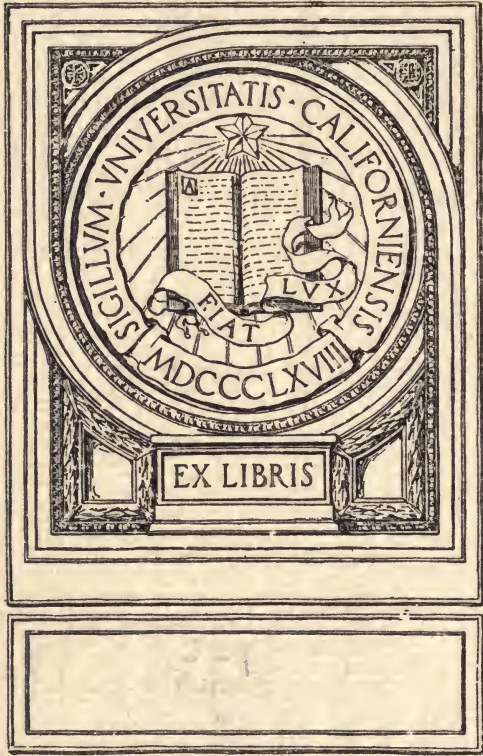# Elementary
Organic Analysis

F. G. BENEDICT

The Chemical Publishing Co.

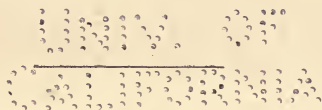# Elementary Organic Analysis.

Elementary Organic Analysis

The Determination of Carbon and Hydrogen

BY

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PREFACE

Perhaps no analytical operation is at once so fundamentally important and exasperatingly vexatious as the organic combustion. Notwithstanding this fact, save for the meager statements in one or two of the larger books on organic chemistry, no description of the process of the determination of carbon and hydrogen is accessible to most students. As a rule a knowledge of the operation is chiefly obtained by word of mouth.

This little manual is presented in the hope that the descriptions of processes here recorded will aid in making this method of analysis more familiar and more satisfactory.

Usually very little, if any, discrimination is exercised in burning the compounds obtained in organic research, and experiment alone is relied upon to secure the proper conditions for complete combustion. It is hoped that the different cases cited in the latter part of the manual will aid in giving some clue to the treatment necessary for many compounds, thereby saving time and, more frequently, valuable material.

While an attempt has been made to describe all operations commonly used it is obviously impossible not to give fuller consideration to such modifications of the general method as have been suggested by an experience with over two thousand combustions. Ac-

cordingly these modifications are treated in detail and as a general rule recommended in preference to the older manipulations.

For the painstaking care and numerous suggestions of Mr. Emil Osterberg, assistant in this laboratory, whose experimental skill has contributed greatly to many of the modifications here presented, the writer is extremely grateful.

MIDDLETOWN, CONN.

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INTRODUCTION

The analysis of organic compounds requires the determination of but few elements, the most important of which are carbon, hydrogen, and nitrogen. This book has to do only with the determination of carbon and hydrogen in organic compounds. The method consists of converting all the carbon to carbon dioxide, all the hydrogen to water, and absorbing and weighing these products.

In bodies containing nitrogen, care is taken to provide that none of its compounds are retained in the systems used to absorb water or carbon dioxide. In general the nitrogen escapes in the gaseous form.

The oxidation of the carbon and hydrogen may be effected by mixing the material intimately with metallic oxides, such as cupric or mercuric oxide, or with oxygenated salts, such as potassium chlorate, potassium dichromate, or lead chromate. In some methods use is made of a current of air or oxygen to facilitate the burning of refractory substances and to regenerate the oxidizing agents. The property of platinum and palladium of condensing large quantities of oxygen on the surface of the finely-divided metal has also been made use of in conjunction with the current of oxygen to effect the combustion of organic substances. The method best adapted for general purposes involves the use of cupric oxide and a current of air or oxygen.

In this last method all volatile organic products are

oxidized by a layer of hot cupric oxide; and air, or better, oxygen is finally introduced to aid in oxidizing any charred residue and to reoxidize the reduced copper. Of the products formed, water is absorbed by calcium chloride or sulphuric acid; carbon dioxide is absorbed by a solution of potassium hydroxide or by soda-lime; and the nitrogen, if present, escapes as such from the tube.

PREPARATION OF OXYGEN

The commonest method of preparing oxygen is by heating a mixture of potassium chlorate and manganese dioxide. The two ingredients should be separately pulverized and, if necessary, dried. Equal weights of each are intimately mixed and heated in a 250 cc. Jena glass Erlenmeyer flask, fitted with a stopper and a wide glass elbow, and clamped on a retort stand. To the elbow is attached a rubber tube with a glass elbow at the other end which permits a free movement of the tube in the pneumatic trough or gasometer. On gradually increasing the heat a rapid though steady evolution of oxygen is obtained. At the end of the reaction and before the lamp is removed the tube must be withdrawn from the pneumatic trough or gasometer to prevent the back suction of the water. If glass other than Jena is used the flask should be protected in heating with a piece of asbestos paper.

The purity of the manganese dioxide is of considerable importance as an admixture of carbonaceous matter of any nature is liable to cause an explosion, be-

sides contaminating the oxygen with carbon dioxide. It is accordingly advisable to test a small portion of the mixture by heating it in a test-tube.

COMPRESSED OXYGEN

The use of compressed oxygen for elementary organic analysis is especially to be recommended as furnishing a constant, ready supply of the gas.[1] It is frequently necessary to refill a gasometer during a combustion, particularly if there is any considerable leakage, and it is not always possible to prepare the gas quickly according to any of the methods ordinarily in use. A cylinder of the compressed gas can be used at any time to refill the gasometer or, what is still more advantageous, to supply the oxygen to the tube without the use of a gasometer.

Progress in the compressed gas industry has reached such a point that it is comparatively easy to secure a strong, thoroughly well-tested cylinder of highly-compressed oxygen. These cylinders are made in all sizes, containing from a few gallons to a hundred cubic feet of oxygen. For the laboratory, a cylinder containing ten cubic feet or seventy-five gallons is of convenient size.

The gas thus compressed contains slight traces of carbon dioxide, water vapor, and nitrogen, but the most vexatious impurities existing in compressed oxygen are volatile hydrocarbons resulting from the superheating of the oils used in lubricating the com-

[1] J. Am. Chem. Soc., **21**, 389.

pressing machinery. With compressed oxygen containing these impurities a preheating furnace[1] is necessary to oxidize the hydrocarbons.

Some manufacturers have replaced the lubricating oils with graphite and in the large number of cylinders of compressed oxygen obtained from the S. S. White Dental Mfg. Co., of Princes Bay, N. Y., and tested in this laboratory, gaseous hydrocarbons, or at least hydrocarbons not completely absorbed by the sulphuric acid of the drying apparatus,[2] were never detected.

Only compressed oxygen free from hydrocarbons is recommended as the preheating furnace is an undesirable addition to an already elaborate apparatus. The gas obtained from the above-mentioned source is comparatively dry and, after being freed from traces of moisture and carbon dioxide, is sufficiently pure to be used in elementary organic analyses.

A cylinder containing ten cubic feet costs about ten dollars. The so-called "commercial" oxygen, which differs from the "medical" only in so far as it has been, perhaps, a little less thoroughly washed and purified, costs at the rate of ten cents per foot; i. e., one dollar per ten cubic feet. This amount is not great compared with the cost of an ordinary Mitscherlich or Pepy gasometer. Inasmuch as the gasometers are used almost exclusively to hold oxygen, it will be seen that they are not indispensable to the ordinary laboratory supplied with a cylinder of the gas. Ten cubic feet

[1] J. Am. Chem. Soc., **15**, 531.
[2] See page 14.

will last for a great many carbon and hydrogen com-
bustions, while the advantage of using a cylinder of
this gas in the lecture room is obvious.

Inasmuch as the oxygen contained in the steel cyl-
inders is under great pressure, some method of regu-
lating the flow of gas as it en-
ters the combustion tube must
be devised. The expensive pre-
cision and reduction valves used
ordinarily with these cylinders
can be replaced by the follow-
ing simple arrangement. A
rubber tube leading from the
cylinder connects with a T-tube,
one end of which dips one inch
under mercury in a small bot-
tle fitted with a rubber stopper
having two holes (Fig. 1). The
second hole is left open. A
rubber tube connects the other
end of the T-tube with the puri-
fying apparatus, which is in
turn connected by rubber
tubing to the combustion tube.
This last rubber tube is sup-
plied with a pinch-cock which

Fig. 1.

is closed. When the valve on the oxygen cyl-
inder is opened slightly the gas will flow out, and,
passing through the trap, produce a bubbling in the
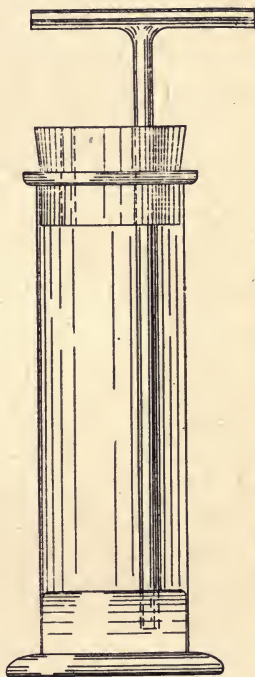mercury. As yet no gas escapes through the purify-

ing apparatus. If, now, one wishes to regulate the flow of gas, the pinch-cock is opened until the desired rate of flow is secured. Any excess of gas still escapes through the mercury trap. It is always possible to adjust the valve on the oxygen cylinder finally, so as to prevent any appreciable loss of oxygen through the mercury.

As the weight of the cylinder, as well as that of the oxygen it contains, is generally given, by keeping a record of the weight of the cylinder it is easy at any time to determine how much oxygen remains. If a high pressure gauge is at hand a similar result may be obtained by recording the diminution in pressure.[1]

GASOMETERS OR GAS-HOLDERS

Where the air or oxygen used is not under pressure

Fig. 2.

in cylinders or pipes connected with a constant supply, some form of gasometer is necessary. A Pepy gasometer (Fig. 2) constructed of zinc or preferably of copper is less liable to be broken than the Mitscherlich or glass form though there is great advantage in being able to see at a glance the amount of gas remaining in the apparatus. For elementary analysis alone the Pepy form has one unnecessary pipe and stop-cock
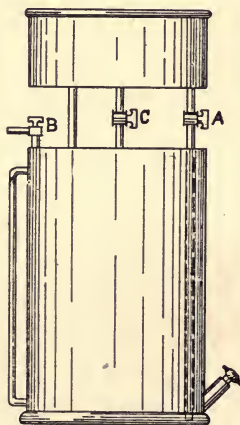
[1] Müller: Ztschr. physik.-chem. Unterricht, 12, 26.

(C) which is used to direct gas into cylinders filled with water and inverted in the upper vessel.

The gasometer is filled with water by closing the opening near the bottom and opening all valves at the top and then conducting into the upper pan a current of water which flows through the connecting pipes and soon fills the lower chamber. The rise of the water is noted by means of the side gauge tube. When the gasometer is completely filled all the cocks are tightly closed and the screw plug or cock near the bottom removed. A little water will run out, especially if the chamber has not been completely filled with water. After the first few cubic centimeters have escaped no more water should run out and gas from a generator or cylinder may be conducted by means of a bent tube through the opening in such a manner that it rises inside the chamber, the displaced water running out at the opening. Consequently it is necessary in filling a gasometer of this form to conduct the operation at a sink or to provide in some other way for the displaced water. When filled with gas the lower chamber is tightly closed and the upper pan is filled with water. On opening the stop-cock A, the water in the pan flows down through a tube extending to the bottom of the lower chamber until the internal pressure of the gas is sufficient to sustain the column of water in the tube. By carefully opening stop-cock B, gas may be withdrawn as desired. As gas is withdrawn the water flows through the valve A into the lower chamber and provision must be made to furnish occasionally a sup-

ply of water for the upper pan as otherwise as soon as
all the water in the pan has run into the lower chamber, the flow of gas would cease. Instead of intermittently adding water to the upper pan a simple device
may be used for maintaining a constant level of water
in the pan. This consists of a rubber tube conducting water from a tap through a twenty centimeter
length of small lead pipe, bent in the form of a U and
hung over the edge of the pan. A hole is made in the
side of the pan about half way down and a cork carrying a tube leading to the sink is carefully inserted.
Water flowing through the lead U fills the pan to the
level of the opening and all excess of water flows away
through the overflow to the sink.

The Mitscherlich form of gasometer is manipulated in essentially the same manner, the operation of the valves differing in no way from that in the Pepy form. The adoption of
the device for maintaining a constant level in the upper jar
is rendered somewhat difficult, as a hole is not as readily
made through glass as through metal. However, any one
may, with a broken file and emery and camphor, grind a hole
of suitable size through the glass. By slipping a piece of
thick-walled rubber tubing over the glass tube used as an
overflow it can be inserted in the orifice which accordingly
need not be unnecessarily large.

The use of gasometers of these forms is, however,
open to considerable objection, for if constructed of
metal they soon leak, owing to the attacks of acid
fumes and vapors always present in a laboratory, and
are constantly needing repairs, and glass gasometers,
though they do away with the large mass of metal,
rely on metallic pipes, cocks, and connections to re-

ceive and deliver the gas. These connections are equally liable to the attack of acid, resulting in leakage and consequent loss of gas. The fragile nature of such gasometers and the necessity for transportation to the sink, when being filled, make their handling difficult. Consequently it is only by exercising great care in the lubrication of stop-cocks and in the general treatment of this form of gas-holder that satisfactory service can be obtained.

A much simpler though less convenient form of gas-holder (Fig. 3) consists of two carboys, demijohns, or large bottles

Fig. 3.

fitted with two-holed rubber stoppers through one hole of which a glass tube extends to the bottom of the vessel. The other hole in one of the stoppers is provided with a glass elbow carrying a short piece of rubber tubing and a screw cock. A rubber tube once and a half as long as the vessel is high, connects the two long glass tubes in the two vessels. One bottle is completely filled with water and the screw pinch-cock closed. The other is then lowered until its mouth is about on a level with the bottom of the bottle containing water.

The delivery-tube of the gas generator from which only a gentle current[1] of oxygen must be escaping is connected with the short rubber tube, the screw-cock having been previously opened,[2] and the gas entering the bottle forces the water through the long rubber tube into the other bottle. At the end of the operation the gas generator is removed and the screw-cock immediately closed. By raising the bottle containing water to a position somewhat above the level of the bottle containing gas, almost any degree of pressure may be obtained. The gas is drawn off by slowly opening the screw pinch-cock.

Bottles having tubulatures at the bottom are used with a one-holed stopper carrying, in the one case, a short glass elbow and screw-cock, while the hole in the other stopper is left open. The long rubber tube connects short pieces of glass tube thrust through stoppers in the tubulatures. The manipulation differs in no wise from that given.

Another convenient form of gasometer is a modification of the foregoing, consisting, however, of only one vessel fitted with a two-holed rubber stopper, the holes of which are plugged with four centimeter lengths of glass rod or glass tubing sealed at one end. The vessel is filled with gas at a pneumatic trough and the stopper firmly inserted while the neck is still under water. The vessel is then placed on the table, one of the plugs withdrawn and a glass elbow, carrying a short piece of rubber tube and a screw-cock, quickly thrust into the hole in the stopper. A glass elbow in the end of a rubber tube connected to a tap is first filled with

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[1] Determined by dipping the tube for a moment under water in a beaker and noting the rate of bubbling.

[2] The cock is opened and in case there was sufficient water in the long rubber tube to cause it to act as a siphon the action is momentarily stopped by pinching the connecting tube with the fingers, care being taken to release the pressure on the tube as soon as the oxygen generator is connected. By using care in filling the bottle no water is driven over into the rubber tube and the siphon is not started until the pressure of the gas in the generating apparatus forces the water up through the bend of the long glass tube into the rubber connecting tube whence it falls into the other bottle.

water by allowing the water to flow through the tube for a moment, and then thrust into the second hole of the stopper after removing the plug. The connection is made between the rubber tube and the purifying apparatus and the screw-cock is opened. By admitting water through the glass elbow, gas in desired quantities may be forced through the system. If a three-holed stopper is used and a two or three centimeter layer of water is left in the bottom of the vessel a long glass tube may be thrust through the third hole far enough to dip under water in the bottom and thus serve as a pressure gauge.

A fundamental objection to all forms of gasometers is the great inconvenience experienced in filling them at a sink with gas or water, requiring, as they do, transportation of a bulky apparatus filled with water. Accordingly whenever obtainable the use of pure compressed oxygen in steel cylinders is strongly recommended.

AIR

In some methods of analysis air is substituted for oxygen during the greater part of the combustion, oxygen being used only to oxidize refractory carbonaceous residues. The use of air in gasometers is identical with the manipulation described on page 7 with the exception that the filling is accomplished by opening the lower seal and the valve from which the gas is usually drawn at the top. For most organic bodies oxygen must be substituted for air before complete oxidation can be assured, hence two aspirators and purifiers are often used.

Air under pressure may also be conveniently obtained from any of the numerous forms of water-blast.

PURIFYING APPARATUS

Impurities other than carbon dioxide and water-vapor are seldom present in oxygen or air used for analysis, though in the compressed oxygen furnished by some manufacturers material quantities of hydrocarbons are often present. These hydrocarbons are effectually removed by conducting the gas direct from the gasometer or cylinder through a heated glass, porcelain,[1] or brass[2] tube containing cupric oxide where they are oxidized to water and carbon dioxide. In general the removal of carbon dioxide and water-vapor only is necessary.

The removal of water-vapor is effected by use of calcium chloride or concentrated sulphuric acid, while potassium or sodium hydroxide in sticks or in concentrated solution, or soda-lime is used to remove all traces of carbon dioxide. The relative merits of the various absorbing agents are discussed at length under the head of absorbing agents on page 31.

The essential feature of the purifying system is that it should hold a considerable quantity of the reagents and not become exhausted until after a large number of combustions. The gas entering the purifying apparatus is generally very moist from standing over water in a gasometer and contains but a small quantity of carbon dioxide. The gas leaving the combustion tube contains as a rule even more water and a great deal more carbon dioxide, so much more in fact

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[1] Dudley and Pease: J. Am. Chem. Soc., **15**, 530.

[2] Shimer: *Ibid.*, **21**, 560.

that the absorbing reagents ordinarily used become exhausted after one or two combustions.

Of the various absorbents of carbon dioxide and water the systems most commonly used are: Potassium hydroxide followed by calcium chloride ; potassium hydroxide followed by sulphuric acid; sulphuric acid, potassium hydroxide, and sulphuric acid ; sulphuric acid, potassium hydroxide, and calcium chloride, etc., etc., and sulphuric acid, soda-lime, and sulphuric acid.

The last combination is remarkably efficient and hence is first considered.

A simple form of purifying apparatus consists of a Drechsel gas washing-bottle one-third filled with concentrated sulphuric acid, a U-tube containing soda-lime,[1] and a U-tube containing pumice stone drenched with concentrated sulphuric acid. The sulphuric acid in the bottle retains the water (in case a cylinder of compressed oxygen, which is itself very dry, is used, the gas washing-bottle with sulphuric acid may be discarded), the soda-lime retains the carbon dioxide, and the sulphuric acid and pumice stone U-tube the moisture escaping from the soda-lime. The gas issuing from this system is free from carbon dioxide and contains no moisture that can be retained by sulphuric acid.

The three pieces of the absorber above described may be combined by using a calcium chloride jar filled as is shown in Fig. 4.[2] The tubulature should be as

[1] Page 32.
[2] Am. Chem. J., **23**, 332.

near the top of the lower compartment[1] as possible, to

Fig. 4.

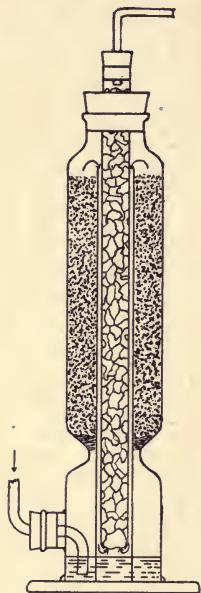permit the introduction of the maximum quantity of concentrated sulphuric acid.

A piece of glass tubing of an external diameter a little less than the internal diameter of the constriction in the jar is cut off long enough to rest on the bottom and reach within thirty millimeters of the top of the jar. A one-holed cork on the end of a glass rod is loosely inserted in the upper end of the tube and a layer of glass wool or long fiber asbestos is packed around the tube to a depth of three or four millimeters. Sodalime prepared as described on page 32 and pulverized into pieces approximately two millimeters in diameter is then introduced and the jar

filled to within one centimeter of the top of the inner

[1] Calcium chloride jars are furnished by Whitall, Tatum & Co. with the tubulature inserted at any point desired in the lower compartment at a cost but slightly in advance of the regular goods. As ordinarily made a jar " 12 inches high" will have the tubulature in such a position that about 20 cc. of concentrated sulphuric acid can be introduced without flowing out of the orifice or coming in contact with a rubber stopper inserted in the tubulature. Where gas from a cylinder of compressed oxygen is used this amount of acid suffices to dry a great many liters of gas, but if the gas is drawn from gasometers over water the reagent is more rapidly exhausted. Twenty cc. of acid will absorb effectually six grams of water and taking the temperature of a gasometer in use as $28°$ C., the gas leaving it would contain twenty-seven milligrams of water-vapor per liter. An average of 1.5 liters of oxygen are used per combustion in the method described beyond, hence twenty cc. of acid would serve for two hundred combustions, a number rarely exceeded by any one operator. The chief advantage of that form of jar having the tubulature near the top of the base is that there is much less liability of getting concentrated acid on the rubber stopper in the tubulature.

tube. A "12-inch" calcium chloride jar will require about one hundred and seventy-five grams of soda-lime. The layer of glass wool or asbestos prevents the soda-lime from falling through into the lower compartment.

A long glass tube approximately ten millimeters external diameter is thrust through the one-hole rubber stopper inserted in the top of the jar. This tube is slightly constricted at the bottom and is filled with pumice stone which is subsequently drenched with concentrated sulphuric acid. The glass tube extends from about one centimeter above the cork to within two centimeters of the bottom and should be of a diameter small enough to slide easily through the upright tube passing through the constriction of the jar. The upper end of the tube is closed with a one-holed red rubber stopper carrying a glass elbow and a piece of rubber tubing with a screw pinch-cock. This stopper may be sealed with paraffin if desired. With this arrangement the only chance for leakage that could contaminate the gas is in the stopper at the top of the glass tube. A leak at the other stoppers would be effectively counteracted so far as moisture (the greatest danger in leaks) is concerned by the long column of pumice stone and sulphuric acid.

Concentrated sulphuric acid is poured down the central tube thoroughly drenching the pumice stone and collecting in the base. The first lot of acid is often contaminated with foreign material from the pumice stone and should be poured out of the tubulature; enough acid is then poured through the tube to

fill the lower compartment to within five millimeters of the one-holed rubber stopper in the tubulature. The cork is then replaced in the tube and the pinch-cock closed. A glass tube bent downwards is thrust through the hole in the rubber stopper in the tubulature in such a manner that a current of gas passed through it bubbles through the acid in the base of the jar. The gas rises, passes through a long column of soda-lime at a very slow rate, and then turns and passes down through the annular space between the two glass tubes, finally entering the base of the tube filled with pumice stone and issuing at the top. The greater portion of the water is removed as the gas bubbles through the acid; the carbon dioxide is completely removed by the soda-lime, and the unabsorbed moisture, including that lost from the slightly moist soda-lime, is removed as the gas passes over the pumice stone and sulphuric acid. The gas issuing at the top is free from carbon dioxide and as free from moisture as is possible with sulphuric acid. In case the sulphuric acid becomes exhausted, to regenerate the purifier it is only necessary to drain the acid out of the lower compartment and pour fresh acid through the tube containing the pumice stone. This operation should be performed at the end of every fifty combustions. The soda-lime need not be renewed until it becomes three-fourths white.

Numerous forms of apparatus, more or less complex, for holding the various absorbents for the purification of the air or oxygen used in organic combustions, are described in chemical literature and are furnished by most of the dealers in chemical supplies. Some are suited for the absorbing com-

bination sulphuric acid, soda-lime, sulphuric acid and many were especially devised and are described as being filled with the other absorbents in any of the other combinations. Liquid reagents, such as potassium hydroxide solution or concentrated sulphuric acid, are generally held in gas washing-bottles though sometimes they are poured over broken pumice stone in long U-tubes. Solid reagents, such as calcium chloride, stick potassium hydroxide, and soda-lime, are generally placed in large U-tubes or calcium chloride jars. The remarkable absorptive power of soda-lime for carbon dioxide renders it unnecessary to have a great length of this reagent through which the gas must pass.

RUBBER TUBING AND STOPPERS

Rubber tubing is used to make all connections between the oxygen supply, the purifier, and the combustion tube, and only fresh tubing, not cracked or deteriorated, must be used. Often strong sulphuric acid is carelessly allowed to suck back into the rubber tube connecting the supply of oxygen with the purifier. The tubing becomes hard and brittle and should immediately be removed.

Red or maroon tubing, " 5/32 inch " inside diameter, is a convenient size and withstands the action of heat better than most other kinds. A twenty to forty centimeter length is required to conduct the gas from the purifier to the combustion tube, but the gas issuing from the combustion tube does not come in contact with any length of tubing as it is advisable to have the glass tubes of the various absorbers touch,[1] using a two centimeter length of rubber tube simply to hold

[1] Pflüger : Arch. f. d. ges. Physiol., 18, 133 ; Lieben, cited in " Manual of Organic Chemistry," by Lassar-Cohn, p. 373 ; Berthelot : Compt. rend., 110, 684.

2

the glass tubes together.   If glass touches glass a
minimum exposure to rubber is obtained.

The rubber stoppers used in the purifier and in the
absorbing tubes may be of the ordinary quality though
red rubber is preferable.   Those used in the ends of
the combustion tube ought to be of red rubber as it is
much less affected by heat than any other kind.

COMBUSTION FURNACES

The accuracy demanded in organic elementary analy-
sis at the present day renders the use of a gas com-
bustion furnace almost imperative.   The earlier forms
of charcoal furnace are occasionally used in localities
where gas is not at hand, but they are not of sufficient
importance to warrant special consideration here.

Where illuminating gas is accessible any one of the
numerous forms of furnace may be advantageously
used.   In general the furnace, which is about eighty
centimeters long, consists of a series of twenty to thirty
Bunsen burners provided with air as well as gas regu-
lating devices, screwed into a gas pipe of size large
enough to supply all the burners with sufficient gas,
giving a heating length of about seventy-five centi-
meters.   The flames are generally confined and made
to impinge on fire clay tiles in such a manner that the
combustion tube is heated on all sides as evenly as
possible.   A good pressure as well as a good supply
of gas is necessary and, owing to the great heat and
the large quantity of the products of combustion, the
furnace should be installed in a hood provided with a

good draft. Sufficient room for the gasometer or oxygen cylinder and the purifying apparatus as well as the absorbing system is necessary. A gas cock to which a Bunsen burner with a long rubber tube is attached should be at hand. The gas pipe with which the furnace is connected should be not less than " ¾-inch" standard size.

Many designs of furnaces are in the market, each constructed with a view of attaining the greatest and most even heating of the combustion tube with the minimum consumption of gas. The progress made in developing the combustion furnace is not as great as the complex nature of many designs would indicate, and there is very little, if any, choice in the selection of a furnace. All are a great improvement on the charcoal furnace, and all have their salient points. As a rule the increase in complexity of construction and in cost is not accompanied by a proportionate increase in utility. Equally satisfactory results with the "Bunsen," "Erlenmeyer-Babo," and "Glaser" furnaces have been obtained in this laboratory.

The "Glaser"[1] furnace is provided with a series of iron U pieces placed side by side, forming a trough in which the combustion tube is placed. Difficulty is often experienced, however, as the pieces become separated and allow the free flame to impinge on the unprotected glass, a fracture of the tube being almost certain to result at the point of overheating. If the tube is well protected at the bottom with two or three layers of asbestos paper the liability to accident is much decreased.

[1] Ann. Chem. (Liebig) Suppl., **7**, 215.

In most other forms of furnace, including the two others above mentioned, the combustion tube is laid in a heavy sheet iron or tile trough.

Tiles possess the advantage of not becoming twisted or warped on heating, but owing to their fragile nature and their non-conductivity for heat, thus necessitating considerable time to heat and cool, they are not to be recommended.

Iron troughs are open to the serious objection that they warp and twist and constantly form scales of iron oxide which clog the burners. On the other hand, they are very cheap, conduct heat much better than tile, and if constructed of sheet iron two millimeters in thickness do not warp sufficiently to cause any considerable difficulty. Any plumber or tinner can make them by hammering a piece of thick (two millimeters) sheet iron over a gas pipe. They may be renewed before any considerable amount of scale is formed and are on the whole the most satisfactory form of trough to use.

The trough, whether it is of iron or tile, should be lined with two or three layers of asbestos paper which will protect the tube.

A fifteen centimeter square of rather thick asbestos card having a two centimeter hole in the center is thrust over each end of the combustion tube as a protection to the corks.

The consumption of gas varies not only with the form of furnace, but more especially with the nature of the substance to be burned. A number of experi-

ments made with different forms of furnaces coupled direct to a gas meter gave an average consumption of forty-five cubic feet of gas per hour.

In some forms of furnace, provision is made for raising or lowering the burners which is often an advantage in securing the best regulation of the flames. The furnace should be raised some three or four centimeters at the anterior end by placing a block of wood of the required height under the support. (Fig. 12, p. 51.)

COMBUSTION TUBES

The cupric oxide used to oxidize the volatile portions of the material to be burned is heated in a platinum, porcelain, or glass tube. Platinum tubes are expensive and consequently but rarely used. Porcelain tubes are much used in technical work, but as a rule are too fragile and expensive for ordinary laboratory use. Glass tubes are almost invariably used in all other than technical laboratories. As the old bayonet form of tube originally used by Liebig has been almost universally replaced by the tube open at both ends, the former need not be considered here. The long-continued high heat to which a glass combustion tube is subjected requires that it be of glass of unusual resistance to heat, i. e., not melting easily and capable of withstanding rapid fluctuations in temperature.

Bohemian glass.—An especially hard glass containing potassium instead of sodium, i. e., Bohemian glass, has been used for this purpose with satisfactory results for a number of years. It is drawn in tubing of a con-

venient size, generally from twelve to fifteen milli-
meters internal diameter, designated as combustion
tubing, which, unless otherwise ordered, comes in
lengths of approximately two meters.

Jena glass.—Recently a new glass of a remarkably
high melting-point and small coefficient of expansion
has been introduced which promises to prove of great
value in organic analysis. A special kind of Jena
glass, made expressly for combustion tubing, which
must not, however, be confused with the softer glass
used for preparing sealed tubes, furnishes a tube that
leaves very little to be desired and which is nearly as
resistant to heat as are the more expensive porcelain
tubes.

In this laboratory the average number of combus-
tions made with Jena glass tubes is over fifty, while
four tubes have withstood heating in ninety-seven,
ninety-nine, one hundred and four, and one hundred
and sixteen combustions respectively.

Owing to its infusibility there is much less danger
of breaking Jena glass tubes by fusion to tile or iron
troughs, a source of many accidents with the other
forms of glass. Fortunately the price of this glass is
no greater than that of other kinds of combustion
tubing.

For use in the furnace the tube should be cut of a
proper length and the sharp edges should be rounded
to prevent their cutting the stopper and introducing
bits of rubber which might easily be swept into the
heated part of the tube. One end of the length of

combustion tube should be cut off square, if it is not already so, and then a length equal to the length of the furnace plus ten centimeters[1] marked off with a file scratch on the glass. A sharp triangular file is necessary for the purpose. If a deep scratch is made the tube may readily be broken at the scratch in case it is of Bohemian glass by following a line around the tube in the direction of the scratch with a hot glass rod, or better with a gas flame burning from a fine jet. The gas flame is held in a tangential position and the tube rapidly revolved three or four times to produce excessive heating in a narrow band around the glass including the scratch. Then by directing the flame on the scratch for a few moments the crack will usually start and instantly run clear around the tube in the heated zone leaving a sharp cut. With Jena glass tubing it will be necessary to file a deep scratch clear around the tube. On applying the heat from a fine gas jet as described the tube is then cut with no great difficulty.

After cutting the tube in the desired length the sharp edges of the cuts are rounded off either by filing with a round file or better by fire-polishing, *i. e.*, partially fusing the edges in a blast-lamp. The fire-polishing is done by carefully heating one end of the tube in a smoky flame of a blast-lamp until the glass is covered with soot. The air is then admitted to the blast-lamp and the temperature gradually increased

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[1] As the furnace is generally eighty centimeters long the glass tube is cut ninety centimeters, thereby allowing five centimeters to protrude at each end of the furnace.

till the edges are fused. The cooling should be slow and is brought about by cutting off the air from the blast-lamp and gradually turning off the gas till the end of the tube is again covered well with soot. The flame is then extinguished and the tube allowed to cool in the air. The covering of soot equalizes the radiation of heat and prevents cracking.

When cool the tube is carefully wiped and washed inside and outside with water and then rinsed with 10–20 cc. of alcohol which is allowed to drain out. The alcohol adhering to the walls of the tube is removed by rinsing with a few cubic centimeters of ether and the tube is then gently warmed by moving a Bunsen burner along its entire length, removing the ether-vapor by a blast of air or by suction from a filter-pump.

OXIDIZING AGENTS USED IN THE COMBUSTION TUBE

Cupric oxide. —The ease with which this compound gives up its oxygen to reducing substances renders it of the greatest value in organic combustions.

For general purposes the wire form, consisting of short pieces of copper wire that have been completely converted to the oxide, is the best. This form is readily obtained in the market. Approximately four hundred grams of the oxide in the wire form are required to fill a combustion tube.

Granular copper oxide obtained by igniting the nitrate is often used. The powdered oxide is used in small quantities to cover highly refractory substances. Each time before being used it should be heated

strongly in a Bunsen flame and then allowed to cool in a desiccator where it should be preserved. Both forms are readily obtained in the market.

Spirals of copper oxide are used and are prepared by winding stout copper wire tightly around a glass tube of such a size that the finished spiral, some twelve centimeters long, can easily be inserted in a combustion tube. The wire is bent in a ring form at each end to facilitate its withdrawal. The spiral is then strongly heated in a Bunsen flame till the oil is all burned off and an outer coating of black cupric oxide is formed. It is then cooled and kept in a desiccator until used. Another form of spiral which is, however, more readily disintegrated, is prepared by rolling a piece of copper gauze, ten centimeters square, around a piece of stout copper wire some eleven or twelve centimeters long, with a loop made in each end. The wire gauze is compactly rolled and the roll when finished must easily slip into the combustion tube. The fine copper wire of which the gauze is made, readily oxidizes when heated in a flame which burns off any shellac, varnish, or oil. The brittle nature of the cupric oxide renders such spirals extremely fragile and they soon have to be replaced. Though presenting less surface of cupric oxide no difficulty will be experienced in using spirals of stout wire provided they are at least twelve centimeters long.

Spirals of this form are often used to reduce oxides of nitrogen when present as a product of combustion and are reduced to the metallic form as described on page 64.

A succession of spirals[1] has been used in place of the wire form of cupric oxide.

Lead chromate is the only other oxidizing agent that is extensively used in ordinary methods of combustion. This material in the fused form is coarsely granulated and introduced into the combustion tube. It is used in burning substances containing sulphur or the halogens (p. 66). No special preparation is necessary as the material is furnished ready for use in the market.

A mixture of nine parts of lead chromate and one part of potassium dichromate was introduced by Mayer,[2] but is not generally used.

The low fusibility of lead chromate is the serious disadvantage in its use and to obviate this difficulty De Roode[3] mixes one part of red lead with four parts of the chromate.

A fused mixture of lead monoxide and cupric oxide was successfully used by Schwarz.[4]

Platinized asbestos[5] and quartz,[6] asbestos covered with finely divided cupric oxide,[7] manganese sesquioxide,[8] mercuric oxide,[9] potassium dichromate,[10] and potassium chlorate,[11] are occasionally used but belong rather to special methods.

Other oxidizing agents that are occasionally used to cover refractory substances in a boat, are potassium dichromate, potassium chlorate, platinum sponge, and powdered cupric oxide.

[1] Blau: Monatshefte, 10, 357.

[2] Ann. Chem. (Liebig), 95, 204.

[3] Am. Chem. J., 12, 226.

[4] Ber. d. chem. Ges., 13, 566.

[5] Kopfer: Ztschr. anal. Chem., 17, 4.

[6] Dennstedt: "Die Entwicklung der organischen Elementaranalyse," p. 103.

[7] Lippmann and Fleissner: Monatshefte, 7, 9.

[8] Dudley: Am. Chem. J., 10, 433; Ber. d. chem. Ges., 1, 3172.

[9] Mitscherlich: Ztschr. anal. Chem., 15, 374; Frerichs: Ber. d. chem. Ges., 10, 26.

[10] Johnson and Hawes: Am. J. Sci., 7, 465.

[11] Schulze: Ztschr. anal. Chem., 5, 269.

FILLING THE COMBUSTION TUBE

The tube cut to length, cleaned and dried as described on page 22, is filled by first inserting either a plug of previously ignited fibrous asbestos or a short copper oxide spiral five centimeters from one end of the tube   (Fig. 5).

· Fig. 5.

The asbestos is best introduced by using a plunger consisting of a glass rod about ten centimeters long on the end of which is fastened a cork whose largest diameter is a little smaller than the internal diameter of the tube.   The cork is inserted in the tube a distance of five centimeters, crowding before it a small wad of asbestos.   Holding the glass rod and the combustion tube firmly in a vertical position and keeping the cork five centimeters in the tube, the asbestos is packed down by a similar plunger with a long glass rod or tube inserted in the other end of the combustion tube.   More asbestos is added, if necessary, till a plug eight to ten millimeters long is obtained.

If cupric oxide spirals are used they must be prepared by rolling a strip of copper gauze, one centimeter wide and ten centimeters long, into a roll that will snugly fit the interior of the combustion tube.   The roll should be thoroughly ignited in a Bunsen flame before being used.

To the asbestos plugs there is the possible objection that a little longer time is required to oxidize all products of dry distillation that may be deposited on them in the course of a combustion, while with the cupric oxide spirals or rolls the

oxidation of such material would be effected almost imme-
diately. On the other hand the cupric oxide spirals are
easily disintegrated. Asbestos plugs have been exclusively
used in this laboratory.

A forty-five centimeter[1] layer of cupric oxide in the
wire form (p. 24) is then introduced and an asbestos
plug or a short cupric oxide spiral is placed on top of it.
Owing to the weight of the column of cupric oxide
the plug or spiral should be supported from beneath by
the short plunger described above. A ten centimeter
space is then left for the boat in which the substance
to be burned is generally placed and the large cupric
oxide spiral is inserted in the tube, leaving about two
centimeters between the boat and the spiral. The
remainder of the tube is unoccupied.

Well-fitting, one-holed, red rubber stoppers are in-
serted in each end of the tube. The oxygen or air is
admitted at the anterior end of the tube, *i. e.*, that con-
taining the long cupric oxide spiral, while the prod-
ucts of combustion issue from the other or the exit
end of the tube. The stopper in the anterior end is
generally furnished with a well-fitting glass tube which
is connected directly by means of rubber tubing with
the purifier. It is highly desirable to use a straight
glass stop-cock (Fig. 12, p. 51) in place of the glass
tube. Where rubber and a screw pinch-cock are used
the cock often cuts the rubber, causing leaks which
may mean loss of carbon dioxide and water. The
glass stop-cock does away with this difficulty, and

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[1] A forty centimeter length of cupric oxide will suffice to burn most ma-
terials, but a forty-five centimeter length is much safer to use.

furthermore furnishes a length of tubing easily examined for traces of condensed products of distillation or sublimed material which has diffused backwards and escaped oxidation by the cupric oxide spiral. Such condensation rarely occurs, however, if the combustion has been properly conducted. The stopper in the exit end of the tube is connected directly with the water absorbing tube of the absorption apparatus. It is important, therefore, to see that the hole in this cork is of a proper size to take snugly the glass connecting tube of the water absorber.

The combustion tube thus prepared is placed in the furnace and is ready for the preliminary " burning out " described on page 45.

BOATS

The material to be burned, if a solid or a high boiling liquid, is almost invariably placed in a porcelain, copper, or platinum boat which is introduced into the combustion tube by means of a long wire with a bend on the end. The boat should preferably have a ring handle or extension to facilitate inserting and withdrawing it.

Porcelain.—The porcelain boat should be approximately seventy-five millimeters long and not too wide to enter the combustion tube readily. This boat is especially advantageous for beginners as the charring of the material is well seen against the white background. Furthermore, it is seen at a glance by the absence of any black color in the boat when all the carbonaceous residue has been oxidized.

Copper.—Occasionally substances are met with that
are unusually refractory and require either unusual
heat or length of time for their complete oxidation.
Such materials may often be burned to advantage in
a copper boat which has been heated till a coating of
oxide has been formed.   While at a high heat the car-
bonaceous residue resists the action of the oxygen
alone, it is readily oxidized by the cupric oxide coat-
ing of the copper with which it is in contact and the
copper thus reduced is again instantly oxidized, there-
by acting as a carrier of oxygen.

In burning substances with the copper boat care
should be taken when heating to prevent frothing, and
the boat should be covered with a bit of sheet copper
which protects the tube from being spattered.

Copper boats may be obtained in the market. Owing
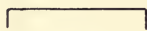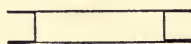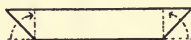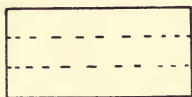to their rapid disintegration by alternate oxidation
and reduction, it is better to prepare
them as desired, using moderately
thick sheet copper.   A rectangular
piece is cut twenty-one by sixty-eight
millimeters and by making two folds
lengthwise of the sheet a copper
trough of rectangular cross-section
with a base seven millimeters wide
and sides seven millimeters high is
obtained (Fig. 6).   A pair of flat-
nosed pliers are used to bend up each
end and a serviceable boat is easily made.   A piece of
sheet copper sixty-eight millimeters long and seven

Fig. 6.

millimeters wide has a strip five millimeters long bent down at each end. This cover when placed on top of the boat prevents spattering on the glass.

Platinum.—The expense of a platinum boat is so great as to prohibit its general use. Platinum absorbs gases and hence the use of a boat of this metal in a current of oxygen hastens oxidation as does, in a much greater degree, the use of finely divided platinum in the form of platinized asbestos or platinum sponge.

ABSORBING AGENTS

The products of combustion issuing from the combustion tube, _i. e._, water and carbon dioxide, are retained in some absorbent and weighed.

As absorbers of water calcium chloride, concentrated sulphuric acid, phosphorus pentoxide, and, at times, solid potassium hydroxide may be noted. Carbon dioxide may be absorbed by strong solutions of potassium or sodium hydroxide, solid potassium hydroxide, soda-lime,[1] and barium hydroxide.

Calcium Chloride in the granulated form is obtained in the market and should be sifted to remove all of the finer powder which is liable to be mechanically carried along with the current of gas. It should be in granules of from two to three millimeters in diameter. It is well to dry the chloride before use by heating in an evaporating dish over a Bunsen flame, care being taken not to fuse the salt. Fused calcium chloride, unless in small lumps, is not an active dehydrating agent, but the coarser, more granular, and porous form may be used in larger pieces. The chloride should be chemically pure and as free from basic compounds as possible.

[1] Mülder: Ztschr. anal. Chem., **1**, 2; Dennstedt: "Die Entwicklung der organischen Elementaranalyse," p. 105; Benedict and Tower: J. Am. Chem. Soc., **21**, 389.

Potassium hydroxide in stick form or in concentrated solution is very generally used. The stick contains about twenty-five per cent. of water. A concentrated solution is prepared by dissolving one part of stick potassium hydroxide in two parts of water and cooling the solution. Another method consists of dissolving stick potassium hydroxide in a small amount of water and diluting the cooled solution until its specific gravity is 1.27.[1] If impurities in any appreciable quantity are present in the hydroxide the solution should be allowed to stand and the supernatant portion should be decanted off and preserved for use.

Soda-lime when used to absorb carbon dioxide must contain appreciable quantities of moisture; hence, the dry fused soda-lime, sold for use in the determination of nitrogen by the method of Will and Varrentrapp, or for drying gases, is not suited for the absorption of carbon dioxide.

A soda-lime that has given excellent satisfaction is quickly and easily prepared as follows: One kilogram of commercial caustic soda, "Greenbank Lye," is treated with 750 cc. of water in an iron kettle, forming a strong solution, or more properly a thin paste. While still hot one kilogram of quicklime, coarsely powdered, is rapidly added, stirring constantly with an iron rod or a piece of gas pipe. The lime is slaked by the water of the caustic soda solution and soon the whole mass heats and steams. While in this stage it is advisable to keep the mass stirred and the lumps broken. No outside heat is necessary and as soon as cool the product is coarsely pulverized and placed in wide-mouthed bottles and the corks sealed in with

[1] Auchy (J. Am. Chem. Soc., **20,** 245) prefers a sp. gr. of 1.40.

paraffin or wax. When cool it should not be moist enough to show water as such, *i. e.*, no particle should glisten in strong light. If too dry, a small quantity of water can be readily added after the soda-lime is made, though the great danger lies in adding too much water, thereby making the lime too pasty for the most efficient absorption. The addition of dry soda-lime to a product that is too moist will, in many instances, render it suitable for use. The granules of soda-lime should not be more than two millimeters in diameter to secure the most efficient absorption. As the material is damp there is no danger that dust particles will be carried along mechanically with the gas.

Phosphorus pentoxide[1] is but seldom used as an absorbent of water in organic combustions. When used the greatest efficiency and least possibility of clogging the tube is obtained by mixing the powder with ignited asbestos. Asbestos cord consisting of two or three strands is unwound and the strands cut in pieces about one centimeter long. The pieces are then strongly ignited in an iron dish and cooled. A quantity of phosphorus pentoxide is placed in a dry wide-mouthed bottle, the pieces of asbestos added, and the bottle tightly corked. The bottle is well shaken and the asbestos becomes coated with the powder which clings to it. The pieces are then quickly transferred to the tube in which they are to be used. The hygroscopic nature of this material renders the use of U-tubes fitted with ground glass stoppers necessary.

ABSORBING APPARATUS

The absorbing system, though performing the same function as the gas purifier, must be so constructed as

[1] Löwe : Ztschr. anal. Chem., **11**, 403; Mitscherlich : *Ibid.*, **15**, 388; Schmitz : *Ibid.*, **23**, 515.

to conform to certain conditions in regard to efficiency of absorption, compactness of form, and minimum weight, for it is necessary to absorb all the products of
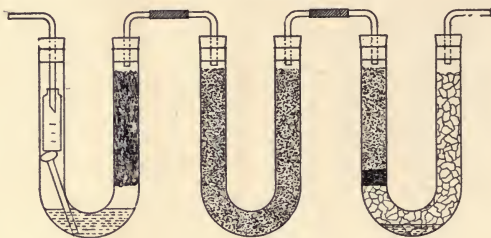

Fig. 7.

combustion in an apparatus not too large or too heavy to weigh on an ordinary analytical balance. In general, the solid reagents are held in the various modifications of the U-tube and the liquid agents are held in the various modifications of the " potash bulb."

In combustions of most organic substances more water is formed than is sufficient to saturate the gas leaving the combustion tube ; hence a varying amount of water condenses about the stopper in the exit end of the combustion tube. The water formed in the process of a combustion is generally collected in a U-tube having a bulb on the arm nearest the combustion tube which serves to collect the condensed moisture and thus to prevent unnecessary exhaustion of the absorbing agent. As this bulb fills it may be emptied, and consequently a number of combustions may be made with the same absorbing tube. The Volhard and the Marchand form of U-tube are most commonly used.

A simple and efficient absorbing system is shown in Fig. 7 and consists of three plain five-inch U-tubes five-eighths inch in diameter. The first contains a small glass vial, concentrated sulphuric acid, and glass wool drenched with concentrated sulphuric acid; the second is filled with soda-lime prepared as described on page 32; the third is one-third filled with soda-lime and the remaining volume with pumice stone drenched with sulphuric acid.

In this form of absorber the vial serves the purpose of the bulb in the other U-tube. It should be somewhat smaller in diameter than the U-tube and so supported on a bit of glass rod flattened at one end that the glass tube conducts the products of combustion into the neck of the vial. Water condensing in the tube falls in drops to the bottom of the vial and the gas saturated with aqueous vapor at the temperature of the apparatus passes through the U-tube where it is dried and thence into the carbon dioxide absorbers.

A plug of coarse glass wool is inserted in the other arm and extends from the stopper to the point where the bend begins. Enough commercial concentrated sulphuric acid is slowly poured through the glass wool to saturate it thoroughly and just seal the bend at the bottom of the U-tube in such a way that the gas will have to bubble through it. The lower end of the glass wool will then be about one centimeter above the surface of the liquid, the air space preventing too much acid from being carried up mechanically into the glass wool. When this happens it is not unusual for the

acid to be carried over into the carbon dioxide ab-
sorbers. The air space is otherwise valuable as it per-
mits isolation of each bubble and consequently better
regulation of the rate of the combustion. If the bend
is just sealed the minimum pressure only is necessary
to force the gas through the tube. The greater por-
tion of the water-vapor is retained by the acid in the
bend of the tube as the gas bubbles through, while the
last traces are removed by the acid adhering to the
glass wool. Thus in one plain U-tube are incorpo-
rated three distinct drying operations; condensation of
excessive moisture, removal of the major part of the
water-vapor, and final absorption of remaining traces
of moisture. The tubes are closed with well fitting
one-holed rubber stoppers furnished with glass elbows.
One elbow extends far enough below the stopper to be
thrust into the neck of the vial. The tubes are finally
closed with short bits of red rubber tubing fitted with
short glass plugs. The rubber tubes are removed be-
fore weighing. Inasmuch as all the tubes in the ab-
sorbing train can be used for a number of combustions
before refilling, the rubber stoppers can be replaced
by corks which are crowded down and cut off flush
with the ends of the U-tube. The corks may then be
coated with sealing wax. This precaution is hardly
necessary as good rubber stoppers give excellent re-
sults. A tube prepared in this manner may safely be
relied on to absorb about one gram of water-vapor ex-
clusive of the water condensed in the vial. In a series
of experiments on the combustion of sugar where ap-

proximately 0.12 gram of water was weighed each
time, it was found that about three-fourths of the water
condensed in the vial. No direct estimate can be made
of the length of time such a tube will last, owing to
the varying amounts of water formed in different com-
bustions, though, if the vial is marked with a file
scratch at the points indicating cubic centimeters, by
deducting the amount of condensed water from the in-
crease in weight of the tube, a ready check on the
amount of water actually absorbed is at hand.

The second tube of the absorbing system is filled
with soda-lime prepared as described on page 32, and
when freshly filled, will last for from six to fourteen
combustions, the number depending on the size of the
lumps of soda-lime, the quantity in the tube, and the
weight of carbon dioxide absorbed in each combustion.

The last tube of the system serves the dual purpose
of retaining any moisture lost from the soda-lime tube
and any traces of carbon dioxide that may have es-
caped absorption in case the soda-lime becomes ex-
hausted. With soda-lime the change in color is a
very accurate indication of the absorption of carbon
dioxide, and hence it is only necessary to replace the
tube with a fresh one before it has been completely
whitened.[1]

The increase in weight of the last tube is ordinarily
not more than seven milligrams for each combustion,
and consequently when the increase is greater it is an
additional sign that the soda-lime tube is nearly ex-

[1] J. Am. Chem. Soc., **21**, 394.

hausted. An increase of more than ten milligrams indicates the necessity of a new tube.

One arm and the bend of the last tube of the system are filled with dry lumps of pumice stone. Concentrated sulphuric acid is then allowed to trickle slowly down over the pumice until it becomes thoroughly saturated, but there must not be acid enough left in the bottom of the U-tube to seal the bend. A ten millimeter layer of glass wool is then laid over the pumice stone in the partially filled arm and the remaining space filled with soda-lime. The glass wool must not come in contact with the acid at any point.

In case sufficient carbon dioxide to exhaust the soda-lime does not enter the tube, it should last for twenty-five or more combustions, since the sulphuric acid would completely absorb at least one-half gram of water, and if ten milligrams were retained from each combustion the possible efficiency would be fifty combustions. The ease with which the last tube is prepared, however, renders it more satisfactory to change it after twenty-five or thirty combustions.

All tubes are closed with two centimeter lengths of red rubber tubing fitted with bits of glass rod. The edges of the glass plugs should be fire-polished.

The tubes are conveniently placed in a small pasteboard box nineteen centimeters long, thirteen centimeters high, and eight centimeters wide, open at the top. Similar boxes are furnished to be used with potash bulbs.

Bredt and Posth[1] have devised a special form of tube with ground-glass stoppers for holding soda-lime.

Barium hydroxide has been used by Claesson[2] and Kreusler[3] as an absorbent of carbon dioxide. Its action is similar to that of soda-lime.
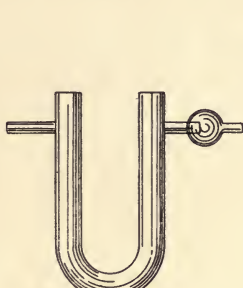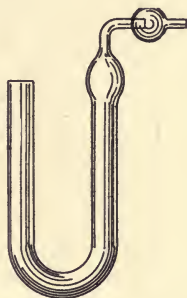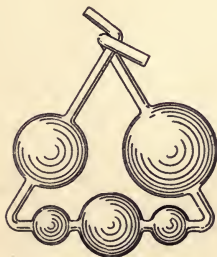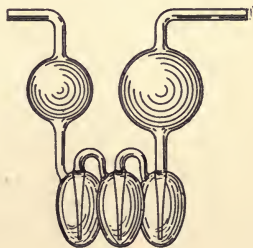

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

The most familiar and one of the oldest absorbing systems consists of a Marchand (Fig. 9), or Volhard[4] (Fig. 8) U-tube

[1] Ann. Chem. (Liebig), **285,** 385.

[2] Ber. d. chem. Ges., **9,** 174.

[3] Ztschr. Chem. (1866), 292.

[4] Ann. Chem. (Liebig), **176,** 339. The earlier forms of Marchand and Vol-hard tubes do not contain the small extension tube in the bulb suggested by Mixter. This tube aids materially in preventing drops of water entering the arm of the U-tube.

filled with granular calcium chloride followed by a Geissler (Fig. 11), Liebig (Fig. 10), or Mohr potash bulb containing a concentrated solution of potassium hydroxide.

The calcium chloride tube of this system is designed to absorb the water in a number of combustions, consequently, after filling the arms of the U-tube with the calcium chloride (page 31) corks are inserted and preferably coated with sealing wax. At times the arms to which side tubes are attached are closed by sealing off the glass after filling. The tube is provided with a length of fine platinum or aluminum wire to facilitate suspension on the balance arm. This is unnecessary if the hanger mentioned on page 45 is used.

Calcium chloride almost invariably contains basic compounds which absorb not only water but carbon dioxide, and which consequently introduce a serious error in analysis. It is necessary, therefore, to conduct a slow current of dry carbon dioxide through the tube after it is all prepared, to neutralize any basicity that may exist. The tube is best filled with carbon dioxide, tightly closed with bits of rubber tubing and glass plugs and left over night. The unabsorbed carbon dioxide must be carefully expelled by gently sucking dry air through the tube for half an hour. Though the efficacy of this treatment has been doubted,[1] probably the error introduced by subsequent absorption of carbon dioxide is not very great.

The tube thus prepared may be used until about one-third of the calcium chloride has deliquesced. Löwe[2] has suggested coating the inner arm of the U-tube with tallow to prevent deliquesced calcium chloride from adhering to the wall of the tube and thereby stopping the gas. In case this method is used obviously the limbs of the tube cannot be sealed off.

The "potash bulb" of Liebig is the earliest form of apparatus for holding concentrated potassium hydroxide to absorb

[1] Winkler: Ztschr. anal. Chem., 21, 545 (1882).
[2] *Ibid.*, 11, 403 (1872).

carbon dioxide in organic combustions. This bulb has been largely superceded by the more elaborate and fragile bulbs of Geissler and Mohr which have the advantage that they can be placed on the pan of the balance and need no support while the Liebig bulb must of necessity be suspended. The potassium hydroxide solution is introduced into a Liebig bulb by applying gentle suction with the mouth through a rubber tube attached at one end of the bulb. The other end is dipped in the potassium hydroxide solution and sufficient liquid is drawn into the apparatus nearly to fill the three bulbs on the lower arm. The end which was dipped into the concentrated potassium hydroxide is then carefully cleaned inside and out, introducing long pointed rolls of filter-paper to absorb the excess of potassium hydroxide adhering to the inside of the glass tube. When the bulb is filled the ends are closed with bits of rubber tube and glass plugs. Such a bulb should be refilled after two combustions. A prolong consisting of a small straight "calcium chloride" tube, filled with small lumps of potassium hydroxide, is attached to the exit end of the Liebig bulb to retain any moisture lost from the concentrated potassium hydroxide as well as any traces of carbon dioxide escaping absorption.

The Geissler bulb requires a little more care in filling with concentrated potassium hydroxide. The prolong, if attached, is removed and a rubber tube is connected with the arm of the tube on which the smaller bulb is blown. When the prolong is connected with a ground-glass joint the rubber tube is slipped over the ground end on the limb. The other end is then dipped in concentrated potassium hydroxide solution (p. 32) and sufficient liquid is drawn into the apparatus to fill each of the three lower chambers a little more than half full. The filling is easily accomplished by inclining the bulb and applying gentle suction. The greatest care must be taken to avoid sucking concentrated lye into the mouth. An empty wash-bottle may be inserted between the mouth and

the bulb or a very gentle suction with the filter-pump may be used. The suction should first be started and then the tube connected with the bulb. After filling the bulb the tube that was dipped in the liquid should be carefully cleaned as described above and the apparatus plugged ready for weighing. The solution should be renewed after two combustions.

The prolong contains either stick potassium hydroxide, fused soda-lime, or granulated calcium chloride, and serves to retain the water vaporized from the potassium hydroxide solution as well as any traces of carbon dioxide. While solid potassium hydroxide has been used for many years the use of calcium chloride is more logical as the gas entering the bulb is dried over calcium chloride and hence should be dried over this reagent before leaving. If the prolong is filled with calcium chloride it is unnecessary to conduct carbon dioxide through it before using.

Of the other modifications of the potash bulb those of Mitscherlich,[1] Winkler,[2] De Koninck,[3] Kyll,[4] Delisle,[5] Gomberg.[6] Bender and Hobein, and Bowen may be mentioned.

WIPING AND WEIGHING THE APPARATUS

The greatest difficulty is experienced in securing the correct weight of the absorption apparatus before and after a combustion on account of the great inequality in the amount of moisture and gases condensed on the surface of the glass. This inequality is often of sufficient magnitude to render an analysis useless. Attempts are made, therefore, to have the apparatus at

[1] Ztschr. anal. Chem., **15,** 389.
[2] *Ibid.,* **21,** 545.
[3] Ber. d. chem. Ges., **3,** 287.
[4] Chem. Ztg., **18,** 1006.
[5] Ber. d. chem. Ges., **24,** 271.
[6] J. Am. Chem. Soc., **18,** 941.

the same temperature and with the same surface condensation after the combustion as before. To this end it is usually recommended that the apparatus should be lightly wiped with a clean soft cloth and then allowed to stand a half hour beside the balance before being weighed. This operation is fairly effective in good weather and doubtless gives a close approximation to correct results, but the differences in the amount of condensation on days in which the atmospheric conditions are not the same, are very considerable. When the conditions to which the glass is exposed in the course of the combustion are considered, *i. e.*, the wiping, the handling with moist fingers, the sojourn of at least an hour in close proximity to a combustion furnace, together with the considerable internal heat from the absorption of the carbon dioxide by the reagent, the assumption that the surface condition remains the same after as before, even with all precautions, is rather broad.

In an operation of this kind obviously the simpler the form of absorber and the smaller the surface, the more readily can the apparatus be brought into condition for weighing. With the absorber first described (p. 34) it is possible to have constant surface conditions before and after analysis and thus be independent of the weather. By carefully wiping the U-tubes with clean, dry cheesecloth, it is possible to clean the apparatus till there is no longer any loss in weight. This point is taken as the standard condition and the tubes are so wiped before and after each combustion.

The rubber plugs are removed from the first U-tube and the tube wiped thoroughly with a piece of clean, dry cheesecloth in each hand in such a way that the glass does not come in contact with the fingers. It is necessary to give the tube a hard, thorough rubbing. The tube is then placed on the balance, brought to equilibrium, then removed and thoroughly wiped again and weighed. It will probably have lost somewhat in weight. The operation is repeated until the weight remains constant. After a little experience it is seldom necessary to wipe the tube more than three times. The tube is then plugged and the weight recorded. At the end of the combustion the operation is repeated and the condensation on the surface of the glass thereby eliminated. The importance of using clean, dry cheesecloth cannot be too much emphasized. A tube so cleaned rapidly increases in weight owing to the condensation on its surface, but the increase is not too rapid to prevent making an accurate record of the weight.

This method would be impossible if applied to a Liebig or a Geissler potash bulb. The fragile nature of such bulbs would not permit of careful, thorough wiping of their excessively large surface, and consequently the procedure must be that usually recommended, outlined on page 43. The use of a counterpoise when weighing potash bulbs has been recommended.[1] The counterpoise should consist of a simi-

[1] Regnault : Handwörterbuch, Suppl., 189 ; Blair cited by Dudley : J. Am. Chem. Soc., 19, 96.

lar bulb which, however, is not filled with the reagent. Each tube and piece of apparatus may be provided with a loop of fine platinum or aluminum wire though it is much easier to use a hook made from a piece of stout copper wire so bent as to hang on the arm of the balance and furnish suspension for the U-tubes.

WEIGHT OF MATERIAL USED

The amount of material used is generally dependent on the amount of carbon it contains. From two- to three-tenths of a gram is ordinarily used. Where the approximate composition of the substance is known it is advisable to use an amount that will yield, when burned, from three- to four-tenths of a gram of carbon dioxide. In case of compounds of higher carbon content the carbon dioxide formed may rise to five-tenths of a gram, but should not ordinarily exceed that amount.

In burning compounds mixed with sugar or benzoic acid, as described on page 60, the carbon dioxide from the admixture must be considered in calculating the total amount that must be absorbed.

BURNING OUT THE COMBUSTION TUBE

When a new tube is filled there are always particles of dust and a considerable quantity of moisture adhering to the tube and the materials, which must of necessity be removed before making an analysis. This is most readily accomplished by heating the tube in the furnace and conducting a current of oxygen through

it.   The moisture is all expelled by the heat and the
current of gas, while all organic matter is completely
oxidized to water and carbon dioxide which are finally
expelled by dry oxygen.   An old tube which has stood
some time since being used should likewise be burned
out.   The tube filled as described on page 27 is placed
in the combustion furnace, a slow current of pure, dry
oxygen is conducted through it, and the heat gradu-
ally raised until the whole tube is heated to a low red.

No operation connected with the making of an or-
ganic combustion is attended with as many accidents
as is the heating of the tube.   The utmost care must
be exercised to secure an even heating which is grad-
ually increased to the desired point.   If Jena glass is
used, and proper care is exercised in protecting the
tube by layers of asbestos in the iron or tile trough,
and in applying the heat judiciously, no difficulty
should be experienced.   At the start the burners
should all be turned on full force, the air holes closed
and the combustion tube either removed from the fur-
nace or supported on the tiles used to cover the tube
during combustion in such a manner that it is not
heated.   The gas is then turned on full at the main
cock, allowed to rush through the burners a moment,
then it is nearly shut off, and the burners are lighted
from beneath.   The flame will run along till all the
burners are lighted and burning with a smoky, lumi-
nous flame.   The gas is then turned down till the
flames are not more than seven to ten millimeters high
and the tube is placed in the trough.   In five minutes

the tiles are closed over the tube and at the end of five more minutes the gas is turned on more and the flames made non-luminous by opening the air holes at the base of the burners. The gas should be turned on at each burner till the flame is non-luminous without striking back. After this stage the heat may be increased with greater rapidity until the desired temperature is attained.

The temperature to which the tube should be heated is variously given from just below red heat to a cherry-red which limits would extend from 500° to 1000° C.

With Jena glass tubing the heat may be safely carried to a strong cherry-red without danger of having the tube blow out or become very much distorted. By properly supporting the absorbing system and the glass stop-cock in the entrance end of the tube so as to bring no great leverage on the tube no appreciable bending will occur.

With Bohemian glass the heat must be much more carefully regulated and not carried beyond a low red heat. In either case unnecessary heating is to be avoided as wasteful of gas and deleterious to the tube. A low red heat will serve to burn most all substances.

A new tube should be heated for at least half an hour with a continual current of oxygen passing through it. At the end of that time a short straight calcium chloride tube filled with the granular chloride, which, however, needs no preliminary treatment with carbon dioxide, is inserted in the cork in the exit end of the tube. The small cork in the open end of the

calcium chloride tube is fitted with a small glass tube which is purposely drawn down to a point, thereby allowing expansion and contraction of the gas inside the tube while permitting the minimum diffusion of air through the tip when the combustion tube is cold. Under these conditions, after cooling, the tube may be allowed to stand some time and may be used for a combustion without previous burning out. The calcium chloride tube is effective when the intervals between use are short; *i. e.*, not over one or two days, otherwise the tube should be burned out.

In cooling a combustion tube care must be taken to avoid too sudden changes in temperature. With Bohemian glass tubing the diminution of heat must be made as gradual as possible. The flames are gradually lowered at intervals of three or four minutes until it is necessary to cut off the air supply to keep them from striking back. The luminous flames about one centimeter high are retained for from five to ten minutes longer and the gas is finally cut off. The tiles covering the tube must remain closed till the tube cools.

With Jena glass tubing the cooling process is much more rapid. As a general rule the entire supply of gas may be cut off at once, leaving the tiles closed, without damage to the tube. It is a little safer, however, first to turn the gas off one-half for five minutes and then cut off completely. In any case the tiles should remain over the tube.

When a combustion is to be made, immediately after

burning out the tube, or when successive combustions are to be made, it is unnecessary to cool the whole combustion tube. Usually the anterior portion, *i. e.*, that containing the cupric oxide spiral and the first fifteen centimeters of the layer of cupric oxide, alone is cooled until the hand can be comfortably placed upon it while the gas flames under the remainder are lowered till the tube is just below a dull red heat. This is accomplished by lowering the flames under the anterior portion gradually at intervals of three or four minutes and finally cutting off the gas entirely. The tiles are then thrown back and the tube allowed to cool.

With Jena glass tubes the gas under the anterior portion is completely cut off at once[1] and the tiles thrown back after five minutes. As soon as the hand can be held on the tube it is sufficiently cool and ready for the introduction of the substance to be burned. Obviously the degree to which the tube should be cooled depends upon the volatility of the substance to be analyzed. (See page 73.)

GENERAL PROCESS OF THE COMBUSTION

The combustion tube is first heated in a gentle current of air or oxygen, as described on page 45, to remove moisture, and then the anterior portion including about fifteen centimeters of the cupric oxide layer cooled down till the hand can be held on it. The cur-

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[1] When cutting off any considerable quantity of gas it is important to see that the remaining flames do not burn unnecessarily high by reason of the greater supply of gas.

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rent of air or oxygen is then cut off by means of the glass stop-cock or screw pinch-cock, and after removing the small calcium chloride tube the water-absorbing tube is inserted in the cork in the exit end of the combustion tube. The U-tube is suspended on a wire hook resting on a long glass rod horizontally clamped (Fig. 12). The carbon dioxide absorber is then attached by means of the short bit of red rubber tubing used as a plug. To insure good connections the ends of the glass tubes should touch inside the rubber tube. This is especially necessary when using potash bulbs owing to the considerable pressure required to force the gas through the liquid. By using a small aspirator[1] the pressure may be neutralized. In case the aspirator is used it is advisable to insert an unweighed calcium chloride tube between the aspirator and the absorbing system to prevent back diffusion of moisture. Such a guard tube may also be used after any system of absorbers, though if the combustion is properly conducted there is no necessity of having back suction.

After connecting the absorbing system to the tube the cork is removed, the long cupric oxide spiral withdrawn upon an iron, porcelain or previously ignited asbestos plate by means of a long wire with a hook on the end, and the boat containing the weighed substance is carefully thrust into the tube. The boat is pushed along the tube until within one centimeter of the asbestos plug. Since the tube becomes discolored

[1] Glaser: Ann. Chem. (Liebig), Suppl., **7**, 213.

and opaque with age it is advisable to insert the boat by placing the hook of the wire in the ring at the rear of the boat, pushing it into the tube until it touches the asbestos, withdrawing it one centimeter and raising the hook out of the ring.

The cupric oxide coil is thrust into the tube to within two or three centimeters of the boat and the cork inserted. This operation may be quite deliberate if the substance is not volatile, but in the case of volatile compounds the introduction should be as rapid as possible.

The cupric oxide coil is first heated to prevent back distillation of volatile organic material, and when the coil is hot enough to oxidize such material the boat is heated. As a rule the three burners directly under the coil are lighted, turned on full, and the tiles above closed. The tiles covering the boat should be opened for five centimeters on each side of the boat

Fig. 12.
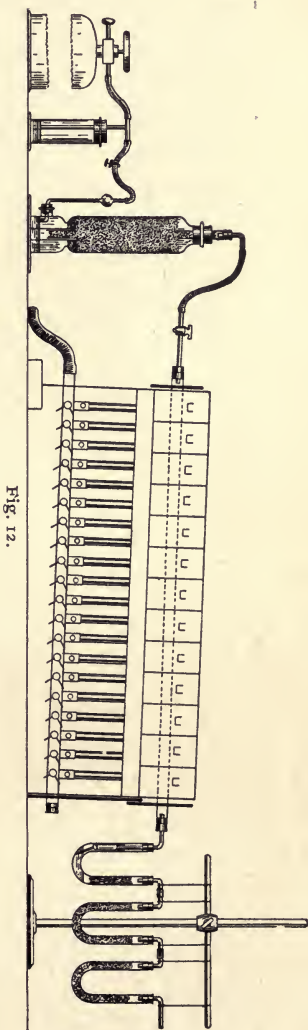
to prevent premature heating of the boat.   If an iron trough is used the heat will be conducted along the trough and heat the tube, though the layers of asbestos will serve to protect the tube somewhat.

The greatest difficulty in the whole operation of making an organic combustion is heating the substance properly.

As soon as the cupric oxide coil is at a low red heat the tiles over the boat are closed and the boat is gradually heated.   It should be borne in mind that the heat is conducted along the iron trough and consequently those burners nearest the boat should be lighted only after some time.   The whole operation is easily regulated by the rate of bubbling in the sulphuric acid U-tube of the absorbing system (Fig. 7), or in the potash bulb in case potassium hydroxide is used to absorb carbon dioxide.   In case a " 5/8 inch " U-tube containing sulphuric acid (Fig. 7) is used the bubbling should not be faster than one bubble per second.   With potash bulbs which contain tubes of much smaller caliber two bubbles per second are permissible.   This ratio, 1 : 2, by no means expresses the relation of the volumes of gas passing the tubes as the rate is much greater in the U-tube.   Potassium hydroxide is not so good an absorbent of carbon dioxide as soda-lime, hence the current of gas must be much slower.

During the preliminary heating of the cupric oxide coil the air in the tube will expand and bubble through the liquid.   As the temperature approaches redness the bubbling will be much slower.   Heating the boat

will again cause an expansion of air in that portion of the tube and consequent increase in the rate of bubbling. As soon as the material begins to volatilize and either through sublimation or dry distillation to come in contact with the hot cupric oxide, it is oxidized to form water and carbon dioxide which increase the volume of gas inside the tube and again increase the bubbling. As soon as the bubbling indicates an increase in the evolution of gas the burners nearest the boat are turned off and, if necessary, the tiles thrown back.

To be on the safe side, it is advisable to heat very slowly and at each indication of rapidly increasing rate of bubbling, to cool the tube considerably by cutting off the gas burners nearest the boat and opening the tiles. The cooling should be rapid and one should err on the side of cooling too much as by subsequent heating the combustion is immediately continued. As soon as bubbling becomes very slow heat may again be cautiously applied. By alternately warming and cooling (taking care to anticipate any great increase in the rapidity of bubbling) the combustion may be so regulated that oxidation is complete and no carbon dioxide or water escapes absorption in the absorbing system.

Volatile substances gradually sublime and some time is required to burn all the material. Some substances, such as sugar, melt and char rapidly, giving off a great deal of water-vapor and gases, leaving a charred residue. The manipulation varies with the substance,

but only in the case of very volatile bodies or sub-stances more or less explosive is any great difficulty experienced in regulating, by proper manipulation of flames and tiles, the rate of combustion.

When the bubbling has nearly ceased a very gentle current of oxygen is admitted, the rate being observed by the bubbling in the purifying apparatus rather than in the absorbing system. As a large quantity of cupric oxide has been reduced the oxygen will all be absorbed at first in reoxidizing the cupric oxide spiral. If the gas current is very rapid as soon as the free oxygen reaches the charred residue in the boat, carbon dioxide will be formed and a great rush of gas will force its way through the absorbers with the consequent liability of escape of unoxidized material. A regular bubbling of the oxygen in the purifier is the only safe guide. The charred mass will glow and burn brightly in the oxygen. This will serve to indicate the progress of combustion if the tube is too discolored to be trans-parent. As soon as the contents of the boat have been entirely oxidized the anterior portion of the tube may be cooled ready for a second combustion. The current of oxygen is continued till a good test for oxygen is obtained at the open end of the last tube in the ab-sorbing system. Splinters made of cigar-box wood retain their sparks a long time and are especially to be recommended for this purpose.

As soon as the oxygen is admitted the moisture con-densed in the entrance end of the combustion tube should be driven off by playing a Bunsen flame over

the surface of the glass, exercising care not to over-heat the rubber stopper. As soon as the cooling process is begun the moisture condensed in the exit end of the tube should be in a similar manner driven over into the water-absorbing tube.

The combustion requires in general about one hour from the introduction of the boat to the removal of the tubes. Five to ten minutes are required to heat the cupric oxide spiral; twenty minutes to heat the material in the boat till no more gas bubbles through the liquid in the absorbers; fifteen minutes till the tube is ready to cool ; and fifteen minutes to cool the tube and get ready for the next combustion. During the last half hour oxygen is conducted through the combustion tube and consequently all unoxidized organic material, as well as the copper, is thoroughly oxidized and the products of combustion are swept out of the combustion tube leaving the tube ready for another combustion. About one and a half liters of oxygen are required for the combustion. With materials which volatilize unchanged and leave no carbonaceous residue, it is necessary to heat a longer time before admitting the oxygen, but on the other hand, less time is required to complete the oxidation with oxygen. After oxygen is admitted the combustion practically runs itself, save for the time required to cut off the gas and cool the anterior portion of the combustion tube.

When succeeding combustions are to be made, the absorbers may be weighed, filled with oxygen be-

fore and after use. The openings through the glass elbows or connecting arms are so small as to prevent any considerable diffusion during the short time they are open for weighing. The weight of the set removed would, of course, be taken as the original weight of the set for a new combustion.

It is better, however, unless one is unusually skilled in combustion work to replace the oxygen by dry air. A U-tube similar to the last tube in the absorbing system (Fig. 7), is used to free the air from moisture and carbon dioxide. As usually conducted the limb of the purifying tube containing the greater quantity of pumice stone is connected by a short rubber connector to the entrance end of a water-absorbing tube, *i. e.*, the limb of the U-tube (Fig. 7) containing the glass vial. A twenty centimeter length of small rubber tubing, having an eight centimeter length of small glass tube inserted in one end, is connected to the exit limb of the water absorber. The short glass tube is placed in the mouth and air is drawn through the tube for a few moments. The air taken in at one long breath is sufficient to remove all oxygen. Obviously the air current must not be rapid enough to cause the acid to bubble up into the glass wool and run out of the tube.

The carbon dioxide absorber is likewise connected with the purifying U-tube and two long breaths of air drawn slowly through the system. In case it con-

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[1] Dudley and Pease (J. Am. Chem. Soc., **15**, 540) find, when using a small potash bulb, that eight hundred cc. of air should be aspirated to remove al oxygen. Much less would be required when a soda-lime tube is used.

sists of two pieces (Fig. 7), both should be connected as used in order that the moisture lost from the soda-lime (or potassium hydroxide) may be retained in the second tube or prolong.

The same care must be exercised in preparing the purifying tube as is used in preparing the absorbing tube described on page 38. Sufficient glass wool must be between the soda-lime and the acid. A great excess of acid is to be avoided. The purifying tube should last for twenty-five or thirty combustions. It is then well to refill it. The rate at which the air is being drawn through may be readily determined by connecting an instant with a gas washing-bottle or the mouth tube of an ordinary wash-bottle. Air will bubble through the water and after a few trials the rate is easily controlled. With a little experience no indicator is necessary. If too much air is drawn through the wash-bottle the soda-lime will rapidly become pasty and inefficient.

Burning in a closed tube, *i. e.*, with no current of oxygen, is liable, under certain circumstances, to cause a slight back suction. At times this is caused by the scaling off of cupric oxide from the large spiral, exposing fresh surfaces of unoxidized copper which immediately absorb oxygen, resulting in a contraction in volume. In this case if the spiral is hot enough to absorb oxygen the preliminary steps in heating the material in the boat may be taken and the expansion of the air in the tube will soon stop the back suction. If this is not immediately effective a very slow stream

of oxygen may be admitted, just enough to prevent back suction, but not enough to cause the gas to bubble out of the tube. As soon as the tendency to back suction is overcome the oxygen is cut off. Sufficient oxygen may be introduced into the purifying apparatus to cause a slight pressure. By slowly opening the stop-cock one or more bubbles of oxygen may be admitted to the combustion tube to prevent back suction.

COMBUSTION OF NITROGENOUS SUBSTANCES

Certain compounds containing nitrogen when decomposed yield varying quantities of nitric oxide which reacts with oxygen or air and water, forming many of the series of oxides and oxy-acids of nitrogen which go under the general name of the oxides of nitrogen. Chief among these is nitrogen peroxide which often appears in the combustion tube as red fumes. While neither nitrogen nor nitric oxide[1] would be retained in the absorbing reagents, nitrogen peroxide is readily soluble in sulphuric acid, soda-lime, or potassium hydroxide, increasing the percentage of hydrogen and carbon respectively. Furthermore, the interstices of a solid reagent such as calcium chloride or soda-lime afford an excellent opportunity for the retention of oxygen which would combine with any nitric oxide and would subsequently be absorbed.

Nitrogenous substances may be subdivided into two classes: one in which the nitrogen is attached to an

[1] Nettlefold: Chem. News, **55**, 28; Russell and Lapraik: J. Chem. Soc., **2**, 28 (1877); Emich: Monatshefte, **13**, 90; Lunge: Ber. d. chem. Ges., **18**, 1391.

oxygen atom, and the other in which no oxygen is connected with the nitrogen. To the first class belong the nitro, nitroso, isonitroso, and azoxy bodies, oximes, etc., while the second class includes practically all other nitrogenous organic compounds; amines, amides, nitriles, etc.

It is only in dealing with bodies of the first class that any modification in the method of combustion is necessary. The unoxidized nitrogenous bodies are burned exactly as described on page 52. The oxidized nitrogenous compounds when heated are especially prone to liberate oxides of nitrogen and some provision is necessary to eliminate any possible effect of their presence on the final results. These precautions consist of one of two essentially different operations. The oxides formed are absorbed by lead peroxide,[1] manganese dioxide,[2] potassium chromate,[3] or metallic silver[4] or more commonly they are reduced by metallic copper.[5] The absorption of the oxides is almost always adapted to special methods and is open to grave objections.

The reduction by metallic copper is by far the simplest and most satisfactory operation. The metallic copper may be reduced in the form of a spiral, by hydrogen, methyl or ethyl alcohol, formic acid, or

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[1] Kopfer: Ztschr. anal. Chem. (1878), 28.

[2] Perkin: J. Chem. Soc., (1880), 457; Ber. d. chem. Ges., 13, 581.

[3] Perkin: J. Chem. Soc., 37, 121.

[4] Dennstedt: Gazz. chim. ital., 28, 78.

[5] The use of a copper spiral to reduce oxides of nitrogen has recently been investigated by Klingemann: Ber. d. chem. Ges., 22, 3064; Tower: J. Am. Chem. Soc., 21, 596; Benedict: Am. Chem. J., 23, 334.

coal gas, and after cooling introduced into the exit end of the combustion tube.

Another method for the decomposition of the oxides of nitrogen consists in reducing a quantity of cupric oxide in close proximity to the boat by charring or vaporizing a known weight (50 to 100 milligrams) of chemically pure sucrose, benzoic acid, or naphthalene in the tube. The metallic copper thus reduced is heated strongly and the material to be burned then heated. As the oxides of nitrogen pass over the hot copper they are completely reduced.

Of these two methods the latter[1] is much the easier, requiring, as it does, no change in the method of filling the combustion tube. The reducing material, sucrose, benzoic acid, or naphthalene, must be perfectly pure. Pulverized rock candy from which the strings have been separated, furnishes a remarkably pure sucrose. It is unnecessary to dry the material unless it is pulverized on an especially damp day. It is preserved in a test-tube closed with a good rubber stopper and furnishes an excellent standard material for making check combustions. Kahlbaum's pure benzoic acid and naphthalene have also given excellent satisfaction as reducing materials in this laboratory.

The material to be analyzed is placed in a boat leaving a free space about a centimeter in length in the forward end. The greater portion of the sucrose, benzoic acid, or naphthalene is placed in this space and the remainder sprinkled over the top of the layer of

[1] Am. Chem. J., **23**, 343.

substance. The end of the boat containing the sucrose is first inserted in the combustion tube and the boat pushed in till it nearly touches the asbestos plug. The boat should not touch the cupric oxide, but be separated by a centimeter layer of air. After heating the spiral in the anterior end of the tube the heat is brought toward the boat from the middle of the combustion furnace, hence the cupric oxide becomes thoroughly heated before the end of the boat containing the reducing material is heated. The sucrose melts at 143° and distils towards 200°, giving off empyreumatic vapors which reduce a portion of the contiguous cupric oxide which becomes still more heated as the flames are turned on. The melted sucrose often mixes with, or possibly partially dissolves, the substance to be burned and when the sugar finally chars there is a large excess of carbon to aid in reducing the nitro group. Furthermore, the hot copper may produce a decomposition of the benzoic acid vapor which passes over it.

When a new combustion tube is used the presence of reduced copper is readily seen as a layer, some two or three centimeters long, appearing in front of the boat while the end of the rear cupric oxide spiral, inserted after the boat, is always seen to be partially reduced.

Few nitro bodies are decomposed with an evolution of oxides of nitrogen below the temperatures necessary to secure the vaporization of benzoic acid or naphthalene, or the dry distillation of sucrose. It may be necessary, however, in some cases to place the redu-

cing material in a small copper boat a little ahead of
the porcelain boat containing the material to be ana-
lyzed.   In this case the copper can be reduced before
the material is heated.   Volatile nitro compounds are
vaporized in a current of nitrogen as described on
page 75 and conducted over copper reduced by a known
weight of either of these reducing materials.

In determining the percentages of carbon and hydro-
gen it is necessary to calculate the weight of water
and carbon dioxide resulting from the combustion of
the reducing material and deduct these weights from
the total increments of the tubes.   The difference rep-
resents the weight resulting from the combustion of
the material to be analyzed.   By multiplying the
weight of material used by the corresponding factors[1]
the weight of water and carbon dioxide is readily
calculated.

Sucrose and benzoic acid require no special care in
weighing and burning, but naphthalene, owing to its
volatility, necessitates rapid weighing and introduc-
tion to avoid loss from vaporization.   Of these three
substances naphthalene is much the best reducing agent,
weight for weight, benzoic acid next, and sucrose last.
Unless the material is very volatile, sucrose will be
found to give most excellent results.

The most familiar method of reducing oxides of nitrogen
is that requiring the introduction of a reduced copper spiral
in the exit end of the combustion tube.   A ten centimeter
layer of cupric oxide is removed from this end of the tube and
a reduced copper spiral of equal length introduced.   Where

[1] See Appendix, p. 82.

a number of combustions of different materials are to be made two tubes may be held prepared, one with the spiral and the other filled as described on page 27. If the last ten centimeters of the layer of cupric oxide are replaced by a coil prepared of stout copper wire thoroughly oxidized, the tube may be used for the combustion of oxidized nitrogen bodies by simply withdrawing the cupric oxide spiral and inserting a reduced copper spiral.

The general process of the combustion does not differ materially from that described on page 52. In order to prevent oxidation and consequent diminution in reducing power of the reduced spiral it is advisable to expel the oxygen in the combustion tube by air[1] before introducing the spiral or connecting the absorbing system. The U-tube used to purify the air drawn through the absorbers after a combustion is connected directly with the stopper in the entrance end of the combustion tube. A gentle suction by the mouth or an aspirator is applied through a rubber tube connected with the stopper in the exit end of the combustion tube and sufficient air is slowly drawn through the tube to remove all oxygen. The reduced spiral is then introduced, the absorbers connected, the boat inserted, and the combustion carried out as previously described. As soon as the oxygen is admitted the burners under the copper spiral should be turned off. When the oxygen is escaping from the last tube of the absorbing system the combustion is at an end and, after five minutes to insure removal of all traces of moisture and carbon dioxide, the absorbers may be removed.

The copper will, on being heated, absorb the oxygen in the air in the tube and consequently cause a back suction. While this can be partly counteracted by admitting a very gentle current of oxygen through the glass stop-cock, it is advisable to attach an unweighed calcium chloride tube to the final tube in the absorbing train to prevent the entrance of mois-

[1] Tower: J. Am. Chem. Soc., 21, 597.

ture.   The small calcium chloride tube used in the end of the
combustion tube when cool can here be used to advantage.

The copper spirals prepared, as described on page 25, are
best reduced by heating strongly in a Bunsen flame and then
thrusting into a large test-tube containing about one cubic
centimeter of ethyl, or better methyl, alcohol. The hot copper
vaporizes the alcohol and the cupric oxide is immediately re-
duced.   To prevent reoxidation a good rubber stopper is in-
serted in the mouth of the test-tube as soon as the liberation
of gases has ceased.   The cork may be laid loosely in the
mouth of the tube and firmly inserted as soon as possible.
The spiral, after cooling, is freed from adhering vapors by
placing it in a vacuum desiccator for several hours.   It may
also be dried in a current of carbon dioxide, or even in an air-
bath, at 100°.

The preparation of the reduced copper spiral and the sub-
sequent removal of the reducing agent have been the subject
of much discussion.[1]   The method described has given sat-
isfaction.

Many nitro bodies can be burned very satisfactorily
by simple admixture with three or four volumes of
pure dry powdered silica such as is used in glass works.
The mixture is placed in a porcelain boat and the
combustion carried out as described on page 52.   The
sand renders the substance non-explosive, and a regu-
lar combustion takes place.

If the absorbing system (Fig. 7) is used the oxides
of nitrogen will almost invariably be retained by the
sulphuric acid and consequently the percentage of
hydrogen alone will be affected.   If the substance

[1] Neumann : Monatshefte, 13, 40 ; Johnson : Chem. News, 67, 99 ; Thudi-
cum and Hake : *Ibid.*, 33, 218 ; Weyl : Ber. d. chem. Ges., 15, 1139 ; Lietzen-
mayer : *Ibid.*, 11, 306 ; Schwarz : *Ibid.*, 13, 559 ; Erdmann : J. prakt. Chem., 76,
96 ; Schrötter : *Ibid.*, 76, 480 ; Lautemann : Ann. Chem. (Liebig), 109, 301 ;
Ritthausen : Ztschr. anal. Chem., 18, 602.

burns with explosive violence and the gas bubbles through the sulphuric acid tube faster than one bubble per second a portion of the oxides of nitrogen may be carried over into the soda-lime.   When the percentage of hydrogen is not especially desired the admixture with pure silica will often be found a very simple and rapid method of determining the percentage of carbon and in most cases the percentage of hydrogen will not be excessively high.

COMBUSTION OF BODIES CONTAINING THE HALOGENS

When compounds containing chlorine, bromine, or iodine are burned in the manner described on page 52 the corresponding cuprous haloid is formed.   The volatility of the halogen compounds of copper renders it almost impossible to prevent their sublimation into the water-absorbing tube.   Furthermore, at a high temperature and in the presence of oxygen they easily lose a portion of their halogen.

The retention of the halogens is often effected by introducing a reduced copper spiral,[1] ten centimeters long, in the exit end of the combustion tube, removing a ten centimeter length of the cupric oxide for the purpose, exactly as was done in reducing the oxides of nitrogen, as described on page 62. The halogens are retained by this spiral which is heated only to a very low red heat, care being taken not to volatilize the cuprous haloid.   During the final combustion in oxygen gas the spiral must be cooled to prevent interaction of the haloid and the oxygen.

[1] Glaser: Ann. Chem. (Liebig), Suppl., **7**, 213; Städler: *Ibid.*, **69**, 335.

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The great objection to the retention of the halogens as copper haloids is their ready action with oxygen. Völcker[1] suggests a mixture of cupric oxide and lead oxide in which the halogen is converted to the non-volatile lead compound. The basicity of lead oxide, however, renders it liable to absorb carbon dioxide.[2]

By using metallic silver instead of copper, halogen compounds are obtained unacted upon by oxygen and withstanding a high heat ; *i. e.*, non-volatile. Silver[3] in the lace, molecular, foil, or spiral form when heated combines readily with the various halogens.

In using a silver spiral the combustion tube is filled as described on page 27, removing a ten centimeter length of cupric oxide from the exit end to make a place for a similar layer of metallic silver in either of the above-mentioned forms. All oil or organic matter should be burned off in a preliminary heating which can be effected in a current of oxygen since silver is not acted upon by oxygen. The silver halogen compounds, if formed in large quantities, are liable to fuse the silver to the glass. By removing the silver and heating it in a current of pure hydrogen the haloid is completely reduced to the metal which can be used repeatedly.

Moissan[4] recommends burning bodies containing fluorine in a copper tube filled with eighty parts of cupric oxide and twenty parts of litharge which retains the fluorine liberated.

The most satisfactory method of burning bodies containing halogens involves the use of lead chromate instead of cupric oxide as the oxidizing agent. The tube is filled precisely as when the latter reagent is used (p. 27). The cupric oxide spiral in the anterior part of the tube is likewise inserted. Since lead chro-

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[1] Chem. Gaz. (1849), 245.
[2] Kopfer: Ztschr. anal. Chem. (1878), 30.
[3] Stein: *Ibid.*, **8**, 83 ; Kraut: *Ibid.*, **2**, 242.
[4] Compt. rend., **107**, 992.

mate[1] is hygroscopic it is necessary to burn out the tube in a current of oxygen as described on page 45. The tube should not be heated enough to melt the chromate. The halogen in the substance burned combines with the lead, forming the corresponding lead haloid. These haloids are somewhat volatile and it is important that the last ten centimeters of the layer of chromate should be heated only high enough to prevent the condensation of moisture. The sublimed haloids condense on the cooler portions of the chromate and are not carried along to the water-absorbing tube. The combustion is finished as before in a current of oxygen which does not, however, regenerate the oxidizing agent as in the case of reduced copper oxide, hence it is necessary to refill the combustion tube with fresh material.

The complete retention of the halogens is at times attended with great difficulty as the following instances show:

Meyer and Wachter[2] found that in burning iodosobenzoic acid the halogen was not retained by lead chromate even with the addition of several long silver spirals.

Mauthner and Suida[3] found too large a percentage of carbon when burning tribromacrylic acid even when using lead chromate and a silver spiral.

The low fusibility of lead chromate has led to several suggestions for a substitute of higher fusing-point. Liebig[4] recommends a mixture of lead and potassium chromates.

By mixing one part of red lead with four parts of finely

[1] Erdmann : J. prakt. Chem., 81, 180 ; Bruce-Warren : Chem. News, 71, 143.
[2] Ber. d. chem. Ges., 25, 2632.
[3] Monatshefte (1881), p. 111.
[4] Anleit. z. Anal. organ. Körper, p. 32.

powdered lead chromate de Roode[1] obtains a mixture which is at least less fusible and has much greater surface for action.

This mixture was found especially serviceable by Remsen in burning the chloride of orthosulphobenzoic acid and allied bodies.[2] It was necessary, however, to mix the substance with powdered potassium dichromate.

In burning compounds containing boron and fluorine Landolph[3] found that a ten centimeter layer of lead chromate, if not heated too high, retained all boron and fluorine.

BODIES CONTAINING SULPHUR

When bodies containing sulphur are burned in the ordinary way with cupric oxide, cupric sulphate is first formed and is then decomposed by a high heat, liberating sulphur dioxide[4] which is absorbed in the carbon dioxide tube.

The retention of the oxides of sulphur may be accomplished at the expense of the hydrogen determination by mixing a small quantity of chromic oxide or potassium dichromate with the sulphuric acid in the water-absorbing tube. All sulphur dioxide is retained. Winkler[5] suggests a determination of the sulphur present by titration of the unreduced chromic acid.

The sulphur dioxide may also be absorbed by a layer of pure lead dioxide[6] placed in the exit end of the combustion tube and warmed to 150° or 180° to prevent the condensation of moisture. The combustion tube must be somewhat longer than that usually employed and so filled that a ten centi-

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[1] Am. Chem. J., **12**, 226.

[2] *Ibid.*, **18**, 803.

[3] Ber. d. chem. Ges., **12**, 1586.

[4] In the case of substances containing iron, sulphur trioxide is also liberated. Ztschr. anal. Chem., **14**, 16.

[5] *Ibid.*, **21**, 545 (1882).

[6] Warren : Am. J. Sci., 2nd ser. **41**, 40 ; Kopfer : Ztschr. anal. Chem. (1878), 28.

meter layer of lead oxide is in that portion of the tube protruding from the furnace. The rest of the tube is filled as described on page 27. The layer of lead oxide is kept warm by a small air-bath or sheet iron hood. All the sulphur dioxide is retained as lead sulphate.

$$PbO_2 + SO_2 = PbSO_4.$$
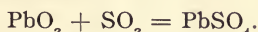
With pure, specially prepared lead dioxide there is no danger of the retention of carbon dioxide though if lead monoxide is present some of the gas will be absorbed.

Precipitated manganic peroxide mixed with a concentrated solution of potassium dichromate containing one-tenth of its weight of potassium chromate and dried forms a mixture that Perkin[1] uses in place of lead dioxide to retain sulphur dioxide and nitrogen peroxide. The mixture is placed in the exit end of the combustion tube and is maintained at a temperature of 200° to 250° by means of a small air-bath. The material is regenerated by heating strongly in a current of oxygen.

In burning bodies containing sulphur it is better to use a combustion tube filled with lead chromate or the mixture of de Roode described on page 68. The sulphur dioxide is all retained as lead sulphate, and if a ten centimeter layer of the lead chromate nearest the exit end of the combustion tube is not too strongly heated the lead sulphate will condense there and not pass into the absorbing apparatus. The manipulation is identical with that given for the combustion of substances containing halogens.

Volatile compounds containing sulphur and nitrogen must be burned very slowly as otherwise sulphur dioxide is liable to escape.[2]

[1] Ztschr. anal. Chem., **21,** 273.
[2] V. Meyer and Stadler : Ber. d. chem. Ges., **17,** 1577.

BODIES CONTAINING THE ALKALI METALS

Compounds of this class when burned retain in the ash material quantities of carbon dioxide which should either be determined and added to the carbon dioxide collected in the absorbing system or the substance to be burned should be mixed with some material such as potassium dichromate,[1] chromic oxide,[2] cupric phosphate,[3] tungstic[4] and silicic[5] acids to expel the combined carbon dioxide.

Lead chromate with an admixture of one-tenth its weight of potassium dichromate is the best reagent for this purpose.

If a calcium salt is being burned Leiben and Zeisel[6] suggest igniting the boat and ash in the blast to drive off the carbon dioxide which is determined by the loss in weight. To prevent contamination from adhering cupric oxide, the boat is introduced into the combustion tube in a cylinder of platinum foil.

DIFFICULTLY COMBUSTIBLE BODIES

Much difficulty is often experienced in securing determinations of carbon and hydrogen in bodies which are difficult to oxidize completely. In such bodies either the carbonaceous residue is of a very resistant character or the gases given off in the decomposition of the molecule, such as carbon monoxide, methane, aldehyde, or acetylene, are not easily oxidized by the cupric oxide.

[1] Wislicenus: Ann. Chem. (Liebig), **166**, 13.
[2] Schwarz and Pastrovich: Ber. d. chem. Ges., **13**, 1641.
[3] De Chaubray: Compt. rend. (1842), **1**, 645.
[4] Cloez: Jahresberichte, 1864.
[5] Schaller: Bull. Soc. Chim., **2**, 414.
[6] Monatshefte, **4**, 27.

Few substances will not be completely burned when the combustion is carried out in a current of oxygen (p. 49). Certain bodies containing nitrogen, halogens, or sulphur require special precautions in burning to effect a complete oxidation of the carbonaceous residue.

Hippuric acid is not readily burned in a porcelain boat, but when a copper (cupric oxide) boat is used the combustion is complete. The copper boat should have a cover (p. 30).

Malonic nitrile,[1] containing as it does about forty-two per cent. of nitrogen, leaves a very resistant residue.

A platinum boat, owing to the condensation of the oxygen on the metal, facilitates combustion. This property of platinum may also be made use of by covering the material in the boat with three or four times its volume of well ignited platinum sponge.[2]

Of the oxidizing mixtures finely-powdered cupric oxide is especially effective. Owing to its hygroscopic nature it is important to ignite it thoroughly in a crucible and allow it to cool in a desiccator before using in the combustion tube. At times the material may be so hard to burn as to necessitate mixing with cupric oxide and introducing into the tube in the form of a powder, filling the space usually reserved for the boat. In such cases the old bayonet form of tube[3] may be advantageously used.

Cyanogen compounds[4] are incorporated intimately

[1] Hesse : Am. Chem. J., **18**, 727.
[2] Demel : Ber. d. chem. Ges., **15**, 604.
[3] Meyer and Jacobsen : " Lehrbuch der organischen Chemie," p. 15.
[4] Lippmann and Fleissner : Monatshefte, **7**, 9.

with a mixture of one part potassium dichromate and ten parts lead chromate. Powdered lead chromate is also hygroscopic and requires special drying before use.

A layer of potassium chlorate may be fused into the boat and the substance then added and weighed.

Substances which, when heated, decompose into gases which are not readily combustible must be burned with a very long layer of cupric oxide at a high heat[1] and at a very slow rate.

Zincke[2] found, in studying the derivatives of the lactone of o-phenylglycerinecarbonic acid, that satisfactory results could not be obtained with cupric oxide. The carbon was always three per cent. too low. By using lead chromate, however, he obtained the theoretical results. The decomposition of these bodies forming carbon monoxide, which escapes unburned, seemed to him to be the difficulty.

The special methods of organic analysis relying on a short layer of oxidizing material are inadequate for the combustion of this class of compounds as a long layer of highly heated oxidizing material is essential.[3]

Zeisel[4] found that Kopfer's method could not be used in analyzing the derivatives of the methyl ester of colchicein as the carbon and hydrogen were, owing to incomplete oxidation, respectively two and one per cent. too low.

Herzig[5] and Skraup[6] found that Kopfer's method could not be used satisfactorily with ethyl or acetyl quercetin or chincholeupon hydrochloride.

[1] Haber and Grinberg: Ztschr. anal. Chem., **36**, 558.
[2] Ber. d. chem. Ges., **25**, 408.
[3] Blau: Monatshefte (1889), 357; Wislicenus: Ann. Chem. (Liebig), **242**, 27.
[4] Monatshefte, **7**, 573.
[5] *Ibid.*, **9**, 540.
[6] *Ibid.*, **9**, 807.

Wegscheider[1] found that the true esters of opianic acid can not be burned with cupric oxide, while with lead chromate satisfactory results may be obtained.

Among other cases in which difficulty was experienced are the following:

Claissen,[2] in burning a number of ethyl esters, found insufficient oxidation of the liberated gases.

Skraup[3] had difficulty in burning some esters in the mucic acid series.

Smith[4] emphasizes the necessity of a very slow combustion with phenylimidocarbonicdiethylester, owing to the escape of unoxidized gases.

Guareschi and Graude[5] found that hydrocarbons (methane and ethylene) were formed during the combustion of dicyan-methylhydroethyldioxypyridine.

COMBUSTION OF LIQUIDS AND VOLATILE BODIES

Certain modifications in the method of weighing and introducing the substance are necessary in burning liquids or volatile bodies.

If the material has a boiling-point above 170° C., it may, as a general rule, be weighed in the boat as directed for solids. It is best to weigh the boat and material just before using and transfer immediately to the combustion tube.

Dudley[6] uses a small bottle, through the cork of which a bulb pipette or medicine dropper is thrust. The bottle is weighed, liquid drawn into the pipette, delivered into the boat and the bottle again weighed, thereby giving the weight

[1] Monatshefte, **14**, 313.
[2] Ber. d. chem. Ges., **25**, 1768.
[3] Monatshefte, **14**, 476.
[4] Am. Chem. J., **16**, 391.
[5] Rendiconti Acad. Torino, **33**, 16.
[6] Ber. d. chem. Ges., **21**, 3172.

of liquid used.   The boat should be immediately thrust into the combustion tube as the weighing-bottle need not be weighed till later.

Reichardt[1] recommends weighing heavy oils, not too hygroscopic, by dropping them on a layer of cupric oxide powder in the bottom of a boat.   A weighing-bottle is used and the amount determined by difference.

Liquids boiling from 100° to 150° may be weighed in a glass tube, sealed at one end, about three millimeters internal diameter and twenty-five millimeters long.   The tube is easily filled by means of a fine pipette made by drawing out one end of a piece of tubing (five millimeters internal diameter) to a fine jet. In weighing, it is advisable to bend a piece of moderately stout copper wire in a form to rest on the balance pan and support the glass tube in an upright position.   The glass tube should be placed in the boat on a layer of cupric oxide (to prevent fusion of the glass to the porcelain) with its open end directed towards the exit end of the combustion tube and sufficiently raised to prevent loss of liquid.   It should be previously determined if the boat and the tube can be inserted into the combustion tube.   A bent piece of sheet copper whose surface is thoroughly oxidized may be used as a carrier for the glass tube.   The rear end of the tube should be so braced that it cannot slide back and cause the front end to drop.

Reichardt[2] places powdered cupric oxide in the tube to absorb the liquid.

A small loosely fitting stopper (Fig. 13) may be

[1] Archiv. der Pharm., **227**, 640.
[2] Loc. cit.

made by softening and flattening the end of a glass rod of a diameter to fit the tube.

Liquids boiling under 100° are best vaporized out-
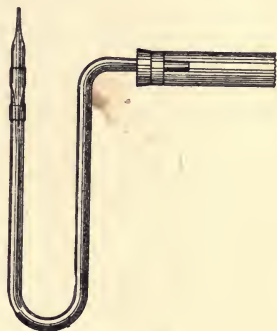
Fig. 13.   Fig. 14.   Fig. 15.

side the tube[1] and the vapor driven into the tube by a current of nitrogen, air, or oxygen. As these last two form explosive mixtures with many vapors they cannot often be used.

A simple arrangement for vaporizing such liquids is shown in Figure 15 and consists of a piece of glass tubing, five millimeters internal diameter, which is bent in a U, one arm of which is again bent at right angles and drawn down so as to be inserted conveniently in the stopper in the entrance end of the combustion tube. The other arm is left in a vertical position. The liquid to be analyzed is drawn into a previously weighed piece of three millimeter glass tubing drawn out at both ends. The ends are sealed by fusion, and after again weighing, the tube is tightly

[1] Dudley : Ber. d. chem. Ges., **21**, 3172.

inserted in a short piece of rubber tubing slipped over
the open arm of the U-tube. By pressing the long
point on the side of the U the end is broken and the
liquid will drop into the bend of the U. To remove
all liquid a rubber tube conducting the purified and
dried nitrogen (air or oxygen) is slipped over the other
end of the drawn-out tube and the slender tip broken
by pressing with a pair of pinchers. A very slow
current of the gas is conducted through the tube, and
by gently warming the U-tube (by immersing it in a
beaker of warm water for example) the liquid is va-
porized and driven into the combustion tube at any
desired rate. By immersing the U-tube in cold water
or a freezing-mixture, liquids of very low boiling-
points can be very readily burned, as their vaporiza-
tion can be easily controlled by raising or lowering
the beaker containing the freezing-mixture. When
nitrogen is used, as is generally the case, the gas freed
from carbon dioxide and moisture should previously
be conducted through the small U-tube and the com-
bustion tube until all air is expelled. Under these
circumstances the light hydrocarbons, ether, etc., can
be vaporized in a current of nitrogen with no danger
of an explosion.

Nitrogen for this operation is best prepared as fol-
lows: A current of air is caused to bubble through
strongest ammonium hydroxide and then to pass over
a heated copper spiral. The copper undergoes alter-
nate oxidation (by the oxygen of the air) and reduc-
tion (by the ammonia), yielding nitrogen containing

an excess of ammonia which is removed by bubbling through sulphuric acid. The gas is held in some form of gasometer (p. 6).

One hundred and fifty cc. of strongest ammonium hydroxide are placed in a two-necked Woulff bottle or a wide-mouthed bottle fitted with a two-holed rubber stopper. Air is forced or drawn through a glass tube, dipping under the surface of the ammonium hydroxide and the air containing a considerable quantity of ammonia gas is conducted over a ten centimeter copper spiral (page 25), (preferably constructed of stout wire), which is heated in a thirty centimeter length of Jena glass combustion tubing. A good Bunsen burner with a fish-tail top will give enough heat.

The gas is then conducted through a gas washing-bottle containing thirty per cent. sulphuric acid, to which a few drops of litmus solution have been added. The gas freed from the excess of ammonia is conducted into the gasometer. The air current may be maintained in many ways. A water-blast, if accessible, is the most convenient form of apparatus for this purpose.

If all the connections between the various parts of the apparatus are tight the air may be drawn through the system by suction either from the valve C in the Pepy gasometer (Fig. 2) or its corresponding valve on the Mitscherlich gasometer. A rubber tube connects the gas washing-bottle containing the sulphuric acid and litmus solution directly with valve C. The orifice at the base of the gasometer is opened and the valve C slowly turned. As water rushes out at the bottom, air is drawn in at the top. After drawing a liter of gas through the system and displacing all air by nitrogen the gasometer should be filled again and the operation repeated. The gas now entering the gasometer is pure nitrogen and the vessel may be completely filled.

A filter-pump having a long rubber tube attached to its

exit tube may also advantageously be used to fill the gasometer with nitrogen. A current of air is drawn through the apparatus by means of the pump and the gas mixed with water is allowed to flow into the opening at the base of the gasometer. The air current should be maintained for several minutes before the gas is finally collected.

By observing the color of the copper spiral the operation can be well regulated. As there should always be an excess of ammonia gas in the air, all the spiral but the front end should be in the reduced state. As soon as it begins to oxidize for any distance it is an indication that the supply of ammonia is becoming exhausted and the bottle containing the ammonium hydroxide must either be warmed by immersion in a crystallizing dish of hot water or the air current must be stopped and the ammonium hydroxide renewed. A few preliminary trials should be made. No difficulty will be experienced in preparing from fifteen to twenty liters of nitrogen with the amount of ammonium hydroxide used. If the sulphuric acid turns blue a fresh supply of acid must be added.

The gas is purified by passing it from the gasometer through any of the purifying systems, though sulphuric acid should be used as a drying agent to remove the last traces of ammonia gas.

Warren[1] and Kassner[2] vaporize volatile liquids from small capillary bulbs in an arm of the combustion tube extending outside the furnace and slanting upward.

Low boiling liquids may be sealed in small bulbs with capillary openings, introduced into the combustion furnace, and there vaporized.

A small bulb holding from three- to four-tenths of a cubic centimeter is blown on the end of a tube which has been drawn out to a capillary (Fig. 14) and the

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[1] Am. J. Sci., 2nd series, **38**, 387.

[2] Ztschr. anal. Chem., **26**, 585.

bulb tube weighed.   By warming the bulb to expel
the air, dipping the end of the capillary in the liquid
and cooling the bulb, sufficient liquid may be drawn
up to fill it nearly.   After driving all liquid out of the
capillary the bulb is finally sealed.   Just before intro-
ducing the bulb into the combustion tube a file scratch
is made a few millimeters from the end of the capil-
lary, and, holding the tube by the capillary rather than
by the bulb, the tip is broken off.   The bulb is laid
in a boat with the open end pointing towards the exit
end of the combustion tube and the boat instantly
thrust into the tube.   The relative size of bulb and
boat should be previously determined to see if the two
can be inserted in the tube.   Also provision should
be made to prevent the bulb from sliding back, there-
by lowering the capillary tube.   The criticism has
been made that a certain residuum of gas remains un-
oxidized in the bulb, but nevertheless this method is,
and has been, almost universally used for liquids of
low boiling-point.

A longer capillary,[1] with or without a bulb,[2] facilitates in
the slow evaporation of liquids if the heat is inadvertently
carried above the boiling-point.

Hempel[3] seals the end of the long capillary with a fusible
alloy of Wood's metal ten parts and mercury two to three
parts which, on solidifying, does not expand and break the
glass.   By gentle heat the metal is melted and the capillary
is opened.

[1] Kopfer (Ztschr. anal. Chem., **17**, 15) used a capillary six centimeters
long.

[2] Zulkowsky (Monatshefte, **6**, 450) used a two millimeter tube thirteen
centimeters long.

[3] Ztschr. anal. Chem., **17**, 414.

COMBUSTION OF EXPLOSIVE BODIES

Compounds, such as diazo and nitro bodies, that explode on heating must be mixed or diluted with some inert material such as powdered lead chromate, cupric oxide, or quartz.

Fine cupric oxide[1] is mixed with the material which is best placed in a long copper boat. At times the mixture is separated by dams of pure cupric oxide to isolate small portions.[2]

Picric acid and picramid and allied bodies are easily burned when mixed with three or four volumes of finely powdered quartz.[3]

For the combustion of the more explosive compounds such as nitroglycerine, etc., recourse must be had to one of the special methods ; for instance, that of Hempel,[4] of burning in a vacuum.

CALCULATION OF RESULTS

As three-elevenths of the carbon dioxide is carbon the per cent. of this element is found by means of the formula :

$$\text{Per cent. carbon} = \frac{\text{wt. carbon dioxide} \times 300}{\text{wt. substance} \times 11}.$$

As one-ninth of the water is hydrogen the per cent. of this element is found by means of the formula:

$$\text{Per cent. hydrogen} = \frac{\text{wt. water} \times 100}{\text{wt. substance} \times 9}.$$

[1] Schwarz: Ber. d. chem. Ges., **13**, 559 ; Janowsky : Monatshefte, **6**, 462 ; *Ibid.*, **9**, 836 ; Eder : Ber. d. chem. Ges., **13**, 172.

[2] Jackson and Lamar (Am. Chem. J., **18**, 676), in burning dinitrophloroglucindiethylester, found this procedure necessary.

[3] Am. Chem. J., **23**, 346.

[4] Ztschr. anal. Chem., **17**, 414.

The logarithmic calculations, using the factors given in the appendix, are as follows:

Log. wt. $H_2O \times 100 =$	·		Log. wt. $CO_2 \times 100 =$	
Log. factor	$= 1.04883$		Log. factor	$= 1.43573$
Colog. wt. subs.	$=$		Colog. wt. subs.	$=$
Log. per cent. H	$=$		Log. per· cent. C	$=$

Where known weights of sucrose, benzoic acid, or naphthalene are used in the tube to effect reduction, the resulting carbon dioxide and water must be deducted from the weights found before making the final calculations (see p. 60).

APPENDIX

ATOMIC WEIGHTS[1]

Carbon	12.001
Hydrogen	1.0075
Oxygen (standard)	16.000
Nitrogen	14.045
Chlorine	35.455
Bromine	79.955
Iodine	126.85
Sulphur	32.065

LOGARITHMIC FACTORS[2]

Carbon in carbon dioxide	1.43573
Hydrogen in water	1.04883

One gram of sucrose, $C_{12}H_{22}O_{11}$, yields:

    0.5791 gram H_2O.   log. factor = 9.76272−10.

    1.5430 grams CO_2.   log. factor = 0.18836.

One gram of benzoic acid, C_6H_5COOH, yields:

    0.4428 gram H_2O.   log. factor = 9.64622−10.

    2.5235 grams CO_2.   log. factor = 0.40201.

One gram of naphthalene, $C_{10}H_8$, yields:

    0.5627 gram H_2O.   log. factor = 9.75025−10.

    3.4357 grams CO_2.   log. factor = 0.53602.

[1] Compiled by T. W. Richards in the Proceedings of the American Academy of Arts and Sciences, April, 1899.

[2] Atomic weights given above are here used.

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