

UNITED STATES DEPARTMENT OF THE INTERIOR

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SAMPLING MINE GASES
AND USE OF THE BUREAU OF MINES
PORTABLE ORSAT APPARATUS
IN THEIR ANALYSIS

REVISED JUNE 1936

By

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UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1936

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SAMPLING MINE GASES AND USE OF THE BUREAU OF MINES PORTABLE ORSAT APPARATUS IN THEIR ANALYSIS¹

By W. P. YANT and L. B. BERGER

INTRODUCTION

Since 1911 the Bureau of Mines has given instruction in first aid and in the use of rescue apparatus, but this training does not include instruction in recovery operations after mine disasters. To supply this the Bureau initiated a course of instruction in advanced training in mine rescue and recovery operations.

This publication is a revision of "Advanced Mine Rescue Training. Part II. Instructions in Methods of Sampling and in the Use of the Bureau of Mines Portable Orsat Apparatus for Analyzing Mine Gases," and proposes to present the second of a series of four miners' circulars to be used in a course of training which will prepare mine officials to organize men for mine rescue and recovery operations. This part describes Bureau of Mines methods of sampling mine gases and use of the portable Orsat apparatus for analyzing mine gases and gives instruction in its manipulation. The first of this series of circulars deals with mine gases and the various methods of detecting them; the third tells of the means of protection against gases encountered in mines; and the fourth explains the procedure in sealing and unsealing mine fires and in recovery operations.

ACKNOWLEDGMENTS

The writers are indebted to the Bureau's field engineers for making suggestions and for reviewing these instructions.

IMPORTANCE OF SAMPLING AND ANALYZING MINE ATMOSPHERES

The close relation between the composition of air and problems of health and safety in mines, tunnels, and similar confined places where explosive or poisonous gases may be present makes the sampling and analysis of gases an important part of safety work in these localities. This statement applies to means for averting accidents by

¹ Work on manuscript completed October 1928; printed 1929. Revised and reprinted 1936.

detecting the occurrence of dangerous gases and assuring adequate ventilation and for ascertaining the composition of atmospheres as a basis for planning safe procedures when conditions are dangerous, as when extinguishing mine fires by sealing and when conducting rescue and recovery work following explosions. Although approved portable detecting devices, such as the flame safety lamp, methane detectors, and carbon monoxide detectors, are widely used for examining mine atmospheres, all have a definite lower and upper limit to their range of detection. Moreover, they are designed primarily for the detection of a single gas constituent, whereas in many cases a complete analysis or determination of all the constituents of the atmosphere is necessary.

Where the information desired is outside the scope of portable detecting apparatus samples of the atmosphere are collected and later subjected to chemical analysis, usually by gas-volumetric methods. The apparatus for conducting such analyses may be of a portable type which can be taken to a place near the site of collection of the samples; or, if analyzing apparatus is not available, it is usually possible² to collect the samples in bottles or tubes that can be tightly sealed and then shipped to a laboratory for analysis. The bureau maintains a laboratory at its Pittsburgh Experiment Station for analyzing samples collected and submitted by its field engineers. Also, in emergencies where there is mutual interest, this service is extended to the State departments of mines, mine operators, and others.

ACCURATE ANALYSES VERSUS APPROXIMATE ANALYSES AND QUICK RESULTS

When a high degree of accuracy is desired and there is no immediate need of results the sample should be sent to a well-equipped laboratory where the conditions under which the analytical apparatus is used permit more refinement in design and consequently greater accuracy than can be conveniently embodied in a portable apparatus. However, when moderate accuracy is satisfactory and compatible with the problem at hand the use of portable apparatus is advised, as it not only avoids delay in obtaining results but also avoids the loss of samples or contamination by leakage before analysis is made. A central laboratory often has a large number of samples on hand awaiting analysis, and delays are unavoidable.

² Frequently the gas laboratory of the Pittsburgh Experiment Station receives samples in the ordinary vacuum-tube containers with the request that they be analyzed for sulphur dioxide, hydrogen sulphide, or oxides of nitrogen. With the low concentrations of these gases usually found it is not possible to make a satisfactory determination with the sample of ordinary size. Also, these gases react with dirt, moisture, etc., in the container or decompose so that by the time the sample is analyzed they have disappeared from the gas mixture. These determinations should be made in the field by direct sampling into an absorbing reagent.

The need of immediate results is very obvious in mine fires or in recovery work after explosions when the results of analysis must be known within a day or even an hour after the sample is collected, as the next move may depend entirely on the composition of the air. This need for immediate results therefore necessitates the use of a portable type of gas-analysis apparatus that can be transported to the scene of the investigation; this in turn creates the need for personnel familiar with the technique involved in collecting and analyzing mine atmospheres. The following instructions have been prepared with this in view.

The type of apparatus to which these instructions particularly apply is a portable Orsat modified to suit the needs of field use. It is not designed for the precise analysis of mine air, such as is required for most ventilation studies, but is only intended for the analysis of the samples usually taken in emergency cases (fires and recovery work) as a guide to safe and effective procedure. It can, however, be used satisfactorily to check the occurrence of methane in headings and rooms, to determine oxygen depletion and black damp, and for other uses described later. It is not accurate enough for the analysis of return air of coal mines to ascertain the quantity of methane or to determine the presence of carbon monoxide from the standpoint of health or the extinguishing of mine fires.

The apparatus and its operation are described in detail, much of which may seem unimportant to persons acquainted with the technique of gas analysis. However, it has been primarily prepared to instruct engineers, chemists, and mining men who are unacquainted with the technique and who infrequently have occasion to make analyses. On this basis the detail is thought justified. Also, the authors believed that rather than list a number of procedures specific to each of the wide variety of samples for which the apparatus might be used confusion would be avoided by giving a general procedure that would take care of the majority of cases and difficulties presented in the field. For some samples the operations and precautions as given in the general procedure could be omitted without affecting the results, and as the persons making analyses become more familiar with the technique of gas analysis the omissions and short cuts will become apparent.

Although the chemistry and procedure involved in gas analysis are simple, practice and experience are required to attain a technique that will give satisfactory results and avoid some of the difficulties encountered, especially when dealing with a wide variety of samples. In view of this it is not merely necessary for beginners to read these instructions; they are also advised to obtain an apparatus and actually carry out the various operations while reading the text.

SAMPLING MINE GASES

The field investigator may be the collector of the samples as well as the analyst; therefore, a section of these instructions has been devoted to a description of suitable procedure for taking samples. In describing these it will not be possible to consider all of the varied situations that might arise, but the suggestions and information given may be helpful to engineers and chemists who are inexperienced in mine-gas work.

In determining the composition of mine gases by analysis the collection of a representative sample and the preservation of that sample until it can be analyzed are the most important and most difficult parts of the procedure. Analytical work has been standardized for the most part, and it is fairly well known that by following a certain sequence of manipulations and measurements carefully and precisely a result within certain limits of error will be obtained. On the other hand, the collection of the samples requires planning and ingenuity, in many cases, to insure their being representative of conditions. Improper and nonrepresentative sampling gives erroneous or irrelevant results. Erroneous results lead to incorrect interpretations or conclusions that may cause either a false sense of security or undue anxiety, and they may be used as a basis for unsafe or unnecessary recommendations.

Many suggestions for sampling have been devised, and some of those which have been found most practical and efficient by the bureau have been described in a previous publication³ dealing with the analysis of mine gases.

However, it was not possible to give in Bulletin 197 many of the apparently minor but essential details which have been found by experience to be necessary in collecting samples. In view of this the following instructions, which deal almost entirely with a specific field of work, have been prepared to supplement the information given in that bulletin.

TYPES OF GAS SAMPLES

Gas samples may be divided into two general classes, which characterize the rate at which the samples are taken. These classes are termed "grab" (sometimes called "spot," "snap," or "instantaneous") samples and "continuous" samples.

Grab samples are taken over a short duration of time, say, a few seconds to a minute or two, and represent the gas at some particular place and instant. These constitute the large majority of samples taken in mines.

³ Burrell, G. A., and Seibert, F. M., *The Sampling and Examination of Mine Gases and Natural Gas*: Bull. 197, Bureau of Mines, revised in 1926 by G. W. Jones, 108 pp.

Continuous samples are collected over a period of longer duration than grab samples and are usually taken where the stream of gas to be sampled is of varying composition; that is, homogeneous at a particular instant and varying throughout a comparatively long period, but not varying as regards stratification in a cross section. A sample taken continuously throughout the period will give the average composition. There is seldom occasion for taking continuous samples in mines, even when information regarding the average condition is desired; a number of grab samples taken at predetermined intervals will generally be more informative than one continuous sample. The principle of slow sampling in taking continuous samples, however, may be applied to the collection of gas from feeders or other similar places where the supply of gas is not large enough to fill the container instantaneously.

A grab sample may be taken from one point in a cross section of the mine, or the opening to the container may be moved during the sampling so that gas from several points may enter and thus form a composite sample representing the cross section. It is often thought that the latter method may be used to obtain an average sample from a stratified atmosphere. If the air is moving and only slight stratification is anticipated, it is good practice to move the opening of the tube vertically across the place of sampling when the gas is entering the tube. In still air, however, where marked stratification may occur, it is not possible to obtain an average sample by this method unless special facilities are used to control the rate of movement of the opening and the rate of entrance of the gas. The use of such facilities is not ordinarily practicable for routine sampling in mines; also, a number of grab samples taken from various points in the cross section will give more information.

SAMPLING EQUIPMENT

TYPES OF SAMPLE CONTAINERS

The Bureau of Mines recommends the use of the vacuum-tube type of sample container shown in Figure 1 for all samples of mine air taken for shipment to its gas laboratory at the Pittsburgh Experiment Station. This type of container has been found most suitable for effective sealing by field men, durability for shipping, and preserving the samples where considerable delay may occur between the sampling and the analysis, as in shipment to a distant laboratory.

In field work where analyses are made within a relatively short period after sampling and it is not necessary to make shipment other types of containers can be used. They are often more available than vacuum tubes, are refillable, and may be used many times, which makes their use less expensive than vacuum tubes unless a laboratory

or glass-blowing shop equipped to make, repair, and reevacuate the latter is available.

VACUUM TUBES

The vacuum-tube gas-sample containers shown in Figure 1 and used by the bureau for sampling mine gases are glass bulbs from which

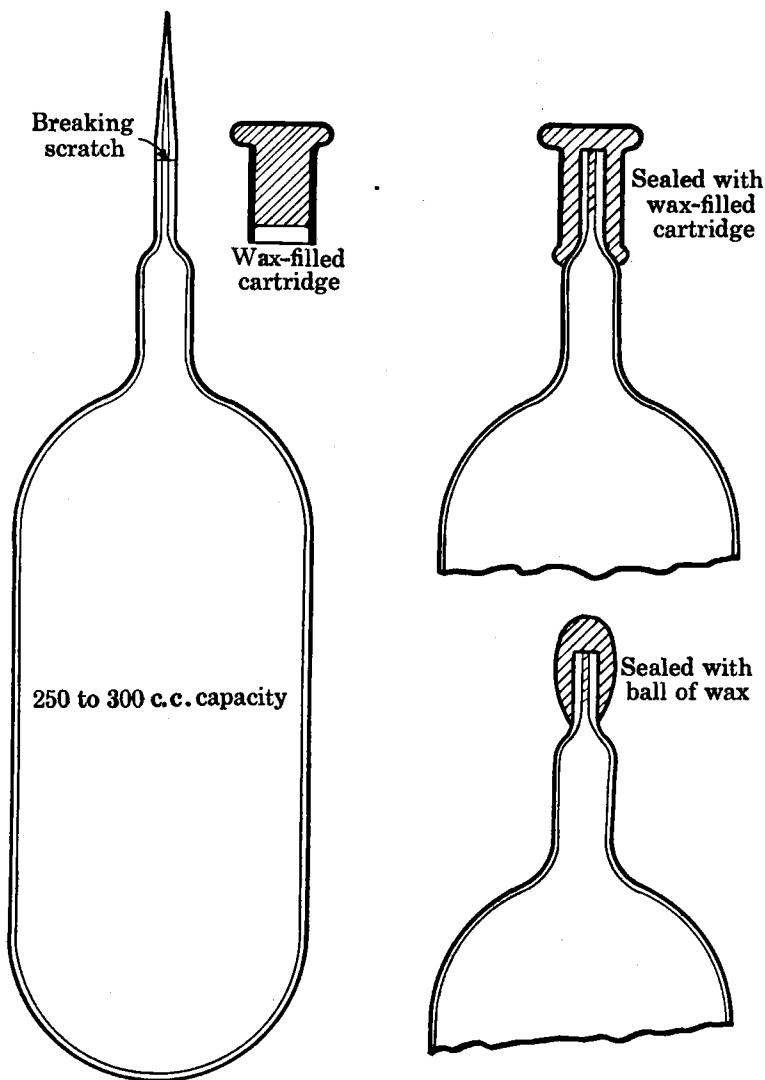


FIGURE 1.—Vacuum-tube gas-sample container

99.97 per cent or more of the air has been removed by a vacuum pump and the necks of which have been hermetically sealed by heating and drawing during the final stage of evacuation. This results in an inclosed space which has practically no internal pressure but which

at ordinary altitudes has an atmospheric pressure of 13 or 14 pounds per square inch on the outside of the bulb. The tube remains in this condition until the seal is broken, when the air rushes in and fills the internal space to a pressure equal to that outside. It is then sealed with wax and shipped to the laboratory for analysis. The size used for ordinary mine-gas investigations has a capacity of approximately 250 c. c. However, in special investigative work when larger samples are required a tube with a capacity of 1,000 c.c. is used.

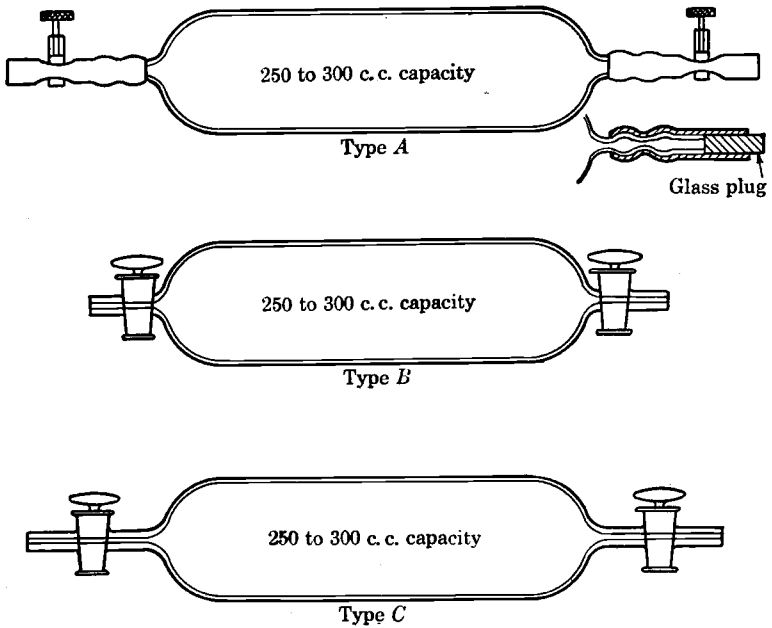


FIGURE 2.—Gas-sample containers, gas or liquid displacement type

GAS OR LIQUID DISPLACEMENT CONTAINERS

Containers filled by gas or liquid displacement include the forms supplied by laboratory-supply houses, as shown in Figure 2, and ordinary bottles, preferably the kind used in drug stores for magnesium citrate.

Figure 2, *A*, shows a glass tube approximately 1½ inches in diameter, with short pieces of glass tubing of small diameter sealed on each end to provide for closing. The closing device is a short piece of heavy-wall rubber tubing and a screw clamp. Pinch clamps are sometimes used instead of screw clamps, but they are not satisfactory.

Short pieces of glass rod or glass plugs may be used and are more satisfactory than either screw clamps or pinch clamps if they form a tight fit with the tubing and are inserted until a glass-to-glass contact is made with the end of the container.

The type *A* container, when fitted with good rubber tubing and properly closed with screw clamps or glass plugs, is satisfactory for

confining samples of mine gases, especially when analysis will be made within a few days. These containers are not as convenient for filling with gas from accessible places or as durable for shipping as vacuum tubes. They are often more convenient, however, for sampling gases in inaccessible places, as behind fire seals, tanks, etc. These tubes may be filled by either gas or liquid displacement, as described later.

The container shown in Figure 2, *B*, is similar to the type *A* container except that the rubber tubing and screw clamp are replaced by a glass stopcock. This container has the same field of use for sampling mine gases as the type *A*. Also, when the stopcocks are well greased there appears to be less danger of leaks during storage. On the other hand, the type *B* container is more expensive and less durable for shipment. Purchasers of this type should insist that the stem between the body of the container and the stopcock be as short as possible, preferably entirely eliminated, and not as shown in Figure 2, *C*. By eliminating this stem and cutting the extension beyond the stopcock to not more than $1\frac{1}{4}$ inches breakage will be markedly reduced.

The ordinary size of types *A* and *B* containers for mine gases is 250 to 300 c. c. capacity. The tubes should be made from heavy-wall glass with 2 to 3 mm. inside diameter and approximately 7 to 8 mm. inside-diameter capillary-tubing stems.

METAL-TYPE GAS-SAMPLE CONTAINERS

Metal containers, similar in other respects to types *A* and *B* glass containers, may be purchased from laboratory-supply houses. However, iron or tinned-iron sample containers are not recommended. The gas laboratory at the Pittsburgh Experiment Station has received samples in tinned-iron containers in which the oxygen had been reduced from 20 to less than 10 per cent, due to rusting of the metal on the inside of the tube. However, copper and zinc tubes are used by a number of laboratories for samples to be analyzed shortly after collection. Metal containers with stopcocks have the disadvantage of being more liable to leakage than the corresponding ones of glass design; however, if they are fitted with good stopcocks properly greased and kept in good condition, they are fairly satisfactory for routine work when the samples are analyzed within a day. If it is necessary to keep them for several days before analysis can be made, the ends may be coated with paraffin, as described later.

Hydrogen sulphide, sulphur dioxide, and oxides of nitrogen react with metal containers and accordingly distort results for these gases. However, no type of container suitable for routine sampling of mine air has been found which is entirely satisfactory for preserving these reactive gases for extended periods. Clean glass containers may be used for short periods, but even then the amount of hydrogen sul-

phide, sulphur dioxide, or oxides of nitrogen ordinarily found in mine air is so small that the 250 to 300 c. c. sample bottle contains insufficient gas for making a satisfactory determination. A method in which the gas is determined at the time of sampling or absorbed in a suitable reagent for later determination is more desirable.

ORDINARY GLASS-BOTTLE SAMPLE CONTAINERS

Bottles used by druggists for magnesium citrate make satisfactory containers. These bottles are closed by a rubber washer under a cap held in place by a strong spring. A supply of extra rubber washers or gaskets should be kept on hand for renewals. Unless the samples are to be analyzed within a day or two the tops of the bottles should be dipped in molten paraffin or sealing wax after collection. This coating should be applied by successive rapid dips and subsequent cooling to produce several thin layers. Thin layers make a more effective seal and avoid undue heating, which would cause the gas to expand and possibly to leak outward; on cooling, the gas would then contract and tend to draw in air.

It may sometimes be necessary to use ordinary bottles with cork or rubber stoppers for taking a gas sample, although this is not recommended. Under such circumstances the end of the stopper should be cut off a little below the top of the neck and the recess filled with sealing wax or paraffin, as described above.

ASPIRATING DEVICES

When filling containers in accessible places by gas displacement and when taking samples through tubes leading into inaccessible places an aspirating device may be needed to purge or sweep the original air or gas content from the tubing and to create a stream of gas through the container. This procedure is obviously unnecessary when gas is being sampled from behind seals that are under enough positive pressure to cause a flow of gas through the tubing and the container. Many convenient devices, such as motor-driven air pumps and steam injectors, are used for aspirating gases, but the most convenient for underground use is a double-acting rubber-bulb aspirator, a double-acting foot pump, or aspirator bottles.

RUBBER-BULB ASPIRATORS

Rubber-bulb aspirators of the type shown in Figure 3 may be obtained from apparatus-supply houses and may be used for either suction or pressure. As a rule, the aspirator is connected with the valves so that the pressure and relief on the bulb will draw the air out of the container and admit the gas as shown in Figures 5 and 6, *A*, although in some cases it is used to force the gas into the container as shown in Figure 7, *C* and *D*. Fifty compressions of an ordinary 40 to 60 c. c. capacity bulb will replace the air in a 250 c. c.

sample container. A factor of safety is provided, because the bulbs become less efficient with use. Their usefulness can be fairly well determined, however, by compressing the bulb, closing the intake end, and noting whether there is any leakage, and then by repeating the process endeavoring to compress the bulb with the outflow end

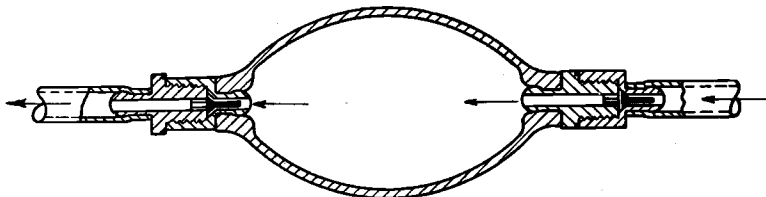


FIGURE 3.—Rubber-bulb hand aspirator

closed. A little dust sometimes lodges on the valve seats, causing them to leak. A seemingly defective bulb is often remedied by the removal of such dust and by wetting the valve seats with water. An added precaution during sampling is to connect a hose to the outflow end and place the exit under a water seal or water trap of 1 or 2 inches. This prevents air contamination through leaky valves.

FOOT PUMPS

Where it is necessary to purge long tubes leading to inaccessible places, as through seals and bulkheads, the use of a rubber-bulb aspirator may be laborious if the dead space is rather large. Then a double-acting foot pump (also procurable from laboratory supply houses) may be used. The principle and use of this device are identical with that of the rubber-bulb aspirator, although it is not

thought to be as free from sources of air contamination when the sample container is on the discharge outlet, as in Figure 7, *C* and *D*, page 21. When this is necessary it is good practice to use the pump to purge the connections and a rubber bulb for filling the container.

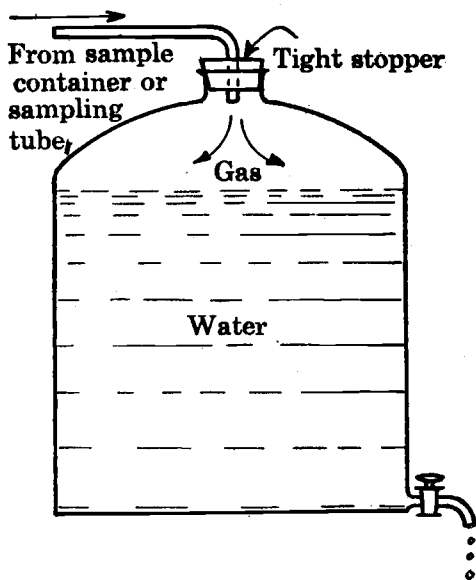


FIGURE 4.—Aspirator bottle or can

ASPIRATOR BOTTLES

If a foot pump is not available, the gas may be aspirated by means of a bottle or can filled with water, as shown in Figure 4. As the

water escapes from the can gas is drawn through the tube to replace the water. The size of the can is determined by the volume of gas necessary to purge the tube and sample container. The can may, of course, be refilled several times during the sampling, the only precaution necessary being that of closing the connection between the container and the can during the filling process.

FILLING SAMPLE CONTAINERS

Filling a sample container with gas is merely replacement of the original content of the container with the gas to be sampled, and the most satisfactory method for accomplishing this is one that will insure complete replacement and not change the composition of the sample. The latter has particular reference to the partial solubility of some of the constituents in liquids and consequently their loss to the sample.

The methods for filling sample containers in accordance with the medium displaced in each case are (1) vacuum displacement, (2) air or gas displacement, and (3) liquid displacement.

Vacuum displacement is the principle employed in vacuum tubes, in which the tube from which the original gas content has been previously removed is allowed to fill with the gas desired for analysis.

Air or gas displacement is the method in which the original gas content is swept out by causing a stream of the gas to be sampled to flow through the container.

Liquid displacement refers to replacement of the original gas or air in the container with a liquid, such as water, salt solution, or mercury, and later replacement of the liquid with the gas to be sampled. This method obviates the necessity of sweeping large volumes of gas through the container and often avoids the need of an aspirator to produce a stream of gas.

SAMPLING IN ACCESSIBLE PLACES

APPRECIABLE AIR MOVEMENT

Moving air in main air courses, splits, etc., is usually well mixed, and a sample of average composition can be obtained without special precaution in selecting the sampling point. However, in all cases the air should have traveled under conditions favorable for mixing since it passed the last point or source of significant contamination with gas of markedly different composition (as a large feeder), gas from abandoned or poorly ventilated sections, the junction of two splits of different composition, etc. Such sources of gas cause streaming currents of varying composition which may persist for a considerable distance. Turns and irregularities in airways cause turbulence, which obviously aids mixing and decreases the distance that streaming will persist.

In sampling air where there is appreciable movement, select a rather straight section of the air course and stand facing the air current with the tube at arm's length. Avoid exhaling breath into the zone to be sampled. Open the sample container and allow it to fill rapidly. As a precaution against possible stratification, the tip or incoming opening to the container may be rapidly moved in a plane at right angles to the current and gas thus obtained from several points in the cross section. If the time of sampling is short, as when using vacuum tubes, the inlet to the container may merely be passed in a vertical line across the current.

SLOWLY MOVING OR STILL AIR

The composition of still air or slowly moving air that has had no opportunity to mix may vary widely in vertical cross section at a particular place. In still air methane almost invariably accumulates near the roof of the place where it is being emitted. In relatively still air methane will also flow along the roof to places of higher elevation and fill recesses and potholes in the roof. If issuing in dead ends of rise workings, it will fill the entries and workings in a manner almost exactly opposite to that in which water fills dips, and with a difference of only 1 foot in elevation a sample of gas may vary in composition from a low percentage of methane and almost normal oxygen content to as much as 50 to 75 per cent of methane and a marked deficiency of oxygen.

On several occasions the gas laboratory of the bureau received samples of mine atmospheres that the collector stated indicated less than 2 per cent of methane when tested with a flame safety lamp, whereas the samples actually contained an explosive mixture (5 to 15 per cent) to as high as 65 per cent of methane. In all probability the discrepancy was due to the fact that the point of sampling and the point of making the lamp test were not identical, because samples may be collected several inches nearer the roof than it is possible to test with a flame safety lamp.

When the air is still, however, black damp or atmospheres depleted of oxygen by oxidation unlike methane and like water generally collect at the bottom of the workings. They also flow along the bottom to places of lower elevation. Places have been observed where enough oxygen was present to sustain life when the air 3 or 4 feet from the bottom was breathed, but if men sat down or fell down so that their heads were below that level they very quickly became unconscious from lack of oxygen, much the same as if falling into water.

SAMPLING PRODUCTS OF COMBUSTION OF EXPLOSIVES

The procedure for sampling mine air to determine slight degrees of contamination by gaseous products of the combustion of explosives

is the same as that for sampling moving air. However, when taking samples of these gases near the place of blasting and when there has not been enough time or cause for mixing the atmosphere may be markedly stratified or heterogeneous, and a representative or average sample will be difficult to obtain. The method of dividing a cross section into imaginary rectangles, described under Procedure for Collecting Gas Samples, is not adequate, because the contaminating gas may be in pockets and may be stratified in a given section; the former is especially true if there are a number of intermittent shots. A detailed description of procedures for obtaining average samples under such circumstances has been described recently in Bureau of Mines Bulletin 287.⁴

PROCEDURES FOR COLLECTING GAS SAMPLES

If the composition at localized places is desired, as is usually the case in sampling still or slowly moving air in mines, the procedure consists merely of holding the tip of the container at the desired place while filling. Care should be taken to avoid disturbance of the air and contamination during both sampling and sealing.

If an average analysis of an atmosphere that is not of uniform composition and is practically still air is desired, it is advisable to take several samples from a cross section. In doing this, divide the cross section as nearly as can be judged by the eye into equal rectangles, one of which represents each of the anticipated zones of variable composition, and take a sample of gas in the center of each. Usually four samples are enough to give an average of the conditions. In collecting these samples, take care to avoid contamination by the breath and to avoid undue disturbance of the air.

In collecting samples from blowers and feeders, from leaks in plugged and sealed gas wells, and from similar places where gas issues, a satisfactory procedure for obtaining a sample of highly concentrated gas (diluted as little as possible with air) is to place a tin or glass funnel, tin can, bucket, or small keg, with the bottom removed, over the place of emission and provide for collecting the gas from a hole in the top. The receptacle may be sealed with mud around the bottom. Before sampling, it should be purged by allowing concentrated gas to flow in and remove the original air. The time necessary for this operation can be judged from the rate of flow of gas and the size of the receptacle. The sample may be taken by any of the methods previously described. Where the flow of gas and the receptacle are small a type of container that can be slowly filled as gas is emitted should be used.

Sometimes, however, the volume of gas liberated from blowers, crevices, etc., is large enough or enough gas is already at hand to per-

⁴ Gardner, E. D., Howell, S. P., and Jones, G. W., Gases from Blasting Tunnels and Metal-Mine Drifts: Bull. 287, Bureau of Mines, 1927, 96 pp.

mit direct sampling—that is, without the use of a funnel or collecting device—by merely holding the tip in the stream and breaking it according to the manner described later for filling vacuum containers.

FILLING VACUUM TUBES

In taking samples where there is an appreciable air movement, stand facing the air and hold the bulb at arm's length (avoiding contamination of the sampling zone by the collector's breath) as near as possible to the point to be sampled. Break off the end of the capillary tube at the file mark or scratch. This may be done by holding the shoulder of the tube firmly in one hand and with the other attempting to bend the capillary tube at the mark. As the fractured edges are often sharp it is well to use a glove, piece of cloth, or handkerchief for protection of the thumb and fingers used to grip and bend the tip. A suitable breaking device is a $\frac{1}{4}$ by 3 inch pipe nipple or a small piece of hardwood with a hole slightly larger than the capillary neck, bored in the end. Insert the neck nearly to the scratch and press downward or attempt to bend the tube; this will break the neck. Common pliers, the head of a cabinet-lock key, or similar devices may be used. Do not strike the tube against the roof, ribs, or timbering or with any object, as this is unnecessary and frequently breaks the tube at other than the desired place, making it difficult to seal the tube if not entirely spoiling it. If the scratch mark does not appear on the neck, a suitable mark may be made with a common file.

When the end is broken a hissing noise will be heard as the air rushes in. Often a grain of glass will lodge in the capillary opening and may slow down the entrance of gas and consequently the time of collection to such an extent that the collector will unknowingly seal the container before it has been filled with gas. The end should always be watched for such stoppages, the tip being kept in the zone of air being sampled, and any obstruction should be removed. Observation should be made to ascertain whether breaking the tip has severed the capillary opening. The bureau's gas laboratory has received vacuum tubes which the collector thought were filled with gas but which really contained their original vacuum.

SEALING VACUUM TUBES

After breaking the tip, hold the sample container in the place of sampling for about five seconds after the hissing noise has stopped, then remove the tube and seal it by filling the neck with the special sealing wax furnished with the bottles. The preparation of this wax is described in Bureau of Mines Bulletin 197 already cited. Do not use chewing gum, paraffins, or tar, as they do not adhere tightly to the glass. The wax is usually supplied in the form of wax-filled

metallic cartridges. The vacuum tube should be sealed by working the cap over the end of the tube with a twisting motion so that the wax is forced into the capillary opening but not so that it enters the sample container. It is important not to force the wax into the container. Finally, force the cap on as tightly as possible and make a tight joint between the cartridge and the shoulder of the tube by smoothing the wax that exuded from the cartridge. (See fig. 1.) If a small piece of wax has been used instead of a wax-filled cartridge, work it well into the capillary tube and finish the sealing by modeling a small egg-shaped lump over the tip; cover it with a small piece of thin paper to keep it from adhering to other objects, such as packing in the shipping cases.

Do not melt or heat the wax, because combustible vapors will be formed and spoil the sample.

**FILLING OPEN-END
TUBES AND ORDINARY
BOTTLES BY
GAS DISPLACEMENT**

Where large amounts of gas and aspirating facilities are available the containers shown in Figure 2 and ordinary bottles are filled by gas displacement.

Figure 5 suggests how the containers may be filled. In each instance the gas is removed from the container, thus allowing it to fill with the desired atmosphere. In sampling stratified atmospheres it is good practice to discharge the exit gas at a level below that of the container for methane and at a level above for black damp. About 10 times the volume of the sample container should be passed through for taking a satisfactory sample. On that basis it will require 50 squeezes of the ordinary 50 c. c. displacement bulb to take a 250 c. c. sample.

After the required amount of air has been passed through, the tube is held in the sampling position until the bulb arrangement is removed and the container closed.

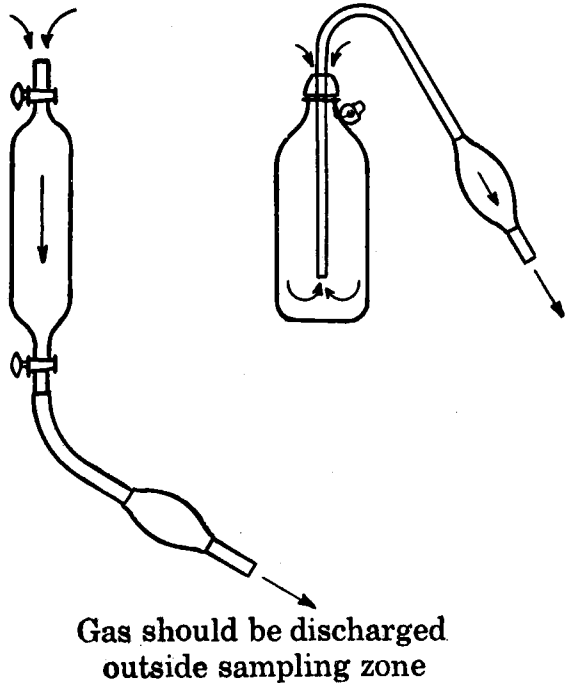


FIGURE 5.—Suggestions for filling container from accessible places by gas displacement

FILLING BY LIQUID DISPLACEMENT

Containers of the types shown in Figure 2 and ordinary bottles can be filled by liquid displacement. Salt solutions, water saturated with the gas to be sampled, and mercury are sometimes used instead of ordinary water with this method to obviate solubility errors when gases containing large amounts of carbon dioxide and other constituents that are appreciably soluble in water are sampled. However, from a practical standpoint this precaution is not necessary for ordinary samples of mine gases. Oxygen, carbon monoxide, hydrogen, methane, and nitrogen are not soluble enough in water to cause appreciable error. Carbon dioxide is more soluble, and where the amount of that constituent is of unusual importance ordinary water can not be used; in these cases, mercury, salt solutions, or water saturated with the gas to be sampled should be used for the liquid-displacement method.

Briefly, water may be satisfactorily used for taking samples of ordinary mine air to determine the oxygen, methane, hydrogen, carbon monoxide, and nitrogen content. The results for carbon dioxide will be slightly low but will not ordinarily vitiate the interpretation of the results as a whole, in relation to mine-fire and explosion hazards.

The only advantage of the water-displacement method for filling containers in accessible places is convenience and time for filling.

The method for filling containers in accessible places by water displacement consists of filling them with water, taking them to the place of sampling, draining or pouring out the water, and closing. The container is held in the zone of the gas to be sampled. Facing the current, holding the container at arm's length, and other precautions previously given for filling vacuum tubes obviously apply to sampling by water displacement.

SAMPLING FROM INACCESSIBLE PLACES

In mines the only inaccessible places usually sampled are behind fire or gas seals. The place of sampling and mode of collection depend on the particular place and facilities for sampling and the ingenuity of the collector.

CHOICE OF PLACE OF SAMPLING

There is not much choice in the place of sampling in mine fires which have only one or two seals. However, if there are more than this number of seals, the choice of the place of sampling is usually a significant factor in obtaining samples that are most representative of the conditions around the fire. The most important items to be considered in this connection are (1) distance of place of sampling from fire and probable course of gases coming from the fire; (2) changes in

barometric or fan pressures that would affect the extent or direction of air change in the sealed area; (3) occurrence of water seals or falls or previously constructed temporary seals that would isolate the place of sampling from the fire area; and (4) position of sampling in the seal, mainly with respect to elevation. These items are considered in more detail under their respective headings.

PLACE OF SAMPLING WITH RESPECT TO FIRE

Samples should be obtained from the seal nearest the supposed course of the gases coming from the fire. This is not always, however, the seal nearest the fire. It is governed more by the position of the seal with respect to differences in ventilation pressures that might cause a slow but gradual air change over the fire, the direction being in general from the place of higher to that of lower pressure. This is a very important consideration in choosing the place or places for sampling.

CHANGES IN BAROMETRIC OR FAN PRESSURES

When the place of sampling has been selected its suitability should be observed each time thereafter that a sample is collected. Frequently a seal breathes; that is, it exhales or gives off gas part of the time and inhales or takes in air at other times. A sample collected when the seal is taking in air is worthless, because the air immediately behind the seal will be contaminated to an unknown degree with normal mine air. In these instances other seals (if present) should be examined as a change in pressures may have occurred that would cause others to be exhaling at this time. If all seals are taking in air, due possibly to increased barometric pressure, cooling of the area, or both, the sampling should be postponed until the conditions are more favorable for obtaining a representative sample. If these observations regarding the seal are not made, erratic results are often obtained which may lead to wrong conclusions or be inexplicable and cause undue anxiety. The pressure conditions on the seal are sometimes difficult to ascertain. A U gage filled with water will indicate appreciable pressure differences. In lieu of this, a film of water or saliva may be placed over the end of the outlet tube and observed for the direction of breaking or bulging of the film. Another method is to sift a little fine dust across the opening in the seal and by use of a flash light or electric cap lamp observe the motion, if any, in the suspended dust.

OCCURRENCE OF WATER SEALS, FALLS, OR PREVIOUSLY CONSTRUCTED TEMPORARY SEALS BETWEEN PLACE OF SAMPLING AND FIRE

Occasionally water seals form in dips, or falls occur after sealing, which isolate the chosen place of sampling from the fire. The possibility of these occurrences should be considered. Frequently one or more temporary seals of wood or canvas are present either imme-

diately inside the permanent seal or a considerable distance in by the latter; these are erected as air checks or temporary seals during fire fighting or preparatory to the erection of permanent seals. Although these canvas and loose (not plastered) board stoppings apparently have no marked effect when the seals are under positive pressure and leaking outward, they confine relatively small bodies of gas that prevent obtaining representative samples. If these temporary seals are within a few feet of the permanent stopping, they may be penetrated after the permanent seal is in place by inserting a $\frac{1}{2}$ to $\frac{3}{4}$ inch pointed copper tube through the sampling hole or section of pipe usually placed in the permanent seal and ramming a hole through the temporary canvas or board stopping. Copper should be used as a precaution against sparks which might be caused by friction between an iron pipe and nails or rock. If time and facilities permit, these temporary seals should be penetrated with a piece of small ($\frac{1}{4}$ to $\frac{1}{2}$ inch) iron pipe before closing up with a permanent seal. This pipe should be extended through the large vent pipe (usually 2-inch size) in the permanent seal and bushed or cemented to make a tight fit.

The length and size of the invisible part of the vent pipe should be known to the collector of samples, as they regulate the time and volume required to purge the pipe before sampling.

POSITION OF SAMPLING POINT IN SEALS

Although there is considerable difference in the density of some of the gases and air (methane, 0.55; carbon dioxide, 1.53; and air, 1), there has seldom been marked stratification behind seals in flat or comparatively flat coal seams that are exhaling gas. If the individual constituents of a gas mixture once become well mixed, they do not later separate but remain in a homogeneous state regardless of differences in density. The gases are usually well mixed, probably by convection currents or changes in pressure causing breathing or movement. The most probable places for stratification would be at seals close to the fire and bordering on rises or dips from the fire, in rise workings in pitching seams where there are strong feeders near the seals, or at leaky seals when there is no positive pressure. Where stratification is suspected it is well to sample the gases at two positions—about one-fourth of the vertical distance from the top and the same distance from the bottom. However, unless conditions are unusual, one place of sampling near the middle of the seal and as far behind the seal as it is convenient to reach with the sampling equipment is satisfactory.

SAMPLING EQUIPMENT FOR INACCESSIBLE PLACES

The same types of sample containers as were previously shown in Figures 1 and 2 can be used for taking samples from inaccessible

places of the nature of sealed territory. Also, if the gas behind the seal is under enough pressure to cause a marked stream to issue from the opening from which the sample is to be taken, the container, if necessary, may be filled directly by some of the methods described for accessible places. When sampling directly the stream of gas must be large and of enough intensity that the inlet to the sample container is enveloped at all times with the gas to be sampled. A very small amount of air, which might enter if the container inlet is moved slightly outside the stream or the stream is momentarily deflected from its course, will vitiate the sample. The direct-sampling method, however, should be used only when the devices, sampling tubes, and aspirating equipment described later are not available.

DIRECT SAMPLING FROM SEALS UNDER POSITIVE PRESSURE

As already stated, samples may be obtained direct from holes in seals if other equipment is not available, provided that the stream of

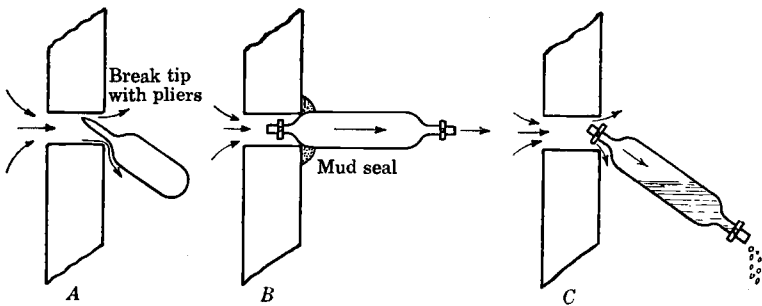


FIGURE 6.—Suggestions for sampling direct from holes in seals

gas issuing is large enough to avoid the possibility of contamination by air and that the procedure is carefully followed. Suggestions for this procedure are given in Figure 6. The method shown in *A* consists merely of inserting the neck of a vacuum tube into the hole or pipe opening and breaking the tip. Long-nose pliers are convenient for the latter. *B* is a gas-displacement method, and the container may be sealed into the hole with mud or other similar means or through a suitable 1-hole rubber stopper. The exit end of the container should be examined for flow of gas, which should be readily perceptible, and the container should be left in place for about five minutes to obtain a satisfactory sample. Method *C* is by ordinary water displacement and, owing to the slow rate at which a sample may be taken, is perhaps the most satisfactory method from the standpoint of avoiding air contamination. This method may be improved by placing a short extension of rubber or glass tubing on the intake end. Care should be taken, however, to purge the extension by having it filled with water before inserting it in the hole.

SAMPLING THROUGH EXTENSION TUBES

Most samples are taken from inaccessible places by means of tubes or extensions leading through the seal to the gas to be sampled. The term "sampling tube" is applied not to the sample container but to an extension leading to the source of supply of the gas. The tube may be any rubber, iron, glass, or copper tubing of small diameter and should extend as far behind the seal as practical because unless the seal is under continuous positive pressure causing it to leak outward the air immediately inside the opening may be contaminated with the outside atmosphere. Also, the annular space between the extension tube and the hole in the seal should be closed tightly to prevent either an ingress of outside air during the purging and sampling or unnecessary contamination of the air outside of the seal with poisonous and flammable gases.

The extension or sampling tubes may be permanent arrangements or merely devices taken by the collector for use at the time of sampling. For temporary use, $\frac{1}{8}$ inch inside diameter, heavy-wall, well-annealed copper tubing is the most satisfactory type, because it is durable, may be coiled for convenience in transportation, and is rigid enough to extend 2 or 3 feet horizontally back of the seal when inserted through the opening. Connections to the sample container and aspirating devices may be made by short pieces of rubber tubing, but care should be taken to see that they fit tightly over the copper tubing.

Copper, iron, or rubber tubing is not suitable for sampling gases containing hydrogen sulphide, sulphur dioxide, or oxides of nitrogen; glass tubing only should be used. Rubber tubing is also very undesirable for sampling gasoline or petroleum vapors, because these vapors readily dissolve in the rubber and will be lost to the sample. Also, in using the same rubber tubing later for sampling gas which contains less or none of these hydrocarbon vapors some of the vapors previously dissolved will be given up to the air passing through the tubing. Copper, iron, or glass should be used for heavy hydrocarbon vapors. Rubber couplings may be used for joining the glass or metal tubes for both the reactive gases or the heavy hydrocarbon vapors if the joints are butted tightly together.

Although it is impossible to describe devices applicable to all of the many variable conditions that are presented in sampling mine gases from inaccessible places, a few general suggestions are shown in Figures 7, 8, and 9. The exact application of these is governed by the facilities at hand and provision for inserting tubes through the seal. Sometimes arrangements for sampling may have been provided in the form of pipes inserted at the time of construction of the seals; then it is only necessary to make suitable connections to the sample container.

FILLING SAMPLE CONTAINERS THROUGH EXTENSION TUBES

The method of filling the container depends on the opening in the seal, the pressure at the seal, and the sampling facilities at hand. If the seal has a vent pipe, the original gases should be removed from this pipe first. When the seal is under appreciable positive pressure this may be accomplished by merely opening the pipe and allowing the gases to flow long enough to remove the original gas. If the pressure is practically zero or not enough to cause a steady flow, the pipe may be purged by any of the aspirating devices previously described, such as a double-action foot pump, aspirator bulb, or aspirator bottle.

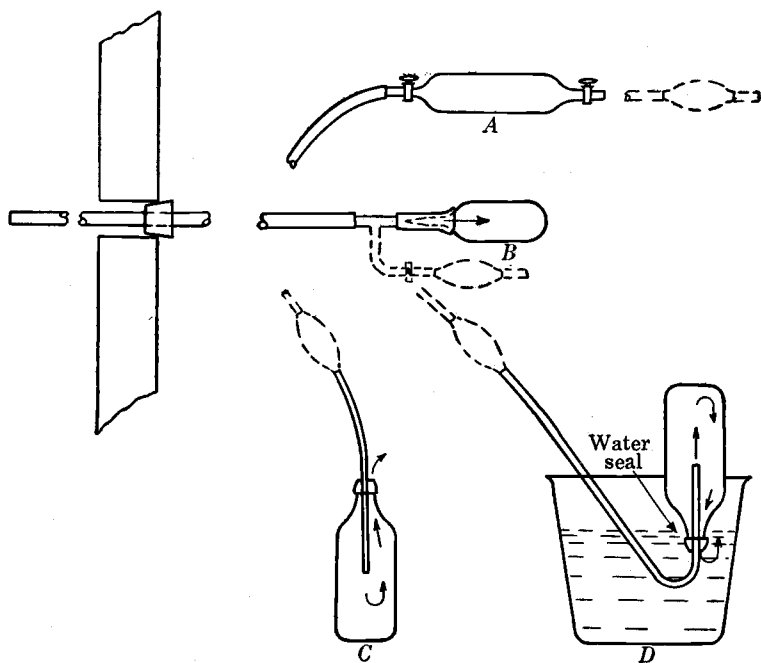


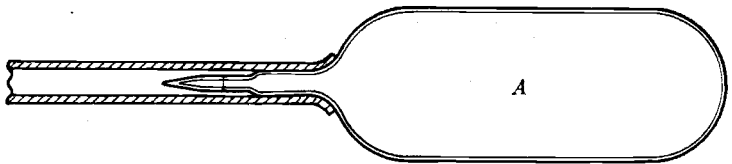
FIGURE 7.—Suggestions for taking samples from inaccessible places by gas displacement. Aspirator bulbs shown in dotted lines are for use when there is insufficient pressure to cause flow of gas

An amount of air estimated to be ten to fifteen times the capacity of the vent pipe should be removed. In this connection it is obvious that the collector should know the size and length of extension tubes. A particular instance is recalled where the collector of samples was unaware that a 20-foot extension of 2-inch pipe had been placed behind the seal and accordingly had been collecting samples after purging what he thought was a 2-foot section.

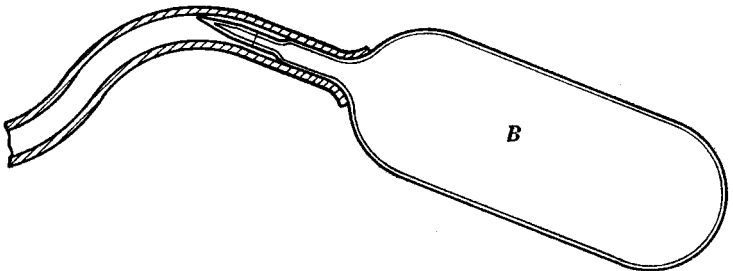
If the seal has a positive inward flow of air, no samples should be collected as they would be worthless except to show that air was entering the zone behind the seal.

After the vent pipe has been purged of its original air the sample containers may be attached to the sampling tube and filled with gas. If the outward pressure is almost imperceptible, it may again be necessary to use an aspirating device to fill some types of containers. (See fig. 7, *A*, *C*, and *D*.)

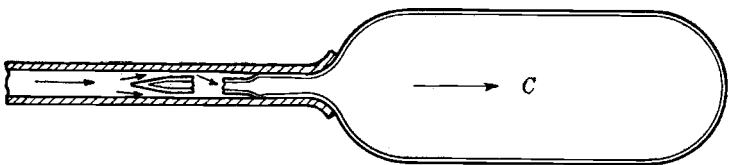
One should always remember that the oxygen content in samples of air from mine fires is of utmost importance, and all sources of contamination from atmospheric air should be excluded. This



After purging hose tightly insert shoulder of container.



Break tip by grasping tip in one hand and container in the other and bend hose.



Allow gas to flow past loosely fitting end of broken tip into container

FIGURE 8.—Method for filling vacuum containers through extension tubes leading to inaccessible places

should be considered by making the very fundamental observation that the seals are not under reduced pressure and drawing air inward and by making tight sampling connections, by purging the sampling tracts, by filling the containers, and finally by sealing these containers so that no contamination will occur between the time of sampling and analysis. To reiterate, there should be full realization of the fact that the samples are collected, preserved, and analyzed in atmospheric air, a medium that contains markedly higher percent-

ages of oxygen than are ordinarily found in gases from sealed areas. For this reason the prevention of contamination by air is not always an easy matter; it has been found to constitute the largest and most general source of error and difficulty in this kind of work.

Vacuum tubes.—In using the vacuum tube for obtaining samples from inaccessible places it may be joined to a sampling-tube extension by a short piece of medium-wall rubber tubing of a size that will fit tightly over the shoulder of the tube but will leave a free space around the capillary neck, as shown in Figures 7 and 8. Insert the tip and shoulder of the vacuum tube into the end (noting the approximate position of the file scratch on the tip) and when tightly in place

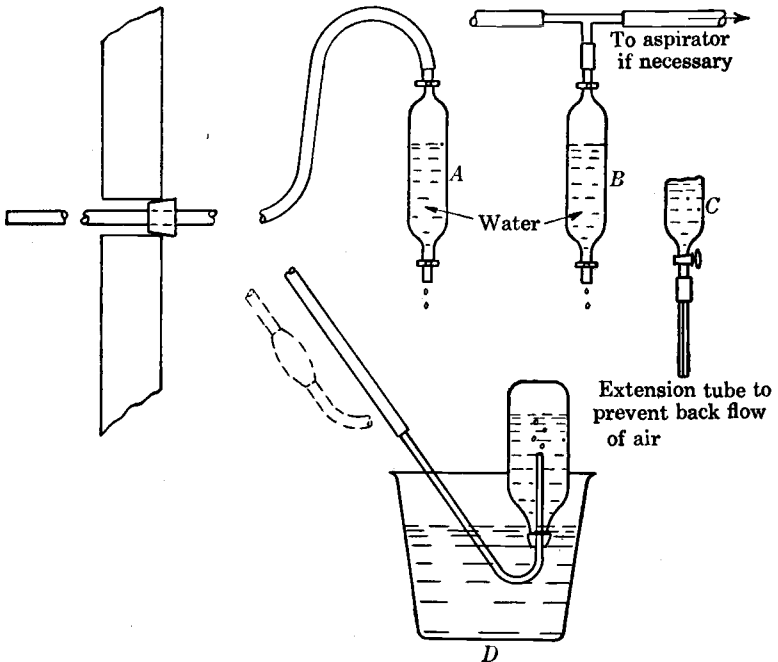


FIGURE 9.—Suggestions for taking samples from inaccessible places by water displacement

purge the entire system by the aid of a foot pump or aspirating device. When the system has been completely purged close the screw clamp between the T connection and aspirator and then by bending the hose break the tip at the mark. The gas will rush past the broken piece of tip and fill the bottle. Before removing the container rub the broken end (by bending the rubber tubing as before) to remove any grains of glass that might have lodged in the capillary opening and might cause impediment to the flow of gas. After waiting about one-half minute remove the tube and quickly seal with wax.

If there is no perceptible flow and a T connection for the aspirator bulb as shown in Figure 7, B, is not available, a straight tube may be

used. The hose connection to receive the sample container is then pinched near the end with the fingers after purging and the sample container carefully inserted, air contamination being avoided by forcing the tip and neck into the opening while the tubing is held pinched together.

Open-end tubes and ordinary bottles; gas displacement.—Open-end tubes and ordinary bottles can be filled by gas displacement by adopting convenient methods from those previously described under sampling from accessible places and by referring to Figure 7 for suggestions. After the sampling tube is purged, the sample container is tightly connected in series and approximately 10 to 15 times the container volume of gas is drawn through the system. If the seal is under distinct pressure, the gas will flow through without the aid of an aspirating device. If there is a distinct flow of gas from the sample container, it should be left in place for about five minutes to obtain a satisfactory sample. If there is only a moderate or just perceptible flow, the time should be extended.

When using aspirating devices the sample containers of the types shown in Figure 2 should be between the sampling tube and aspirator, to avoid contaminating the sample in case air leaks into the aspirator. Making a water seal at the outflow end of the aspirator bulb or pinching off the exit tube with the fingers during the intake stroke of the aspirator is an added precaution.

When the gas-displacement method is used for filling magnesium citrate bottles or other types of bottles with gas from inaccessible places the aspirator must be placed between the container and the sampling tube. If means for a water seal are available the neck of the bottle should be inserted about 1 inch under water and the gas led under the water and into the bottle, as shown in Figure 7, *D*. If a seal is not available, the hose leading into the bottle should be pinched off with the fingers during the intake stroke of the bulb to avoid contamination from leaky valves. Aspirating should be continued while the hose is slowly withdrawn from the bottle and a stream of gas played on the top while closing.

Filling by liquid displacement.—Containers of the types shown in Figure 2 and ordinary bottles can be filled by liquid displacement, but in so doing the carbon dioxide content will be affected. This topic was discussed under the use of liquid displacement for sampling from accessible places. The containers shown in Figure 2 also have the advantage that where aspirating devices are not available the need for them can be obviated by filling the sample container and the sampling tube with water. The latter can then be thrust through the opening in the seal and the water drained out of both the tube and container through the bottom outlet of the container. Thus, the system is completely purged with the water. When the

last portion of water is draining from the sample container care should be taken to prevent air from entering at the bottom due to negative pressure in the container. To guard against this use a 6 or 8 inch small-bore tube extension at the lower end of the container, as shown in Figure 9, *C*. Such an extension will remain filled with water and in effect will be a hydrostatic head that will prevent air from entering the container unless the negative pressure is greater than the weight of the water column in the extension.

Ordinary bottles are filled by an arrangement similar to that shown in Figure 9, *D*. In all sampling by water displacement the water should be completely drained from the container. If the sample is taken rather slowly, say in two or three minutes, the walls will drain satisfactorily during the sampling period.

INFORMATION TO BE COLLECTED AT TIME OF SAMPLING

The value of collecting and analyzing samples of mine air lies in the interpretation of the results in terms of the conditions at the time the sample was collected. It is essential therefore to collect accurate detailed information regarding each sample. Attention should be paid not only to the information needed to answer immediate questions but to making the analytical results as far-reaching as possible and to contributing information that will be of fundamental value to the mining industry when similar conditions are met elsewhere. In the past the value of many analyses of mine gases made by the Bureau of Mines gas laboratory has been greatly curtailed by lack of detailed information regarding the sample.

BUREAU OF MINES BLANK FORMS FOR SAMPLERS

Experience has shown that there is certain fundamental information that the collector should endeavor to get for each sample in addition to special detailed notebook information which may be specific to the immediate problem. As a consequence, the Bureau of Mines gas laboratory requires the collector to fill out a form sample card and submit it to the laboratory with each sample sent to the laboratory for analysis. When vacuum sample containers are sent out in the regular mailing case the blank card (blue form 562) is usually placed in the case compartments between the corrugated pasteboard liner and the side wall. After it has been filled out it should be replaced in this position and returned with the sample.

When properly filled out the sample card embodies the information that is needed for—

1. Identification of the sample.
2. Record and filing.
3. Interpretation of results.
4. Assistance to the laboratory in making the analysis.

The portion applying to each of these items is in most cases obvious from the nature of the data; however, certain essential items will be discussed in detail. In this discussion reference is made to the symbols in parentheses shown in the following reproduction of the form sample card:

Face of card

MINE-AIR SAMPLE

<i>Laboratory record</i>		Laboratory No. (w)
Bottle No. (a)		
Sample of (b)		
Mine (c)	Operator (d)	
State (e)	County (f)	
Town (g)	Name of coal bed (h)	
Location in mine (i)		
Method of sampling (j)	Date sampled (k)	Hour
Velocity air (l)	Area (m)	Quantity (cu. ft. per min.) (n)
Pressure on seal (o)	Barometer: Inside (p)	Outside
Temperature, ° F.: Wet bulb (q)	Dry bulb (r)	Humidity (s)
Mailed (t)	Received (v)	
Collector (name and title) (u)		

(FILL OUT THIS CARD AND SEND TO THE LABORATORY WITH GAS SAMPLE)

Referring to the letters on the face of the card—

(a) This should be the number shown on the bottle and should always be filled in by the collector for identification, record, and filing.

(b) The source of sample, as: Coal-mine air, iron-mine air, railroad-tunnel air, etc., should be given.

(c), (d), (e), (f), and (g) The type of information desired is obvious and should always be filled in completely for identification, reports of analyses, record, and filing. If this is not given, the gas laboratory must look it up in directories or communicate with the collector.

(i) The exact location in the mine of the place of sampling should be given in detail and made as descriptive as possible. If taken through a stopping or seal, over a fall, from a borehole, etc., be sure to add that information; also whether sampled close to roof, to floor, etc. It has been observed frequently that collectors confuse "Location *in* mine" with "Location *of* mine", inserting the name of a town in this space, whereas it should contain information describing the entry, room, or other location where the sample was taken.

(j) Insert method of sampling and type of container.

(k) The date and exact time of sampling should be given as they often have a very important bearing on interpreting or explaining the results of analysis.

(l) and (m) The velocity as measured by an anemometer in linear feet per minute and the square feet in the cross-sectional area of the place of sampling are essential data in calculating the quantity of gas emitted or produced and in explaining variations in composition of the air. If the air is still or is moving too slowly to be measured, a descriptive statement should be made instead of leaving the space blank. Where at all feasible velocity and area should be taken at the point of sampling and recorded on the sample card.

(n) This is obviously the value obtained by multiplying the cross-sectional area in square feet by the velocity in linear feet per minute. The result is cubic feet of air per minute.

(o) If the sample is of gases from behind a seal or stopping it should be recorded whether the gas pressure on the seal is positive (blowing out), negative (drawing in), or neutral (pressure the same on both sides of seal). If the pressure measurement is made by means of a water gage the reading, in inches of water, positive or negative, should be recorded.

(p) The barometric pressure or change in barometer very often has an important bearing on the emission of gas, condition of seals, etc., and should, if feasible, be taken as constituting important information relative to the sample.

(g), (r), and (s) The temperature and humidity of mine air have a very important bearing on health and comfort and influence the inflammability of coal dust and the use of rock dust for preventing coal-dust explosions; and, while the specific purpose for which samples are collected may not include these factors, a record of this information may be of marked value in connection with later problems not only in the particular mine where the samples are taken but also in dealing with those subjects in general. The determinations are usually made by the use of a sling psychrometer.

(t) The date of mailing should be included as a matter of record.

(u) The name of the collector who actually obtained the samples should be given. If he collected them for some other person, it should be so stated. If the collector is not a Bureau of Mines employee, his title and position should be stated.

(v) This is filled in by the gas laboratory where the samples are received.

(w) The laboratory number is a consecutive number given the samples after they are received in the laboratory and is used entirely for reference and filing.

Reverse side of card

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

-
1. State kind of sample; as, normal mine air, from fire or gas seal, taken following a mine explosion, products from explosives, etc. If from sealed area state if pressure behind seal is positive or negative.

 2. If, in the collector's judgment, by safety-lamp tests or other tests, the methane content is more than 2 per cent, give estimated percentage.

 3. State constituents to be determined.

 4. Send results of analysis to (give name, address, and number of copies).

General information pertaining to the sample should be given on the reverse side of the "Laboratory Record" section of the form. In the following brief explanations the numbers refer to the item numbers on the card.

1. The collector should state the kind of sample. The constituents usually determined in a "normal mine air" are CO₂, O₂, CH₄, and N₂. If it is desired by the collector that constituents other than these be determined, "normal mine air" should not be designated.

2. The information requested is very important and desirable for the laboratory, because it aids in selecting a method of analysis that will avoid the occurrence of explosions that break the apparatus and also jeopardize the safety of the analyst.

3. The collector should state the constituents to be determined, as, CO₂ and O₂; CH₄, only; complete analysis, which for mine atmospheres includes CO₂, O₂, CH₄, and N₂; complete analysis including CO; etc.

4. The laboratory frequently lacks the information necessary for distribution of the analytical reports. If a deviation from the usual practice of sending reports to the bureau's district engineer is desired, state the names and addresses of persons to whom reports should be sent directly from the laboratory.

The data for the sample card should be taken at the time of sampling and recorded either directly on the sample card or in a notebook. In either case, to guard against loss of information, the collector should have another record of the samples besides the card which

accompanies the sample. *Do not try to remember data and later record them.* If they have been recorded first in a notebook, carefully check the accuracy of the sample-card copy.

MOST COMMON VITAL OMISSION OF DATA

The most common vital omission of data accompanying samples of mine air sent to the Bureau of Mines gas laboratory is the quantity of air, the factor through which composition is correlated with ventilation. The determination of methane in moving air in most cases is practically worthless and does not justify the cost of analysis when information as to the quantity of air is not given.

SUMMARY OF RULES FOR OBTAINING SATISFACTORY SAMPLES AND ANALYSES OF MINE GASES

No analysis is better than the sample, and no chemist can improve the quality of the sample.

1. Have clearly in mind your problem and the purpose for which you desire an analysis of the air and choose sampling points with that object in view. A few samples collected at well-planned locations will usually give better information than a much larger number collected at random.

2. Select a sample container that will preserve the sample during the period between sampling and analysis free from leaks or change in composition and that will be sturdy and practicable if shipment is necessary.

3. Be sure the gas entering the tube is that for which you desire information. In this connection consider source, stratification, homogeneity, and contamination during sampling.

4. Close or seal the sample tightly and avoid contamination by gas of different and undesirable composition entering between the time of sampling and the time of sealing the tube.

5. Collect all information regarding the sample that is pertinent to your problem as well as that which in your experience may make the sample of value to other problems. Be careful to identify the sample and the place and date of sampling accurately. Include such information as will assist the analyst who makes the analysis. Send the data cards with the samples and follow these with a letter to the laboratory telling the type of sample, purpose of analysis, and the constituents in which you are interested; this information will serve as a guide in selecting the most suitable method of analysis and conduct of the work to give results best suited to your problem. Moreover, include the number of samples and bottle numbers, as they will enable the laboratory to ascertain whether the entire group of samples has been received.

PRINCIPLES OF GAS ANALYSIS

In gas analysis as applied to mine gases the various constituents in a mixture are with few exceptions estimated by a system of successive measurements of change in gas volume produced by treating the mixture of gases with suitable absorbents (as in the case of carbon dioxide (CO_2), oxygen (O_2), and frequently carbon monoxide (CO)), or by subjecting the mixture to a combustion with oxygen (as in the case of methane (CH_4), hydrogen (H_2), and sometimes carbon monoxide (CO) if the latter has not been determined by absorption). The successive steps in absorption and combustion are carried out so as to remove or measure the constituent in question without altering the amount of the residual or remaining gases to be determined later. The order in which each gas is determined depends, then, upon the various gases present and the reagents used. This procedure of gas analysis which depends on the measurement of volumes is usually known as gas volumetric or gasometric, and the results are given in per cent by volume and not per cent by weight. Also as the measurements are made with the gas saturated with water vapor, the results obtained are on a dry basis and do not include the percentage of water vapor in the sample.

The gas volume is measured in what is termed a "burette," which is essentially a glass tube or vessel having a series of suitable graduations or calibration marks. The gas is confined within this tube by a mechanical closing device, such as a pinch clamp, a stopcock, or a series of stopcocks at the top; and it is sealed at the bottom by a confining liquid, such as water, brine, or mercury. The bottom of the burette is usually connected by a rubber hose to a movable reservoir for the confining liquid, so that by raising or lowering the reservoir the level of the liquid in the burette can be made to rise or fall, either expelling or drawing gas through the opening at the top or, if the opening is closed, increasing or decreasing the pressure of the confined gas. The volume of gas in the burette is measured by observing the graduation mark which corresponds to the level (usually termed "meniscus") of the confining liquid within, necessary precautions being taken to insure known condition of temperature and pressure. These are described later.

A gas mixture is generally treated with absorbents in an auxiliary vessel or vessels filled with a specific solution which, when in contact with a mixture of gases, will absorb and remove the desired component from the mixture. Thus, by noting the volume before the mixture is subjected to this solution and by measuring the residual volume afterwards one can easily ascertain how much was absorbed and consequently how much of that particular gas was present. In the portable Orsat apparatus these reagent vessels or pipettes are arranged

in a row, all being connected to a manifold through which communication with the burette can be made by merely opening a stopcock. In the combustion analysis the entire residue that has been unabsorbed by the various reagents is burned in a suitable pipette in the presence of an excess of air or oxygen⁵ and the percentage of methane calculated on the basis of the contraction in volume produced by burning and the amount of carbon dioxide formed.

The nitrogen which is unabsorbed by ordinary gas-analysis procedures and is incombustible is determined by subtracting from 100 the sum of the percentage of all other gases found. This is usually expressed as percentage of nitrogen (N_2) and contains about 1 per cent of argon, which, however, has physical and chemical properties similar to nitrogen and for practical purposes may be considered as such.

TYPES AND LIMITATIONS OF GAS APPARATUS USED BY THE BUREAU OF MINES FOR MINE-GAS ANALYSIS

The three types of apparatus used by the bureau for complete analysis of mine atmospheres are the Haldane,⁶ the laboratory Orsat,⁷ and the portable Orsat.⁸

HALDANE APPARATUS

The Haldane apparatus is designed for the analysis of air contaminated with small amounts of carbon dioxide, methane, carbon monoxide, hydrogen, and nitrogen and deficient in oxygen. All of these constituents in a gas mixture can be determined (by complete analysis), or the procedure may be modified to include one or more as desired. If, for example, only the methane content is needed, the procedure is much shorter, and far less time is required than when a complete analysis is made. *The collector of samples should always advise the laboratory as to the analysis desired.*

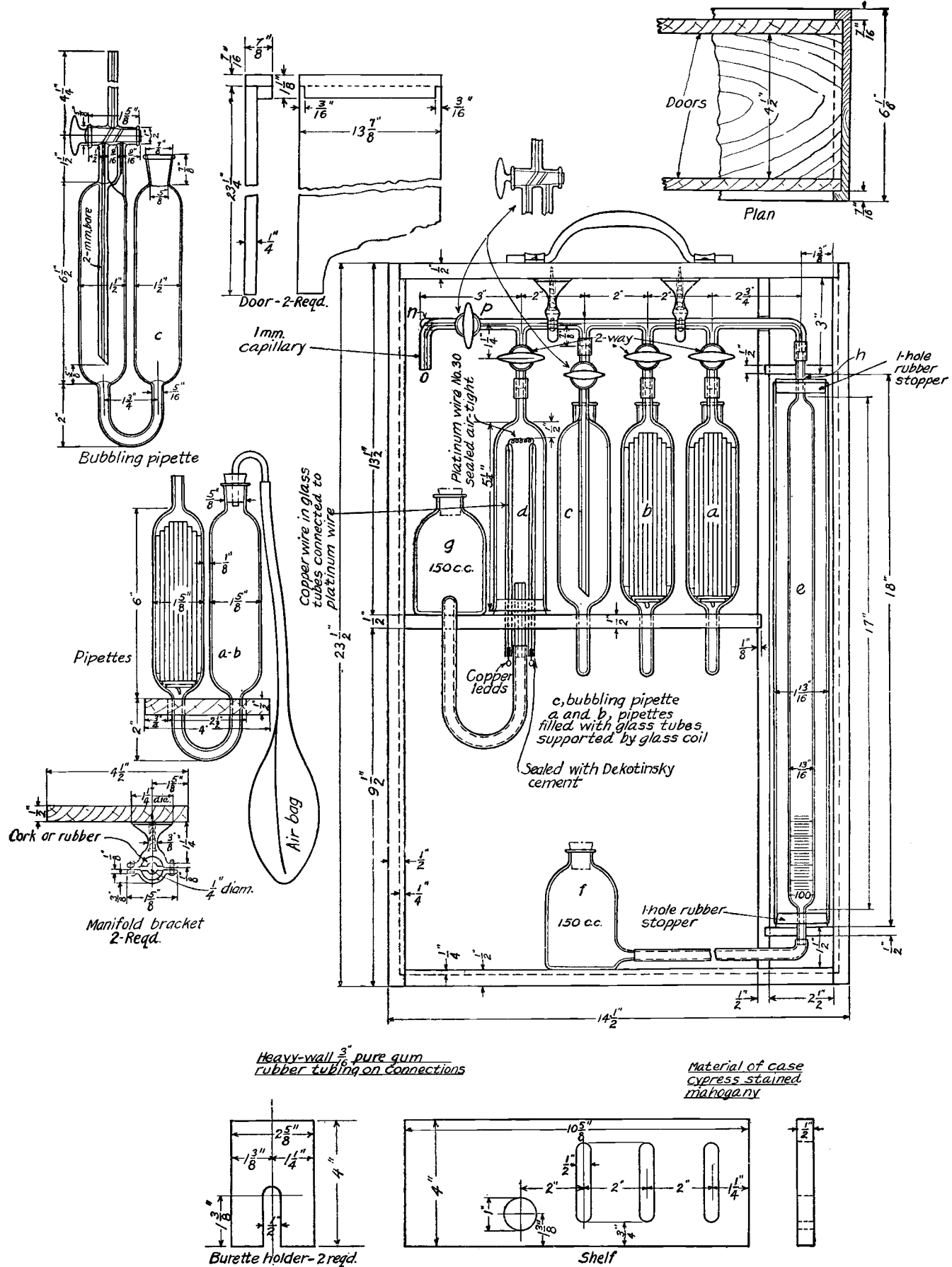
Samples to be analyzed by the Haldane apparatus must not contain an explosive mixture of combustible gases (methane, hydrogen, and carbon monoxide). Also, they must contain enough oxygen to burn completely all of the combustible gases, because no means for adding oxygen for combustion or for handling explosive mixtures are provided, as with the Orsat types. Therefore, the collector is re-

⁵ This applies to the type of apparatus for mine-fire gases described in these instructions. With the laboratory type of Orsat, described in Bull. 197, Bureau of Mines, Sampling and Examination of Mine Gases and Natural Gas, by G. A. Burrell and F. M. Seibert, revised by G. W. Jones, 1926, 108 pp; or Tech. Paper 320, The Bureau of Mines Orsat Apparatus for Gas Analysis, by A. C. Fieldner, G. W. Jones, and W. L. Holbrook, 1925, 18 pp., the CO and H₂ are determined by passing the gas slowly through copper oxide heated to 300° C., which oxidizes the CO to CO₂ and the H₂ to H₂O. The residue which contains the methane is burned afterwards by slow combustion with oxygen.

⁶ Burrell, A. G., and Seibert, F. M., Sampling and Examination of Mine Gases and Natural Gas; Bull. 197, Bureau of Mines, revised by G. W. Jones, 1926, 108 pp.

⁷ See Fieldner, A. C., Jones, G. W., and Holbrook, W. L., The Bureau of Mines Orsat Apparatus for Gas Analysis, Tech. Paper 320, Bureau of Mines, 1925, 18 pp. See also footnote 6.

⁸ See footnote 6.



quested always to advise the laboratory whether or not the sample contains more than 2 per cent of CH_4 . While methane is not explosive until 5 per cent or more is present the margin of safety afforded by stating when there is more than 2 per cent is desirable.

The principal advantage of the Haldane apparatus is its accuracy, as it can determine the amount of each gas within 0.02 to 0.03. This is about 10 times as accurate as the Orsat types described later. The samples usually analyzed are normal mine air, where the amounts of CO_2 , O_2 , and CH_4 (below 5 per cent) are desired for ventilation studies pertinent to health and safety. This apparatus is especially useful in calculating quantities of methane from an analysis of total return air from coal mines or air from splits. In these cases the total amount of methane may be only a few tenths of 1 per cent, and an error of 0.2 or 0.3 (as obtained by the Orsat) would change the quantities 100 per cent or more. Other types of samples analyzed with the Haldane apparatus are air contaminated by leaks from fire seals, by afterdamp, and by diluted products of combustion of explosives, when the amount of combustible gas is below an explosive mixture and when the samples contain enough oxygen to burn completely all of the combustible gases present.

ORSAT TYPES OF APPARATUS, LABORATORY AND PORTABLE

The Bureau of Mines portable Orsat apparatus (figs. 10, 11, and 12) is used to analyze the same kind of samples of mine gases in the field as the laboratory type analyzes in the laboratory. These samples constitute atmospheres in which the contamination is greater than can be determined by the Haldane apparatus, such as samples collected from behind fire or gas seals, concentrated samples of afterdamp, and atmospheres markedly depleted in oxygen and containing amounts of methane within or above the explosive limits. In general, all samples that contain an explosive mixture or greater than an explosive mixture of methane and an insufficient amount of oxygen for combustion are analyzed with the Orsat type of apparatus. The only advantage of the laboratory type over the field type is that the former is slightly more accurate, because mercury is used instead of water as the confining liquid in the burette and combustion pipette and because copper oxide heated to 300°C . is used to remove the hydrogen and carbon monoxide. The latter permits the amount of hydrogen to be determined, which can not be done satisfactorily with the portable type, and makes it possible to determine the amount of ethane if it is desired as an indication of the occurrence of natural gas in mine atmospheres.

The error⁹ of the laboratory type of apparatus is 0.2 as compared with 0.2 to 0.4 for the portable apparatus. The greater accuracy of

⁹ These values do not mean that the error is 0.2 to 0.3 per cent of the amount of a constituent found by analysis but that the results as obtained in per cent are within 0.2 or 0.3 of the amount present.

the laboratory type is not a significant advantage in analyzing the types of mine-gas samples for which the portable apparatus is recommended, because the errors of sampling are usually as large as the error of analysis. Even if it were possible to collect better samples, these limits are within the range of practical use and interpretation of results.

Also, the use of the laboratory type of apparatus in most cases involves shipment of samples, which results in delay and allows time for leaks, in many cases causing far greater error than if the samples

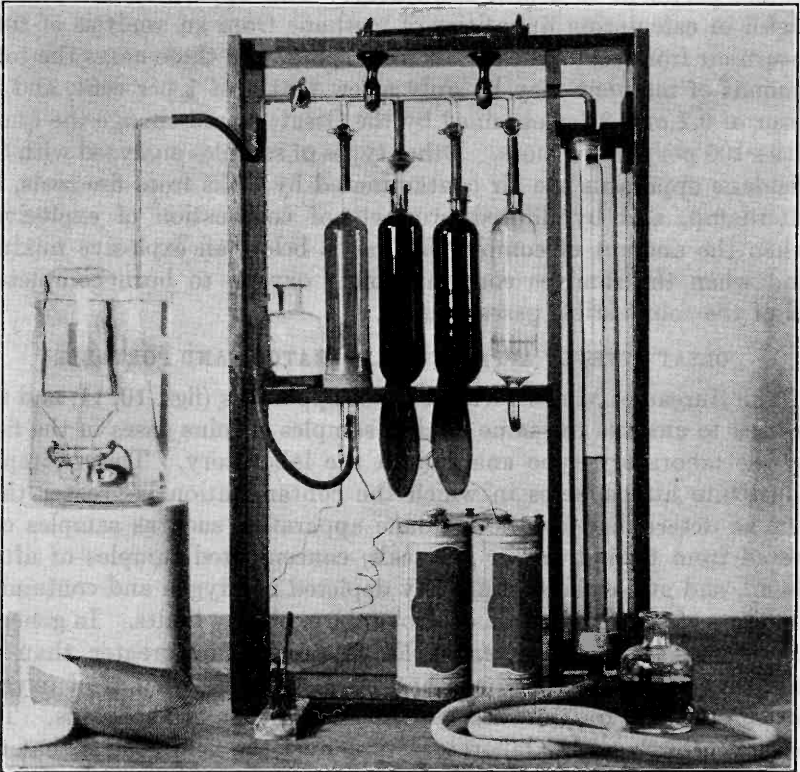


FIGURE 11.—Front view of portable Orsat gas apparatus

were immediately analyzed by the portable type of apparatus. Because the oxygen content is of major importance in mine-fire gases more samples of that type are vitiated by air contamination after taking than by all other causes.

Another advantage of the portable apparatus is the possibility of obtaining immediate results. In the case of samples taken from sealed areas which contain active mine fires, the samples represent only the composition at the time of sampling, and the composition may be entirely different the next day. For this reason a lapse of even a few days may change the condition to such an extent that the

results of analysis of samples sent to a distant laboratory may have no value other than perhaps that of interest, record, or general information. Under some conditions it is absolutely necessary to have results on the same day or within an hour or two after the samples are taken. This applies especially to recovery work where the next move of a crew may depend upon the composition of the air.

The laboratory Orsat provides for the determination of hydrogen and ethane in addition to the constituents that can be determined

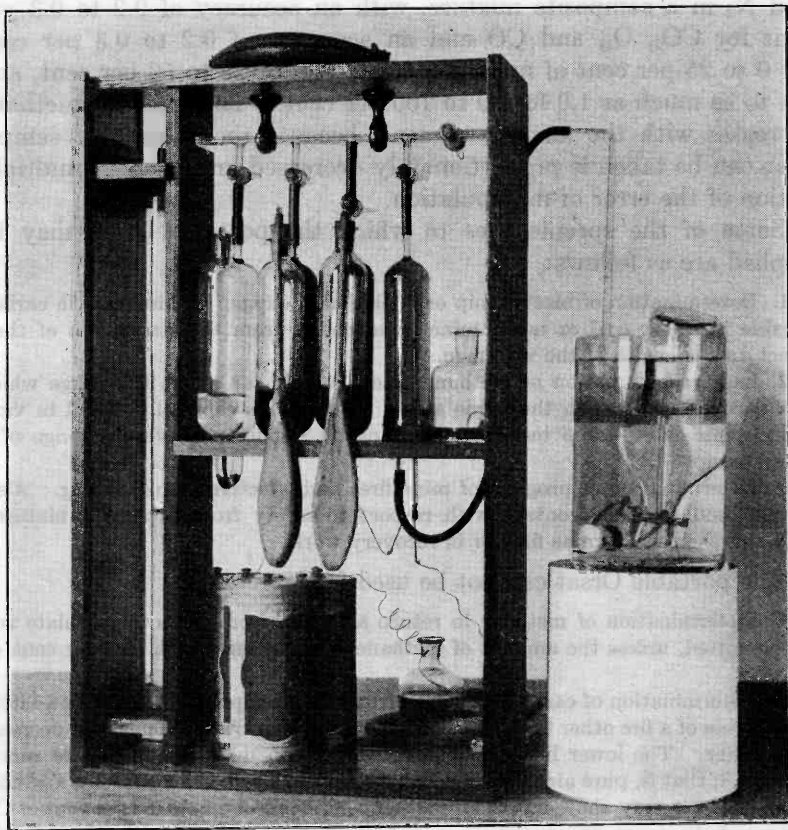


FIGURE 12.—Back view of portable Orsat gas apparatus

by the portable type. However, hydrogen is not a significant constituent, except perhaps during a short period after sealing very active mine fires. Also, with the portable type the hydrogen is burned with the methane, and its contribution toward the explosibility of the atmosphere is evaluated to a fair degree of accuracy in terms of methane. As for ethane, which might be present in small amounts immediately after sealing, it is likewise evaluated in terms of methane. There are conditions, however, where a determination of ethane in mine atmospheres is desirable, as in the leakage

of natural gas into the mine. These samples must be analyzed with the laboratory type to obtain satisfactory results.

In summing up the merits of the laboratory as compared with the portable type of apparatus, the advantages of the latter outweigh its disadvantages for the particular uses set forth in the following.

FIELD OF USE OF PORTABLE ORSAT

The portable Orsat can be used to determine CO_2 , CO , O_2 , CH_4 , and N_2 in a composite mixture, with an accuracy of 0.2 to 0.3 per cent for CO_2 , O_2 , and CO and an accuracy of 0.2 to 0.3 per cent for 0 to 25 per cent of methane, 0.3 to 0.4 for 25 to 50 per cent, and 0.4 to as much as 1.0 for 50 to 100 per cent. The error for methane increases with the amount present, because the volume of sample that can be taken is proportionately decreased and causes a multiplication of the error of manipulation.

Some of the specific uses to which the portable Orsat may be applied are as follows:

1. Determination of black damp or depletion of oxygen and increase in carbon dioxide in either coal or metal mine atmospheres from the standpoint of their effect on the health of the workmen.
2. Large accumulation of methane below, within, or above the range which can be determined with the flame safety lamp. It is especially useful in verifying flame safety-lamp tests or examining atmospheres above the range of a safety lamp.
3. Determination of progress of mine fires and effectiveness of sealing. Also, oxygen and methane content with respect to safety from explosive mixtures, either in the case of mine fires or in recovery work.

The portable Orsat can not be used for—

1. Determination of methane in return air or air from splits to calculate volume emitted, unless the amount of methane is exceedingly high (2.0 per cent or more).
2. Determination of carbon monoxide from the standpoint of health and safety or progress of a fire other than to show a general trend toward increase or decrease in activity. The lower limit of detection of carbon monoxide is plus or minus 0.2 to 0.3; that is, pure air may show 0.3 per cent when no CO is present, and contaminated air may show 0.0 when 0.3 per cent is present. As 0.3 per cent of CO is enough to cause unconsciousness in half an hour or less, with exercise, the apparatus is obviously unsatisfactory; likewise, it is entirely too inaccurate for determining the proper time for unsealing mine fires.

In both of the examples given it is highly desirable to have results for carbon monoxide that are accurate to 0.01 per cent. For this purpose the pyrotannic method¹⁰ is recommended for use with the portable and laboratory Orsat.

¹⁰ For details see Sayers, R. R., and Yant, W. P., The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and in Air: Tech. Paper 373, Bureau of Mines, 1925, 18 pp. For brief description see Burrell, G. A., and Seibert, F. M., Sampling and Examination of Mine Gases and Natural Gas: Bull. 197, Bureau of Mines, revised by G. W. Jones, 1926, 108 pp.

DESCRIPTION OF PORTABLE ORSAT

The apparatus shown in Figures 10, 11, and 12 consists essentially of a burette, *e*, and four pipettes, *a*, *b*, *c*, and *d*. The burette has a total capacity of 100 c. c. and is divided into 100 large divisions, each of which is further subdivided into 5 small or 0.2 c. c. divisions. The pipettes contain the following solutions: Pipette *a*, potassium hydroxide or sodium hydroxide solution for the removal of carbon dioxide; *b*, alkaline pyrogallate solution for the removal of oxygen; and *c*, acid cuprous chloride solution for the removal of carbon monoxide. Pipette *d* is the slow-combustion pipette for burning the methane. Pipettes *a* and *b* are filled with glass tubes to increase the absorption surface of the reagents. Pipette *c* may be similar to *a* and *b*, but preferably it should be of the bubbling type, because cuprous chloride solution is not viscous enough to spread out a large absorption surface on the glass tubes as does caustic or pyrogallate but rapidly drains and leaves the tubes nearly dry. The bubbling pipette is provided with a 2-way cock, one branch of which communicates with a capillary tube extending to within about five-eighths inch of the bottom of the pipette and the other with the top. The cock should be turned first so that the liquid is just displaced from the short tube and then turned through 180° and the remainder of the gas slowly forced out the long tube in a stream of small bubbles. The cock is then turned through 180° and the gas withdrawn through the short arm to a point just below the short-arm outlet. This procedure should be repeated five or six times. The gas is drawn up each arm in turn to a mark on the tubes.

The platinum combustion element inside of the slow-combustion pipette *d* is made from about 2½ to 3 inches of No. 28 or 30 B. & S. gage wire formed into a ⅜-inch coil and supported by two glass tubes. As a rule, the platinum wire is hermetically sealed through the upper ends of the supporting tubes and welded to copper wires that pass down through the tubes to the exterior. Connections to a storage battery or other source of electric current are made with the lower ends of these copper wires. A current of about 5 amperes at approximately 4 to 6 volts is desired and may be obtained by connecting a number of cap-lamp batteries or dry cells in series. Where electric current, as from lighting circuits, is available the desired current may be obtained by the use of a lamp-bank resistance, or (if alternating current) a more satisfactory device is a toy or electric-bell transformer that will give enough current to heat the platinum coil. Most of these transformers are made for 110-volt primary current and will burn out if used for 220 volts.

When cap-lamp batteries or dry cells are used the temperature may be regulated by a combination of partly used units with fully

charged ones. A variable rheostat may be made by placing a 12-inch piece of 20-gage nichrome wire in series with the coil. One end of the wire is fixed to a copper lead from the coil, and the other is made variable by slipping it through the eye of an ordinary screw binding post to which the corresponding lead from the source of current is attached. A small variable resistance similar to that used for radio apparatus can be used, provided that it has enough resistance and is so constructed that the mounting will not burn or melt.

The solution reservoirs of pipettes *b* and *c* are closed with 1-hole rubber stoppers to which are attached air bags or rubber expansion bags, shown in Figures 10 and 11. These bags prevent interchange of air during the operation of the pipette and thereby extend the life of solutions that are affected by constituents of the air. They may be connected singly—that is, one to each pipette—or a common manifold may be made, in which case only one bag is required for all of the pipettes. Pipette *a* does not need protection while in use and can be closed with a rubber or cork stopper when not in use.

The marks on the pipette stems that indicate the height to which the solution is to be drawn are usually etched into the glass. If not, a suitable mark can be made by pasting a narrow strip (about one-sixteenth inch wide) of gum label, the sealing edge of an envelope, or adhesive tape around the stem about one-fourth to one-half inch below the lower end of the rubber connections. This distance gives space for observing and adjusting the level of the liquid and eliminates dead space as much as possible. "Dead space" is the term usually applied to the space in the manifold and capillary glass-tubing connections that can not be conveniently filled with displacing liquid during the operation of the apparatus.

READING GAS VOLUMES WITH THE BURETTE

DESCRIPTION OF BURETTE

The gas-measuring vessel (burette *e*), for the type of apparatus shown in Figure 10, is a tube that has a total volume capacity of 100 c. c. and is divided by horizontal calibration marks into 100 equal whole portions called cubic centimeters and marked in even numbers, 0, 2, 4, 6, etc. (see fig. 13), beginning with 0 at the top or bottom and reading both ways in some cases. The odd figures, 3, 5, 7, etc., are generally omitted, due to lack of space. These unit portions are then further divided into smaller portions, usually five equal parts, each one of which represents one-fifth of 1 c. c. or, expressed in decimals, 0.2 c. c. For laboratory apparatus the markings are usually consecutive, as 0, 1, 2, 3, 4, 5 (see fig. 13, *C*), and the small units are subdivided into 10 equal portions, each representing 0.1 c. c. The horizontal scratches or marks generally correspond in length to the magni-

tude of the division; that is, the 1 c. c. units are the longest and may extend half or entirely around the burette, whereas the 0.2 or 0.1 c. c. marks are only across a portion of the face.

In reading the volume of gas in an ordinary clear-glass burette the lowest point of curvature of the water level, termed "meniscus,"

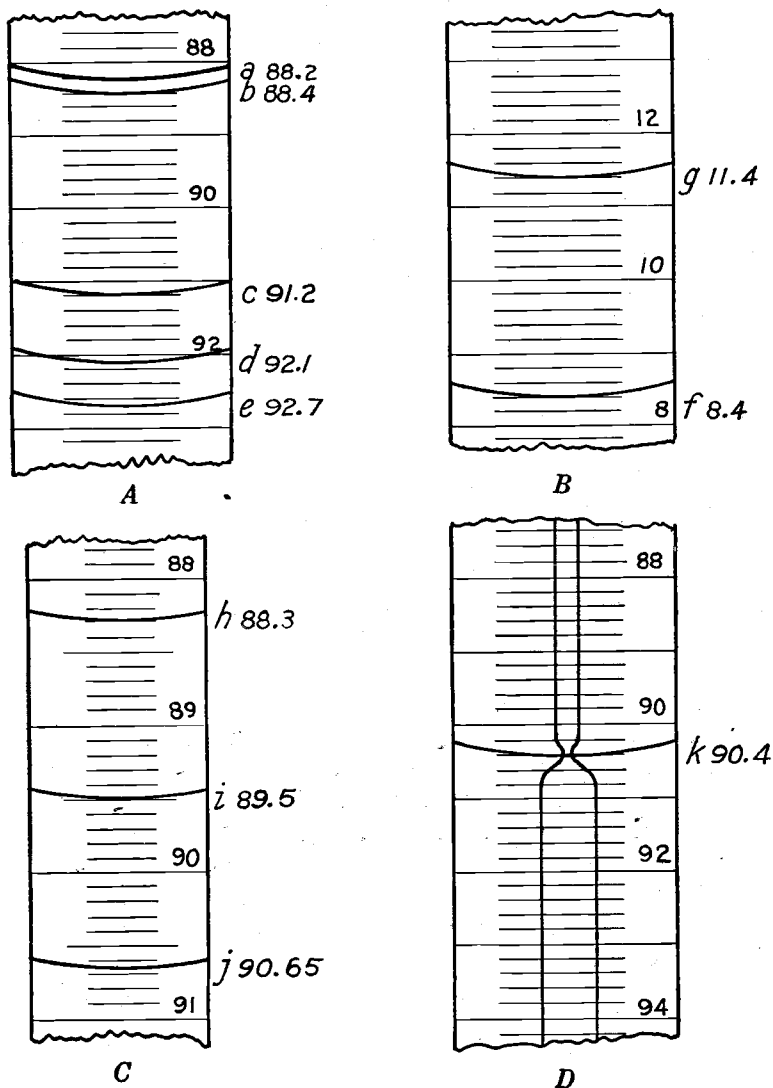


FIGURE 13.—Sections of various types of burettes for portable Orsat gas apparatus

is always compared to a mark on the burette. However, with burettes of the Schellbach type, which have a milk-glass back with a vertical blue or colored line (fig. 13, *D*), the liquid in the burette magnifies the line below the meniscus, but the portion above appears

without magnification. In reading volumes with the Schellbach type the point where the magnified and nonmagnified portions meet is compared with the calibration marks.

With burettes having numbers increasing from top to bottom (fig. 13, *A*), the readings of whole and part units are taken in the same order; in other words, the gas space between the 0 mark at the top of the burette and the liquid is measured. With burettes numbered from bottom to top (fig. 13, *B*), the reverse order is followed; that is, the space between the 0 mark at the bottom and the top of the liquid is measured. A few specific cases will serve to illustrate the manner of reading volumes. In *A*, each large subdivision (marks extending entirely around the burette) equals 1 c. c. and each small division 0.2 c. c. It follows that meniscus *a* equals 88 whole units and 1 part unit with a value of 0.2. Consequently, the reading for *a* is 88.2 c. c.; likewise, that for *b* is 88.4. In *c* the meniscus appears in one of the odd or unnumbered whole units; but from the even-numbered unit above (which is 90) it is known that the unnumbered whole unit is 91; and this, with one small division having a value of 0.2, makes the reading 91.2. In *d* the bottom of the meniscus does not fall exactly on any line but comes midway between, so that the reading is 92 plus one-half of a division whose value is 0.2, or 92.1. The same is true of *e*; the reading is 92 whole units, 3 full small units, and one-half small unit, the sum of which is 92.7. In Figure 13, *B*, when the burette reads from bottom to top, *f* equals 8 whole units from the bottom and 2 small ones, or 8.4. Similarly *g*, which falls in an unnumbered unit, equals 11.4.

Burettes that are numbered from 100 at the top to 0 at the bottom are designed to give the net volume lost after the gas is subjected to a given reagent by subtracting the total volume as measured before absorption in each successive step in the procedure from the volume after absorption; burettes calibrated from 0 at the top to 100 at the bottom (fig. 13, *A*) give the net volume lost after absorption by subtracting the volume after absorption from the volume before absorption. For most people this latter type appears the easiest to read as well as the easiest from which to keep records and calculate results, as it permits setting all readings in a vertical column and subtracting one reading from that above to obtain the data for a specific constituent.

PROCEDURE FOR MAKING BURETTE READING

After the gas has been drawn into the burette from either the sample container or one of the pipettes and the stopcocks have been closed, allow one minute for the water to drain down the sides of the burette. Then, by holding leveling bottle *f* close to burette *e* (the bottle may be steadied, if necessary, by holding it against the side of the case), bring the level of the water in *f* to the same height as that in *e*. Hold

in this position and, with the eye about 15 inches from the burette and at the height of the liquid in *f*, sight horizontally across the burette and find the graduation mark that coincides with the bottom of the meniscus, at the same time noting the value of the mark as so many units and parts of units. (See fig. 14.) The position of the meniscus should be estimated to the nearest mark or half-division mark, as *c* or *d*, *h* or *j*, Figure 13. The meniscus and graduation marks can be illuminated by holding an electric light (extension cord), flash light, or cap lamp behind them. The ordinary clear-glass electric-light bulb is too bright for this purpose unless it is screened.

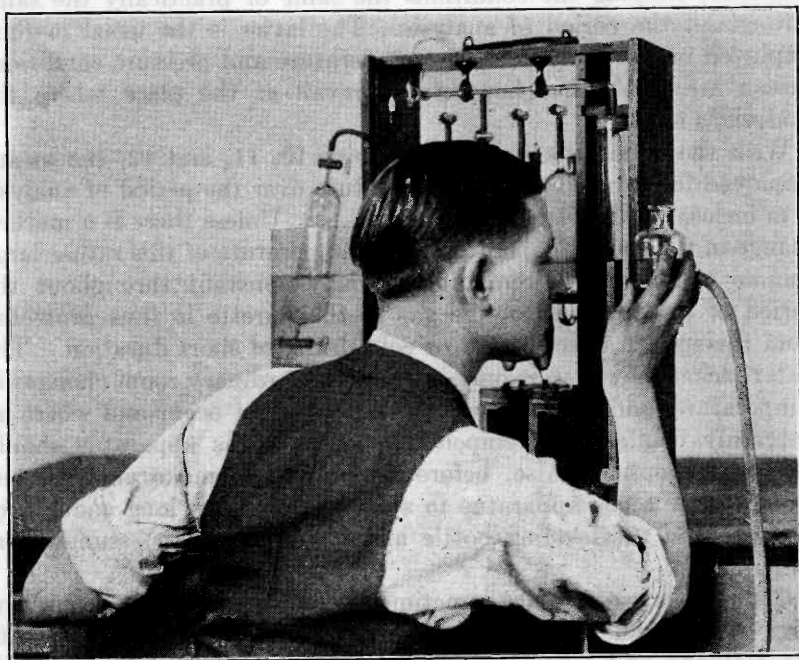


FIGURE 14.—Position of leveling bottle and line of sight in making burette reading

A correct burette reading depends entirely upon (1) having the line of the water in *f* the same as that in *e* to bring the gas to atmospheric pressure and (2) having the eye at the same level to make the line of sight in the same horizontal plane as the water levels. Record the volume immediately after making a burette reading.

CONTROL OF TEMPERATURE AND PRESSURE DURING MEASUREMENT

The volume of liquids and solids, such as water, steel, etc., changes comparatively little with ordinary changes in pressure and temperature, and these factors are not usually considered in ordinary measurement. Gases, however, change markedly with changes in temperature

and pressure, and as the ordinary procedure for analyzing them is based on successive comparative measurements of contraction in volume caused by absorption or combustion it is necessary to know or to control the temperature or pressure at which each measurement is made. Otherwise, one could not ascertain whether the differences in readings were due to removal of a constituent or to a change in the conditions under which the gas was measured.

The temperature and pressure are controlled either by measuring them at the time of making each successive reading and transforming each volume by calculation to one standard condition or by devising means for keeping the conditions the same or practically the same throughout the period of analysis. The latter is the usual method employed in gas analysis. The temperature and pressure conditions chosen are those that happen to prevail at the place where the analysis is made.

With the apparatus shown in Figures 10, 11, and 12, the means employed for controlling the temperature over the period of analysis is to inclose the burette in a water jacket. Unless there is a marked change in the room temperature, the temperature of this rather large volume of water will remain practically constant throughout the period of analysis. Also, the gas in the burette is thus protected from the sudden effect of hot or cold drafts of short duration. The water jacket, however, is only intended for ordinary room changes in temperature, and where marked changes do not occur and where an ordinarily comfortable temperature exists a gas apparatus should always be housed. Also, before attempting to make analyses one should allow a gas apparatus to stand in the room long enough for the water in the leveling bottle and water jacket to assume room temperature.

Changes in pressure are sometimes taken care of by compensating devices independent of atmospheric pressure. These are used with the Haldane and laboratory Orsat¹¹ types, but with the portable Orsat shown in Figures 10, 11, and 12 the pressure is controlled by bringing the gas within the burette to the existing atmospheric pressure. The barometric-pressure changes over the period of analysis (say, 30 minutes) will seldom be great enough to cause a significant error.

To make the pressure of the gas in the burette the same as that outside before each measurement is taken, hold leveling bottle *f* close to burette *e* and raise or lower *f* until the liquid in the bottle is the same as that in the burette. This virtually makes a U gage, one arm of which is the burette and the other arm of which is the hose and leveling bottle. When the levels are the same, the pressures on each are the same.

¹¹ See footnote 6, p. 31.

PREPARATION OF SOLUTIONS

The absorbing solutions are most conveniently prepared in a chemical laboratory where facilities are available; then they are shipped to the field. However, in emergency cases when there is no time for ordering them from a distant laboratory it may be necessary to prepare them in the field. The chemicals used in preparing the solutions for carbon dioxide and oxygen are common and can be obtained from a drug store or photographic supply house. Those required for making the cuprous chloride can be obtained from a university or commercial chemical laboratory.

CARBON DIOXIDE

Potassium hydroxide (KOH) or sodium hydroxide (NaOH) is generally used for absorbing carbon dioxide. As a rule these chemicals are solids marketed in stick form and contained in stoppered bottles to exclude moisture and air. The grade of hydroxide known as electrolytic and not the product purified by alcohol is recommended for gas absorbents, not because the electrolytic grade is better for absorbing carbon dioxide but because it should be used in preparing alkaline pyrogallate solution for oxygen, and because by using the electrolytic for both it is unnecessary to provide two grades in the laboratory.

A considerable amount of heat is produced when potassium or sodium hydroxide is dissolved in water, and if dissolved rapidly the water may even boil. For this reason the solution should be made by dissolving one stick or only a few sticks at a time and by cooling the bottle or flask (an ordinary table dish is suitable if other apparatus is not available) by letting it stand or by holding it under a stream of water, otherwise the heat might cause it to crack. The vessel should never be stoppered while the caustic is being dissolved, but it should be stirred or the contents rotated gently. After the solution has been prepared it should be allowed to cool. A small amount of sediment will settle on standing, and the clear liquid can be poured or decanted off for filling a pipette or can be transferred to storage bottles. Magnesium citrate bottles are convenient containers.

Potassium hydroxide solution.—Dissolve 300 grams in 1,000 c. c. of water.

Sodium hydroxide solution.—Dissolve 200 grams in 1,000 c. c. of water.

Distilled water is recommended for preparing absorbing solutions and can usually be obtained from a drug store or garage; if unobtainable, however, rain water or ordinary drinking water may be used.

In preparing either solution a greater or less amount can be made as long as the proportion of each chemical is kept the same; for

example, for 200 c. c. of water 60 grams of potassium hydroxide should be added. Potassium or sodium hydroxide, either in stick form or in solution, is poisonous and corrosive to the skin and clothes. The action is similar to that of ordinary lye.

OXYGEN

Alkaline pyrogallate is used for absorbing oxygen. It consists of a mixture of potassium hydroxide solution and pyrogallic acid (ordinary "pyro," as used in photography) solution. These two solutions are prepared separately and then mixed. In making the potassium hydroxide solution the same precautions given under carbon dioxide absorbents should be taken regarding skin burns, effect on clothing, and heating of solution. No precautions need to be taken with the pyrogallic acid except to avert stains on the skin and clothing.

Potassium pyrogallate solution.—Dissolve 50 grams of pyrogallic acid in 150 c. c. of water. In a separate bottle, flask, or ordinary dish dissolve 1,200 grams of potassium hydroxide (electrolytic grade) in 800 c. c. of water. Smaller amounts of the solutions, even just enough to fill a pipette, may be made by proportionately decreasing the amounts of each chemical; that is, divide each by 2, 5, 10, etc., as desired. After cooling the potassium hydroxide solution add the pyrogallic acid solution, mix, and immediately place in a tightly stoppered bottle to avoid contact with the oxygen of the air. A better and more convenient procedure is to place 250 c. c. of the potassium hydroxide solution in each of a suitable number of bottles of approximately 325 c. c. capacity, such as magnesium citrate bottles. Add 45 c. c. of the pyrogallic acid solution to each and immediately close. These small containers are better than large bottles, as only a small portion of solution is subjected to air if opened, whereas if stored in a large container all of the solution would be exposed to air each time a pipette is filled. Of course, large bottles having siphons or drains for removing the solution would prevent this, but they are not considered satisfactory for field use.

Alkaline pyrogallate solution is poisonous and corrosive to the hands and clothing.

CARBON MONOXIDE

Cuprous chloride solution.—Either ammoniacal cuprous chloride (blue solution) or acid cuprous chloride (straw colored) solution is suitable for absorbing carbon monoxide. However, the acid solution is recommended, as the ammonia vapors given off from the ammoniacal preparation may cause error by making the moisture or drops of water in the manifolds alkaline, thereby prematurely absorbing CO_2 from the gases.

Acid cuprous chloride solution is prepared by either the "copper reduction" or "stannous chloride reduction" method.

Acid cuprous chloride solution.—Dissolve 100 grams of c. p. cuprous chloride in 600 c. c. of concentrated c. p. hydrochloric acid. Oxygen is readily absorbed by this solution and oxidizes some of the cuprous chloride, hence it should be excluded as much as possible during the preparation. Even slight oxidation causes the solution to be dirty black or greenish black immediately after preparation or on standing. It can not be used in this condition but must be reduced until it is a clear straw yellow.

Reduction by copper.—To the above solution in a bottle add some copper turnings, strips of sheet copper, wire, or copper gauze. Several days may be required to reduce the solution to a straw-yellow color; but after reduction has been effected the remaining copper will keep it reduced, unless, of course, the bottle is not tightly closed.

Reduction with stannous chloride.—The reduction can be effected immediately if stannous chloride is used instead of metallic copper. Drop the stannous chloride in the solution piece by piece, preventing the entrance of air as much as possible, or add small portions of a solution made by dissolving 25 grams of stannous chloride in 100 c. c. of a solution of equal parts of c. p. concentrated hydrochloric acid and water. Insert the stopper after adding each portion and shake gently. Continue in this manner until the solution becomes straw color (not merely greenish), then add another portion of stannous chloride in excess. This solution is ready for immediate use. If a large quantity has been made, it should be stored in accordance with the instructions given for alkaline pyrogallate.

Acid cuprous chloride is poisonous and fairly corrosive to the hands, clothing, shoes, metal, etc.

Cuprous sulphate beta naphthol.—Under the method for determining carbon monoxide the use of cuprous sulphate beta naphthol instead of cuprous chloride is discussed. Also, it is stated that the solution is rather difficult to prepare, hence no method is given here. Persons interested in preparing it, however, may consult the references given.¹²

CONFINING LIQUID FOR BURETTE AND COMBUSTION PIPETTE

The water used in the burette and combustion pipette should be kept slightly acidic with sulphuric acid. Also, it is desirable to color it red with an indicator such as methyl orange,¹³ because the color not only facilitates reading the meniscus but it also changes to a rather pale yellow if the confining liquid becomes alkaline, thus giving a warning to add more acid.

The acid solution is made by adding a few drops of concentrated sulphuric acid to the leveling bulb or burette reservoir and then

¹² Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Gases, 3d ed., 1927, 187 pp. Prepared by a Committee of Chemists. Same method in *Gás Chemists' Handbook*, Am. Gas Assoc., 1928.

¹³ Methyl orange is a water-soluble organic compound which is red in acid solution and yellow in alkaline solution. It is commonly used in chemical analysis and may be obtained from any chemical-supply house.

adding a few drops of the methyl-orange indicator, or a stock of 10 per cent sulphuric acid solution containing the indicator may be prepared and small portions added as need arises. Any clear drinking water may be used to prepare the confining liquid.

LIFE OF SOLUTIONS

As the solutions absorbing carbon dioxide, oxygen, and carbon monoxide from gas samples will also absorb carbon dioxide or oxygen from the air, their life depends on (1) the effectiveness of protection from air when in the pipette or the storage bottle and (2) the amount of gas they absorb in the analysis of successive samples. Preservation during preparation and storage is referred to under "Preparation of solutions," and in the pipettes they are protected by rubber bags which preserve the solutions from deterioration when not in use. However, one can not always be sure that the bags will not leak air, and the solutions should be changed if they have stood two months or more, even though the apparatus has not been used. However, if an emergency arises and new solutions are not available, the old ones may be used, but more attention should be given to insuring complete absorption by checking each absorption as described in the analytical procedure for the various gases. Cuprous chloride deteriorates faster than any of the others and is more liable to be inefficient after prolonged standing. If it has turned quite dark, it is worthless.

The approximate life of solutions during use depends on the manner of preparation of the original solution and how well it was preserved. The following facts are approximately true for average solutions and may be used as a guide to changing them, although toward the latter part of their life the speed of absorption and completeness should be observed occasionally, and if slow or inefficient the solution should be changed, even though its estimated life has not expired.

Sodium or potassium hydroxide.—Either of these solutions is capable of absorbing large amounts of carbon dioxide, and as many as 100 or 200 mine-fire samples can be analyzed before they are "worn out"; in fact, the solutions are generally changed due to other reasons, such as turbidity, sediment, or solid matter in the stems, etc.

Alkaline pyrogallate.—After alkaline pyrogallate has absorbed about 10 times its volume of oxygen its action becomes slower, and 9 to 12 passes into the solution may be required in making the determination. When the solution has absorbed 15 to 20 times its volume of oxygen it should be discarded. One filling of the pipette may be used satisfactorily for approximately 75 to 100 samples of mine-fire gases. This, however, depends upon the original preparation and how well it was preserved.

Cuprous chloride solution.—Cuprous chloride is a rather unsatisfactory absorbent, because it never completely absorbs all of the carbon monoxide from a gas mixture. The amount that it absorbs depends upon the amount that it has previously absorbed and the amount in the particular sample. For example, a new solution will absorb nearly all of the carbon monoxide from the first few samples and then leave more and more in the gas of succeeding samples. If it has already absorbed a considerable amount of gas from previous samples it may even give up small amounts of carbon monoxide to samples that contain only traces or none of that constituent. In types (not shown in figs. 10, 11, and 12) of gas apparatus used for analyzing samples containing large amounts of CO, such as water gas, producer gas, blast-furnace gas, etc., two cuprous chloride absorption pipettes are used in series, the gas being passed into the first to remove the major part of the gas and later into a comparatively fresh one to remove most of the remaining gas. The solutions are changed alternately; that is, as soon as the first one is worn out it is replaced by fresh solution and becomes the pipette to be used for the second absorption.

The portable apparatus shown in Figures 10, 11, and 12 has only one cuprous chloride pipette, *c*. This, however, will give satisfactory results for mine-fire gases, afterdamp, etc., which contain relatively small amounts of CO, provided, of course, that the solution is changed frequently. The solution should be changed after every 8 to 10 analyses (not samples) if the samples contain 1.5 to 3 per cent of CO. With 0.5 to 1.5 per cent the solution should be changed every 15 to 20 analyses and with lower amounts of CO (0.5 per cent or less) the same solution may be used for 25 to 35 analyses if not previously darkened from oxidation by atmospheric oxygen.

If the results of analysis of several successive samples taken from the same place, as the same seal of a mine fire, show a continual trend toward decrease in carbon monoxide content, the cuprous chloride solutions should always be changed to ascertain whether the trend is due to actual decrease in the carbon monoxide content or due to the solution becoming worn out and leaving more and more of the carbon monoxide in the gas.

OPENING SAMPLE CONTAINERS

Although preliminary connections to sample containers may be made, no containers should be opened and the gases exposed to the displacing water (which will absorb carbon dioxide) until everything is in readiness to draw a sample into the burette. All containers should be opened under water and care taken to avoid contamination by air.

Open vacuum tubes by carefully making a file scratch on the shell tubing stem about midway between the point where the capillary

tip is attached and the body of the tube. Avoid excessive pressure on the stem lest it be crushed or break prematurely at the file scratch. Then, while holding the tube in a vertical position, tip down and end under water, break the neck at the scratch in a manner similar to the breaking of the tip in filling. To avoid the possibility of cutting the fingers, a handkerchief or rag may be used to grip the neck. If the vessel containing the confining water for displacing samples is not large enough to get the hand in, to grasp the tip for breaking, the tube may be broken by carefully striking the neck beyond the point where the file scratch has been made against the side of the vessel or against an iron rod or other object placed therein. In either event, take care to keep the open end under water, thus sealing it against contamination by air.

SUPPLY OF OXYGEN FOR COMBUSTION

If the ordinary compressed oxygen made from air or electrolytic oxygen contains less than 0.1 per cent of combustible gases, it is suitable for making combustion analyses. A convenient way to use oxygen is to fill a double-end sample container from the cylinder of compressed gas, place the container in water, and when oxygen is desired make a connection to n (fig. 10) similar to that described for connecting sample containers. The oxygen reservoir is connected to n only when it is desired to draw portions into the burette, and it should therefore be equipped with a screw clamp or pinch clamp for closing when not in use.

The sample container used as an oxygen reservoir may be filled with oxygen by just cracking the valve of a cylinder of compressed gas and inserting a 1-hole stopper in (or holding it against) the valve outlet. A short piece of glass tubing is inserted in the stopper for making the connection to the tube or reservoir. The exit end of the reservoir must be open when the compressed oxygen enters, and the containers must not be subjected to high pressures, as they will break and possibly endanger the operator. The filling may be done by air or water displacement; that is, by first filling the container with water and then displacing it with oxygen or by allowing the oxygen to flow through the container until all of the air has been removed.

PREPARING APPARATUS FOR USE

GREASING STOPCOCKS

When occasion arises to use the apparatus after it has been in storage for some time (refer to Care and Storage, p. 85) remove the stopcocks, being careful not to interchange them, and carefully clean out the paper strip if this has been used to keep the stopcocks from sticking. Do not scratch with iron or steel implements but use a copper wire

or wood splinter. If small particles of paper remain, soak them with water and remove the last traces of them by wetting the plug, inserting it in the barrel, and turning it a few times.

Heavy-grade vaseline may be used; in fact, it is recommended where solutions or water come in contact with the grease. However, if precautions are taken to prevent this contact with water, a rubber-beeswax-vaseline preparation¹⁴ will give a better seal and will need to be renewed less frequently than vaseline.

In greasing a stopcock remove the plug and wipe it and the barrel free from all water or grease. Then, by using a piece of copper wire bent at right angles or the end of an ordinary pipe cleaner remove particles of grease or dirt from the bore in the plug and from the outlets of the barrel. Wipe the barrel and plug again. Apply a thin uniform film of grease to the plug, remove any grease that may have entered the bore, insert the plug in the barrel, and turn it a few times, after which a transparent film should be formed throughout the barrel. If streaks occur, traces of either water or dirt were present or insufficient grease was applied. Remove the plug, wipe it clean of grease, regrease, and proceed as described.

Whenever streaks appear in the film when in use the stopcocks should be regreased before the next analysis is attempted. Also, in some instances grease will collect in the bore during use and form a plug that will cause a stoppage in the gas flow. In most cases the particular analysis can be finished by forcing the flow, but the cock should always be removed and regreased before the next analysis is attempted. When vaseline is used the cocks may become tight; this indicates that the film is too thin, and the cocks should be regreased even though the film appears clear.

Properly greased stopcocks are important in avoiding leaks and consequent errors in analysis.

FILLING THE BURETTE AND COMBUSTION PIPETTE

The water jacket and leveling bottles should be filled with clear water. Any water suitable for drinking purposes may be used. The leveling bottles *f* and *g* (fig. 10) should be nearly filled with water and enough of the colored 10 per cent sulphuric acid solution added to give the solution a distinctly sour taste and red color. (See Preparation of Solutions, p. 42.) The acid is desirable, although not entirely essential if the water is not normally alkaline or if none of the caustic solution or alkaline pyrogallate gets into the burette. If the displacing water is alkaline, it will absorb some of the carbon dioxide from the sample before the determination for that constituent is made, in which case less than the correct amount will be found.

¹⁴ For formula and method of preparation, see Burrell, G. A., and Seibert, F. M., Sampling and Examination of Mine Gases and Natural Gas: Bull. 197, Bureau of Mines, revised by G. W. Jones, 1926, p. 30.

The use of acid water will neutralize small amounts of the caustic, and the red methyl orange, which is an indicator, will lose its color when the water becomes alkaline, thus giving a warning of the condition. The red color also facilitates observing the level of the meniscus in making burette readings.

FILLING ABSORPTION PIPETTES AND MAKING RUBBER CONNECTIONS

Fill each of the pipettes about half full of the appropriate absorbing reagent and set them in the proper place in the apparatus. Loosen the manifold in its support, having previously cleaned the stems and greased the stopcocks. To avoid accumulation of caustic spray in the manifold wash it out occasionally with dilute acid water. This may be done conveniently at the time of removing the solution. Cut $1\frac{1}{2}$ to $1\frac{3}{4}$ inch pieces of 4 or 5 mm. (inside diameter) pure-gum tubing for each connection. The translucent type of pure-gum tubing is preferred, as entrapped bubbles of air or solution can be observed in the covered portions of the capillary glass tubing. Wet the inside and the ends of each glass tube with water or saliva and slip one piece of tubing half its length over each branch to which connection is to be made. Then carefully slip the other half over the end of the pipette stem (wetting the tube as before). This should be done carefully by twisting the tubing back and forth around the stem. Continue this until the end of the branch and the pipette stem are butted firmly together, then raise the pipette stand (if the apparatus has adjustable stands) and secure it in place. If all pipettes are to be attached at the same time, it may be easier to start each one and then work them all into place by successive operations (moving each a short distance at a time) than to slip the connection completely over the stem of each before connecting the next one. If the pipette stem is too long, cut it off by making a file scratch at the desired place and break it in a manner similar to that used in breaking the tips of the vacuum tubes used in sampling gases. Round off the sharp edges or spicules with a file or emery cloth. If the stem is too short and the apparatus is not equipped with adjustable stands, seal an extension on the stem or slip a small piece of capillary glass tubing into the rubber connection so that the gap between the end of the pipette stem and the manifold arm will be filled.

When all pipettes are in place the solution should be brought exactly to the mark on the stem. The cock should then be closed and the air discharged from the burette.

If there is not enough solution in the pipettes to draw to the marks, add to the pipette reservoir until about three-fourths to 1 inch of solution remains therein when the solution is at the mark on the absorbing side. Attach the air bags to protect the solution

from atmospheric air; but before attaching each bag blow air into it until there is perceptible inflation, pinch off the tube between the thumb and finger, and while holding it in this manner insert the stopper in the tubulure of the reservoir. Both alkaline pyrogallate and cuprous chloride solutions absorb oxygen, and if this inflation is not made the removal of the oxygen from the air in the reservoir will reduce the volume until it will be at negative pressure when the solution is at the mark on the pipette stem.

PROCEDURE FOR WITHDRAWING GAS FROM PIPETTES

Careful technique is required to withdraw the gas from the pipette and bring the liquid exactly to the mark on the pipette stems and at the same time to avoid drawing it into or through the stopcocks. If the latter is done in the course of an analysis, the liquid must be washed out of the manifold, because otherwise the gas would be exposed to traces of the particular reagent in the manifold and certain constituents would be prematurely absorbed, thereby causing erroneous results.

To withdraw the gas from the pipette, lower *f* rather quickly until the liquid in the pipette reaches a point about three-fourths inch below the rounded top. Then stop momentarily and hold the reservoir steady until the flow of gas nearly stops. This is necessary, because *f* may have been lowered fast enough to cause negative pressure in *e*. After this stop, continue to lower *f* but do so slowly and cautiously, working more and more slowly as the liquid reaches the stem. Now, with one hand on the stopcock to the particular pipette, lower the leveling bottle a little more and very carefully and slowly draw the liquid to the mark on the stem. As soon as it reaches the mark turn the cock.

FLUSHING OR CLEANING MANIFOLD

A good way to flush out the manifold if sodium or potassium hydroxide solution, alkaline pyrogallate, or cuprous chloride has been drawn up into the vertical stem above the cock is to transfer the first half of the gas to the combustion pipette and then pass the other half into the pipette to be cleaned out, with a little acid water from *f*. The combustion pipette is used because the composition of the gas will not be affected by absorbent. Also, as the combustion pipette contains acidified water the capillary stem need not be flushed out if the liquid is drawn through the stopcock. Close the cock, withdraw the half of the gas which has been stored, and run it into the pipette to be cleaned. This will drive the slug of water down through the cock. Finally, withdraw all the gas and proceed with the analysis. If, however, the reagent has been drawn up into the

horizontal part of the manifold, bring the level of the solution to the mark in the pipette in question, then open the cock to *d*, and pass the sample back and forth several times, each time running a little acid water from *e* to *d* and from *d* to *e* and finally withdrawing it to the mark on *d* and closing the cock. The gas is then passed into all pipettes that have previously been used, and the slug of water in the branches above the cocks is swept down into each pipette, as otherwise water would occupy space previously occupied by gas and the burette reading would be increased. The gas should not be passed into pipettes that have not been used previously, because some of the constituents, if present, would be prematurely absorbed. All that can be done with slugs in these cases is to allow them to remain and estimate the error they might cause. At the most the error will not be more than 0.1 to 0.3 c.c. In some cases it is possible to store the sample in the combustion pipette, close the cock, draw in a burette full of air, remove the oxygen, use the nitrogen residue to sweep out the slugs of water, and then discard the nitrogen. This causes the loss of the small volume of sample that occupies the manifold dead space but does not markedly alter the results from a practical standpoint.

The procedures just discussed for flushing out manifold or pipette stems are intended mainly to save an analysis. This may be very desirable if there is not enough sample available for a second trial or if the results are needed immediately. If time permits, however, and enough sample is available for another trial, it is best to remove the manifold, wash it out, and regrease the stopcocks.

REMOVING RESIDUALS OF PREVIOUS SAMPLE

Precaution should always be taken to avoid contaminating a sample during analysis by air or oxygen or the residuals of the previous analysis left in the capillary stems or dead space of the apparatus. For example, if the previous sample contained 30 per cent or more of methane, enough may be left in the capillary stems of pipettes *b* and *c* (for oxygen and carbon monoxide, respectively) to be picked up in the course of a succeeding analysis and cause a significant error if the latter contains a relatively low amount of methane. This methane in the capillary stems was lost from the previous sample, but the error is not usually significant with amounts as large as 30 per cent.

In the combustion procedure the methane trapped below the stopcock of the stems to pipettes *b* and *c* can not be picked up as in *a*, where it is picked up during the absorption of CO_2 which follows the combustion (see Determination of Methane, p. 62) and is then burned during the second combustion. The absorbents in pipettes *b* and *c* (alkaline pyrogallate and cuprous chloride, respectively)

absorb oxygen; and, if the gas after the first combustion is passed into them to sweep out the stems, some of the oxygen present for the combustion will be absorbed and will thereby vitiate the combustion data for methane.

In the analysis of all samples such as mine-fire samples for which the oxygen content is of marked importance, precaution should be taken before starting the analysis to purge all connections to the apparatus, the manifold, and the stem of pipette *a* below the stopcock of all oxygen or air which may be present usually as a residual from the preceding analysis. There is no need to purge the stems to *b* and *c* of oxygen, as the absorbents in these remove oxygen. However, they should be purged to remove methane residuals. If the manifold and the stem to *a* are full of oxygen from the preceding analysis, there may be a positive error of as much as 1 per cent for oxygen.

To eliminate these and similar potential contaminations it is good practice to purge the apparatus after each analysis. This may be done by discarding the residual from the previous analysis in the usual manner, then drawing in a 50 c. c. sample of air and passing it directly into pipette *b* until the oxygen has been removed. The alkaline pyrogallate in pipette *b* will also remove any carbon dioxide that might be present. Then pass this nitrogen residue once into all other pipettes in turn and discard it. The entire capillary space of the apparatus will now be filled with nitrogen containing only insignificant traces of other gases. However, the analyst familiar enough with the various steps in the procedure can evaluate the extent of contamination from these sources and judge which are negligible in particular cases.

For example, if with a particular apparatus the capillary stem below the stopcock and above the level of the liquid in the stems is small or the concentration of the contaminating constituent therein is relatively low or both, there will not be contamination enough to affect the results from a practical standpoint; accordingly, it will be unnecessary to take precaution further than to sweep out the manifold above the stopcocks during the process of drawing in and discarding some of the sample as described under Analytical Procedure, page 57. This eliminates the time and wear on the alkaline pyrogallate solution caused by taking out the oxygen and sweeping out the stems.

ADJUSTING TEMPERATURE OF PLATINUM COIL AND REPAIRING BROKEN COILS

In adjusting the temperature of the platinum coil the operator should start with less than the estimated voltage, increase the amount until the wire becomes red hot, and then increase it further until the wire assumes a yellow tinge. A mere red heat will burn methane

slowly and will thus tend to give low results; or in "feeding in" an explosive mixture, described later, the operator will be misled into thinking that the methane is burning and he is averting an explosive mixture whereas the methane is not being burned and an explosive mixture is accumulating in the combustion pipette. A slight rise in the temperature, either of spontaneous origin or due to a change in resistance, will cause an explosion. This nearly always destroys the combustion pipette and adjoining pipettes and breaks the manifold, not to mention the danger to the operator from flying glass. *Always keep the wire heated until it shows a yellow tinge. If adjustments of temperature are necessary, do not try to make them while gas is going into the pipette. Stop gas flow and then make adjustment before resuming gas flow. See precautions given under Procedure for Methane, page 64.*

The platinum coils used to burn the gas frequently break or melt, due to excessive heating. In some cases they may be temporarily repaired by merely twisting the broken ends together, but if the wire has been in use for a considerable time it may be brittle and may break on being twisted. In repairing the coils, remove the pieces where they are fastened to the leads at the end of the tubes, straighten each piece, and join the ends by a short tight splice.

When the ends are joined, wind the coil evenly around a $\frac{5}{32}$ or $\frac{3}{16}$ inch mandrel made from a glass tube, bolt, or piece of wood and then carefully attach each end firmly to the leads. Replace the assembled coil in the pipette and adjust its height until the top of the coil is about one-half inch (see fig. 1) from the top of the pipette and directly under the capillary opening to the stem.

As the length of the wire in the coil has been shortened, it will have less resistance than before, and it will be necessary to increase the resistance through the rheostat before heating it the first time; otherwise the coil will be fused.

To avoid possible delay in making important analyses, several linear inches of No. 28 or 30 B. & S. gage platinum wire should be kept on hand. A new platinum coil can be made in a few minutes by winding a 3-inch piece on a mandrel as just described. About three-eighths inch of each end is used for attaching to the leads.

TESTING APPARATUS FOR LEAKS

If an apparatus has not been used for some time or if new connections have been made, it should always be tested for leaks before an analysis is begun. Likewise, it may be desirable to make occasional tests before analyzing very important samples or if there is an apparent nonagreement of duplicate results of analysis.

Open *p* to connect to the outside through *n* and discard the gas from the burette by raising *f* until the water just reaches *h*. Immediately lower *f* and draw in 15 to 20 c. c. of air and again discard

the gas by raising f . This washes or sweeps the original gas from the manifold. Now lower f and draw in about 50 c. c. of air, close cock p , and by raising f and opening the cock to b pass the gas into b and absorb the oxygen and traces of carbon dioxide. The nitrogen is then passed once into each pipette, and the liquids in turn are carefully brought to the marks on the stems. Discard the gas through n until the water in e just reaches h . Immediately lower f and draw in 95 to 100 c. c. of normal air, allow the burette to drain one minute, and read the volume accurately. Now raise the leveling bulb as high as possible and hold it there for two or three minutes. Return the bulb to its position near the 100 c. c. mark, allow it to drain one minute, and again read the volume. If the reading is the same as the previous one, plus or minus 0.2, the apparatus may be considered free from leaks in the burette connections and stopcocks.

The sample of air is then subjected to a complete analysis by passing it into the various pipettes (including the combustion pipette) according to the regular procedure. If the results obtained are within 0.2 per cent of the composition of normal air—that is, carbon dioxide, 0.03; oxygen, 20.93; carbon monoxide, 0.00; and nitrogen, 79.04 per cent—the apparatus with but few exceptions can be considered in good working condition. The operator should remember that if this air test is conducted in a mine where the sample is taken from a room or in a return air course where the air may contain some black damp, the results obtained will vary from those for normal air. *No tests involving combustion analyses should be conducted underground or in other places where there may be combustible gases or vapors; also the battery equipment for combustion analyses should not be taken underground.* The use of the electrically heated platinum spiral presents obvious sources of ignition and can be considered similar in effect to open lights or flames.

If, however, the pressure test on the burette reveals a decrease in volume greater than 0.2, a significant leak has occurred. The test (raising f with all stopcocks closed) should then be repeated, using the same sample of gas and noting if there is additional decrease in volume. If the original loss was only slightly greater than 0.2, the burette may have been read erroneously, and this may be apparent after the second test.

However, if the second reading shows a further decrease in volume, the apparatus is apparently leaking either at the burette connection or around the stopcocks. If it is leaking at the pipette cocks, it is usually due to circular channeling in the grease, and the liquid in the stem of the faulty cock will drop below the mark. Should this occur, the particular cock or cocks should be regreased, after which the liquid should be drawn back to the marks as before. If no

evidence of a leak is apparent through the falling of the liquid in the stems of *a*, *b*, *c*, and *d*, cock *p* should be regreased; and if this does not remedy the condition, the rubber connection to the burette and to *c*, if it is of the bubbling type, should be replaced. The proper size of pure-gum tubing usually fits tightly if the glass tubes are clean, and there should be no difficulty in making a tight joint if the lap over each end of the capillary stems is approximately $1\frac{1}{2}$ to $1\frac{1}{2}$ inches. However, if the leak appears to be at the connection, the tubing should be examined for holes, especially at the seams. If none are found, the hose should be replaced or ferrules made at about the mid-point of each end by wrapping them with either two or three turns of soft copper wire, several turns of rubber band, or string, drawing it tight and twisting or tying the ends.

If no leaks occur in the pressure test but the results of analyzing the sample of air fail to agree closely enough with those for normal air, one of three things may be the cause: (1) Leaks at the pipette connection, (2) poor or worn-out solution if the error is in the oxygen value, or (3) wrong technique or procedure. In making this test analysis the percentage of each constituent should be calculated immediately after each successive step in the procedure, in which case the occurrence of error is noted at once, and certain tests can be made to ascertain the cause. The first thing to do is to see if the liquid has been brought exactly to the mark on the pipette stem and to check the burette reading. If no apparent error has been made in measurement, the following methods should be tried to ascertain the cause: (1) If the percentage is too low, as with oxygen or carbon dioxide, the sample should be passed again into the solution, as the error might be due to incomplete absorption, and more passes should be employed or the solution changed. (2) If the percentage is too high or continues to increase or decrease with successive passes into the same reagent, the cause is leakage. In most cases the leak is in the connection to that particular pipette or there is a leaky stopcock, but leakage is sometimes due to unusual causes, such as one of the tubes inside the pipette sliding down into the opening below and when gas is rapidly forced into the pipette some of it being driven down this tube and traveling around the U connection into the reservoir in the back. The presence of carbon monoxide indicates incomplete removal of oxygen and an increase in the volume of the gas after it passes into the acid cuprous chloride pipette may be due to incomplete removal of the acid vapor. Leaks in the combustion pipette may be due to faulty connections or to cracks in the tubes which support the platinum wire if the type which has an incased copper wire lead is used. These leaks can usually but not always be discerned by water entering the inside of the glass tube which incases the leads.

CONNECTING SAMPLE CONTAINER TO APPARATUS

OPENING SAMPLE CONTAINERS

If double-end tubes are used for containers, fill the capillary or the rubber hose of one end of the sample container with water to expel the air and place it in a vessel of displacing water. (See fig. 15.) The displacing vessel should be larger in diameter than the container and at least two-thirds as deep. An ordinary water bucket, crock, etc., is suitable. If the tube tends to float horizontally, fasten it in a vertical position by tying it with string or wire. The temperature of the water should be about the same as that of the room or slightly higher, otherwise the gas will be cooled suddenly and will contract in volume, which augments conditions for inward leaks of air. Connect the other end (keeping it closed) to *o* (fig. 10) by a short piece of small

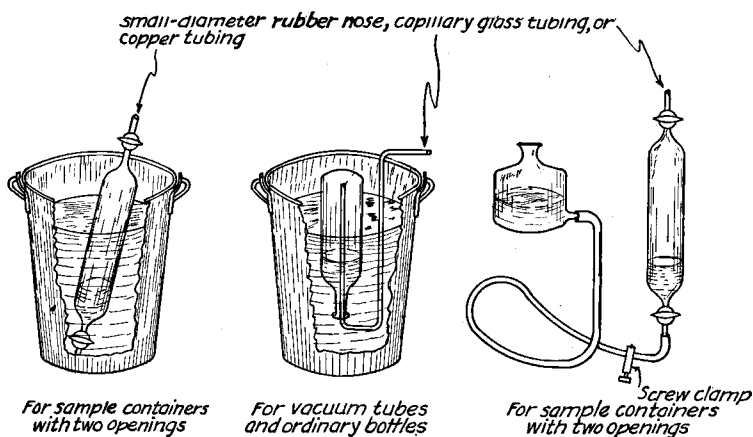


FIGURE 15.—Suggestions for removing sample from container

(inside diameter approximately three-sixteenths inch) rubber tubing. If available, 2 mm. capillary glass tubing is better, as it holds a smaller volume of dead air. In using the latter make slip connectors to the sample tube by using pure-gum tubing.

If the samples have been collected in magnesium citrate bottles, ordinary bottles, or vacuum tubes, it is necessary to insert a tube or hose into the neck of the bottle while it is in an inverted position with the neck under water. A U tube made from $\frac{1}{8}$ -inch inside diameter copper tubing or 2 mm. capillary glass tubing, one arm of which is a little shorter than the depth of water in the bucket or vessel, is more convenient than a rubber hose. With one arm of the U tube connected to *o* in the manner described above and with as short a piece of hose as possible, hold the other end about 1 inch under water and insert it in the container opening by bringing the latter over the top of it but without breaking the water seal, as that would contaminate

the sample with air. When the arm has been inserted allow the container to sink as far as it will and then fasten it in an approximately vertical position. If this is not done and the displacing water vessel is wide, the bottles will tend to float horizontally, and the water seal may become broken. The container should not, however, be fastened tightly enough to prevent its sinking farther in the water when gas is removed.

In using ordinary bottles or vacuum tubes a means of closing the connecting tube where it is attached to *o* should be provided if the type of stopcock shown at *p*, Figure 10, is not employed, so that the sample container may be closed after the first sample is withdrawn and the remainder of the sample preserved for a duplicate analysis. The most convenient arrangement is permanently to attach a 1-way capillary stopcock to *o* by means of a short rubber connection. However, a screw clamp will suffice or the short arm of the U tube or hose may be removed from the neck of the container, although the latter is somewhat inconvenient and wastes the sample. As stated, this closing device is not needed if the type of cock shown in *p* (fig. 10) is used.

The end of the connection between the sample container and *o* should always be closed either by a screw clamp or by previously connecting to *o* with *p* closed before inserting the hose or U tube in the sample, otherwise the sample may be lost or become contaminated.

ANALYTICAL PROCEDURE

PREPARATION

Before starting an analysis take care of all preliminary items such as greasing stopcocks, purging the dead space of air or residuals from the previous analysis, and adjusting the filament current and supply of oxygen for combustion (if oxygen is needed). These operations have previously been described in detail.

OBTAINING SAMPLE

Bring the solutions in pipettes *a*, *b*, *c*, and *d* exactly to the marks on the capillary stems and close the cocks. Connect the sample container to *o* by any suitable means, as shown in Figure 15, and have the stopcock *p* closed between *o* and the sample. With *p* open to *n*, raise *f* until the water just reaches *h*, turn *p* to connect with *o*, lower *f*,¹⁵ open all connections to the tube, and allow gas to flow

¹⁵ In using vacuum tubes or bottles where a U tube (see p. 56, Connecting Sample Container to Apparatus) is required to withdraw the gas, the latter will be filled with water which would be drawn into the manifold ahead of the gas. This can be avoided by closing the hose to *f* with a screw clamp when the water is at *h*. Open the cock to *d* and lower *g*. Then open connections to the sample container and draw off water and a little gas into *d*. Close cock *p* to the sample container and turn *p* to connect through *n* to the exterior, raise *g*, and discard the gas. Bring the water to the mark and close the stopcock to *d*. Now turn *p* to again connect to *o* and proceed in obtaining a sample as given herein.

from the sample container through *o* into the burette. When about 20 c. c. of gas has been drawn into the burette turn *p* to connect the manifold with the exterior through *n*, raise *f*, and discard the gas through *n*. As soon as the water reaches *h* close *p* to *n*. This sweeps out the gas left in the manifold from the preceding analysis, which, if not removed, would probably give high results for oxygen.

Avoid waste of gas in flushing connections or purging the apparatus. With the ordinary 250 c. c. sample it is necessary to use the gas sparingly, otherwise there will not be enough for duplicate analyses.

Turn *p* to connect to the sample through *o*, lower *f* until the water falls approximately to the lowest division on the burette, pinch off the leveling-bottle hose (between *e* and *f*) with the thumb and finger, and quickly close stopcock *p*. Release the hose, and with *f* on the table or at approximately the height of the bottom of *e* allow one minute for the water to drain from the sides of the burette, then read the volume according to the instructions given under Reading Gas Volume With the Burette, page 37. If the volume is 100 c. c. or less, record it and proceed with the next step in the analysis. If the volume is more than 100 c. c. (which falls below the lowest graduation mark and hence outside the range of measurement with the burette), raise *f*, at the same time observing the meniscus; and when the latter coincides with 100 c. c. again pinch off the hose. Now turn *p* to open the manifold momentarily to the exterior through *n* and allow the excess gas to escape. Close *p* and read the volume, which should be recorded as "original volume of sample." The sample is now ready for absorbing the first constituent, namely, carbon dioxide.

DETERMINATION OF CARBON DIOXIDE

Since mine atmospheres always contain carbon dioxide the procedure for determining that constituent must be followed, even though the results may not be desired.

Raise the level of the water in *f* a little higher than that in *e* to insure against drawing solution over from the pipette, open the cock to the sodium or potassium hydroxide pipette *a*, and pass the gas into *a* by raising *f* until the level of the liquid is near but not above *h*. Allow the gas to remain three to five seconds in *a* for contact and then withdraw it by lowering *f* until the solution in *a* is about one-half inch below the stem. Immediately raise *f* again and pass the gas back into *a*. Repeat this procedure five or six times. It is not necessary each time a pass is made to bring all of the gas out of the pipette or to raise the level of the water in *e* exactly to *h*, as five or six passes will eventually allow contact of all of the gas with the reagent and avoid the danger of drawing or forcing liquid into the manifold. When five or six complete passes have been made withdraw the gas and bring the liquid exactly to the mark on the stem

of *a*, being careful not to draw it into the stopcock of the manifold. (See p. 50, Procedure for Withdrawing Gas from Pipettes.) Close the cock, allow the burette to drain one minute, and read the volume. Beginners should now repeat the entire procedure for absorbing carbon dioxide to ascertain if complete absorption has been effected. (If any carbon dioxide escapes absorption at this time, it will be removed during the determination of oxygen by the alkaline pyrogallate, and the amount of carbon dioxide will not only be too low but the oxygen will be erroneously increased.)

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

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

For example, if the original sample volume was 98.85 c. c. and the volume of sample after absorbing the carbon dioxide 95.30, the calculation is as follows:

$$\text{Volume of carbon dioxide} = 98.85 - 95.30 = 3.55 \text{ c. c.}$$

$$\text{Per cent of carbon dioxide} = \frac{3.55}{98.85} \times 100 = 3.6.$$

Actually, the percentage found is 3.59, but as the error of the portable Orsat method is approximately 0.2 for this determination it is useless to report figures closer than the nearest tenth; in fact, it is misleading to report results in the second decimal place.

DETERMINATION OF OXYGEN

If the sample does not contain carbon monoxide and a direct determination of oxygen is not desired, the procedure for determining oxygen can be omitted. The determination of oxygen must be omitted at this time if it is desired to use the special procedure described on page 79 for methane in normal mine air containing less than 5 per cent methane and more than 14 per cent oxygen.

Again raise *f* a little above the level of the liquid in *e*, open the stopcock to *b*, and pass the gas into the alkaline pyrogallate solution in the manner described for carbon dioxide. Alkaline pyrogallate solution does not remove oxygen from a gas mixture as rapidly as the sodium or potassium hydroxide solution removes carbon dioxide, consequently more contact must be allowed between the solution and the sample. Eight or nine passes are usually enough. An experienced analyst can ascertain from the color of the solution as it drains down the pipette whether or not a sample contains oxygen and when it is nearly all absorbed. If the thin film of solution on the walls of the pipette as the solution recedes is a deep brownish

red, it indicates a reaction with oxygen; but if it is greenish, little or no oxygen is present. Hence, if oxygen is present in the sample, the film will first be reddish and later turn to the green when nearly all the oxygen has been absorbed. After the latter is noted two or three more passes are usually enough to complete the absorption.

Upon completing the absorption draw the solution to the mark, close the cock, allow the burette to drain one minute, and read the volume. Beginners should repeat the procedure to insure complete absorption. This check should be applied especially after the alkaline pyrogallate solution has been used for a considerable number of analyses. If all of the oxygen is not removed, it will be absorbed later by the solution used for determining carbon monoxide, and the results of analysis will not only be low for oxygen but also high for carbon monoxide. In the latter case an error is usually of marked significance.

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

The method for calculating results to a percentage basis is the same as that previously given for carbon dioxide.

$$\text{Per cent of oxygen} = \frac{\text{Volume of oxygen}}{\text{original volume of sample}} \times 100.$$

DETERMINATION OF CARBON MONOXIDE

If the sample does not contain carbon monoxide or less than 0.2 per cent, which is within the limits of error of the portable Orsat, the procedure for carbon monoxide can be omitted. Traces of carbon monoxide can be determined in another sample or remaining portion of the same sample by use of the pyrotannic method. (See footnote 10.)

If the ordinary type of pipette filled with glass tubes, similar to those for carbon dioxide and oxygen, *a* and *b*, is used for the carbon monoxide absorbent (acid cuprous chloride), the gas is passed into *e* in the manner already described for carbon dioxide and oxygen, and after six or eight passes it is completely withdrawn and measured as before.

If the bubbling type of pipette is used, the 2-way cock is turned to connect with the short arm, and a little gas is forced over to displace the solution so that it will not be drawn up in the manifold later. The cock is then turned through 180° and the remainder of the gas slowly forced out the long stem in a stream of small bubbles. When the liquid in *e* reaches *h* the cock is turned back through 180° and the gas is withdrawn through the short arm; the analyst should be careful not to draw the solution into the cock or manifold. As it approaches the top of the pipette the cock is again turned through 180° and the gas forced into the pipette as before. This procedure

should be repeated five or six times, after which the liquid should be drawn to the mark in each arm. The carbon monoxide is now absorbed, but the residual gas may contain hydrochloric acid vapors given off by the acid cuprous chloride solution. The water in the burette will absorb the greater part of these vapors, but to insure removal of the final traces the gas should be passed two or three times into pipette *a* in the manner described for carbon dioxide, after which it should be withdrawn and the volume read and recorded. Any carbon monoxide that is not absorbed by the cuprous chloride will be determined later with methane in the combustion analysis. However, with mine atmospheres the amount is usually so small that the effect on the amount of methane is not very significant.

The volume of sample after absorbing the carbon monoxide and removing the acid vapors subtracted from the volume after absorption of oxygen equals the volume of carbon monoxide.

The method for calculating results to a percentage basis is the same as that previously given for carbon dioxide.

$$\text{Per cent of carbon monoxide} = \frac{\text{Volume of carbon monoxide}}{\text{original volume of sample}} \times 100.$$

As discussed under Life of Solutions, page 45, cuprous chloride is not a very satisfactory reagent for gas analysis, and no great dependence can be placed on the results when the amount present is under 0.3 per cent and then only when care is taken in the analytical procedure. Any results below that amount (including 0.0) are not dependable, and in view of the significance of even considerably lower amounts from the standpoint of health or the progress of a mine fire percentages below 0.3, including 0.0 per cent, should be checked by the pyrotannic method. (See footnote 10.) This method gives a positive lower limit of detection of 0.01 per cent of carbon monoxide and an upper limit of approximately 0.15 to 0.20 per cent.

Cuprous sulphate beta naphthol solution is a more satisfactory absorbent than cuprous chloride for carbon monoxide in mine gases, as it removes carbon monoxide more completely. The action is slower than that of cuprous chloride, although this is not important when dealing with the relatively small amount of carbon monoxide present (usually less than 2 or 3 per cent by volume). Cuprous sulphate beta naphthol is, however, much more expensive than cuprous chloride, is difficult to make, and has the further disadvantage that on standing or when exposed to cold temperatures a suspension settles out which "plugs" the pipette at the curved connection at the bottom and the long stem of the gas inlet tube if the bubbling type of pipette is used. The bubbling type of pipette is recommended, however, as the bubbles of gas stir the suspension, and when analyses are made frequently no settling difficulties are experienced. It is

recommended for investigations where a large number of analyses are to be made; but it is not thought suitable in all respects for field apparatus where only occasional analyses are made, unless the analyst removes it each time after completing the particular work and preserves the solution in a well-stoppered bottle.

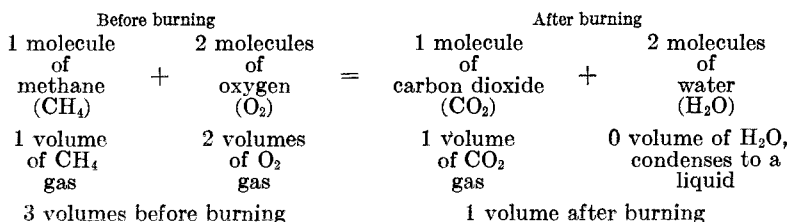
DETERMINATION OF METHANE

The following warning should be made at this point: *During a combustion analysis a wire gauze should always be placed around the pipette, and the operator should stand in such a position as to be protected from flying pieces of glass in case of an explosion. Moreover, no combustion analyses should be made or combustion-analysis equipment in the form of dry cells, batteries, etc., taken underground or any other place where there might be inflammable gases or vapors.*

Methane can not be absorbed readily like carbon dioxide, oxygen, and carbon monoxide, hence it is determined by slow combustion with oxygen in the presence of a hot platinum coil. In this manner the methane is changed to carbon dioxide and water, and the oxygen is consumed, resulting in a definite volume change that can be measured similarly to the changes attending the direct absorption of constituents. Also, by combustion the unabsorbable methane is converted to absorbable carbon dioxide which can be determined as previously described for that constituent.

The chemical reactions involved in the determination of methane are as follows:

Chemical reactions involved in combustion of methane



It will be noted that 1 molecule of methane required 2 molecules of oxygen to burn it, and in burning it forms 1 molecule of carbon dioxide and 2 molecules of water vapor. As the water vapor condenses and occupies a negligible space, the carbon dioxide is the only measurable product of combustion. As a net result, 2 volumes of gas are lost from the burette for each volume of methane burned. From this it follows that the loss or contraction on burning is twice the volume of methane burned, and the contraction in cubic centimeters should be divided by 2 to obtain the number of cubic centimeters of methane burned.

From the same equation it is also evident that 1 molecule of methane forms 1 molecule of carbon dioxide, and it follows that 1 volume¹⁶ of methane will form 1 volume of carbon dioxide. This carbon dioxide can be absorbed by the potassium or sodium hydroxide solution pipette *a*, Figure 10, and the loss or contraction on absorption will be directly equal to the amount of methane present.

The technique involved in the determination of methane is a little more difficult than that for carbon dioxide, oxygen, or carbon monoxide. First, as the oxygen has already been removed, oxygen in the form of pure gas or air must be added to the sample, and with samples containing large amounts of methane it must be added so as to obviate the possibility of an explosive mixture being formed in the combustion pipette. To make space for this oxygen it is usually necessary to discard a portion of the residual gas after absorption of carbon dioxide, oxygen, and carbon monoxide. All of these operations require careful technique to obtain satisfactory results and especially to avoid an explosion in the combustion pipette when explosive mixtures of gases are analyzed.

As the total volume of sample plus air or oxygen that can be conveniently handled in the apparatus in most cases is 100 c. c., the ideal conditions to minimize errors of manipulation as much as possible would be to employ the maximum amount of sample and the minimum amount of air or oxygen to burn the methane completely and yet keep the volume within the 100 c. c. limit. The ideal condition, however, can seldom be attained, because it implies an accurate estimation of the amount of methane present; nevertheless it can be approximated closely enough for practical purposes from the conditions under which the sample was taken, from the analysis of previous samples taken from the same or similar source, or, if convenient, from examination of the gases with the flame safety lamp. Whether or not the sample contains an explosive mixture of gas or a mixture that will be explosive when diluted with the necessary amount of air or oxygen for combustion is of primary importance in selecting the technique of analysis, as described later.

The amount of methane should not be estimated within close limits, unless preliminary trial analyses on which to base the estimation have been made. It is always better to be liberal in the amount of the air or oxygen in the first analysis of a sample, and if the results obtained indicate that a significantly larger volume of sample and less air or oxygen can be used a duplicate analysis governed by the results of the first can be made.

¹⁶ A volume means any unit quantity such as cubic centimeter, cubic inch, cubic foot, etc.

PROCEDURE FOR DETERMINATION OF METHANE

If the sample contains no methane or if analysis for methane is not desired, the procedure can be omitted. The following procedures are designed for residuals of samples from which the oxygen has been removed, either in making a direct determination of oxygen or as a necessary procedure for the determination of carbon monoxide. For the determination of methane in normal mine air which contains less than 5 per cent methane and more than 14 per cent oxygen, the special procedure described on page 79 is used.

In general, the technique employed for the combustion of methane with oxygen depends, as already stated, on whether or not the samples contain an explosive mixture of gases or a mixture that will be explosive when diluted with enough air or oxygen for complete combustion. For practical purposes the samples may then be divided into two main classes: (1) Samples containing less than 5 per cent of methane, and (2) samples containing 5 per cent or more of methane.

Samples containing less than 5 per cent of methane.—If previous analyses or tests with a flame safety lamp indicate that the amount of methane is below 5 per cent (the lower explosive limit of methane), analysis consists merely in mixing the residue left after removal of carbon dioxide, oxygen, and carbon monoxide¹⁷ with enough oxygen or air to burn the methane completely. Attention should be called to the fact that observers using the flame safety lamp for testing gas mixtures sometimes err in giving information regarding the amount present. The gas laboratory at the Pittsburgh Experiment Station of the bureau has occasionally received samples with the advice that "the methane content was near the explosive limit," which in practice means the lower limit or 5 per cent, whereas during analysis it was found to be near the upper explosive limit or 15 per cent.

After completing the determination of carbon monoxide, raise *f* to about the height of *h* and slowly discard a portion of the sample from *c* by opening *p* slightly to connect with *n*. Keep one hand on cock *p* and, as the water level in *e* reaches the 45 to 50 c. c. mark, close *p* quickly. The expulsion of gas should be continuous after cock *p* has been opened and until it is again closed, otherwise air may be drawn back into the sample. Measure the residual volume of gas in the usual way and record the volume. The burette does not need to drain, as the sides above the level of the liquid in *e* have not been wet. Now lower *f* to a point below the lower end of *e*, open *p*, and slowly but continuously draw in air until the level of the

¹⁷ This refers especially to samples from mine fires and explosions. With other samples which do not contain carbon monoxide or where a determination of oxygen is not desired, as described later under Summarized Procedure for Various Types of Mine Atmospheres, the combustion procedure can follow the carbon dioxide or oxygen absorption. See page 76 for detailed procedure.

liquid in *e* is between 95 and 98 c. c. Close *p*, allow one minute for draining, and read and record the total volume.

If oxygen is used instead of air for combustion, it will be necessary to have space for only about 12 or 14 c. c. (including excess) of oxygen, and it may not be necessary to discard any of the sample or at least not to less than 45 to 50 c. c. before drawing in the oxygen. Some analysts use only 85 to 90 c. c. as an initial volume for samples of this type, in which case enough room in the burette for oxygen is assured. Also, after the analyst has become familiar with gas-analysis technique and methods of calculating the quantity of air required for combustion, as described in the procedure to follow, he can use a larger proportion of residual to air than given above, provided the samples are known to contain only 1 or 2 per cent of methane. In either event the final mixture must contain twice as much oxygen or 10 times as much air (plus a small excess) as there is methane in the sample to be burned. The pure oxygen may be obtained by filling ordinary sample containers from a cylinder of compressed gas (hydrogen-free) and then drawing it out of the containers in much the same method as that used to obtain a sample of gas except that the oxygen is drawn in through *n*. Table 1 (p. 72) gives practical proportions of air or oxygen to sample for combustion analysis.

Also, if none of the sample has been discarded, the method of calculation given later for changing the volume of CH_4 found in a portion of the sample to a value representative of the entire sample may be omitted. However, oxygen is not always available or is bothersome to obtain, and for samples containing less than 5 per cent of CH_4 the procedure described for air is entirely satisfactory.

After the air or oxygen has been added and measured raise *f*, open the cock to *d*, and pass all of the gas into *d* to mix thoroughly the residual gas and the air or oxygen. Then withdraw the gas from *d* until the water is about one-half inch below the top of the tubes that support the platinum coil and close the cock to *d*. Place a pad of wet cotton around the stem and over the rounded top of *d* and a wire gauze around the pipette. (See fig. 16.) Stand a little to one side to avoid flying glass in case an error has been made in estimating the amount of methane present, close the switch and heat the platinum coil, and adjust the current if necessary until the temperature of the coil passes through the red-heat stage and appears to have a tinge of yellow. Now open the cock to *d* and pass in the remainder of the gas at the rate of about 15 c. c. per minute. After all of the gas has been passed into *d*, allow the burning to continue two minutes, meanwhile dripping water on the pad from a medicine dropper, glass tube, or another cotton pad used as a sponge. At the end of two minutes draw about one-half or two-thirds of the gas out of the pipette. Do not raise the level of water in *d* above a point approximately one-half

to three-fourths inch below the top of the coil supports, otherwise the supports may be cracked by sudden cooling. Pass the gas back into d , immediately repeat this three times, then allow the gas to remain in the pipette about one minute, open the switch, and allow the pipette to cool until it is only perceptibly warm. Then withdraw the gas, bring the liquid to the mark on d , close the cock, wait one minute for draining, and read and record the volume. The difference between this volume and the total volume after adding air to the sample is the contraction produced by burning the methane and any other combustible gases.

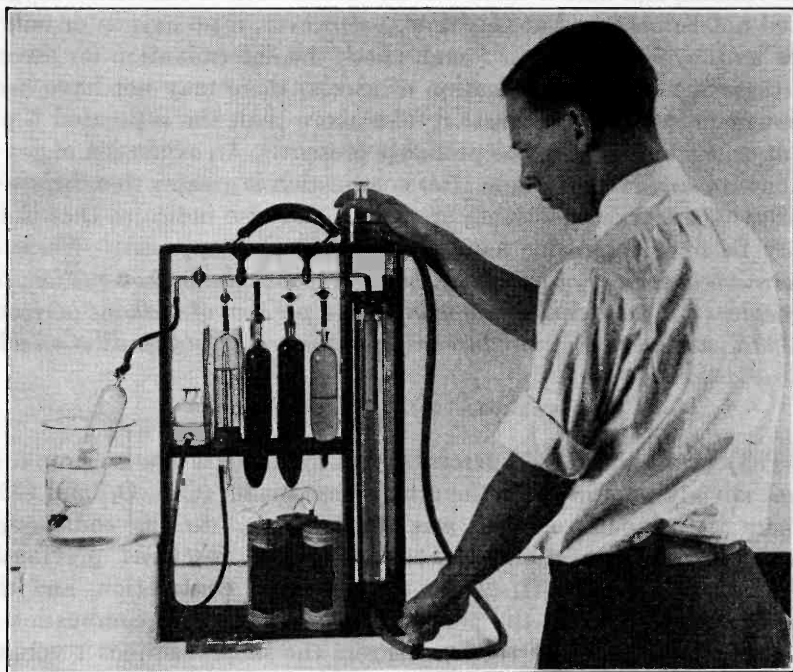


FIGURE 16.—Apparatus with gauze around pipette and ready for combustion procedure

The carbon dioxide produced by the combustion is now determined by passing the gas into a in the manner previously described for carbon dioxide, except that after the third or fourth pass about three-fourths of the gas is withdrawn from a and the cock closed. This gas, which is practically free from carbon dioxide, is then passed into d and immediately withdrawn to pick up the carbon dioxide-laden gas in the manifold and connections to d . After bringing the liquid to the mark and closing d , open the cock to a and continue the absorption of the CO_2 . Read the volume in the usual way and record the result. The difference between the volume after combustion and the volume after absorbing the carbon dioxide is the carbon dioxide

formed by combustion of methane and the traces of CO that may have escaped absorption. The latter is usually a negligible amount. If the analysts are just learning the procedure or if the results are apparently erratic, the entire combustion procedure should be repeated, but it may be carried out more rapidly than before. Contraction on burning or CO₂ produced by the second combustion procedure should be added to the respective values previously obtained.

After completing the combustion analysis, pass the gas into *b* two or three times in the manner previously described for oxygen, measure the volume, and note if there was an excess. All of the excess oxygen need not be absorbed at this time. However, if no oxygen or only a few tenths of 1 per cent is found, check the determination for excess. If there is no further indication of excess, there may not have been enough present for combustion; also more than the estimated 5 per cent or less of methane was probably present. An expansion of gas—that is to say, if the volume after combustion is greater than before—indicates a marked deficiency in oxygen and also indicates that there may be much more methane than previously supposed. *Whenever there is a deficiency of oxygen or the gas expands during combustion, the procedure for gases containing more than 5 per cent of methane is recommended, as an explosive mixture might be formed by further dilution with air or oxygen.*

CALCULATION OF METHANE

The calculation of the percentage of methane is not as simple as that already described for the other constituents (CO₂, O₂, and CO), where the amount of each was exactly equal to the contraction produced by absorption. According to the reactions previously given, 1 volume of CH₄ causes 2 volumes of contraction, and the volume of methane in the portion of sample used for combustion is always one-half the contraction. From the same reactions 1 volume of carbon dioxide is formed for each volume of methane present, and the volume of carbon dioxide found after combustion is equal to that of the methane in the portion of sample taken for combustion. In view of this one might ask, why not take only the contraction and divide it by 2 or take carbon dioxide alone as a measure of the amount of methane? The reason for not taking one or the other alone is that during combustion some of the carbon dioxide formed goes into solution in the water in both *d* and *e*. It is thereby lost to the residual gas mixture after combustion, and the contraction as found is not really the contraction due to burning the methane but is the true contraction plus a certain amount of contraction due to some of the carbon dioxide being dissolved. Thus, the contraction, as found, divided by 2 would give a result for methane that is too high. Also,

the volume of carbon dioxide found after combustion is smaller than it should be, because some of it was taken up by the water before the absorption analysis was made. Consequently, this volume would represent less methane than was present. These errors, however, will be compensating; and the true volume of methane will be found if the contraction in volume produced by burning, which is too high, and the contraction produced by absorbing the CO_2 after burning, which is too low, are added together and the sum divided by 3.

When the methane containing the residue from all of the original volume of sample is taken for combustion (none discarded) no further correction is necessary, and the calculation of the percentage of methane in the sample is as follows:

$$\frac{\text{Total contraction on burning} + \text{total carbon dioxide formed}}{3} = \text{volume of methane.}$$

$$\text{Per cent of methane} = \frac{\text{volume of methane}}{\text{original volume of sample}} \times 100.$$

For example, if the original sample volume was 99.50 c. c., the total residue after previous removal of other gases 81.20 c. c., the total contraction on burning 8.15 c. c., and the total carbon dioxide formed 3.95 c. c., the calculation is as follows:

$$\text{Volume of methane} = \frac{8.15 + 3.95}{3} = 4.03 \text{ c. c.}$$

$$\text{Per cent of methane} = \frac{4.03}{99.5} \times 100 = 4.1 \text{ per cent.}$$

Actually, the result would be 4.05 per cent, but because the error of the portable Orsat method is only about 0.3 for this determination, it is useless to report figures further than the nearest tenth; in fact, it is misleading to report results in the second decimal place.

The value given for the total residue after removal of other constituents was not used in the above calculation. It was unnecessary, as the entire residue was used for combustion. However, if some of the methane containing residual from the original volume of sample was discarded to make room for oxygen or air for combustion, then the combustion data pertains only to a portion of the original methane and must be corrected to a volume which represents the original volume of sample.

On first thought one might suppose that as the original volume was approximately 100 c. c. and the portion used was approximately 50 c. c., the amount of methane found in the latter need only be multiplied by 2 or by a factor

$$\frac{\text{Original volume}}{\text{Portion taken for combustion}}$$

This is incorrect, as at the time the approximate 50 c. c. portion of the residue containing the methane was taken the original sample had

been reduced by previous absorptions (CO_2 , O_2 , and CO) to a volume of about 80 or 85 c. c. In other words, this volume contained all of the methane originally in the entire 100 c. c. sample.

The correct manner of transforming the volume of methane found by combustion of the portion of sample to a volume representative of the original volume is to multiply it by a factor obtained by dividing the total residue before discarding by the portion taken for combustion, or—

$$\frac{\text{Total volume of CH}_4 \text{ in original sample} = \text{volume of CH}_4 \text{ in portion} \times \text{volume of total residual before discarding}}{\text{volume of portion taken for analysis}}$$

$$\text{Per cent of CH}_4 = \frac{\text{total volume of CH}_4 \text{ in original sample}}{\text{volume of original sample}} \times 100.$$

For example, if the original sample volume was 98.85 c. c., the total residual available for combustion 85.50 c. c., the portion taken for combustion 45.60 c. c., the total contraction on burning 4.85 c. c., and the total carbon dioxide formed 2.30, the calculation of per cent of methane would be as follows:

$$\text{Volume of methane in portion of residue} = \frac{4.85 + 2.30}{3} = 2.38 \text{ c. c.}$$

$$\text{Volume of methane in total residue} = 2.38 \times \frac{85.50}{45.60} = 4.46 \text{ c. c.}$$

$$\text{Per cent of methane} = \frac{4.46}{98.85} \times 100 = 4.5 \text{ per cent.}$$

Samples containing 5 per cent or more of methane.—For samples in which the methane is estimated as more than 5 per cent, the operations for performing an analysis are distinctly different from those given for samples with less than 5 per cent of methane. The gas and air or oxygen is not mixed before being subjected to the heated platinum coil. The gas is kept in *e* and the air or oxygen in *d*. Then, when the platinum coil in pipette *d*, which contains only air or oxygen, has been heated to the proper temperature (see Adjusting Temperature of Platinum Coil, p. 52) the stopcock to *d* is opened and the gas passed from *e* to *d* at a rate that will allow the coil to burn the methane as fast as it comes to *d* and not allow an explosive mixture to accumulate. This technique requires care to avoid explosions, but it may be successfully used if the instructions given later are strictly followed.

Proportion of sample and air or oxygen for combustion.—As the amount of methane in this group of samples may range from 5 to as much as 90 per cent or more, no definite sample volume can be prescribed. On the other hand, the proportion of sample and air or oxygen is governed entirely by the particular sample. With gases containing relatively small amounts of methane a comparatively

large sample and a small amount of oxygen are used; but as the methane content increases the volume of sample must obviously decrease to permit the use of more oxygen. When the sample contains 25 per cent or more of methane it is no longer practicable to use atmospheric air, because the size of the sample of gas that could be used would be so small that errors of manipulation would be increased to an extent that would vitiate the results. For example, an error of 0.2 c. c. in reading the volume of a 10 c. c. sample would be an error of 2 in the per cent found, whereas the same error in reading a 50 c. c. sample would be only 0.4.

After the analyst has had experience with samples containing various amounts of methane, he can readily judge the proportion of the residue and the amount of oxygen or air to take for combustion analysis. From the type of sample and the constituents, such as carbon dioxide, oxygen, and possibly carbon monoxide previously determined, he will be able to estimate the amount of methane within a certain range, and from previous experience with similar samples he will know in round numbers what proportions of residue and air or oxygen to take for analysis. From a practical standpoint it is not necessary to have the theoretically optimum proportions; that is, the maximum amount of sample and minimum amount of air or oxygen. That condition need only be approximated, at least for the first analysis of a sample. If greater accuracy is desired, a second analysis can be made, basing the proportions of residue to air or oxygen on the previous analysis.

For the analyst who has had no experience the following method of calculation will be of assistance. In the calculation it is assumed that the oxygen has already been absorbed from the residue. If the oxygen has not been removed, the calculations will still be satisfactory, as the only difference will be that the calculated amount of oxygen will be increased by the amount in the portion of residue finally taken. Even if the amount of oxygen in the residue is known (and usually it is not), the only advantage in considering it would be the possibility of increasing the proportion of residue to oxygen or air, a small and practically insignificant amount.

As methane, unlike carbon dioxide, oxygen, and carbon monoxide, is not removed by previous absorption procedures, all that was in the original volume of sample is contained in the residue, and the amount may be approximated by multiplying the original sample volume by a safe estimate of the percentage of methane in the gas. The theoretical amount of air or oxygen necessary for combustion of the estimated amount of oxygen may be found by multiplying the volume of methane by 2 for oxygen and by 10 for air.

For example, if the original sample volume is 100 c. c. and the sample is estimated to contain 30 per cent of methane, the volume of methane in the original sample and in the residue after absorption procedures

is 30 c. c.; hence, 60 c. c. of oxygen or 300 c. c. of air will be required for combustion. This calculation does not include a 20 per cent or one-fifth excess of oxygen or air which is recommended, at least for inexperienced analysts. For experienced analysts the excess may be decreased.

In deriving the final proportions of residue and air or oxygen to be taken the example just given may be used again to illustrate the procedure if it is further assumed that the total residue after absorption is 80 c. c. In the use of oxygen to burn the entire residue the amount of gas that would be handled would be 80 c. c. of residue plus 60 c. c. of oxygen plus 12 c. c. of excess oxygen, a total of 152 c. c. That is too much to be handled conveniently in the ordinary apparatus, and accordingly the volumes should be proportionately decreased to bring them to a 100 c. c. basis. This may be done by taking $\frac{100}{152}$ of the residue and oxygen volumes, respectively, as

$$\frac{100}{152} \text{ of } 80 = 52.6 \text{ c. c. residue}$$

and

$$\frac{100}{152} \text{ of } 72 = 47.4 \text{ c. c. oxygen.}$$

If a total of 120 c. c. is desired, $\frac{120}{152}$ of each should be taken.

In making these estimations and calculations it is well to be conservative in methane and liberal in the supply of oxygen, at least for the first analysis. If the portion of the residue not taken for analysis is stored in pipette *c* during the first trial, a duplicate combustion analysis may be made, using the reserve portion, for which the amount of methane may be estimated more clearly.

If air and not pure oxygen is used for combustion in the above example, the volume of gases entailed in burning the entire residue is 80 c. c. of residue plus 300 c. c. of air plus 60 c. c. of excess air, or a total of 440 c. c. Proportionately decreasing this to a 100 c. c. basis, the respective values would be—

$$\frac{100}{440} \text{ of } 80 = 18.2 \text{ c. c. residue}$$

and

$$\frac{100}{440} \text{ of } 360 = 81.8 \text{ c. c. of air.}$$

The amount of residue that could be used is evidently only 18.2 c. c. Due to errors of manipulation when small volumes are calculated to a percentage basis, it is recommended that oxygen (if available) be used when the methane content is above 25 per cent. It is even preferred when the methane content is above 15 per cent.

Practical proportions of air or oxygen for samples containing more than 5 per cent of methane.—Table 1 gives practical proportions of air or oxygen to sample for the combustion analysis of samples containing more than 5 per cent of methane. The table has been prepared for the convenience of the beginning analyst who may have these instructions, and who may not have had opportunity to become familiar with the procedure for calculating the air or oxygen requirements for combustion, as previously described.

TABLE 1.—*Practical proportions of air or oxygen to sample for combustion analysis of samples containing more than 5 per cent of methane*

[Values given are approximate; deviations of plus or minus 2 or 3 c. c. are permitted]

Estimated methane in sample, per cent	Air		Oxygen		Remarks
	Volume of air	Volume of sample	Volume of oxygen	Volume of sample	
	<i>C. c.</i>	<i>C. c.</i>	<i>C. c.</i>	<i>C. c.</i>	
5 to 10.....	60	40	25	75	Air or oxygen satisfactory.
10 to 20.....	75	25	40	60	Oxygen preferred for accurate results.
20 to 30.....	80	20	50	50	Do.
30 to 50.....	-----	-----	60	40	Oxygen required for accurate results.
50 to 70.....	-----	-----	68	32	Do.
70 to 100.....	-----	-----	75	25	Do.

Analytical procedure for samples containing more than 5 per cent of methane.—After the carbon monoxide absorption has been completed,¹⁸ estimate the portion of residue to be kept for combustion by the methods previously given, consulting Table 1. Transfer the excess residue to the cuprous chloride pipette *c* by raising *f*, opening the cock to *c*, and closing the cock as soon as the meniscus in *e* has reached the desired calibration mark. Measure accurately (it is unnecessary to allow time for draining), and record the volume. Now store the gas in *a* by opening the cock and raising *f* until the water just reaches *h*. Close the cock to *a* when the water is exactly at the mark *h*. If air is used for the combustion, cock *p* is turned to connect to *n*, and *f* is lowered until the desired amount of air is drawn into *e*. If pure oxygen is used, connect the outlet *n* to a reservoir of oxygen and draw in the desired amount, as for air. In either event close *p*, allow one minute for draining, and read and record the volume. The air or oxygen is then passed into *d* by opening the cock and raising *f* until the water reaches *h*; then close the cock to *d*. Immediately after closing *d* open the cock to *a*, withdraw the sample of residue gas into *e*, and close the cock to *a*. Allow one minute for draining and read the volume; it should be within 0.2 c. c. of the portion of residue originally stored in *a*. The residue containing the

¹⁸ For samples in which carbon monoxide does not occur the procedure for methane may be started after the oxygen absorption or, if the determination of oxygen is not desired, the methane may be determined immediately following the absorption of carbon dioxide. (See Summarized Procedure for Various Types of Mine Atmospheres, p. 76.)

combustible gas is now in e and the oxygen or air in d , with a stopcock closed between them, and everything is in readiness for the actual combustion procedure.

Place a wire gauze around d and a pad of wet cotton over the rounded top and around the stem. Close the switch or connect to the source of current and heat the coil until it shows a bright yellow tinge. (See Adjusting Temperature of Platinum Coil, p. 52.)

While holding the level of f at the level of the liquid in e , so that the gas in e will be at atmospheric pressure, close the hose between f and e tightly with the thumb and finger if the methane is estimated to be below 25 per cent or with a screw clamp if the amount is unknown or is above 25 per cent. Raise f above h by setting it on top of the apparatus case but keep the hose pinched. Note by casual observation if the level in e has changed. It should not, but if it has f should be lowered and the gas in e brought to atmospheric pressure again, otherwise the gas in e will be under pressure and in carrying out the next step (opening the cock to d) a rush of gas would enter d and probably cause an explosion. (See fig. 13 for details.) If the coil is properly heated, open the cock to d cautiously, keeping your head turned away from d . Then slowly and continuously pass the gas sample in e into d by partly releasing the thumb and finger or by carefully releasing and adjusting the screw-clamp connection on the hose from e to f , which was previously closed. The permitted rate of passing gas from e to d without danger of an explosion is approximately 1 c. c. of methane (not residual gases) per minute; that is, in passing over a 40 c. c. sample which is estimated to contain 8 c. c. of methane, approximately eight minutes should be the total time allowed for passing over the gas, the rate being 5 c. c. of the residual gas mixture per minute. The rate should be uniform and continuous, not pulsating or intermittent. A rate slower than the above will do no harm, but a faster rate may cause an explosion or melt the platinum coil. It is always good practice to start with a slow rate and increase toward that rate described as permitted, at the same time observing the coil. If a halo of flame appears over the wire or small explosions or inflammations occur in the pipette, the rate is too rapid and should be decreased.

The entire combustion procedure should be carefully observed, adjustments in the rate of flow being made when necessary. Under no consideration should gas be allowed to enter d if the coil is not up to a satisfactory temperature. When the water reaches h lower f , draw approximately 3 c. c. of the gas back into e , and slowly feed it back into d . Repeat this procedure, using 5 c. c. It is important to remove the gas from the manifold as described, because, if the sample contains high percentages of methane and the residue in the manifold is removed and then rather quickly passed back into d to burn

out the remaining traces of combustible gas, there might be enough methane to make an explosive mixture.

After completing the removal of gas from the manifold, release the thumb and finger or screw-clamp constriction on the hose and rather rapidly pass the gas several times back and forth over the heated spiral, being careful, however, not to bring the water in *d* higher than one-half or three-fourths inch below the glass-tubing supports for the spiral, as otherwise they may break by sudden cooling. Open the switch or connection to the source of current, allow the pipette to cool until it is only just warm, then withdraw the gas and bring the water to the mark. Close the cock to *d*, allow one minute for draining, and read and record the volume.

Next, absorb the carbon dioxide produced by passing the gas into the caustic pipette *a* as described in the first procedure for methane, being careful to sweep the carbon dioxide out of the manifold and stem to *d*. Read and record the volume.

After absorbing the carbon dioxide, pass the gas back into *d*, close the switch, and subject the gas to a second combustion to burn the last traces of methane. No precaution against explosions need be taken if the first combustion has been properly carried out, and the gas can be passed into *d* and the switch closed. Continue the burning about two minutes, pass the gas back and forth over the heated spiral three or four times, open the switch, allow the pipette to cool as before, and withdraw and measure the gas. Again absorb the carbon dioxide formed. Add the contraction and the carbon dioxide formed by the second burning to the respective volumes obtained by the first burning.

To ascertain whether or not enough oxygen was added for complete combustion, pass the gas into *b* two or three times and note any contraction in volume by measuring the volume.

Calculation of results.—Results are calculated as already described under the procedure for methane when only a portion of the residual (after taking out the CO_2 , O_2 , and CO) was taken for the combustion procedure.

NOTES ON COMBUSTION PROCEDURE

If during the passing of the gas from *e* to *d* the platinum coil ceases entirely to glow or even becomes a dull red, due to poor connection or other causes, open the switch at once, and close the cock to *d*. If it is estimated that between the time the coil became dull and the time the cock to *d* was closed an insufficient amount of gas for an explosive mixture has entered *d*, the electrical connections may be repaired and the switch closed cautiously (cock *d* should remain closed at this time). To lessen the danger of an explosion or the possibility of melting the coil, the switch should be closed only momentarily—that is, only until it heats to a red heat—then quickly opened, the opera-

tion being repeated two or three times. If done carefully so as to take advantage of the lag in ignition of methane, some of the methane will be burned at each closing, thus avoiding an explosion with mixtures which might be just above the lower explosive limit but not with mixtures well inside the explosive range. After the three or four periods of momentary closing, the switch may be closed and the resistance adjusted to give the mixture tested a yellow-tinged appearance. Before opening the cock to *d* and admitting more gas from *e*, however, the screw clamp on the hose from *f* should be opened, *f* lowered, and the gas in *e* brought to atmospheric pressure by bringing the level of the water in *f* to the same height as that in *e*. Then the hose is again closed, *f* raised to its original position, and the combustion carried out in the manner previously described. However, an attempt to save a sample after the combustion has been prematurely stopped, as described above, is a rather dangerous procedure for the inexperienced analyst and has accounted for many cases of explosion and damage to the apparatus. Unless there is insufficient sample for another determination, the recommended procedure when the coil "goes out" is to open the switch quickly and discard all gas from *d* and *e*. After this has been done, draw in a burette full of air and pass it once into all pipettes in turn (except *c* if it contains some of the residual that has been stored by a second trial) and then discard the air. This sweeps out any residue of the old sample that might also form an explosive mixture if transferred to *d* during an attempt to repair connections to the coil.

DETERMINATION OF NITROGEN

The residual gas left after the determination of the methane contains the nitrogen in the portion of the original gas taken for analysis, the nitrogen added with the air or oxygen for combustion, and usually some excess oxygen. The direct determination of nitrogen is too difficult and time-consuming, however, to attempt in technical gas analysis. Also, no attempt is made to determine it by calculation from the volume of inert residual. The value reported for nitrogen is merely obtained by difference; that is, the sum of the percentages for all the other constituents (CO_2 , O_2 , CO , CH_4) subtracted from 100, provided that all the known constituents have been determined. If oxygen, carbon monoxide, or methane is present and not determined, the nitrogen can not be determined by difference. Omitting the determination of small amounts of carbon monoxide, however, does not seriously affect the determination of nitrogen if a combustion analysis has been made for methane, because the carbon monoxide will be burned with the methane and determined in terms of methane.

Per cent of nitrogen = $100 - (\text{sum of percentages found for all other constituents})$.

SUMMARIZED PROCEDURE FOR ANALYZING VARIOUS TYPES OF MINE ATMOSPHERES

As stated in the section dealing with Principles of Gas Analysis, the analytical procedure employed for the analysis of complex gas mixtures consists of subjecting the mixture to successive absorption and combustion operations. These are carried out in a manner that will remove from the gas mixture and measure the constituent in question without altering the amount of the residual or remaining gases which are to be determined later. The procedure described satisfies this requirement for gases taken from sealed mine-fire areas and other similar types in which it is desired to determine CO_2 , O_2 , CO , CH_4 , and N_2 .

It may be desirable occasionally to analyze other types of samples, as described under Field of Use of Portable Orsat, page 35, which may not contain all of the constituents just mentioned or for which it may not be necessary to determine all of them. If the analyst has become familiar with the various steps in the analytical procedure, as outlined for mine-fire gases, and understands the reasons for the order of the successive steps, he can readily devise a procedure for the special sample in question. The following rules will suffice for most cases:

1. Sodium hydroxide or potassium hydroxide (pipette *a*) will remove only carbon dioxide.

2. Alkaline pyrogallate (pipette *b*) will remove both carbon dioxide and oxygen, and it is therefore always necessary to remove the carbon dioxide from a sample (by passing it into *a*) before attempting to determine oxygen. If this is not done, the oxygen value will be high by the amount of the carbon dioxide present in the gas mixture.

3. Cuprous chloride (pipette *c*) will absorb both oxygen and carbon monoxide, and it is therefore always necessary to remove the oxygen completely before attempting to determine carbon monoxide in a mixture, lest the oxygen be absorbed along with the carbon monoxide and give a result which is too high for CO . (See discussion under Determination of Carbon Monoxide, p. 60.)

4. In making combustion analyses it is always necessary to absorb previously any carbon dioxide in the sample, otherwise it will be absorbed later during the determination of the carbon dioxide formed by combustion and in many cases will vitiate the results. Also, if carbon monoxide is not absorbed previously, it will be determined as methane.

Table 2 is a key to the procedure to be used for most types of gases which a field man may desire to analyze and for which the accuracy of the portable Orsat is satisfactory. (See discussion of Field of Use of Portable Orsat, p. 35.) The type of gas, probable gases in each mixture, and necessary steps in the analytical procedure are given in the table. The probable constituents are represented by the symbol \times appearing under chemical symbols in the first major column of the table. The necessary steps or constituents to be determined in

the analysis are designated by a numeral appearing under the chemical symbols in the second major heading. The order of the numerals, as 1, 2, 3, etc., is the required order of performance. When numerals do not appear under a particular symbol it is not necessary to carry out the procedure for making a determination of that constituent. For example, when the sample is from a sealed area containing no fire a \times appearing under CO_2 , O_2 , and CH_4 indicates those constituents are probably present; and 1, 2, and 3 appearing under CO_2 , O_2 , and CH_4 , respectively, designate the analytical procedures to be carried out and the order of performance. The procedures and calculations in each case are the same as have been given for the individual constituents.

TABLE 2.—Key to procedure for analyzing various types of mine atmospheres

Method No.	Type of gas	Constituents to be determined				Required procedure			
		CO_2	O_2	CO	CH_4	CO_2	O_2	CO	CH_4
1	Mine-fire gases (coal or metal).....	\times	\times	\times	\times	1	2	1 3	4
2	Concentrated afterdamp.....	\times	\times	\times	\times	1	2	1 3	4
3	Sealed areas containing no fire.....	\times	\times	-----	\times	1	2	-----	2 3
4	Carbon dioxide and oxygen; no fire or explosion.....	\times	\times	-----	(³)	1	2	-----	(³)
5	Carbon dioxide (only); any mixture ⁴	\times	\times	\times	\times	1	-----	-----	-----
6	Oxygen (only); any mixture ⁴	\times	\times	\times	\times	1	2	-----	-----
7	Carbon monoxide (only); any mixture ⁴	\times	\times	\times	\times	1	2	⁵ 3	-----
8	Methane (no fire or explosion); any mixture ⁴	\times	\times	-----	\times	1	-----	-----	3
9	Methane and oxygen (no fire or explosion).....	\times	\times	-----	\times	1	2	-----	3
10	Coal-mine air containing less than 5 per cent methane and more than 14 per cent oxygen (no fire or explosion) ⁶	\times	\times	-----	\times	1	3	-----	⁶ 2
11	Coal-mine air containing more than 5 per cent methane (no fire or explosion).....	\times	\times	-----	\times	1	2	-----	3

¹ Check CO by tannic acid method when amounts are below 0.3 per cent.

² May have high methane content.

³ Methane usually occurs in coal mines.

⁴ 5, 6, 7, and 8 represent the determination of a single constituent in a probable mixture of mine gases.

⁵ Orsat method not suitable for amounts below 0.3 per cent; in these cases use tannic acid method.

⁶ See special procedure for this type of sample, p. 79.

METHOD OF CALCULATION

Table 3 shows the method of calculation for specimen data.

TABLE 3.—*Specimen data showing method of calculation*

[For samples where a portion of initial volume has been discarded before combustion, refer to description of determination of individual constituents]

	Burette reading	Difference	Per cent	Reference to calculation of per cent by volume
Volume of original sample.....	99.7			
Carbon dioxide.....	96.2	3.5	3.5	(1)
Oxygen.....	90.1	6.1	6.1	(2)
Carbon monoxide.....	89.3	.8	.8	(3)
Volume after sample was discarded.....	51.3			
Volume of oxygen introduced into combustion pipette.....	47.6			
Total volume.....	98.9			
Volume after first burning.....	60.7	38.2		
CO ₂ formed.....	42.6	18.1		
Volume after second burning.....	42.1	.5		
CO ₂ formed.....	41.8	.3		
Total contraction.....		38.7		
Total CO ₂		18.4		
Methane.....		33.1	33.2	(4)
Nitrogen.....			56.4	(5)

$$1 \frac{3.5}{99.7} \times 100 = 3.5 \text{ per cent of carbon dioxide (CO}_2\text{).}$$

$$2 \frac{6.1}{99.7} \times 100 = 6.1 \text{ per cent of oxygen (O}_2\text{).}$$

$$3 \frac{0.8}{99.7} \times 100 = 0.8 \text{ per cent of carbon monoxide (CO).}$$

4 $\frac{38.7+18.4}{3} = 19.03$ c. c. CH₄ in 51.3 portion of 89.3 c. c. volume after absorption of carbon monoxide and before discarding. Correction to original volume $\frac{89.3}{51.3} \times 19.03 = 33.1$ c. c. This step in the calculation may be omitted if none of the sample has been discarded as described (see Procedure for Methane) for samples having a methane content that is less than 5 per cent, or at least that will be less than 5 per cent, when the necessary amount of air or oxygen has been added. CH₄ in whole sample (original 99.7). $\frac{33.1}{99.7} \times 100 = 33.2$ per cent of methane (CH₄).

$$5 100 - (3.5+6.1+0.8+33.2) = 56.4 \text{ per cent of nitrogen.}$$

ANALYSIS OF NORMAL MINE-AIR SAMPLES FOR METHANE

Samples of normal mine air may be analyzed with the portable Orsat apparatus to check estimations made with a safety lamp or other type of detector. Results accurate to plus or minus 0.2 can be obtained. When the samples contain more than 5 per cent of methane or less than 5 per cent of methane but not enough oxygen for combustion of the methane, or both, the analytical procedure for methane is the same as that described on page 64. *If the sample contains less than 5 per cent of methane and more than 14 per cent of oxygen, simpler and more accurate analytical procedure may be employed.* These conditions may be ascertained from a general knowledge of the atmosphere or by making a preliminary analysis according to the analytical procedures already described. It also obviously includes all atmospheres for which a flame safety lamp does not indicate an explosive atmosphere or is extinguished due to oxygen deficiency.

The procedure is briefly:

1. Carry out in the manner previously described all the steps in the general procedure up to and including the determination of carbon dioxide.

2. Do not absorb or determine the oxygen, but pass the residual gas from the carbon dioxide determination directly to the combustion pipette *d* and carry out the combustion procedure as described for samples containing less than 5 per cent of methane, page 67; however, omit the instructions regarding the addition of oxygen or air. Consider and treat the residual from the carbon dioxide determination as the mixture of air or oxygen and sample.

3. Calculate results for carbon dioxide and methane the same as previously described for these gases.

4. If desired, determine the amount of oxygen in the original sample by following the combustion procedure with a determination of the excess or remaining oxygen, taking precaution to sweep out and absorb all the oxygen trapped below the stopcocks of the pipettes during the performance of previous procedures. The volume of oxygen (not per cent) found, added to the volume of oxygen consumed in the combustion of methane (two times the volume of methane found—not per cent) is the total volume of oxygen in the sample, or the same as would have been found by absorption of oxygen before combustion. Two times the volume of methane is added, because 1 volume of methane requires 2 volumes of oxygen for combustion, as discussed on page 67.

The calculation of the percentage of oxygen in the original sample is as follows:

Volume of oxygen = volume of excess + (2 × volume of methane)

$$\text{Per cent of oxygen} = \frac{\text{volume of oxygen}}{\text{original sample volume}} \times 100.$$

ANALYSIS OF OXYGEN OR OXYGEN-CARBON DIOXIDE MIXTURES FROM OXYGEN BREATHING APPARATUS OR INHALERS

The portable water Orsat gas-analysis apparatus may be used for the analysis of—

1. Oxygen used in self-contained oxygen breathing apparatus.
2. Oxygen or mixtures of carbon dioxide and oxygen used in inhalers.
3. Samples of air from breathing bags of self-contained oxygen breathing apparatus.

However, as the grade of oxygen used for these purposes usually contains less than 1 per cent of nitrogen, the regular procedure given for mine atmospheres can not be used because the sample taken for analysis would not ordinarily contain enough inert gas satisfactorily to finish the absorption procedure for oxygen or to make a final

burette reading. Also, as small amounts of carbon monoxide may be generated during the process of absorbing high concentrations of oxygen by the use of alkaline pyrogallate solution, there would be a slight error in the amount of oxygen found. The small part of the oxygen that would be converted to carbon monoxide would remain as unabsorbed gas and would lower the oxygen value and increase the nitrogen value. Both these difficulties, however, may be obviated by modifying the procedure of analysis. To provide a larger amount of nitrogen or inert gas a measured portion prepared from air is added to the sample taken for analysis, and to eliminate error due to formation of carbon monoxide the carbon monoxide is removed by combustion just before the oxygen absorption is completed.

PROCEDURE

After completely purging the apparatus, including the pipette stems to the pipette containing sodium or potassium hydroxide and the combustion pipette, draw in 60 c. c. of air and remove the oxygen by passing the gas into the alkaline pyrogallate pipette. When the oxygen has apparently been removed pass the residue gas through the manifold dead space and capillary stems as before, finally drawing the solution exactly to the mark in each case. This picks up the air residues previously trapped in these places. Then pass the gas again into the alkaline pyrogallate pipette to remove the last traces of oxygen. When this has been done bring the absorbing solution exactly to the mark, close the cock, allow the burette to drain two minutes, and read and record the volume of gas in the burette. The burette and the capillary dead space of the apparatus are now filled with nitrogen. Open the cock to the combustion pipette and pass in nitrogen until the water in the burette reaches the mark at the top. Close the cock to the combustion pipette.

Now draw a 50 c. c. sample of the gas to be analyzed into the burette, using the necessary precautions to purge the manifold and all connections to the sample container of their original gas. When the sample has been obtained close the entering cock, allow the burette to drain, and read and record the volume. Next open the cock to the combustion pipette and withdraw all of the nitrogen. The burette now contains a mixture of the sample to be analyzed and nitrogen. Allow the burette to drain and read and record the volume. The total volume should be the sum of the volume of nitrogen stored in the combustion pipette and the sample of gas taken for analysis. Due to slight errors in making readings, a small discrepancy is often found, in which case the final burette reading—that is, the one made after the nitrogen is withdrawn—is taken as being correct. If a marked discrepancy, 0.3 c. c. or more, is found, the samples should be discarded and the analysis repeated, as there

has been a significant error through inaccurately reading the burette or through leaks in the apparatus.

Determination of carbon dioxide.—Carbon dioxide is absorbed with potassium or sodium hydroxide, according to the regular procedure for mine gases. If carbon dioxide is known to be absent, as in pure commercial oxygen, the absorption may be omitted and the analysis started by determining the amount of oxygen.

Determination of oxygen.—Oxygen is absorbed with alkaline pyrogallate as in the procedure for mine gases. However, to obviate the error caused by the formation of carbon monoxide, the absorption must be modified in accordance with either of the following methods:

1. If the cuprous chloride (the absorbent for carbon monoxide) is comparatively fresh solution, the oxygen should be removed in the regular manner by absorption with alkaline pyrogallate and the gas then passed into the cuprous chloride. After the carbon monoxide absorption, the gas is passed several times into the sodium or potassium hydroxide pipette to remove acid vapors given off by the cuprous chloride and to pick up oxygen that may have been trapped in the stem below the stopcock when making the initial carbon dioxide determinations. The gas is passed again into the alkaline pyrogallate pipette to remove the final traces of oxygen; then it is measured as before. It is not necessary to make burette readings between starting the oxygen absorption and completing the final absorption. The total difference is the amount of oxygen present in the sample.

2. If the analyst is uncertain as to the quality of the cuprous chloride or if it is not available, the carbon monoxide may be removed by combustion in the following way: When all but 5 c. c. of the oxygen has been absorbed, which can be judged from the volume of sample taken or by preliminary absorption to completeness, the gas is withdrawn from the alkaline pyrogallate pipette, passed into the combustion pipette, and burned by the method ordinarily used for small amounts of methane. When the burning has been completed withdraw the gas and remove the remainder of the oxygen by passing the gas into the alkaline pyrogallate pipette. Any carbon dioxide formed by the combustion of carbon monoxide will be simultaneously absorbed in the alkaline pyrogallate solution, which obviates the need of making corrections. In other words, the oxygen used in generating the carbon monoxide and also in burning it is finally absorbed by the alkaline pyrogallate in the form of carbon dioxide. Finally, pass the residual gas through the manifold and pipette stems to pick up oxygen residuals and complete the oxygen absorption by again passing the gas into the alkaline pyrogallate. Read and record the volume of residual gas in the usual manner.

Determination of nitrogen.—Nitrogen is determined by difference; that is, 100 minus the sum of other determined constituents.

CALCULATION OF RESULTS

A typical example will illustrate the method of calculating results:

	Cubic centimeters
Volume of air taken (approximately) -----	(1) 60.0
Volume after removing oxygen from air -----	(2) 47.5
Volume sample taken for analysis -----	(3) 50.2
Total volume after withdrawing nitrogen -----	(4) 97.7
Volume after removing carbon dioxide -----	(5) 95.0
Volume after removing oxygen -----	(6) 47.9

Referring to the above numbers—

(1) Is not essential except to check removal of oxygen on basis of (2).

(5) The volume of carbon dioxide = $97.7 - 95.0 = 2.7$ c. c., per cent of carbon dioxide = $\frac{2.7}{50.2} \times 100 = 5.4$ per cent.

(6) The volume of oxygen = $95.0 - 47.9 = 47.1$ c. c., per cent of oxygen = $\frac{47.1 \times 100}{50.2} = 93.8$, and the per cent of nitrogen by difference = $100 - (5.4 + 93.8) = 0.8$ per cent.

This example refers particularly to the analysis of mixtures of approximately 5 per cent of carbon dioxide and oxygen as used in inhalers. For oxygen termed “pure oxygen,” as used in oxygen-breathing apparatus and inhalers, the value for carbon dioxide will be zero (not more than 0.2 to 0.3 per cent, which is the analytical error of the apparatus) for the usual grade of gas.

When analyzing mixtures containing as much as 5 per cent of carbon dioxide a small amount of this gas may be lost through dissolving in the water in the burette; but if the analysis is made immediately after the sample is taken in, the results should be accurate to 0.3, which is satisfactory for ordinary purposes.

Samples of air from breathing bags of self-contained oxygen apparatus are analyzed by the method given for mixtures of 5 per cent of carbon dioxide and oxygen. The nitrogen value, however, is usually higher than that given in the foregoing example.

DUPLICATE ANALYSES

The most dependable results are obtained by making two separate analyses whose results are in satisfactory agreement. Ordinarily, these may be obtained from the same sample, provided that the sample was collected and preserved so as to insure its being a representative sample of the atmosphere in question. However, a better procedure and one that should be employed in all cases of importance is to collect and analyze duplicate samples. Time may be saved by making single analyses of each sample. In both instances, however, the remaining portion of the sample should be preserved in the container, as it may be desired later to make duplicate analyses for the same sample. If the results are in satisfactory agreement, the arithmetical

average is as satisfactory as need be obtained for the gas sampled. If the results do not agree within practical limits, an error has been made in the analysis, the samples were not representative of the same atmosphere, or one or both of the samples have been contaminated. This will necessitate additional analyses of one or both of the samples until agreement is obtained or the cause of nonagreement established. If the two samples are finally found to have a different composition and more samples of the same atmosphere can not be obtained, the sample which contained the lowest amount of oxygen (referring particularly to mine atmosphere) usually can be taken as more closely representative of the condition in question, although in the absence of information to the contrary even this sample may be viewed with suspicion. If, however, the analyst is unable to obtain duplicate results for the same sample that are within satisfactory agreement, he is making errors in his analytical technique or the apparatus is not functioning properly.

There are cases where single samples and even single analyses are satisfactory, such as samples of practically the same atmosphere or successive samples collected at a place where the composition is not subject to marked changes, as in mine-fire seals. In reality, these furnish checks on each other or on the previous samples and need not be analyzed in duplicate unless erratic or inconsistent results are obtained or the accuracy of the result is very important.

AVERAGING DUPLICATE ANALYSES

Whenever duplicate analyses have been made the arithmetical average of all satisfactory results for each constituent except carbon dioxide should be taken as the final result. For carbon dioxide the result obtained by the first analysis should be taken wherever it is significantly higher than the second, because that gas is very soluble in the water used to displace the sample from its container, and the second determination usually gives a lower result, due to an appreciable amount being taken up by the water during the period of standing. The sample for the first analysis should therefore be drawn into the burette and measured as rapidly as possible after the sample container is opened. If, however, the second analysis indicates a higher carbon dioxide content than the first by an amount greater than the analytical error of the apparatus, the discrepancy has been caused by improper technique, leaks, etc.

These rules for averaging results should always be followed unless there is outstanding evidence that one of the analyses has been more liable to error than the other, in which case the more dependable one should be taken alone. In no event, however, should one analysis be chosen merely because its results conform more closely to the expected result or the other discarded merely because its results do not con-

form to them. The analytical procedure and calculation should always be carried out unmindful of interpretation of the results.

ACCURACY OF THE PORTABLE ORSAT AND SATISFACTORY RESULTS

The limits of accuracy of the portable Orsat apparatus when used by an analyst of average skill are 0.2 to 0.3 in the per cent found for carbon dioxide, oxygen, and carbon monoxide and 0.2 to 0.3 for methane in the range of 1 to 10 per cent, about 0.3 to 0.5 in the range of 10 to 30 per cent, and 1 in the range of 50 to 75 per cent. All results of duplicate samples that fall within these limits are as accurate as can be expected and are satisfactory for the intended purpose of the portable Orsat. Frequently, for inexplicable reasons, wider variations will be obtained, but whether or not the results will be unsatisfactory depends on their particular use. For example, an error of 3 when the methane content is 35 to 50 per cent is not as significant as 0.3 when it is near the inflammable limit for checking flame safety-lamp determinations or similar work with comparatively low amounts; or an error of 1 to 2 in the oxygen percentage is usually not as significant in the results of analysis of a sample taken from a fire seal when the oxygen content has fallen below 6 per cent (regardless of the methane content) as immediately after sealing when the content is 10 to 15 per cent and enough methane is present to form an explosive or potentially explosive mixture.

RECORDS AND DATA

The analyst is usually held responsible for analytical results, and for this reason he should keep a permanent record of the history of the sample and the original analytical data as recorded at the time of making the analysis. Only copies of these data should be given as reports. All data should be kept in a legible form in a permanent leaf notebook or card system and not on tablets or scraps of paper.

SOURCES OF ERROR

The principal sources of error in the analysis of mine gases are as follows:

1. Errors and omissions in general technique and procedure of analysis.
2. Faulty and careless technique in measuring gas volumes or bringing solution to marks in pipette stems.
3. Carelessness in purging apparatus or in avoiding contamination of sample during analysis.
4. Insufficient time of contact with absorbing solutions.
5. Insufficient oxygen present for combustion of methane.
6. Leaky stopcocks or apparatus connections.
7. Errors in reading gas volumes.
8. Errors in arithmetic in calculating amounts of constituent present or percentage values.

9. Worn-out absorbing solutions, especially cuprous chloride.
10. Temperature of platinum coil too low to burn methane completely in the usual procedure of analysis.
11. Traces of absorption solutions in the manifold.
12. Alkaline condition of displacing liquid in the burette or combustion pipette.
13. Nonrepresentative sample.
14. Contamination of sample before analysis.

CARE AND STORAGE OF APPARATUS

Frequently the Orsat gas apparatus and sampling equipment for mine-fire gases have not been kept in a usable condition. When need for their immediate use arises, especially in mine fires and explosions, they are either beyond repair or more than a reasonable amount of time is required for putting them in shape for use. It is therefore advisable to add the following instructions and suggestions regarding care and storage of apparatus:

RUBBER CONNECTIONS

Every two months replace all short soft-rubber connections used to hold glass tubing together, as these connections will deteriorate if left longer and may crack or tear and give trouble through leaks. After several months they will adhere tightly to the glass and be difficult to remove. The rubber connections should be renewed every two or three weeks when the apparatus is in constant use. Never replace the same connection after it has been removed for cleaning, renewing solutions, etc.

In renewing and removing the connections apparatus breakage can be avoided by not trying to slip the connections from the stems but by shaving down the side, using a sharp knife, and then peeling off the tubing. Never use gasoline to loosen adhering pieces of rubber, as some of the gasoline might accidentally get into the pipettes or manifold and thus cause erroneous results for methane.

SOLUTIONS

Pour out all solutions and wash, drain, and replace all pipettes. Although the solutions may not be worn out, it is not good practice to save old solutions, as their quality is always uncertain. Solutions that have been but slightly used should be preserved in magnesium citrate bottles.

STOPCOCKS

Before putting the apparatus in storage remove stopcocks and wipe the grease from the barrels and plugs. Clean any accumulation of grease from the bore of the plug and from the barrel outlets. A piece of small copper wire (18 to 20 B. & S. gage) with a short L bend at one end is convenient for cleaning the outlets. After

flushing the manifold and barrels with slightly acidic water, wipe the latter dry, insert a thin strip of paper about one-fourth inch wide the entire length of the barrel and over the outlet leading to the pipette, grease the plug lightly, and place it in the barrel. This will prevent the plug from sticking or freezing (described later) and will also seal the opening to the absorbing solution. Secure the plugs against dropping out and breaking by tying them with wrapping twine or looping a rubber band around the constriction below the handle and passing it over the small end of the barrel. Another convenient method for securing the plugs is to wrap one end of a 3-inch length of about 18 to 20 B. & S. gage copper wire around the constriction at the handle and the other end around one of the

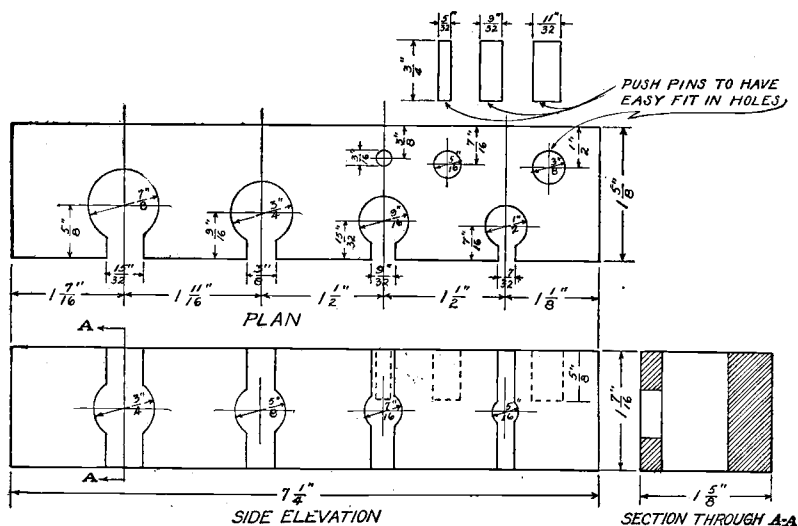


FIGURE 17.—Stopcock stem remover

branches of the stopcock. As stopcock plugs are not interchangeable, it is a good plan to remove, clean, and replace only one stopcock at a time, otherwise they might become mixed.

REMOVING "FROZEN" STOPCOCKS

If a stopcock becomes stuck, warm the barrel rather quickly by placing it in boiling water for a few seconds and then, before it cools appreciably, hold the stopcock in one hand and attempt to turn the plug or tap it gently with a piece of wood. The stopcock may be tapped on the back if the plug sticks through the barrel or on the handle if it is not the hollow-tube type. Repeat the heating from time to time. If this does not remove the plug, the device shown in Figure 17 (which consists of a block of hardwood, such as maple,

bored to receive the handles of the cocks and to support the barrel on the rim so that the plug may be forced out by closing a vise as shown in Figure 18) is often successful. Similar devices may be purchased from laboratory-supply houses.

The method for using the device as shown is to select a hole just slightly larger than the diameter of the plug so that the barrel will fit over the rim, place the bottom of the block against one jaw of an ordinary vise, set a hardwood pin having a diameter slightly less than the small end of the plug against the end of the latter, and close the vise until pressure is exerted on the plug. Avoid strain and allow

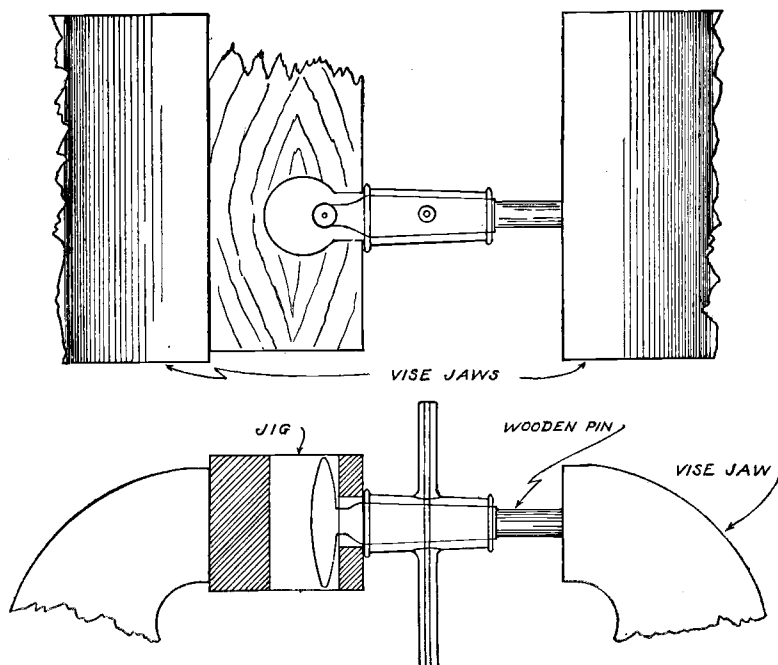


FIGURE 18.—Method of operating stopcock stem remover

free movement of extending arms or attachments to the plug outlets. Continue tightening until the plug is loosened or breaks, because if it will not become loosened in this manner it is almost useless to try other means.

STORAGE

Store the apparatus in an upright position. The other items to be considered in storing it are: (a) Minimize danger of breakage through rough handling; and (b) keep it away from excessive heat, as the latter causes rapid deterioration of the rubber connections and air bags.

SYSTEMATIC INSPECTION

The apparatus should be cleaned, prepared for use, and a sample of gas analyzed at intervals of not longer than two or three months. The sample should preferably be from a sealed-fire area; but if it is not convenient to obtain that type of sample, a sample of automobile-exhaust gas may be used, as it contains all of the constituents ordinarily determined in mine-fire gases—that is, CO_2 , O_2 , CO , CH_4 , and N_2 . Occasionally a sample containing an amount of methane above the explosive limit should be analyzed to check combustion analysis parts and technique.

The practice of periodically analyzing a sample of gas accomplishes two purposes: (1) It assures the usability of the apparatus and gives indication of the need for repairs or new parts; (2) it gives the personnel, whose duty it may be to analyze samples, opportunity to learn and keep familiar with the technique involved.

LIST OF EQUIPMENT FOR FIELD WORK

The following is a list of the equipment which should be on hand for sampling and analyzing mine-fire gases. Articles marked with an asterisk are essential for analyzing gases.

COMPLETE EQUIPMENT

*One Bureau of Mines portable Orsat apparatus with these instructions.

*One set of solutions for portable Orsat apparatus.

*One toy transformer for transforming available alternating current to 4 to 6 volts; or in case of rescue cars having direct current, a lamp-bank resistance or other resistance which will reduce the voltage to 4 to 6 volts; or batteries to give 4 to 6 volts.

*One wire-gauze shield to place in a semicircle around combustion pipette to protect operator from flying glass should an explosion occur during the determination of methane.

*One U tube (8-inch arms) made from $\frac{1}{8}$ -inch inside diameter copper tubing for removing samples from citrate bottles.

*One small tin salve box or tube of stopcock grease.

*One pyrotannic apparatus complete with six air-sample bottles and instructions.

Two water gages.

One aneroid barometer.

Two thermometers.

One rubber aspirator bulb with double-acting valves and hose connections at each end.

Four feet of $\frac{3}{16}$ -inch inside diameter medium-wall copper tubing for sampling through seals.

Six feet of $\frac{3}{16}$ -inch medium or heavy wall ordinary rubber tubing.

*Six feet of 4 or 5 mm. inside diameter, approximate 2 mm. wall, pure-gum tubing (preferably transparent) for renewing connections.

Two 3-inch long pieces of $\frac{3}{16}$ -inch medium-wall ordinary rubber tubing for connecting to other tubing or copper tubing when taking vacuum-tube samples through seals for shipping to the gas laboratory, Pittsburgh Experiment Station.

APPENDIX A.—COLLECTION AND ANALYSIS OF GAS SAMPLES CONTAINING HYDROGEN SULPHIDE, SULPHUR DIOXIDE, OR OXIDES OF NITROGEN

Frequently the gas laboratory of the Pittsburgh Experiment Station receives samples of gas in ordinary vacuum-tube containers with the request that they be analyzed for hydrogen sulphide, sulphur dioxide, or oxides of nitrogen, usually in low concentrations. Frequently the collector of the samples mentions that a "sulphur odor," "rotten-egg odor," etc., was observed, or that the atmosphere was acrid or irritating to the eyes and nose. In virtually every such instance, none of these gases has been found upon analysis, even though there may have been evidence of their presence in the atmosphere sampled. Owing to their highly reactive nature, these gases react with the glass of the sample tubes or with particles of dust and moisture present in the tubes and are diminished in quantity or even lost entirely to the sample before analysis is made.

The result of submitting such samples to the gas laboratory is that no information is gained as to the concentration of hydrogen sulphide, sulphur dioxide, or oxides of nitrogen which may actually have been present at the time of sampling. The quantitative chemical determination of traces to small amounts of these gases, in fact any gas, is difficult, and to obtain dependable results requires special procedures adapted to the particular situation and followed with precision and care by persons who have had experience in their use.

When determination of these gases is considered necessary it should be made in the field. The following procedures are suggestions for use in such cases.

DETERMINATION OF HYDROGEN SULPHIDE

A detector for the quantitative estimation of low concentrations of hydrogen sulphide has been developed, with which it is possible to determine concentrations of this gas ranging from 0.0025 to 0.05 percent. This detector is described in Bureau of Mines Report of Investigations 3276.¹⁹ The device is readily portable and sufficiently accurate to be used in most instances.

A simple and sensitive qualitative test for the presence of hydrogen sulphide may be made by moistening a strip of white absorbent paper, such as filter paper or blotting paper, with a 1-percent solution of lead

¹⁹ Littlefield, J. B., Yant, W. P., and Berger, L. B., A Detector for Quantitative Estimation of Low Concentrations of Hydrogen Sulphide: Rept. of Investigations 3276, Bureau of Mines, 1935, 13 pp.

acetate. The moist paper will turn brown or black if exposed to an atmosphere containing hydrogen sulphide.

Table 1 shows the relation of odor intensity to concentration of hydrogen sulphide in air.

TABLE 1.—*Relation of odor intensity to concentration of hydrogen sulphide in air*

Parts of hydrogen sulphide per million parts of air (by volume)	Percent in air (by volume)	Odor intensity
0.13.....	0.000013	Very faint.
.77.....	.000077	Faint.
4.6.....	.00046	Easily noticeable.
27.0.....	.0027	Strong.

It is apparent from table 1 that hydrogen sulphide has a high odor intensity and can be detected by the sense of smell (majority of persons) in concentrations of 0.13 part per million, or 0.000013 percent. This is below the amount that can be determined quantitatively by any chemical method in use today. It should be remembered that the sense of smell is affected by the inhalation of hydrogen sulphide and cannot be relied upon as a means for estimating the concentration of, or the safety from, this gas after one or two inhalations. Also the odor may be masked somewhat or its character changed somewhat by the presence of other odors.

ESTIMATION AND DETERMINATION OF SULPHUR DIOXIDE

The majority of the samples received at the gas laboratory accompanied by requests for determination of sulphur dioxide content were taken because of an "irritating effect" or an "odor of sulphur dioxide." It does not seem probable that a precise quantitative determination of the sulphur dioxide content of the atmosphere is necessary in most of these cases. A fairly close estimate of the concentration of this gas may be made by observing the odor intensity and the irritating effects produced by breathing such atmospheres. Table 2 may be used as a guide in making such an estimate.

TABLE 2.—*Relation of odor intensity and physiological effect to concentration of sulphur dioxide in air*

Concentration, parts of sulphur dioxide per million parts of air (by volume)	Physiological effect
3 to 5.....	Faintly detectable by smell or taste.
8 to 12.....	Slight throat irritation and tendency to cough.
20.....	Very distinct throat irritation, coughing, constriction of chest, and smarting of eyes.
50.....	More pronounced irritation of eyes, throat, and chest, but possible to breathe several minutes.
150.....	Extremely disagreeable but may be endured for several minutes.
500.....	Causes sensation of suffocation even with first breath.

Where the concentration of sulphur dioxide can be correlated with some other conditions, as in the case of a mine fire in sulphide ore, it is probable that a considerable number of samples would be analyzed and the use of a portable apparatus for the determination of sulphur dioxide at the scene of operations would be justified. A portable apparatus suitable for this purpose is described in Bureau of Mines Bulletin 287.²⁰

DETERMINATION OF OXIDES OF NITROGEN

Samples to be analyzed for oxides of nitrogen should be collected in specially prepared sample bottles and analyzed as soon as possible after collection. A method for the collection and analysis of such samples is described in Bureau of Mines Technical Paper 482.²¹

²⁰ Gardner, E. D., Howell, S. P., and Jones, G. W., Gases from Blasting in Tunnels and Metal-Mine Drifts: Bull. 287, Bureau of Mines, 1927, 96 pp.

²¹ Perrott, G. St. J., Babcock, L. W., Bitting, C. D., and Jones, G. W., Toxic Gases from 60 Percent Gelatin Explosives: Tech. Paper 482, Bureau of Mines, 1930, 30 pp.