of the sample may be stored in the potassium hydroxide pipette.

Mix the gases thoroughly by passing back and forth between the burette and explosion pipette. With the mixture in the explosion pipette, close the pipette stopcock and lower the leveling bulb to create a negative pressure in the pipette. Press the spark button to explode the mixture. Do not permit the spark to vibrate between the electrodes. If the mixture does not explode with several sparks, the proportions are probably wrong. Pass the gas back into the burette and measure carefully, noting any contraction in volume. This decrease in volume corresponds to the contraction "r" in the combustion calculations. Then, determine the amount of carbon dioxide formed. Calculations from combustion data are the same as those applying to the slow combustion method.

DETERMINATION OF NITROGEN

In the usual gas analysis the percentage of nitrogen is obtained by subtracting the sum of the percentage of all the other components from 100.

CHAPTER VII
CALCULATIONS

Absorption

The calculations of the percentages of the components in a gas mixture are based upon the data recorded during the course of the analysis; that is, the changes in volume of the sample observed after the successive absorption and combustion treatments.

In the case of components such as

- Carbon dioxide
- Illuminants
- Oxygen
- Carbon monoxide

which may be removed directly by absorption, the volume of any component is represented by the contraction in volume of the sample after the absorption treatment, and the percentage is calculated by dividing the volume of the component by the volume of the original sample and multiplying by 100.

Volume of sample..... a
Volume after carbon dioxide absorption... b
Contraction, a minus b..... c

$$\% \text{CO}_2 = \frac{c}{a} \times 100$$

Volume after illuminants absorption..... d
Contraction, b minus d..... e

$$\% \text{Ill.} = \frac{e}{a} \times 100$$

Volume after oxygen absorption..... f
Contraction, d minus f..... g

$$\% \text{O}_2 = \frac{g}{a} \times 100$$

Volume after carbon monoxide absorption h
Contraction, f minus h..... k

$$\% \text{CO} = \frac{k}{a} \times 100$$

If the original sample consists of 100 ml. of gas, then the percentage equals the contraction in volume in ml.

Oxidation Over Copper Oxide

The amount of carbon dioxide produced is theoretically equal to the amount of carbon monoxide in the sample, and inasmuch as the hydrogen combines with oxygen from the copper oxide to form

water, the contraction in volume of the sample is a direct measure of the hydrogen present.

Volume after copper oxide combustion.... l
Contraction, h minus l..... m

$$\% \text{H}_2 = \frac{m}{a} \times 100$$

Volume after carbon dioxide absorption... n
Contraction, l minus n..... o

$$\% \text{CO} = \frac{o}{a} \times 100$$

If a = 100 ml., then % H₂ = m and % CO = o

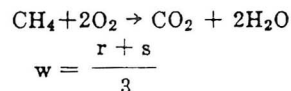
Catalytic Oxidation, Slow Combustion
or Explosion

As described in the text, in any of these methods oxygen is consumed, carbon dioxide is produced, and the gas volume undergoes a contraction as indicated by the reactions on page 9.

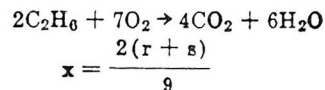
Let

- r = ml. contraction in volume
- s = ml. carbon dioxide produced
- t = ml. oxygen consumed
- y = ml. carbon monoxide
- z = ml. hydrogen
- w = ml. methane
- x = ml. ethane
- v = ml. propane
- u = ml. butane

Methane—The sample undergoes a contraction in volume equal to twice the volume of methane, and the carbon dioxide produced is equal in volume to the methane. The water vapor formed condenses, and is of negligible volume.

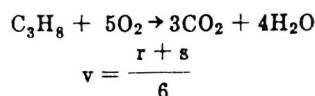


Ethane—The combustion of ethane produces 2½ volumes contraction, and 2 volumes of carbon dioxide.

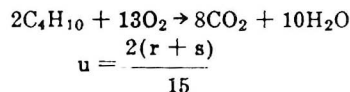


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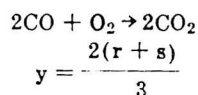
Propane—The combustion of propane produces 3 volumes of contraction and 3 volumes of carbon dioxide.



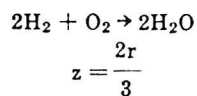
Butane—The combustion of butane produces 3½ volume of contraction and 4 volumes of carbon dioxide.



Carbon Monoxide—The contraction is ½ the volume of the carbon monoxide, and the carbon dioxide formed is equal to the carbon monoxide.



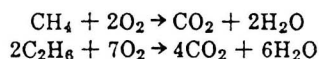
Hydrogen—The contraction is 1½ times the volume of hydrogen.



TWO COMBUSTIBLE COMPONENTS

When two combustible components are present the data used in the calculations are the carbon dioxide produced and the contraction in volume.

Methane and Ethane—The reactions are

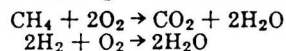


Substituting and solving

$$x = \frac{4s - 2r}{3}$$

$$w = s - 2x$$

Methane and Hydrogen—The reactions are

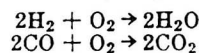


Substituting and solving

$$z = \frac{2r - 4s}{3}$$

$$w = s$$

Carbon Monoxide and Hydrogen—The reactions are



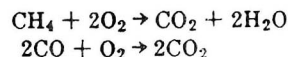
Substituting and solving

$$z = \frac{2r - s}{3}$$

$$y = s$$

CALCULATIONS

Carbon Monoxide and Methane—The reactions are



Substituting and solving

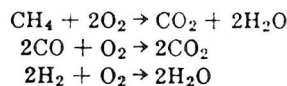
$$y = \frac{4s - 2r}{3}$$

$$w = \frac{2r - s}{3}$$

THREE COMBUSTIBLE COMPONENTS

The oxygen consumed as well as the contraction and the carbon dioxide produced must be determined.

Methane, Carbon Monoxide and Hydrogen—The reactions are



Substituting and solving

$$w = s - y$$

$$y = \frac{(r + 4s)}{3} - t$$

$$z = r - t$$

Volume of Residual Sample Used

If all of the residual gas is used in the combustion or explosion procedure, the percentages are calculated by dividing the volume w, x, y or z of the components as determined by the volume of the original sample a and multiplying by 100 as

$$\% \text{ methane} = \frac{w}{a} \times 100$$

If only a portion of the residual gas remaining after absorption is taken for the combustion, the volume of the component as determined in that portion is used as a basis to calculate the total volume present in the total residual gas according to the following formula.

$$t_1 = \frac{n_1 \times m_1}{o_1}$$

n_1 = ml. of residual gas before catalytic oxidation

o_1 = ml. of residual gas (n_1) taken for catalytic oxidation

m_1 = ml. of component found in portion taken for catalytic oxidation

t_1 = ml. of component present in residual gas (n_1) before catalytic oxidation

p_1 = volume of copper oxide tube in ml.*

*See page 21 for method of calibrating copper oxide tube.

Correction for Combustible Left in Copper Oxide Tube

If the combustible gases have been left unburned in the copper oxide tube, correction for this must be applied to the volume of combustible determined in the residual gas.

$$\left[\begin{array}{c} n_1 + p_1 \\ n_1 \end{array} \right] [t_1] = \text{ml. of combustibles}$$

The percentage of the component in the original sample "a" is then computed as follows:

$$\text{Per cent} = \frac{\text{ml. of combustibles}}{\text{volume of initial sample}} \times 100$$

NOTE: Theoretically the volume of the manifold should be included in this correction, but in actual practice the error introduced by omitting this volume is so small that it may be ignored.

Total Paraffins

Regardless of the members of the series which may be present, the total paraffin hydrocarbon content of a gas mixture may be calculated from the following formula.

$$\text{Total paraffins} = \frac{2r - s}{3}$$

Nitrogen

Per cent nitrogen = 100 minus sum of the percentages of all other constituents.

HEATING VALUE OF GASES

The heating value of a gas may be calculated from analysis by multiplying the percentage, expressed decimally, of each component by its heating value as shown in Table 9 and adding the values obtained. The result will be the gross or net amount of heat in B.t.u.'s which will be given up by a cubic foot of gas completely burned with oxygen under standard conditions, usually expressed as the net B.t.u. value per cubic foot saturated at 60° F. and 30" mercury. The difference between the gross and net figures represents the latent heat or heat of vaporization of the steam produced.

If the gas is free from illuminants, the calculation of heating value from analysis is simplified. It is impossible to separate the components of illuminants by ordinary methods, and a value obtained by other means must be assigned to this group. Neither

does the analysis give a separation of the paraffin group, but the true hydrocarbon content is shown and may be reported with sufficient accuracy as methane and ethane.

If the heating value of a gas as determined by calculation from analysis is compared to the value obtained direct by calorimeter, a value for the illuminants may be obtained which will usually be sufficiently accurate if averaged from a number of determinations repeated periodically.

Watson & Ceaglske, *Industrial and Engineering Chemistry*, Jan. 15, 1932, pp. 70-72, describe a triple-combustion method of determining the average compositions of both illuminants and paraffins. The ordinary analytical procedure is extended to include an additional total combustion with oxygen.

TABLE 9
Heat of Combustion

	B.t.u. per cu. ft.		B.t.u. per lb.	
	Gross	Net	Gross	Net
Acetylene	1499	1448	21,500	20,776
Benzene	3751	3601	18,210	17,480
Isobutane	3363	3105	21,257	19,629
n-Butane	3370	3113	21,308	19,680
Butene	3084	2885	20,840	19,496
Carbon			14,093	14,093
Carbon Monoxide	321.8	321.8	4,347	4,347
Ethane	1792	1641	22,320	20,432
Ethene	1613.8	1513.2	21,644	20,295
Hexane	4762	4412	20,940	19,403
Hydrogen	325	275	61,100	51,623
Hydrogen Sulfide	647	596	7,100	6,545
Methane	1013.2	913.1	23,879	21,520
Isopentane	4008	3716	21,052	19,478
n-Pentane	4016	3709	21,091	19,517
Propane	2590	2385	21,661	19,944
Propene	2336	2186	21,041	19,691
Toluene	4484	4284	18,440	17,620

Fuel-Flue Gases—American Gas Association, N.Y., 1941.

TABLE 10
COMBUSTION DATA

Name	Formula	Molecular Weight	*Specific Gravity 30" Hg(Dry) Air=1	*Lbs./Cu. Ft. 30" Hg(Dry) 60° F.	*Cu. Ft./Lb. 30" Hg(Dry) 60° F.	Combustion Reaction	*Combustion Requirements			*Combustion Products		
							O ₂	Air	Cu. Ft./Cu. Ft. Gas	CO ₂	H ₂ O	N ₂
Acetylene	C ₂ H ₂	26.036	0.9107	0.06971	14.344	2C ₂ H ₂ + 5O ₂ → 4CO ₂ + 2H ₂ O	2.5	11.91	2.0	2.0	1.0	9.411
+Carbon to CO ₂	C	12.01				C + O ₂ → CO ₂	1.0	4.764	1.0			3.764
+Carbon to CO	C	12.01				2C + O ₂ → 2CO	0.5	2.382	1.000			1.882
Carbon Monoxide	CO	28.01	0.9672	0.07404	13.506	2CO + O ₂ → 2CO ₂	0.5	2.382	1.0			1.882
Hydrogen	H ₂	2.016	0.06959	0.005327	187.723	2H ₂ + O ₂ → 2H ₂ O	0.5	2.382			1.0	1.882
Hydrogen Sulfide	H ₂ S	34.076	1.1898	0.09109	10.979	2H ₂ S + 3O ₂ → 2H ₂ O + 2SO ₂	1.5	7.146			1.0SO ₂	5.646
Nitrogen	N ₂	28.016	0.9718	0.07439	13.443							
Paraffins												
Methane	CH ₄	16.041	0.5543	0.04243	23.565	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	2.0	9.528	1.0	2.0	2.0	7.528
Ethane	C ₂ H ₆	30.067	1.04882	0.08029	12.455	2C ₂ H ₆ + 7O ₂ → 4CO ₂ + 6H ₂ O	3.5	16.675	2.0	3.0	3.0	13.175
Propane	C ₃ H ₈	44.092	1.5617	0.1196	8.365	C ₃ H ₈ + 5O ₂ → 3CO ₂ + 4H ₂ O	5.0	23.821	3.0	4.0	4.0	18.821
Isobutane	C ₄ H ₁₀	58.118	2.06654	0.1582	6.321	2C ₄ H ₁₀ + 13O ₂ → 8CO ₂ + 10H ₂ O	6.5	30.967	4.0	5.0	5.0	24.467
n-Butane	C ₄ H ₁₀	58.118	2.06654	0.1582	6.321	2C ₄ H ₁₀ + 13O ₂ → 8CO ₂ + 10H ₂ O	6.5	30.967	4.0	5.0	5.0	24.467
+Isopentane	C ₅ H ₁₂	72.144	2.4872	0.1904	5.252	C ₅ H ₁₂ + 8O ₂ → 5CO ₂ + 6H ₂ O	8.0	38.114	5.0	6.0	30.114	
†n-Pentane	C ₅ H ₁₂	72.144	2.4872	0.1904	5.252	C ₅ H ₁₂ + 8O ₂ → 5CO ₂ + 6H ₂ O	8.0	38.114	5.0	6.0	30.114	
†n-Hexane	C ₆ H ₁₄	86.169	2.9704	0.2274	4.398	2C ₆ H ₁₄ + 19O ₂ → 12CO ₂ + 14H ₂ O	9.5	45.260	6.0	7.0	35.760	
Olefins												
Ethene	C ₂ H ₄	28.051	0.9740	0.07456	13.412	C ₂ H ₄ + 3O ₂ → 2CO ₂ + 2H ₂ O	3.0	14.293	2.0	2.0	2.0	11.293
Propene	C ₃ H ₆	42.077	1.4504	0.1110	9.007	2C ₃ H ₆ + 9O ₂ → 6CO ₂ + 6H ₂ O	4.5	21.439	3.0	3.0	3.0	16.939
Butene	C ₄ H ₈	56.102	1.9336	0.1480	6.756	C ₄ H ₈ + 6O ₂ → 4CO ₂ + 4H ₂ O	6.0	28.595	4.0	4.0	4.0	22.585
Aromatics												
+Benzene	C ₆ H ₆	78.107	2.6920	0.2060	4.852	2C ₆ H ₆ + 15O ₂ → 12CO ₂ + 6H ₂ O	7.5	35.732	6.0	3.0	3.0	28.232
+Toluene	C ₇ H ₈	92.132	3.1760	0.2431	4.113	C ₇ H ₈ + 9O ₂ → 7CO ₂ + 4H ₂ O	9.0	42.878	7.0	4.0	4.0	33.878

*Fuel-Flue Gases—American Gas Association, N. Y., 1941.

+Calculations are based on the assumption that this substance could exist as a gas at 30" Hg and 60° F

CHAPTER VIII
SPECIALIZED GAS ANALYSIS METHODS
AND APPARATUS

This chapter deals with specialized methods and apparatus which have been developed for specific types of gas samples.

The Burrell-Haldane
Gas Analysis Apparatus

The Burrell-Haldane Apparatus is used in the analysis of mine atmospheres or other gaseous mixtures where interest is centered in the accurate determination of small amounts of carbon dioxide, combustible gases, and oxygen.

The principles involved are the same as those applying to other gas volumetric methods of analysis; the chief difference is in design of apparatus.

ASSEMBLY

The burette assembly comprises the burette, compensator, and water jacket (see Fig. 24).

The burette has a total capacity of 21 ml. with a 15 ml. ungraduated bulb at the top and a 6 ml. stem graduated in .01 ml. divisions. Readings may be estimated to .002 ml.

There are three holes in the top jacket stopper. The hole with the slit is for the burette and is positioned to the front of the jacket. Slip the capillary tube just below the burette stopcock through the slit and into the hole. Pass the compensator tube up through the rear right hole and the air tube down through the rear left hole.

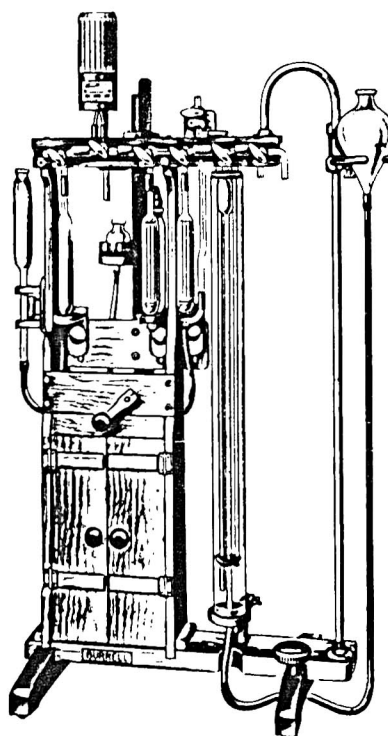
Carefully mount the burette assembly on the support frame. The burette stopcock is fitted into the manifold board while the compensator and agitator tubes slip into place behind the manifold board.

Pass the water jacket up over the burette assembly and seat the top stopper firmly. Wet the lower end of the burette and also the hole in the bottom stopper. Pass the end of the burette through the hole in the stopper and seat the stopper, adjusting so that the burette is perpendicular.

The manifold is in four sections, the flushing end stopcock at the right which connects to the burette stopcock, the flushing manifold (pipette section) No. 39-810-B at the left of the burette, the U-tube stopcock No. 39-825 which carries catalyst tube No. 40-336 and single flushing stopcock No. 39-810-A which connects to the gas reservoir No. 38-888-A.

There is a Burrell contact pipette No. 40-170 for carbon dioxide, a Burrell contact pipette No. 40-190 for oxygen, and the Burrell catalytic assembly for combustibles.

The first pipette to the left of the burette is for carbon dioxide and is of the single barrel type with



38-887
Burrell-Haldane Model VC

a side tubulature at the bottom for making connection to the compensator manometer. The latter has a stopcock at the top and a side tube just below the stopcock for connection to the compensator tube in the water jacket. This pipette contains potassium hydroxide solution.

The oxygen pipette is of the double barrel type and is placed to the left of the carbon dioxide pipette. This pipette is equipped with a rubber gas bag. Alkaline pyrogallol is used for the determination of oxygen.

Next to the left is the catalyst tube mounted on a U-tube stopcock No. 39-825 and then the gas reservoir. The gas reservoir is connected with rubber tubing to a leveling bottle carried on the elevator in the rear.

The reservoir leveling bulb is mounted on an elevator so that the operator may conveniently keep the level of the mercury in the reservoir and leveling bulbs the same during the manipulation of the catalytic assembly. This serves to keep the gas under approximately atmospheric pressure and minimizes the possibility of leaks.

On the outside of the frame at the left is the leveling tube for the carbon dioxide pipette so mounted that the tube may be raised or lowered. The tube is connected to the carbon dioxide pipette by means of rubber tubing.

THE COMPENSATOR

Before taking a sample of gas into the burette turn the compensator stopcock so that the compensator tube in the jacket and the capillary below the stopcock are open to the air.

Adjust the level of the potassium hydroxide solution in the first pipette capillary to the reference mark (about 1/8" below the manifold cock) by raising or lowering the burette leveling bulb.

Tie a single strand of black thread around the compensator capillary and shift the thread until just even with the lower edge of the meniscus curve of the solution in the capillary. Then turn compensator stopcock so that the capillary communicates with the tube in the jacket and both are sealed from the atmosphere. The stopcock and thread are left in this position during the analysis.

The manifold and capillaries leading to the pipettes are then filled with nitrogen (see page 27) and the sample drawn into the burette.

With the gas sample in the burette and with the sample under slight pressure, open the stopcocks so that the burette communicates with the first contact pipette. Then adjust the solution in the pipette capillary back to the reference mark by manipulating the burette leveling bulb.

The solution in the compensator capillary is next adjusted back to the thread by moving the leveling reservoir at the left up or down. Usually, it will be necessary to again adjust the solution in the pipette capillary and also a second adjustment of the solution in the compensator manometer may be necessary. When the solution in both capillaries are exactly at their respective reference marks the pipette stopcock is closed and the burette reading made. The foregoing procedure is followed prior to every burette reading.

ANALYTICAL PROCEDURE

Inasmuch as the Haldane is ordinarily used for the determination of small amounts of impurities

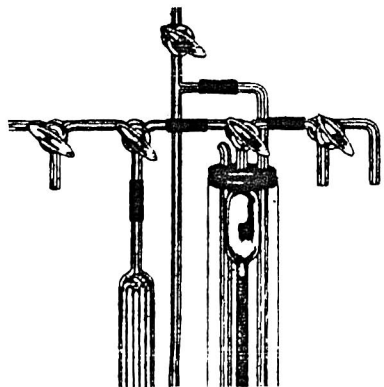


Fig. 24—Haldane Compensator Assembly

in air, carbon dioxide is removed first, then combustible components and then oxygen. The oxygen in the sample is used for burning the combustible. Therefore, the oxygen found by absorption will represent only the amount remaining after combustion. The amount consumed by the combustion must be added.

Since the oxygen of the sample is used to burn the combustible, the sample must contain oxygen in excess of that required for the combustion.

To insure maximum precision, all traces of each particular gas must be "picked up" from the various capillaries during the determination of that gas. In determining carbon dioxide formed by combustion, the major portion of the carbon dioxide is removed in the caustic pipette, and the gas is then passed into the catalyst tube again to pick up the carbon dioxide left in the capillary connections. The gas is then passed into the caustic pipette several times more before making the burette reading. In like manner, the oxygen must be picked up from the caustic and catalyst tube capillaries during the oxygen determination.

In the case of mine atmosphere in which the constituents usually determined are CO₂, O₂, CH₄, and N₂, the following calculations apply.

Volume of sample taken.....	A
Volume after carbon dioxide absorption	B
Contraction (A—B)	C

$$\% \text{ Carbon Dioxide} = \frac{C}{A} \times 100$$

Volume after combustion	D
Contraction (B—D).....	E
Volume after carbon dioxide absorption.....	F
Contraction (D—F).....	H

$$\% \text{ CH}_4 = \frac{\frac{1}{2}E + \frac{1}{2}H}{A} \times 100$$

Volume after O ₂ absorption.....	K
Contraction (F—K).....	M

Inasmuch as the burning of the methane consumed some oxygen, M equals the volume of un-consumed oxygen present.

The volume of oxygen consumed is twice the volume of methane found

Oxygen consumed = 2CH ₄	N
Total Oxygen = M + N.....	P

$$\% \text{ Oxygen} = \frac{P}{A} \times 100$$

% Nitrogen = 100% minus the sum of percentages of CO₂, CH₄, and O₂

When the methane in a sample exceeds 0.25 per cent, a second complete combustion should be made to insure picking up methane from the capillary of the caustic pipette. The first and second contractions on combustion, and the first and second contractions due to carbon dioxide formed in combustion, are added for calculation of methane.

Burrell Gas Purity Testers

ASSEMBLY

Gas Purity Testers are supplied in cabinet models only. All units are completely assembled before shipment so that the glassware may be installed with a minimum of adjustment.

Gas purity burettes are shipped assembled in the water jackets. They are to be mounted on the adjustable platform so that the stopcock is centered on the hole in the manifold support board. Fill the water jacket with water as described on page 16.

All of the models except VP have a single stopcock manifold. Prepare the manifold for use as described on page 16 and connect to burette with piece of rubber tubing $1\frac{1}{4}$ " long by $\frac{3}{16}$ " I. D.

Absorption pipettes are filled as described on page 21 and the Burrell Catalytic Assembly is mounted as described on page 17.

Oxsorbent is recommended for use with Model VE and ammoniacal copper solution for Model VG.

Aqueous salt solution, see page 13, is used as the confining liquid in the burette.

BURETTE

On page 9 will be found paragraphs devoted to reading the burette. However, there is a difference in that the purity tester burette No. 40-000 does not have a rear blue line and the reading is, therefore, made at the bottom of the water meniscus.

It is assumed that the impurities will not exceed 3%. The burette is specially designed to accommodate a full 100 ml. sample and yet permit finer readings. A large ungraduated bulb holding

94 ml. is in the center of the burette. The small diameter stems above and below the bulb each have a capacity of 3 ml. and are graduated in $\frac{1}{25}$ ml. Each milliliter graduation in the stems is numbered, and is divided into five large and twenty-five small spaces.

If the reading should fall in the upper stem, for example below the 2 ml. mark and one large and two small spaces farther down, the volume would be 2.28 ml.

If in the lower stem, below the 98 ml. mark and three large spaces and four small spaces on down, the reading would be 98.76.

In the first case, the volume is two ml. plus a fraction of an ml. The fraction comprises $\frac{1}{4}$ ml. plus $\frac{3}{25}$ ml. or a total of $\frac{7}{25}$ ml. which equals .28 ml.

In the second case, the volume is ninety-eight ml. plus a fraction comprising $\frac{3}{4}$ ml. plus $\frac{4}{25}$ ml. or $\frac{19}{25}$ ml. which equals .76 ml.

When the reading falls in the upper stem (as when testing liquid air oxygen) the sample would be 97.72 pure (100—2.28) and would carry 2.28% of contaminants.

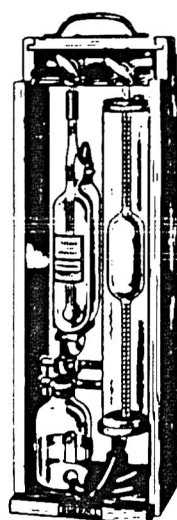
If in the lower stem, the gas would be 98.76% pure and carry 1.24% contaminants (100—98.76).

ANALYTICAL PROCEDURES

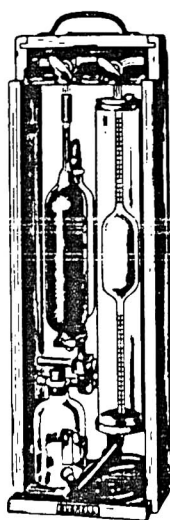
Samples of 100 ml. are taken as described in page 27 and the absorption is made in the case of Models VE and VG as under "Carbon Dioxide" on page 28.

The method of handling the Burrell Catalytic Assembly is fully outlined on pages 30 and 31.

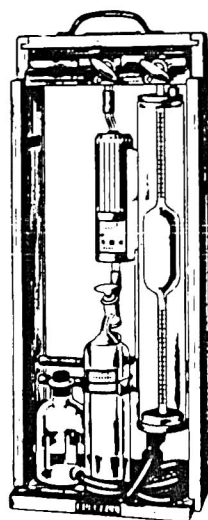
It is well to read through the entire manual to pick up odds and ends of pertinent information on sampling, etc., which apply to gas purity testing, but which may not be specifically pointed out in these abridged instructions.



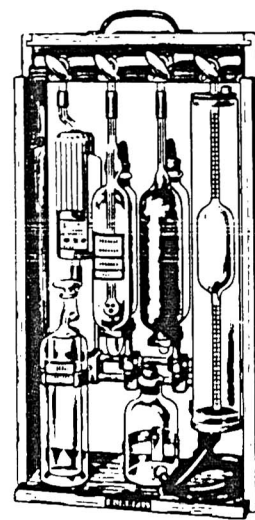
39-556
Model VE



39-557
Model VG



39-558
Model VO



39-564
Model VP

Burrell Gas Purity Testers

Hydrogen Sulfide by the Tutwiler Method

The Tutwiler method is widely applied to the determination of hydrogen sulfide in gas mixtures for control purposes. Mercaptans are absorbed along with hydrogen sulfide.

REAGENTS

Starch Solution—Prepare a thin paste by rubbing 2 grams of soluble starch in 5 ml. of water. Add the paste with stirring to a pint of boiling water. Let stand until cool and decant the clear solution for use. Make up fresh every few days.

Iodine Solutions—For H_2S from 20 grains to 500 grains per 100 cubic feet of gas, dissolve 1.7076 grams of iodine in water with enough added potassium iodide to insure complete solution and make up the volume to one liter. One ml. of this solution is equivalent to 100 grains of H_2S per 100 cubic feet of gas.

For H_2S from 500 grains to 6000 grains per 100 cubic feet, use 5.1228 grams of iodine per liter. One ml. of this solution is equivalent to 300 grains H_2S per 100 cubic feet of gas.

PROCEDURE

Fill burette leveling bulb with starch solution and raise bulb until the solution reaches the stopcock at the top of the burette. Turn the stopcock to the side outlet and fill capillary with starch solution.

Fill the small graduated section at the top with standard iodine solution and make note of the reading.

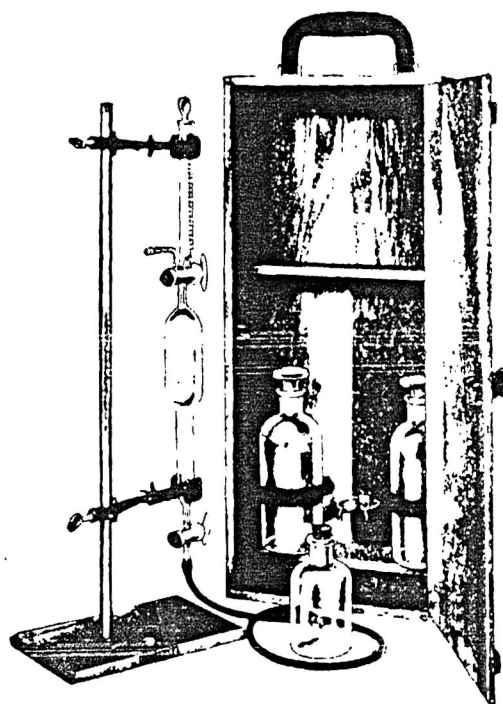
Flush the sample tube outlet with gas sample and connect to side tube of upper burette stopcock. Open lower burette stopcock and draw a little more than 100 ml. of sample into the burette. Raise leveling bulb, open bottom stopcock and permit level of starch solution to rise to the 100 ml. mark. Close bottom stopcock. Open top burette stopcock to the atmosphere to permit excess pressure in the burette to escape, thereby bringing the gas sample to atmospheric pressure.

Close top stopcock and with the bottom stopcock open, lower leveling bulb until the starch solution comes to rest at the 110 ml. mark. Close bottom stopcock. The gas is now under negative pressure.

Admit small increments of iodine solution followed by thorough shaking. Continue until the starch solution assumes a faint, permanent blue color. Record the amount of iodine solution required.

If the first solution has been used, multiply the amount of iodine used by 100 to get the grains of H_2S per 100 cubic feet of gas. If the second solution, multiply by three. If less than 20 grains of H_2S per 100 cubic feet of gas is present, a burette of 500 ml. capacity is preferably employed.

Test each batch of fresh starch solution to determine the blank by filling the burette with the solution to the 10 ml. mark and adding iodine and shaking until a faint permanent blue color is obtained. This blank, usually amounting to 0.2 or 0.3 ml. must be subtracted from the iodine used in each determination.



40-620
Burrell-Tutwiler Apparatus

BURRELL BUILD-UP SUPPORT FRAME

The Burrell BUILD-UP frame for gas analysis apparatus simplifies assembly, permits selection of any desired combination of glass parts, and affords flexibility in alterations as future needs may arise.

The list below and the illustrations on pages 14 and 15 identify the various parts in the make up of the BUILD-UP frame. Each apparatus is completely assembled before shipment, and in disassembling for packing as many as possible of the various clamps are left in place.

A burette can be placed either at the left or right of the pipettes in most BUILD-UP assemblies, or

two burettes may be used, one at each end connected to the same pipettes or each to its own group.

Cross tubes are longer than necessary in laboratory models so that additional glassware may be inserted. Exceptionally long apparatus may require more than two bases to give stability, but as many of these as required may be used and the apparatus made as long as need be, either connected as one apparatus or divided into units each complete in itself.

Extra space in portable apparatus depends upon the size of the case. Without case, the uprights may be spread out as far as necessary.

LIST OF PARTS

Name of Part	Catalog No.
Base, cast iron, laboratory mercury control valve in right leg	GA-2
Base, cast iron, laboratory mercury control valve in left leg	GA-3
Base, cast iron, laboratory	GA-5
Valve, stem and handle only for laboratory base GA-2 or GA-3	GA-6
Upright, portable, with mounting pedestal	GA-8
Upright, aluminum, laboratory	GA-11
Burette, support complete, laboratory, includes platform, rods, nuts and washers	GA-14
Platform, only, for use with GA-14	GA-15
Rod only, with nuts and washers for use with GA-14	GA-16
Base, wood, portable with holes drilled for uprights (Specify Model)	GA-17
Burette Support, metal, portable	GA-18
Cross Tube Clamp, metal, laboratory	GA-30
Cross Tube Clamp, metal, portable	GA-33
Cross Tubes, top pair, aluminum, laboratory	GA-36-1
Cross Tubes, bottom pair, aluminum, laboratory	GA-36-2
Cross Tubes, aluminum, portable, Master TL or 111	GA-39-1
Cross Tubes, aluminum, Portable, Master T or 110 or Senior TL or 211	GA-39-2
Cross Tubes, aluminum, Portable, Senior T or 310 or Junior TL or 511	GA-39-3
Cross Tubes, aluminum, Portable, Junior T or 510	GA-39-4
Manifold Clamp, metal, laboratory	GA-42
Manifold Clamp, metal, portable	GA-43
Pipette Support, metal, laboratory and portable	GA-105
Leveling Rod, laboratory for leveling bulb	GA-111
Leveling Bottle Clamp, steel, portable	GA-115
Ring Clamp, cast iron, laboratory for leveling bulb	GA-117
Leveling Bottle Support, metal, portable	GA-120
Leveling Rod laboratory L type for sampling assembly	GA-123
Electric Outlet Box with mounting clamp and extension	GA-185
Electrical Extension Cord, portable	GA-186
Lower Support, aluminum, for sample tube	GA-210
Upper Support, aluminum, for sample tube	GA-215
Heater Support Clamp, laboratory, build-up type. Supports Perma-Therm heater and U-tube manifold	GA-220
Heater Support Clamp, laboratory cabinet type. Supports Perma-Therm heater and U-tube manifold	GA-225
Heater Support Clamp, portable type, supports Perma-Therm heater and holds gas reservoir	GA-230
Heat Shield	GA-235
Leveling Rod, laboratory, for burette leveling bulb	GA-245
Leveling Rod, short, for gas reservoir	GA-250
Clamp for attaching leveling rod GA-245 to frame	GA-255
Clamp for attaching leveling rod GA-250 to frame	GA-260
Manifold Clamp, laboratory, for attaching Perma-Therm to frame	GA-265
Manifold Clamp, laboratory for attaching leveling rod to frame and supporting flushing end stopcock	GA-270
Cross Tube Clamp, with end cover, laboratory	GA-275
Reservoir Support, laboratory	GA-280
Heat Shield for manifold	GA-290

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*Publication by U. S. Department of the Interior, Bureau of Mines.

†Publication by U. S. Department of Commerce, Bureau of Standards.

GENERAL INDEX

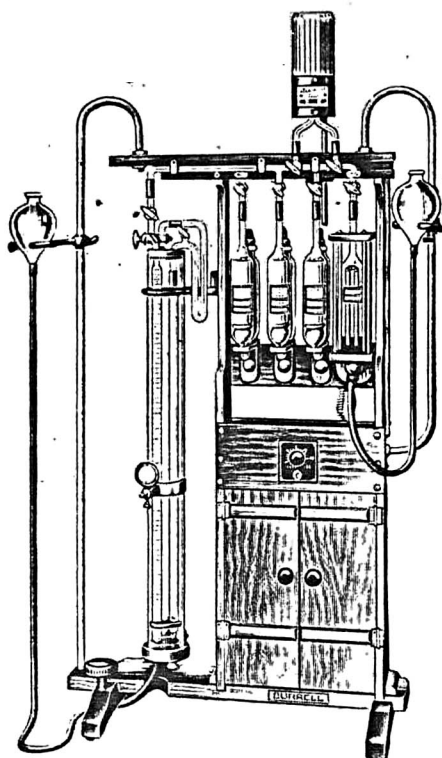
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BURRELL CORPORATION
 SCIENTIFIC INSTRUMENTS AND LABORATORY SUPPLIES
 2223 FIFTH AVENUE, PITTSBURGH, PA. 15219
 Telephone 412 471-2527



8-912

8-912 Gas Analysis Apparatus, Burrell Bureau of Mines Cabinet Model VL, in accordance with specifications in U.S. Bureau of Mines Technical Paper No. 320; capacity of burette 100 ml in 0.1 ml divisions.

This apparatus is standard in the gas laboratories of the U.S. Bureau of Mines, and is in extensive use in other laboratories throughout the country.

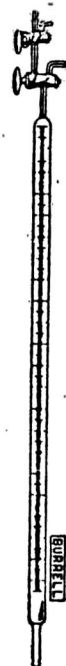
Standard equipment includes three contact pipettes for carbon dioxide, illuminants and oxygen; slow combustion pipette for the determination of methane and ethane; copper oxide assembly (for carbon monoxide and hydrogen) with Perma-Therm heater which is hermetically sealed and pre-set at correct operating temperature (300°C) requiring no further adjustment; gas measuring burette; burette reader; water jacket; compensator; non-flushing type manifold; and leveling bulbs.

Complete with frame, cabinet, and instruction manual, but without solutions or mercury. For 115 volts, 60 cycles, A.C. 385.00

Replacement Parts for 8-912 Burrell Model VL Gas Apparatus

For Burette Water Jacket, Compensator Tube, and Contact Absorption Pipette, see listings under 8-910 Burrell Model J Gas Apparatus.

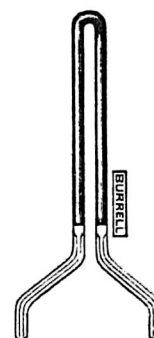
8-912B Burette, Laboratory Type 4, Bureau of Mines Model, 100 ml in 0.1 ml divisions, clear glass, with two stopcocks at top. 32.00



8-912B



8-912D



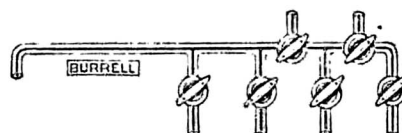
8-912G

8-912D Slow Combustion Pipette, Pyrex glass, with platinum coil and two glass supporting posts; for use with mercury only. Complete with rubber stopper and connections for attaching to filament control box. 11.50

8-912E Ignition Coil, platinum wire, for slow combustion pipette. 1.50

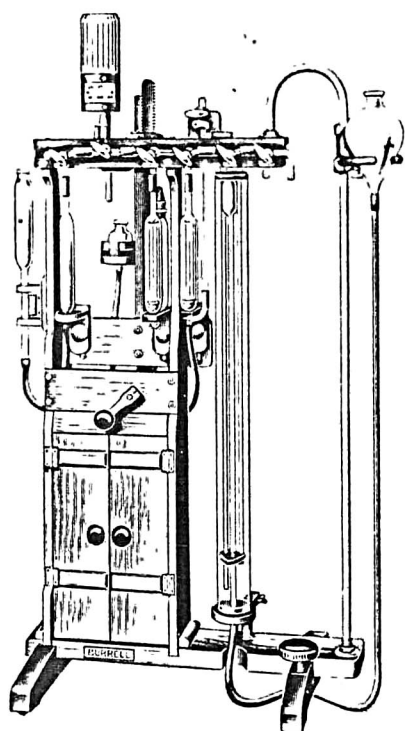
8-912F Copper Oxide Heater, Perma-Therm, cabinet laboratory model, consisting of welded steel cell with fins and removable electric heater which fits lower portion of cell. With mounting rod. For 115 volts, A.C. or D.C. Each 97.50

8-912G Copper Oxide Tube, Bureau of Mines Type, Pyrex Glass, filled with specially prepared copper oxide. Each 7.00



8-912H

8-912H Manifold, Bureau of Mines Type, glass, non-flushing, with six stopcocks, four in vertical legs for pipettes, and two in horizontal header for the copper oxide tube. 33.00



8-913

8-913 Gas Analysis Apparatus, Burrell-Haldane Cabinet Model VC, for accurate determinations of small amounts of impurities in air, and for similar purposes where the components to be measured are present in quantities too slight to yield satisfactory results on other models. The burette has a total capacity of 21 ml with a 15 ml ungraduated bulb at the top and a long stem of 6 ml capacity graduated to 0.01 ml. A specially sensitive compensator manometer is employed and duplicate analysis can be checked to 0.02%.

Standard equipment includes two contact pipettes (one for oxygen and carbon dioxide); catalytic assembly for hydrocarbons and hydrogen) with Perma-Therm heater which is hermetically sealed and pre-set at correct operating temperature; gas measuring burette; water jacket; compensator manometer; flushing manifold; gas reservoir; and leveling bulbs.

Compensator manometer is connected to bottom of first contact pipette and also to compensator tube inside burette water jacket, through stopcock at top of apparatus.

Mercury leveling bulb, connected to catalyst tube reservoir, is raised and lowered by means of chain and sprocket, actuated by hand crank. This feature maintains atmospheric pressure through system which minimizes possibility of leakage.

Complete with frame, cabinet, and instruction manual, but without solutions or mercury. For 115 volts, A.C. or D.C. 390.00

Replacement Parts for 8-913 Burrell-Haldane Model VC Gas Apparatus

8-913A Burette, Laboratory Type 5, Haldane Model, clear glass, straight, with stopcock at top. Total capacity 21 ml, with 15 ml ungraduated bulb at top, and long stem of 6 ml capacity graduated in 0.01 ml divisions. 36.00



8-913A



8-913B



8-913K

8-913B Burette Water Jacket, Haldane Model, laboratory type, Pyrex glass, without rubber stoppers. 7.50

8-913C Compensator, Manometer, Haldane Type.
Each 8.00

8-913D Compensator Tube, Haldane Type. 2.00

8-913E Catalyst Heater, Perma-Therm, with mounting rod. For 115 volts, A.C. or D.C. 97.50

8-913F Catalyst Tube, U-shaped, Pyrex glass, filled with catalyst 9.50

8-913G Gas Reservoir, (Leveling Tube), Haldane Type, connects to end manifold stopcock and 8807H leveling bottle. 4.40

8-913H Gas Reservoir (Leveling Bottle), Haldane Type, connects to 8-913G gas reservoir. 4.40

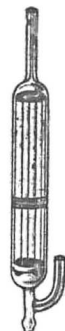
8-913K Reservoir, Haldane Type, for use with absorption pipette having single chamber for carbon dioxide.
Each 4.00

8-913M Flushing Manifold, glass, with two stopcocks in horizontal header. 12.00

8-913N Flushing Manifold, glass, with one stopcock in horizontal header. 6.00

8-910P Flushing Manifold, glass, with single U-tube stopcock, for catalytic tube. 15.00

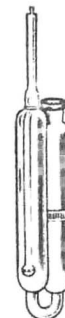
8-910R Flushing End Cock, glass, with stopcock and three outlets, one for sampling, one for flushing, and one for connecting to right hand opening of top burette cock.
Each 7.75



8-913P



8-913R



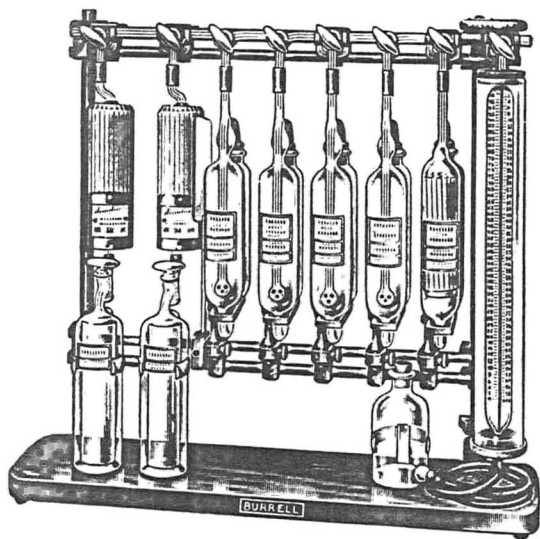
8-913S

8-913P Absorption Pipette, Haldane Contact, Pyrex glass, single chamber, with side tube connection at bottom; for carbon dioxide..... 9.25

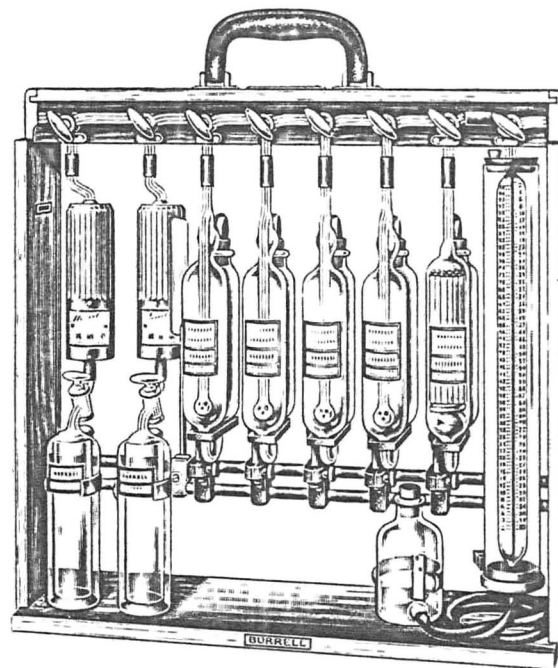
8-913R Absorption Pipette, Haldane Contact, Pyrex

glass, double chamber; for oxygen 10.25

8-913S Absorption Pipette, Burrell Auto-Bubbler, Haldane size, Pyrex glass, for use in place of preceding Haldane contact pipette.... 12.75



8-914



8-915

8-914 Gas Analysis Apparatus, Burrell Master Build-Up Model 111, Portable, for accurate determination of complex gas mixtures containing any or all of following components: carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen (by difference). Apparatus permits use of various methods of analysis.

Standard equipment includes four Burrell Auto-Bubbler absorption pipettes; one contact pipette; copper oxide assembly; catalytic assembly; Schellbach type gas burette, 100 ml in 0.2 ml divisions; water jacket; flushing manifold; and leveling bottle.

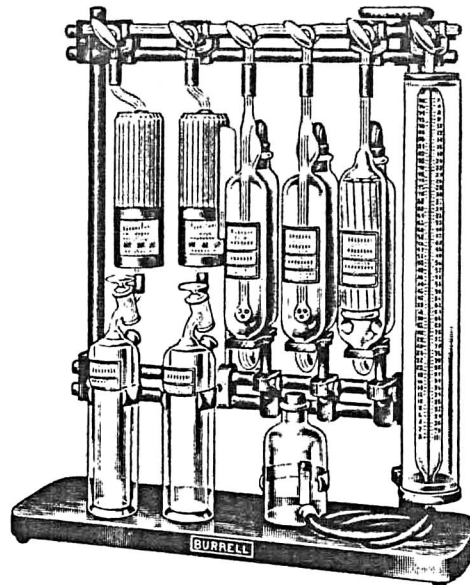
Catalyst assembly does the job of slow combustion pipette with greater speed, safety and accuracy, and supplements the copper oxide assembly for determination

of combustible components. Perma-Therm heaters of both assemblies are hermetically sealed, and pre-set at correct operating temperatures, requiring no further adjustment. Catalyst heater operates at 500°C and copper oxide heater at 300°C.

Build-Up frame comprises standardized, interchangeable parts, including base, with clamps, rods and supports.

Complete with instruction manual, but without solutions or carrying case (For carrying case, see 8819A.) For 115 volts, A.C. or D.C..... 488.00

8-915 Gas Analysis Apparatus, Burrell Master Cabinet Model 211, Portable. Same as 8-914 except mounted in carrying case. Without solutions. For 115 volts, A.C. or D.C..... 488.00



8-916

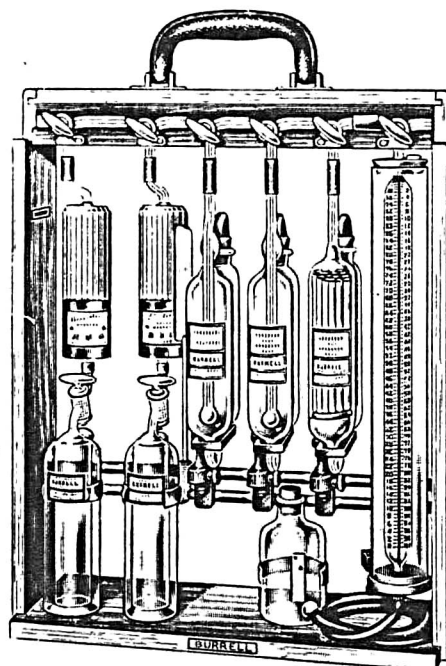
8-916 Gas Analysis Apparatus, Burrell Junior Build-Up Model 511, Portable, a simple unit for analysis of complex gas mixtures containing carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, hydrocarbons, and nitrogen (by difference).

Standard equipment includes two Burrell Auto-Bubbler pipettes; one contact pipette; copper oxide and catalytic assemblies, each with Perma-Therm heaters which are hermetically sealed and pre-set at correct operating

temperatures; Schellbach type gas measuring burette; 100 ml in 0.2 ml divisions; water jacket; flushing manifold and leveling bottle.

Build-Up frame comprises standardized, interchangeable parts, including base, with clamps, rods and supports.

Complete with instruction manual, but without solutions or carrying case. (For carrying case, see 8819B). For 115 volts, A.C. or D.C. 415.00



8-917

8-917 Gas Analysis Apparatus, Burrell Junior Cabinet Model 611, Portable. Same as 8-916 except mounted in

carrying case. Without solutions. For 115 volts, A.C. or D.C. 415.00

Revised

METHODS OF DETERMINATION

DETERMINATION OF FREE OXYGEN IN GAS

POTASSIUM PYROGALLATE METHOD

Procedure.—One hundred ml. of gas are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus

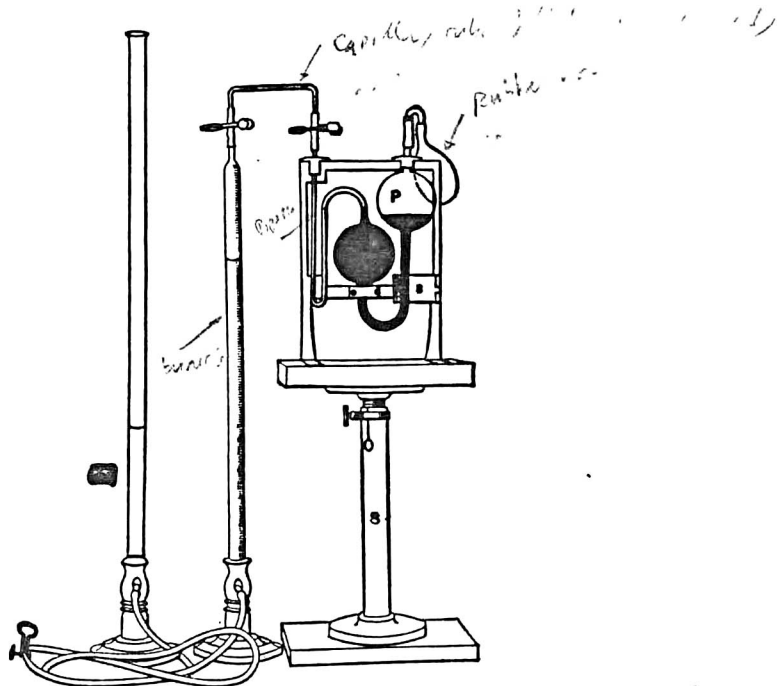


FIG. 34-1. Hempel's Apparatus for Determining Oxygen.

filling the capillary with water; the free end of the capillary is inserted into the pipette connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcocks on the burette and the pipette (Fig. 34-1) are now opened, the gas forced over into the potassium pyrogallate solution (P), and the pinchcock on the pipette closed. After allowing it to stand for fifteen minutes, the residue is drawn back into the burette and the reading taken. Before setting aside the pyrogallate pipette, the number of cubic centimeters of oxygen absorbed should be

Standard Methods of Chemical Analysis. F. J. WELCHER editor

Sixth ed. Vol. 1. Princeton, New Jersey. 1963.

D. Van Nostrand Company, Inc.

noted upon the slate \S on the stand. This must never be omitted with any pipette, save possibly that for potassium hydroxide, as failure to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity—four to five liters of carbon dioxide—of the reagent.

EXPLOSION WITH HYDROGEN METHOD

Procedure.—Forty-three ml. of gas and 57 ml. of hydrogen are measured out, passed into the small explosion pipette, Fig. 34-2, the capillary of the pipette filled

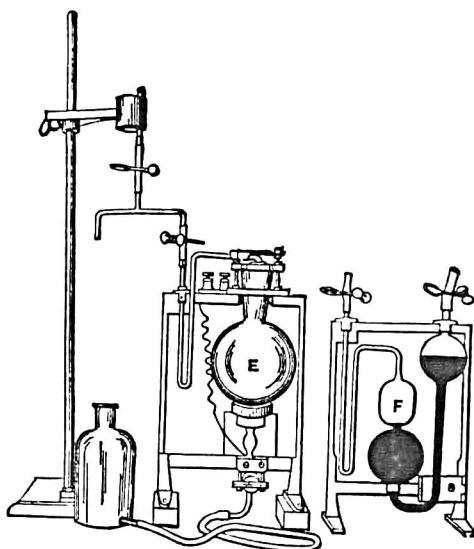


FIG. 34-2. Explosion Pipette (left); Hample Gas Pipette (right).

with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases, otherwise some nitrogen will burn and high results will be obtained; ¹ that is $(H + O):(N + H) = 1:6$.

DETERMINATION OF TRACES OF OXYGEN IN GASES

The apparatus designed by J. G. Dely is shown in the accompanying drawing. The procedure is of special value in the determination of traces of oxygen in the nitrogen-hydrogen gases used in the synthetic catalytic fixation of nitrogen by the Haber or Claude processes or their modifications.

The method depends upon the blue color produced by the action of oxygen on colorless ammoniacal cuprous chloride, and matching with a standard.

¹This is shown in the work of Gill and Hunt, J. Am. Chem. Soc., 17, 987, 1895.

