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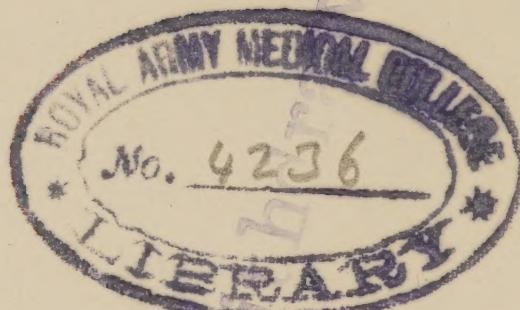
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## METHODS OF AIR ANALYSIS

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# METHODS OF AIR ANALYSIS

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## PREFACE TO FIRST EDITION

IN connection with experimental work in Physiology, Chemistry, and Hygiene, and in the investigation of mine air, products of combustion, etc., methods of air and gas analysis which are both rapid and accurate are greatly needed. This short book contains a description of methods—most of them more or less original—which I have found useful in this class of work. The book is in no sense a complete treatise on gas analysis. The methods described are only such as are designed to meet everyday needs in connection with the analysis of air and comparatively simple gas mixtures. Nearly all the original methods were first described in papers in the *Journal of Physiology*, *Journal of Hygiene*, *Transactions of the Institution of Mining Engineers*, or in Bluebooks ; and several of them were collected in *The Investigation of Mine Air*, now out of print. The descriptions are given in considerable detail, as attention to small matters of detail is often of much importance ; and a number of improvements, the result of extended experience, and not described in the original papers, are embodied in the text.

J. S. H.

*January, 1912.*

## PREFACE TO FOURTH EDITION

In the preparation of the present edition, for which the book has been revised throughout and considerably enlarged, I have had the co-operation of Mr. J. Ivon Graham, Deputy Director of the Mining Research Laboratory, University of Birmingham. The additions, for which Mr. Graham is almost entirely responsible, are mainly in connection with the exact determination of carbon monoxide, other poisonous gases, and dust suspended in air.

J. S. H.

*December, 1934.*

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# METHODS OF AIR ANALYSIS

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## CHAPTER I

### THE COLLECTION OF SAMPLES OF AIR

IN any investigation of the composition of air the first step is the collection of a sample for analysis. In collecting a sample it is necessary to take care (1) that the sample is not altered in the process of collection or storage, (2) that the vessel containing the sample is thoroughly air-tight. It is also very desirable to use a vessel which can be handled conveniently, and from which a portion of the sample can be transferred conveniently to the gas-analysis apparatus.

The simplest case is where the sample can be collected directly in the burette of the gas-analysis apparatus. This method can be used with a portable apparatus for the analysis of air at any point, for instance, in an ordinary room, an air-way in a mine, an experimental respiration chamber, etc. The burette is filled with mercury in the ordinary way described on p. 20, the tap of the burette closed, and the mercury reservoir lowered, so that on opening the tap at the point where a sample of air is wanted the mercury runs out of the burette and air is drawn in. The rate of outflow of the mercury can be regulated by a screw clip on the rubber tubing connecting the gas-burette with the reservoir, so that the collection of the sample is spread over some time ; and during the collection the apparatus, if it is portable, may be carried about in the room. By these

means a fair average sample may be obtained in cases where the air is not uniform in composition. In an experimental chamber uniformity of composition may be ensured by thoroughly mixing the air with an electric fan. Care must always, of course, be taken that the sample is not directly contaminated by the expired air of the person taking the sample.

In other cases it is necessary to collect samples of the air for subsequent analysis at some convenient time and place. Where a large volume of air has to be examined, as in a room, or a mine air-way or working-place, the samples are best collected in 2 or 3 oz. bottles sold as "medicine flats" and fitted with well-ground glass stoppers. These bottles hold 60 to 90 c.c., which is enough for several ordinary analyses, so that any determination can be repeated if necessary. They are cheap, easily obtained, and being flat are readily packed for sending by post where necessary. A number of them can easily be carried about. The stopper of each bottle is greased with vaseline, and after the sample is taken should be turned round until no air-channels are visible in the vaseline. The stopper is held in position by a fairly stout elastic band fixed over it, and a gummed label is placed on the bottle, as shown in fig. 1. Where a small amount of carbon monoxide has to be estimated by the delicate method described in Chap. XI, the sample should be taken in a 12 oz. bottle.

The bottles must be dry and clean. When first purchased, the bottle and stopper should each be marked with the same number and the bottle well washed out with dilute sulphuric acid to remove any free alkali from the glass. They should be cleaned with a brush, rinsed with clean (preferably distilled) water, and dried completely by leaving them on some warm place or blowing them out with air while they are kept warm. Alcohol, ether, etc., should not be used for

drying them, as traces may remain and may cause serious error. If a bottle is wet and dirty, an appreciable amount of carbon dioxide may appear, and oxygen disappear, by bacterial action. To quote an example, after four days the carbon dioxide had increased by 0·05 per cent., and after ten days by 0·12 per cent., in a wet and dirty bottle. If, on the other hand, the bottle is wet and clean the carbon dioxide gradually disappears, as it is absorbed by alkali dissolved out of the glass by the water. For instance, the whole of the carbon dioxide (0·03 per cent.) in a sample of pure atmospheric air had disappeared in a wet bottle in twelve days.

The rubber band is specially desirable for samples taken in mines, as the stopper might otherwise be blown out in consequence of diminution of atmospheric pressure during the ascent to the surface. Bottles with wide glass stoppers should not be used, partly because a wide stopper is more liable to be blown out, and partly because great inconvenience may be caused owing to the fact that a wide-mouthed bottle will not fit into the mercury trough used in transferring the air from the bottle into the gas-analysis apparatus.

The sample is collected as follows. One end of a piece of rubber tubing about 2 or 3 feet long, and  $\frac{1}{8}$  to  $\frac{1}{4}$  inch in internal diameter, is introduced into the bottle to the bottom, the other end of the tube being held in the mouth. A deep breath of air is then sucked in through the tube. The bottle is in this way very thoroughly washed out by the incoming air, since the volume of air sucked through will be

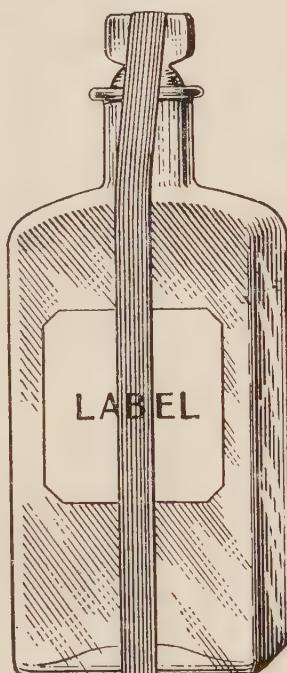


FIG. 1.—  
Sampling Bottle.

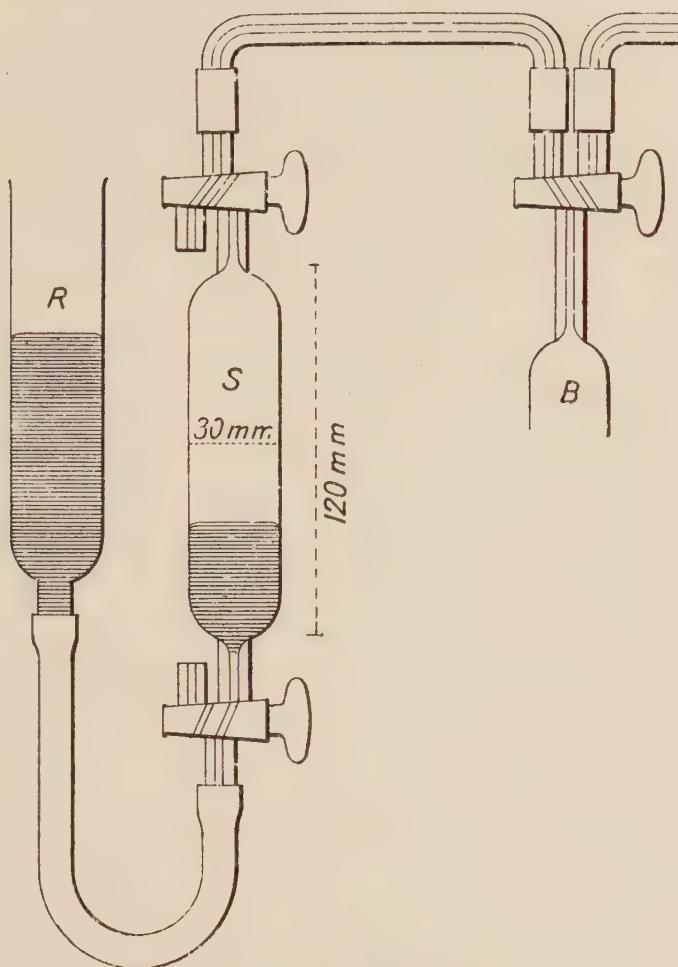
more than ten times as great as the capacity of the bottle. The tube is removed while the air is still being sucked up, so as to avoid any risk of breath passing backwards into the bottle. The stopper is then inserted, turned round, and secured as already described, and the particulars written on the label. Where for the reason mentioned a 12-oz. bottle is used for sampling at least six deep inspirations should be taken, the rubber tube being pinched and withdrawn from the mouth after each inspiration and expiration made with the head turned away from the bottle.

When the gas to be examined is issuing from a pipe or bore-hole a sample may be obtained by arranging a piece of rubber or bent glass tube so as to pass through a plug of clay inserted in the end of the pipe. The free end of the tube is then placed in the bottle, which must be inverted if the issuing gas is lighter than air. The stopper must, of course, be inserted as soon as the tube is withdrawn.

When samples are collected over water, or by emptying vessels of water, the carbon dioxide percentage is not reliable, as the water or wet bottle may have absorbed some of the gas, or the water may have given off carbon dioxide to the air. Samples collected in metallic vessels are unreliable as regards oxygen, if, as is often the case, oxidation of the metal is going on inside.

In physiological work, investigation of furnace gases, etc., the sample has often to be exhausted from a tube or other small space. In all such cases the form of sampling tube shown in fig. 2 is very convenient. It has a capacity of about 70 c.c., and is provided with a three-way tap at each end, the taps being arranged as shown in the figure. In taking a sample the sampling tube may be connected by a rubber tube with the mercury reservoir R in the manner shown. The sampling tube is then filled with mercury by raising R. The upper tap and connecting tubing to the point from which the

gas has to be drawn are also filled with mercury. The upper tap is then closed, and the reservoir R lowered. On opening the upper tap the mercury flows into R, and the sampling tube is filled with the gas. By regulating the lower tap the



S = Sampling tube.  
R = Mercury reservoir.  
B = Gas-burette.

FIG. 2.—Sampling Tube, showing Mode of Connecting with Buretto.

process of filling may be made very slow, if this is required. Another method is to exhaust the sampling tube S first. This is done by lowering R more than 30 inches below S, so that when the upper tap is closed S is completely exhausted. Both taps are then closed and S is disconnected, ready for use. Any connection between S and the source of the gas

should either be filled with mercury or with the gas to be examined. Some of this gas can be sucked through these connections by means of a piece of rubber tube attached to the free limb of the upper three-way tap, which is then turned so as to connect with the vacuous space in S, which is instantly filled with the gas. A series of samples can be taken very conveniently by means of vacuous sampling tubes. The gas is also very easy to transfer to the gas-analysis apparatus by the arrangement shown in fig. 2 and described on pp. 20-1.

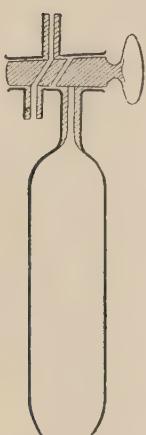


FIG. 3.—  
Bohr's Gas  
Receiver,  
slightly  
modified.

When the gas to be analysed and measured is delivered from a mercury pump, as in blood-gas analyses, etc., the form of receiver shown in fig. 3 is very convenient. This receiver is first filled with mercury (including the bore of the tap), and then placed over the delivery tube of the pump in a mercury vessel, so as to receive the gas, which can afterwards be transferred very easily to the gas-analysis apparatus.

For collecting a sample of gas or air at an even rate over any required period of time, Huntly<sup>1</sup> has devised the form of sampling tube shown in fig. 4. It will be seen from the construction of this tube that the gas is sucked in under a constant pressure until the mercury falls to within half an inch of the lower end of the tube. The rate of inflow was found to be constant within 1 per cent. In other respects, the construction and the precautions needed are the same as in the case of the sampling tube shown in fig. 2.

When samples are sent for analysis to an analyst it may save much trouble if he is informed as to the circumstances under which the sample was taken. If, for instance, the sample is one of mine air and he has been informed that a

<sup>1</sup> *Journ. Soc. Chem. Industry*, 1910, p. 312.

lamp would burn at the point where the sample was taken, he can proceed with the analysis without preliminary tests ; and similarly if he knows that the sample is from a blower of

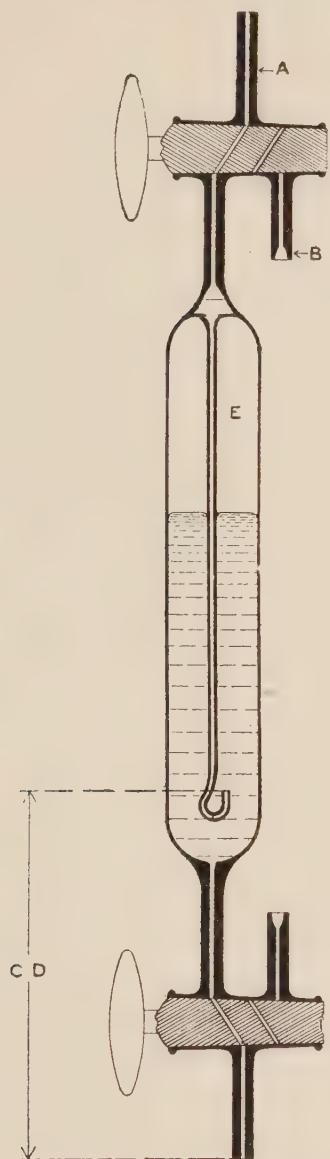


FIG. 4.—Huntly's Gas Sampling Tube.

fire-damp. He should also be informed if there is any reason to suspect the presence of small percentages of carbon monoxide or other unusual gas in small quantity.

## CHAPTER II

### APPARATUS FOR GENERAL AIR ANALYSIS AND GAS ANALYSIS

Two forms of gas-analysis apparatus, the same in principle, will be described. The larger form, which gives the more accurate results, is suited only for use in a laboratory where it can be set up permanently. The smaller form can be moved about easily, and may be used at any place where it is required ; for ordinary purposes, even in laboratory work, it has proved the more useful of the two, though it was originally designed for work outside a laboratory. The method of using the larger apparatus will be described first ; but, allowing for differences in detail, the description applies also to the smaller apparatus.

**Description of Large Apparatus** <sup>1</sup> (fig. 5).—The sample of air is measured in a gas-burette (A, fig. 5) about 32 inches (800 mm.) long, provided at the top with a three-way tap. The upper wide part is about 1 inch (25 mm.) in diameter, and has a capacity of about 15 c.c. The graduation, which is to 0·01 c.c., extends down the narrow part, which is 3·5 mm. in bore, from about 15 to 21 c.c., the capacity being measured from the tap (not including its bore) to the upper surface of the mercury. There are also marks at the first 5 c.c. on the wide part. With such a burette

<sup>1</sup> The various special forms of apparatus described in Chapters II, IV, V, and VI, are made by Messrs. Siebe, Gorman & Co., 187 Westminster Bridge Road, London. The apparatus in its original form was described in the *Journal of Physiology*, vol. xxii, 1898.

it is possible to read without the aid of a telescope to within an error of 0·001 c.c. A magnifying glass is desirable, however, and a good light behind the burette is also needed. The burette must, of course, be most carefully graduated by the maker. The most satisfactory method of

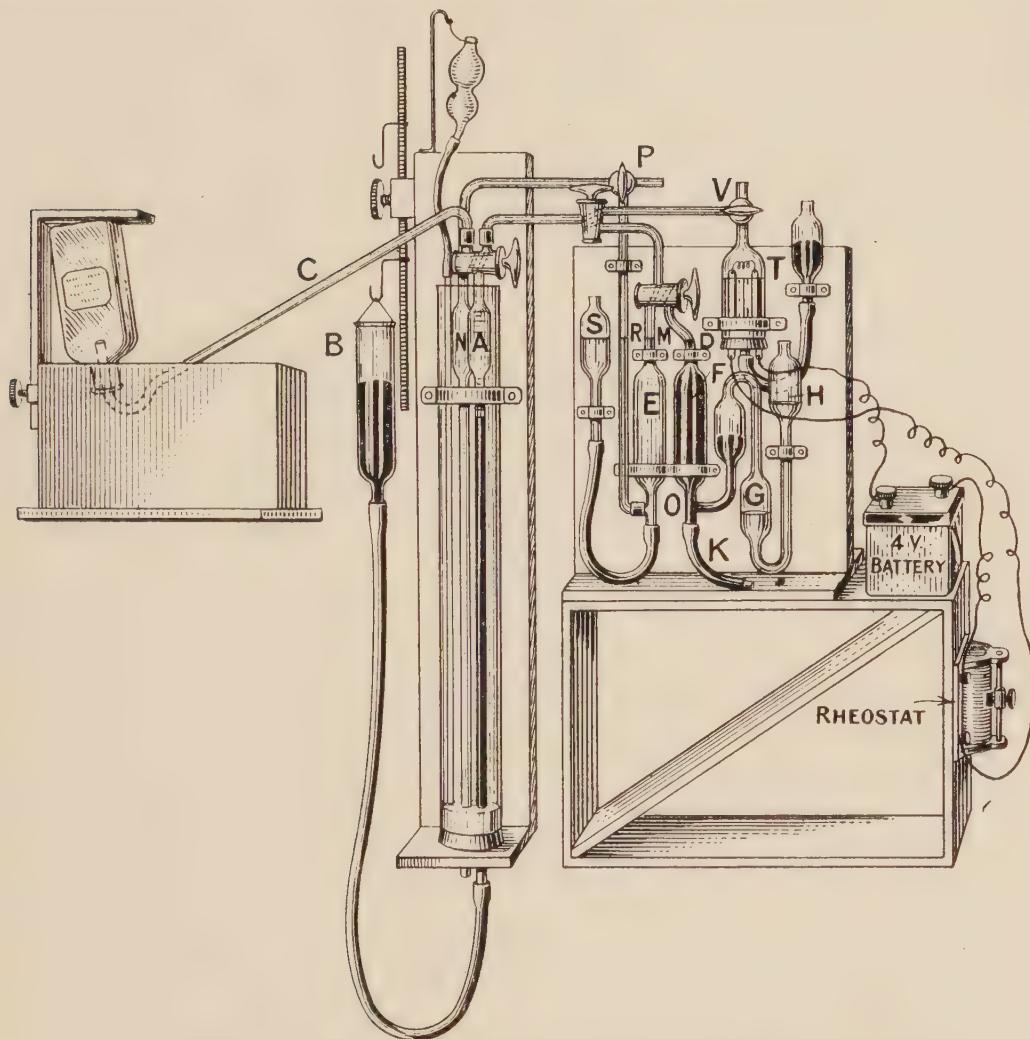


FIG. 5.—Larger Apparatus for Air Analysis.

checking the graduations is to fuse a tap temporarily to the lower end of the burette so that the calibration may be tested with the burette in its working position. The burette is filled with mercury moistened with a small amount of dilute sulphuric acid, as in actual use, and successive portions of mercury, 1 c.c. at a time, are accurately read off, run out

of the burette and weighed. The mercury is allowed to flow out through the tap into a weighed vessel, any hanging droplet of mercury being carefully brushed down before each weighing. Alternatively, to avoid the sometimes difficult task of sealing on a tap, the burette may be reversed and use made of the stopcock already on the instrument for running out the successive and accurately read quantities of mercury. In this case in estimating the volume from the tap to the first graduation it is necessary to add 0·004 c.c. to the volume calculated from the weight of mercury which flows out between these points, as the mercury has its convexity towards the tap when the burette is in its natural position. During the whole operation the temperature of the mercury in the burette must, of course, be kept constant. Another easy method of practically testing the calibration of the burette will be described later. An irregularly calibrated burette is a source of endless trouble, and should be rejected.

Surrounding the gas-burette is a water-jacket about  $2\frac{1}{2}$  inches in diameter, which may be fixed to a wooden stand as in fig. 5 or alternatively supported by an ordinary clamp fixed on a retort-stand, which is itself clamped to the front of the table. The water in the jacket can be mixed by blowing air through a glass tube passing to the bottom. The gas-burette is connected by means of thick-walled rubber tubing of about 3 mm. bore with the levelling vessel B, which may be of the form shown or a tube about 15 mm. in bore. The tube may be held by an easily opened spring clamp fixed to the retort-stand. By raising or lowering the reservoir gas is expelled from or drawn into the burette, and the pressure in the latter adjusted.

If the more compact form of mercury reservoir be employed, greater care is necessary in the levelling. This may be achieved by suspending the reservoir from a rack moved vertically by means of a pinion as depicted in the figure.

This is similar to the arrangement described later for the portable apparatus (p. 43). The rack should be at least 20 inches in height to enable, by means of holes at the top and bottom, the mercury to be adjusted rapidly and with accuracy to any position in the burette.

One of the three-way connections of the tap on the burette is used for taking in the sample, and the others connect the burette with absorption and combustion pipettes, which are arranged as shown. The connecting pieces are of 2 mm. bore, and are joined together by pieces of thick and soft red rubber tubing of the best quality, clean and smooth inside.

The absorption pipettes E and F are about 100 mm. long and 30 mm. in internal diameter. F is filled with glass tubes in order to increase the absorbing surface. The tubing leading up from them must have a bore of about 2 mm. (1·8 to 2·2 mm.). E is filled with caustic potash or soda solution (about 10 per cent.<sup>1</sup>), and is connected with the movable reservoir S by black rubber tubing, as black rubber is less apt than other kinds to give off sulphide to the potash solution. The alkaline pyrogallate solution filling F is made as follows. In 100 c.c. of nearly saturated solution (the specific gravity should be 1·55) of caustic potash 10 grammes of pyrogallic acid are dissolved in a bottle fitted with a rubber bung. This solution is introduced into F through the tube K by means of a large pipette, the open end of K being afterwards securely closed by a piece of glass rod pushed well in. G and H, which have each a capacity of about 30 c.c., are partly filled with some of the strong potash solution. This not only protects the pyrogallate solution from the oxygen of the air, but also prevents the solution from becoming gradually

<sup>1</sup> If gases, such as nitrous oxide, which are very soluble in water, but are not intended to be absorbed by the soda, are present, a saturated solution should be used to prevent solution.

diluted with water, as happens when plain water is placed in G and H.

The solutions last for a very large number of analyses (more than one hundred). When it is found that the oxygen absorption is becoming sluggish the pyrogallate solution should be changed. By mere standing in the absorption pipette it never deteriorates, which is a great advantage. It also has the advantage over phosphorus that it acts equally well whatever the oxygen percentage may be, and is very little affected by temperature. It is important that the solution should be made exactly in the manner described. If the potash is weaker the absorption of oxygen is much slower, and with some mixtures carbon monoxide may be formed.<sup>1</sup> The strong solution has the further advantage that its coefficient of solubility for gases is very low. It produces no measurable carbon monoxide, and is in every way a most perfect and convenient absorbent for oxygen. When freshly made it absorbs much less rapidly than after it has stood for some time. Moreover, it has been shown (*loc. cit.*), that the formation of carbon monoxide is appreciable for about two days with the freshly prepared solution. A stock of matured pyro should therefore be kept for recharging the pipette. Accurate results can be obtained with a freshly made solution, however, if it has been heated for an hour at about 100° C.

The pressure in the burette is adjusted by using the potash pipette as a pressure-gauge, and bringing the potash before every reading of the burette exactly to the mark M. As the potash solution has only about one-tenth of the specific gravity of mercury, and with a tube of 2 mm. bore the level can be adjusted very accurately, it is evident that the pressure can be adjusted with great exactitude.

<sup>1</sup> For recent investigations in this connection, see Haldane and Mackgill, *Analyst*, Vol. LVIII, pp. 378-9, 1933.

In order to make the readings of the burette entirely independent of changes in temperature, barometric pressure and percentage of moisture during the analysis, a control-tube N, which stands beside the burette in the water-jacket, is employed. The connecting tubes from N are of the same diameter and about the same length as those from the gas-burette ; and a three-way tap at P makes it possible to equalise the pressure in N with that of the atmosphere. By means of the T-tube O the potash solution is brought into connection with N. At the beginning of the analysis the potash is adjusted to the mark R by raising or lowering the potash reservoir S, P being open to the air. P is now turned so that the control tube is connected with the potash tube only, and is not again turned till the analysis is complete. Each time a reading of the burette is made the potash is brought to the mark R by raising or lowering S. The potash in the absorption pipette is then brought to the corresponding mark M by adjusting the levelling-tube. The readings of the burette are thus compensated by mechanical means for variations of temperature and barometric pressure during the analysis, so that temperature and pressure may be disregarded. The lower part of the control tube is kept full of water, and particular care must also be taken that the burette is kept moistened sufficiently to make its inner surface wet without fouling the mercury meniscus, so that the air in the burette and control tube is always saturated. The water used for moistening the inside of the burette should be slightly acidified with sulphuric acid in case alkali from the glass should render it alkaline ; and occasional re-moistening is also necessary. It is easy to see whether the burette is moist. The acidified water is introduced through the free limb of the tap, any excess being afterwards expelled by raising the levelling-tube. If the burette is allowed to become dry, very appreciable errors are produced. A sample

of pure air would, for instance, probably increase in volume when passed over into the potash pipette, as the air will take up more moisture than it loses CO<sub>2</sub> in contact with the potash solution.

The use of a control tube in gas analysis was first described by Williamson and Russell,<sup>1</sup> who employed a mercury pressure gauge. The same principle in a much improved form was applied in Pettersson's apparatus,<sup>2</sup> in which the movement of a drop of oil in a horizontal tube connecting the burette with the control tube is used as a pressure indicator, and extreme accuracy in the adjustment of pressure is thus obtained. The Pettersson apparatus is, however, difficult to manage, and the dead space in the glass tube connecting the burette with the pressure gauge cannot be washed out.

The combustion pipette T, which is filled with mercury, is about 80 mm. long by 30 mm. in internal diameter, and contains a spiral of three turns of very fine platinum wire (40 gauge). The current is led to the spiral through the two glass tubes shown. The ends of the wire forming the spiral are of sufficient length to allow of being squeezed into a small bunch which enables retention of the wire within the upper open portion of each tube. Pieces of stout platinum wire pass through the lower sealed ends of the two tubes (each of which is filled with mercury) and are connected through a variable rheostat combined, if necessary, with other suitable resistance, to a 4- or 6-volt accumulator. The combustion pipette is closed at the bottom by means of an india-rubber bung or cork saturated with paraffin wax, through which the two tubes pass as well as a third for connection to the small mercury reservoir, shown in fig. 5. Other forms of tubes for supplying the current required to heat the platinum coil have been used,

<sup>1</sup> *Journ. of Chemical Society*, 1868, p. 238.

<sup>2</sup> *Zeitschr. f. analyt. Chemie*, vol. xxv, pp. 467, 479.

but that described has been found to be the most reliable for the prevention of any minute leakage which, if taking place, will, of course, render an analysis untrustworthy. Tubes showing very slight leakage are a source of endless worry and should be immediately replaced by others which have been thoroughly tested. The bung or cork should be

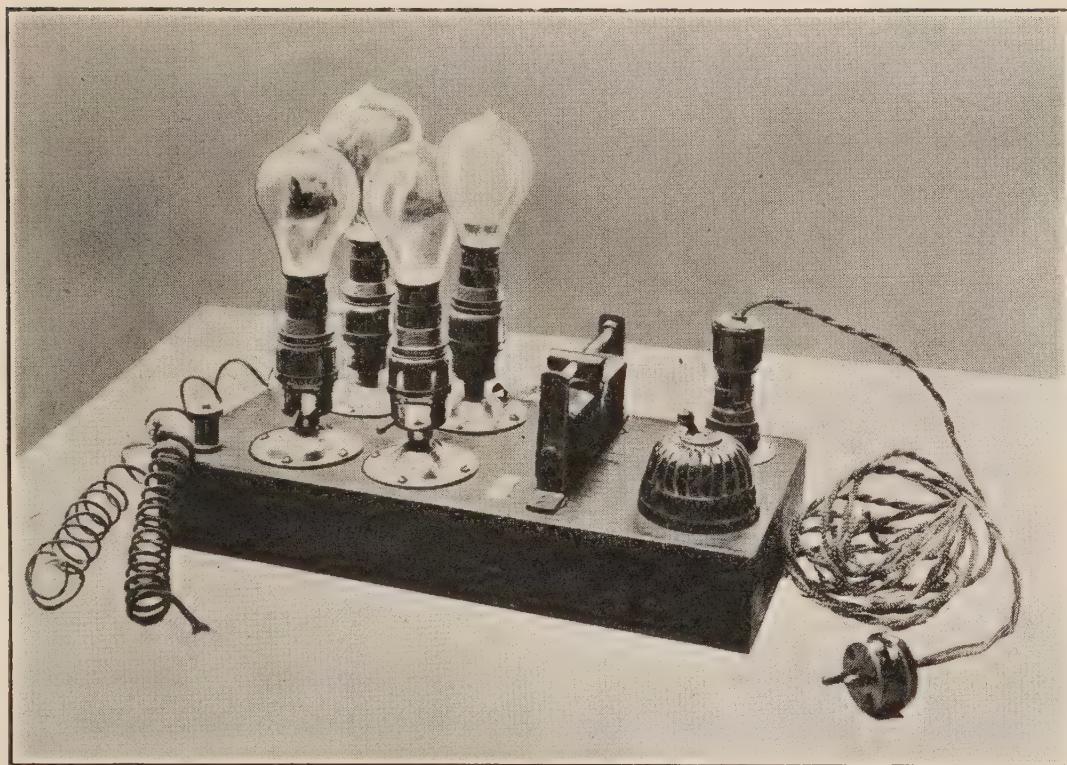


FIG. 6.—Rheostat with Lamp Resistances.

secured by wiring, to prevent its being driven out by an accidental explosion in the pipette.

A small double accumulator, such as is used on motor-cars, is suitable ; dry cells of sufficient size will also answer, or bichromate batteries. But perhaps the most convenient plan is to use the ordinary lighting current, with a suitable lamp resistance and rheostat, as shown in fig 6.<sup>1</sup>

<sup>1</sup> The long form of carbon filament lamp used in radiators is nowadays more easily obtainable than the type shown in fig. 6.

A rheostat is required, so that the current can be gradually increased until the spiral reaches a bright white heat. A lower heat is sufficient in burning hydrogen or carbon monoxide, but almost a white heat is desirable for methane, and the heat should be increased cautiously, as otherwise the wire may fuse owing to the extra heat produced at first by the combustion. A convenient form of small variable resistance is the circular type used for wireless apparatus.

The method of burning combustible gases by means of a heated platinum wire was first introduced by Coquillion<sup>1</sup> for the estimation of methane in mine air. It presents the advantage that where the volume of combustible gas present is less than sufficient to form an explosive mixture with air or oxygen it is not necessary to add hydrogen or detonating gas, as in the older methods of analysis, since, however small the proportion of combustible gas present may be, the combustion occurs very readily in the presence of the heated platinum. The addition of pure hydrogen, oxygen, etc., can thus be entirely done away with in gas analysis, and only air need be added when oxygen is required for the combustion. Since the composition of the outside air is practically constant, except during fogs in large towns, this is a great advantage, as errors arising from slightly impure oxygen, hydrogen, etc., or from the burning of nitrogen in exploding the sample, are entirely avoided, as well as the trouble of preparing pure oxygen, hydrogen, and detonating gas.

By the use of the control tube, pipettes permanently connected for absorption or combustion, the platinum spiral, and the special form of burette, with mercury as a confining liquid, the time required for accurate analysis of air and other simple gas mixtures is enormously reduced as compared with that needed by the older classical methods, and many troublesome calculations are dispensed with. The accuracy

<sup>1</sup> *Comptes Rendus*, vol. lxxxiv, p. 458, 1877.

attained is also greater. The apparatus is not suited for the analysis of very complex gas mixtures, but such analyses are but seldom required.

In order that the greatest accuracy may be attained with this apparatus it is essential that the total volume of the tubes between the burette and the various reagents should be kept as small as possible and the volume of the connections to the compensator be equal to that between the burette and the graduations on the potash pipette.

**Transference of Sample to Gas-burette.**—Before taking a sample of the gas into the gas-burette for analysis it is necessary to see that the connecting tubing to the absorption and combustion pipettes is free from any gas which has to be directly determined, or which might interfere with its determination. For instance, if oxygen has to be determined there must be no oxygen in the connections, or if methane has to be determined there must be no combustible gas in the connections. As a general rule the connections must be filled with nitrogen. A supply of this will probably have been left at the end of the previous analysis; and this nitrogen is always kept, so that the apparatus is ready to start on the new analysis. If, however, it has stood for some hours the connections should be washed through with the gas, so that any oxygen which has diffused in through the rubber joints (as happens if the apparatus stands for long) may be absorbed by the pyrogallate solution. If no nitrogen was left from the previous analysis some air may be taken in, and nitrogen prepared from it. If only carbon dioxide, or some combustible gas, has to be determined, the presence of oxygen in the connections does not matter. The next step is to bring the pyrogallate, mercury and potash to the marks D, V, R and M on the gauges of the absorption and combustion pipettes and of the control tube. The tap connecting with the control tube is then closed to the outside air.

If the sample is in a bottle the mercury trough shown in fig. 7 is needed. It is made either solid, or of two slabs of hard wood, which are so cut out that when they are screwed together a narrow slit open at the top is left between them.

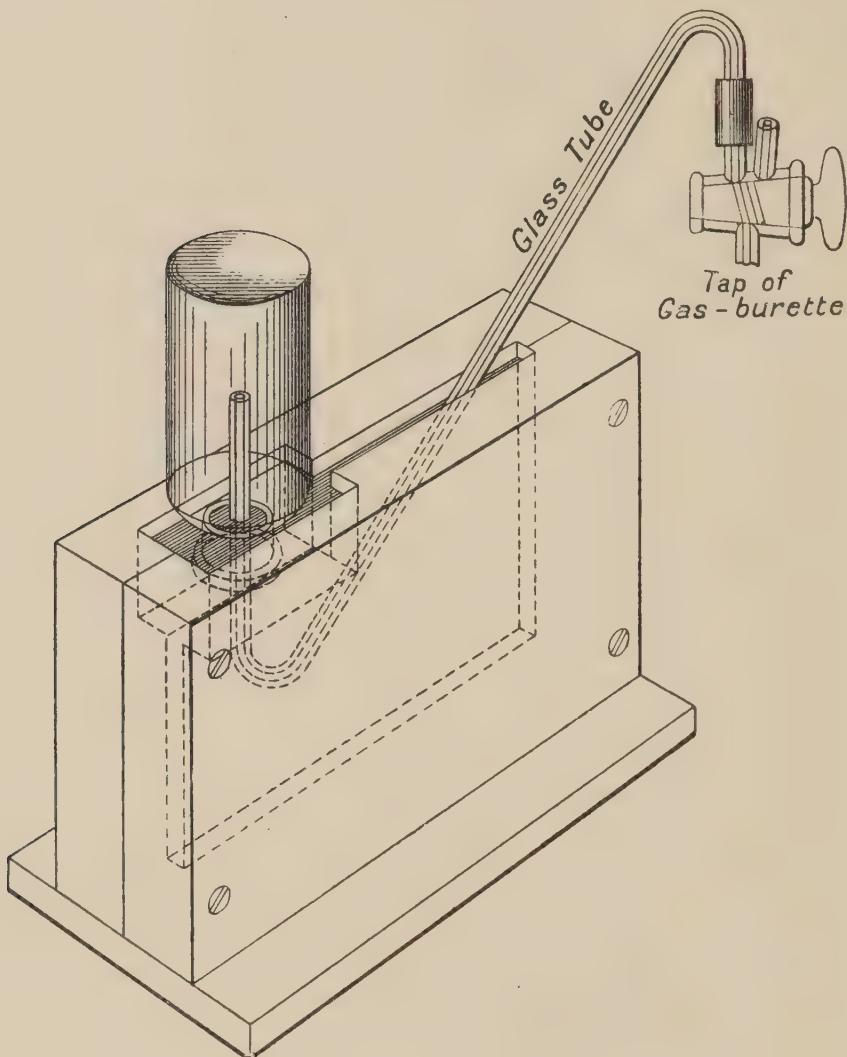


FIG. 7.—Mercury Trough for Sample-Bottles.

At one end of the upper part the slit expands into a rectangular space  $2\frac{1}{2}$  inches long by  $1\frac{1}{4}$  inches wide and  $1\frac{1}{2}$  inches deep, in which the neck of the bottle is received. The slit itself is  $\frac{1}{4}$  inch wide by 6 inches long and 4 inches deep. The trough, if made in two pieces, is rendered tight by a layer of marine glue.

A piece of narrow-bored glass tube, bent as shown in fig. 7, is used for transferring the sample. After the gauges of the burette have been adjusted in the manner already described, the tap of the burette is opened towards the outside, and the contained gas expelled through the bent tube attached to the top of the burette, mercury being allowed to follow until the bent tube is completely filled with it. The tap of the burette

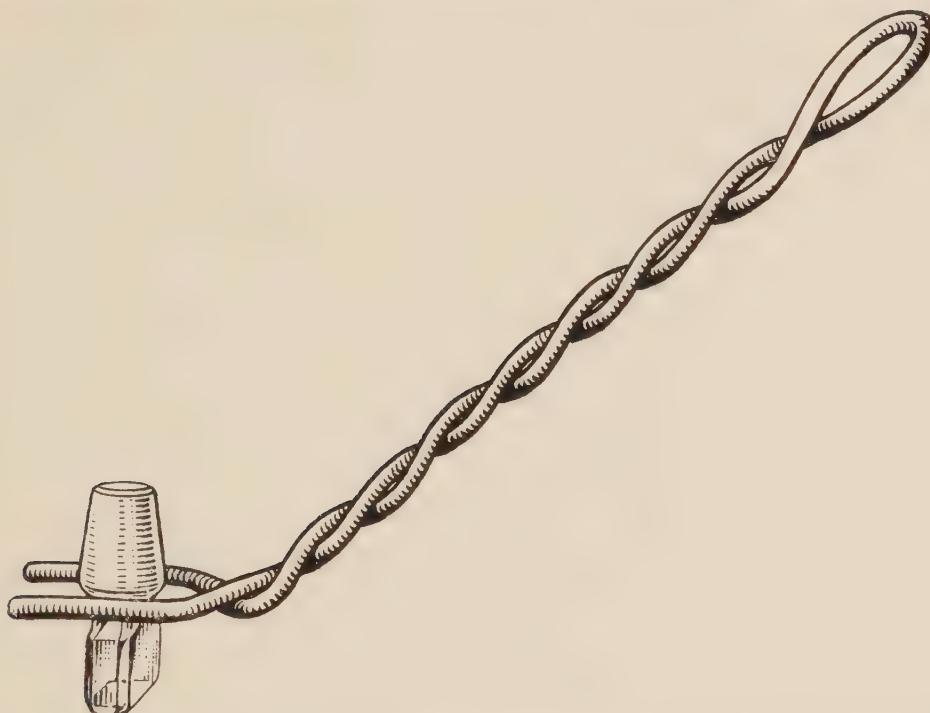


FIG. 8.—Fork for Manipulating Glass Stoppers under Mercury.

is then closed and the levelling tube lowered so as to produce a negative pressure in the burette.

The next step is to turn round the stopper of the sample bottle, so as to loosen it if it is tight. The neck is then inverted under mercury in the trough, and the stopper is removed with the help of a fork (fig. 8) made from stout iron wire.<sup>1</sup> This grasps the neck of the stopper, which can then be easily removed or replaced without letting any air into the bottle. If the stopper is removed under water, which may

<sup>1</sup> The use of a fork was suggested by Fleet-Surgeon Rees, R.N.

sometimes be necessary with an awkwardly shaped stopper, the bottle should first be slightly warmed, so as to ensure that the pressure inside is positive, and no water enters ; the neck is then at once closed by the middle finger and the bottle transferred to the mercury trough.

The free end of the bent tube is now depressed below the mercury level and introduced into the neck of the bottle, and the tap of the burette is turned so as to allow the sample to be sucked into the burette. During this operation the bottle should be steadied with one hand ; as soon as the sample is transferred the bottle becomes steady owing to the fact that mercury has been sucked up inside it, and support by the hand is no longer necessary. More than 20 c.c. of the sample should in most cases be taken in, after which the tap is completely closed by a quarter-turn. The pressure inside the burette is now negative, and must be roughly adjusted to atmospheric pressure by raising the reservoir, B. It is then safe to turn the tap so as to connect the burette with the potash pipette. If there was much negative pressure in the burette the potash might be sucked over on opening the tap. A positive pressure might, on the other hand, drive some of the sample into the potash pipette before the first reading was taken.

The general procedure required when the sample is contained in a sampling tube will be evident from fig. 2. The sampling tube is connected with the mercury reservoir, any air-bubbles being driven out through the free limb of the lower three-way tap. The burette is also connected with one end of the sampling tube by a piece of glass tubing of 2 mm. bore, and bent as shown in the figure. The gas in the burette is then expelled through the free limb of the three-way tap on the upper end of the sampling tube, and mercury is driven over so as to fill the connections up to this tap. Any mercury which escapes can be caught in a small test-tube

hung from the barrel of the tap by a wire. The tap on the sampling tube is then completely closed, and the reservoir B depressed, so that any leakage in the connections, or the presence of any air-bubble, can be detected at once. An air-bubble sometimes sticks at the rubber joint between the connecting tube and sampling tube. To expel this the easiest plan may be to pinch one side of the rubber so as to allow a channel of escape for the bubble. Soft, black rubber should therefore be used in making the joint. When everything is ready the reservoir, B, is lowered and the taps opened so that a sample is sucked into the burette. The pressure inside the burette can then be adjusted to normal by raising or lowering the reservoir R, or B (fig. 5).

If the sampling tube has only plain taps, the glass tubing above the tap must be filled with mercury by means of a fine glass pipette before the sampling tube is joined to the connecting tube. The air is then expelled from the latter after pinching one side of the rubber joint so as to open a channel. The free end of the lower tap must also be filled with mercury before connecting with the rubber tube attached to R. It is then possible to make a connection without including any air.

**Process of Analysis.**—The procedure to be adopted will evidently depend on the composition of the sample, and on what constituents it is necessary to determine. The qualitative, and approximate quantitative, composition of the sample will generally be known beforehand, and will thus be a guide. A series of examples will illustrate the various procedures.

Let us first take the simple, but extremely common, case, in which the sample is known to contain nothing but carbon dioxide, oxygen and nitrogen. A sample of expired air collected in a bag during a respiration experiment will serve as an example.

After the sample has been taken into the burette and the pressure roughly equalised, as already described, the next step is to open the tap of the burette so as to connect with the potash pipette. The level at which the potash stood had previously been adjusted exactly to the mark (M, fig. 5) with the connections to the potash and pyrogallate pipettes filled with nitrogen, as also already described. On opening the tap this level will probably be slightly disturbed, and the potash level at R may also have shifted a little. By raising or lowering S the potash level is exactly adjusted at the mark R, and by raising or lowering the levelling tube the potash level at M is also exactly adjusted. Before doing this, however, some air should be forced through the mixing tube, so as to make the temperature even in the water-jacket. The level of the top of the mercury contained in the burette is now read off exactly to 0·002 c.c. with the help of a lens. The air is then driven into the potash pipette by raising the reservoir B, which is removed from its hook and held in the hand. The mercury is allowed to pass up in the burette to the level of the neck, but not further. The air is then brought back till the potash rises to about M, and this process is repeated about four times, after which all the carbon dioxide will have been absorbed, as shown by the fact that no further diminution of volume occurs. The water in the jacket is again mixed, and the two potash levels adjusted, and a second reading is taken, which shows the volume of carbon dioxide in the sample. The burette is now connected with the pyrogallate pipette, and the air driven over into this, and returned once or twice, after which nearly all the oxygen will have been absorbed. Some oxygen is, however, left in the connection between M and the tap, so this connection is washed out by passing the gas into the potash pipette and back, and then into the pyrogallate pipette and back twice. The washing-out is afterwards repeated to remove the last

traces of oxygen. The levels at D, R and M are then adjusted as previously, and a reading again taken, which shows the volume of oxygen absorbed. If any doubt remains as to the completeness of the absorption of oxygen, the gas should be returned once more to the pyrogallate pipette. If absorption was complete, the reading afterwards should be exactly the same.

The following is an example of the figures obtained :—

	C.c.
Volume of expired air taken .	20·612
After CO <sub>2</sub> absorbed . . . .	19·846
<hr/>	
∴ CO <sub>2</sub>	$= 0\cdot766 = 3\cdot72$ per cent.
After O <sub>2</sub> absorbed . . . .	16·424
<hr/>	
∴ O <sub>2</sub>	$= \underline{\underline{3\cdot422}} = 16\cdot60$ per cent.

As it was known that the sample contained only oxygen, carbon dioxide, and nitrogen (including argon), the latter gas may be calculated by difference, so that the result of the analysis is :—

	Per cent.
Carbon dioxide . . . .	3·72
Oxygen . . . .	16·60
Nitrogen . . . .	79·68
<hr/>	
	<u><u>100·00</u></u>

In this statement of the result no account is taken of errors in the burette. Appreciable errors are nearly always present, however, and must be corrected for. The method of correcting for these errors will be discussed later.

Let us now suppose that the sample contained more than

30 per cent. of oxygen, or carbon dioxide, or of both gases together. It is clear that if the burette has been filled with the sample at first, it will not be possible to get any reading after absorption of the oxygen, as the mercury level will be above the graduations. In such a case sufficient nitrogen to fill the burette to the top of the graduation must be kept from the last analysis, and only enough of the sample taken in to fill up the burette to near the bottom of the graduation. The analysis can then be done without difficulty. We may take as an example the analysis of a sample of commercial oxygen from a steel cylinder. The volume of nitrogen retained from the last analysis, and measured with the usual precautions, was 15.146 c.c. This was then shunted completely into the pyrogallate pipette. About 5 c.c. of the sample were then taken into the burette, the amount being roughly estimated by the coarse graduations on the upper part of the bulb of the burette. The nitrogen was then drawn back from the pyrogallate pipette and the total volume of gas was now measured, and found to be 20.202 c.c., so that 5.056 c.c. of the sample had been taken in. The analysis of this was then proceeded with in the ordinary way, with the following results :—

	C.c.
Nitrogen in burette . . . .	15.146
+ sample taken in . . . .	20.202
<hr/>	
∴ sample . . . .	= 5.056
After CO <sub>2</sub> absorbed . . . .	20.202
<hr/>	
∴ CO <sub>2</sub> . . . .	= 0.000 = 0.00 per cent.
After O <sub>2</sub> absorbed . . . .	15.284
<hr/>	
∴ O <sub>2</sub> . . . .	= <u>4.918</u> = 97.27 per cent.

In this case it is clear that the degree of accuracy of the analysis will be less than when the whole burette has been filled with the sample ; for the readings can only be made to one part in 5,000 (or 0·02 per cent.), instead of one part in 20,000. On the other hand, there will probably be no correction for error in the burette, as will be explained on p. 41.

The next case is that of air containing some one combustible gas, as well as carbon dioxide, oxygen and nitrogen. The following analysis of air from a return air-way in a colliery is a typical example. As the sample was collected at a place where lamps burned, it was known that the air contained sufficient oxygen to burn any methane which was present.

Before the analysis the connections of the combustion pipette, as well as of the absorption pipettes, were filled with nitrogen. About 20 c.c. of the sample were taken in and measured ; the carbon dioxide was then absorbed and the residue measured. The gas was then passed into the combustion pipette, the spiral heated white hot, and the gas passed backwards and forwards over the spiral several times. After waiting a short time for the glass to cool, the mercury in the combustion tube was readjusted to the mark, and the gas measured in order to obtain the contraction on combustion. The CO<sub>2</sub> formed by the combustion was then absorbed in the potash pipette, care being taken to wash out the combustion pipette, so as to remove any CO<sub>2</sub> left in the connections. After again measuring to obtain the volume of CO<sub>2</sub> formed, the gas was passed over the spiral in order to burn the fraction which had escaped the first combustion, owing to the existence of the small dead space in the connection to the potash pipette. Without waiting to obtain the second contraction, the CO<sub>2</sub> formed was absorbed. The total contraction was then measured. After this the oxygen remain-

ing in the sample was absorbed and the residue of nitrogen measured. The actual measurements were as follows :—

	C.c.
Volume of air taken . . .	20.024
After CO <sub>2</sub> absorbed . . .	19.982
	<hr/>
∴ CO <sub>2</sub>	= 0.042 = 0.21 per cent.
After combustion . . .	19.480
∴ contraction	= 0.502
After CO <sub>2</sub> absorbed . . .	19.230
	<hr/>
∴ CO <sub>2</sub> absorbed	= 0.250
After second combustion and CO <sub>2</sub> absorption . . .	19.206
	<hr/>
∴ difference	= 0.024
After O <sub>2</sub> absorbed . . .	15.642
	<hr/>
∴ oxygen absorbed	= 3.564
	<hr/>

In this sample the only combustible gas present was methane (CH<sub>4</sub>). This is indicated, though not conclusively proved, by the fact that the contraction on combustion was, within the error of analysis, exactly double the carbon dioxide formed. A mixture of equal parts of carbon monoxide and hydrogen, or ethane and hydrogen, would also give a contraction which was double the carbon dioxide formed ; but such mixtures do not occur in a mine, so their possible existence need not be considered, and we may assume that the combustion took place in accordance with the equation



As the water condenses, the volume of CH<sub>4</sub> present is

evidently half the contraction on combustion, or one-third of the total diminution of volume after all the CO<sub>2</sub> has been absorbed. This total diminution was 0·502 + 0·250 + 0·024 = 0·776, and this  $\times \frac{1}{3} = 0\cdot259$ , which is 1·29 per cent. of the volume of air taken.

The oxygen which disappeared in the combustion was evidently double the volume of methane, or  $0\cdot776 \times \frac{2}{3} = 0\cdot517$ , and the oxygen left was 3·564, so that the total oxygen present in the air taken was  $0\cdot517 + 3\cdot564 = 4\cdot081$ , or 20·38 per cent.

The result of the analysis was thus :—

	Per cent.
Oxygen . . . . .	20·38
Carbon dioxide . . . . .	0·21
Methane . . . . .	1·29
Nitrogen . . . . .	78·12
	<hr/>
	100·00
	<hr/>

It is often only the methane percentage which is required in an analysis of mine air. In such a case it is only necessary to measure the volume of air taken, pass it directly to the combustion pipette, and then measure again. The methane present is equal to half the contraction.

If the sample does not contain, or is not known to contain, sufficient oxygen to burn the combustible gas, it must first be diluted with a sufficiency of air. The degree of dilution necessary will depend on the nature and amount of the gas known to be actually or possibly present ; and in any case sufficient oxygen must be present in the air to burn completely the maximum of combustible gas which might be present. As a general rule the dilution should be sufficient to ensure that the gas will burn quietly without exploding in the combustion pipette, as, unless the cork of the latter

is very firmly secured, it might be loosened by a sharp explosion. To form a mixture which is just explosive,<sup>1</sup> 12·5 per cent. of carbon monoxide, 4·1 per cent. of hydrogen, 5·6 per cent. of methane, 3·4 per cent. of ethylene, 3 per cent. of acetylene, or 1·5 per cent. of benzene or pentane, must be present ; and for commonly occurring mixed gases the corresponding limits are about 12 per cent. for water-gas, and 8 per cent. for coal-gas. The sample ought, therefore, to be so diluted with air that the percentage of the combustible gas shall not exceed these limits. Thus, if a sample of carbon monoxide is being analysed for purity, as may be frequently necessary in certain kinds of physiological work, not more than 2·5 c.c. of gas should be taken to 20 c.c. of the mixture of air ; or if a sample of fire-damp from a blower or cavity in the roof were being examined, less than 1·2 c.c. should be taken to 20 c.c. of the mixture, since the gas *might* be almost pure methane. It may, of course, turn out that the combustible gas was very dilute. In such a case a second analysis should be done if much exactitude is necessary—particularly if the first analysis showed that the sample could be analysed without any dilution. If, however, anything is known about the sample, or any proper description has been given by the person who may have sent it, a second analysis is seldom needed.

The following analysis of gas issuing through a pipe from behind a stopping in a coal-mine will serve as an example. From indications of the safety-lamps it was known that this gas contained much fire-damp and was possibly almost pure fire-damp. Sufficient pure outside air was first taken in, freed from CO<sub>2</sub>, measured, and shunted into the potash pipette. About 1 c.c. of the gas was then taken in and roughly measured by the coarse graduations, the air added,

<sup>1</sup> Coward, Carpenter and Payman, *Trans. Chem. Soc.*, 1919, Vol. 115, p. 29.

and the analysis then proceeded with as usual, the results being as follows :—

	C.c.
Air (freed from CO <sub>2</sub> ) . . .	18·892
+ sample taken in . . .	20·010
	<hr/>
∴ sample . . .	= 1·118
After CO <sub>2</sub> absorbed . . .	19·976
	<hr/>
∴ CO <sub>2</sub> . . .	= 0·034 = 3·0 per cent.
After first combustion . . .	18·824
	<hr/>
∴ contraction . . .	= 1·152
After CO <sub>2</sub> absorbed . . .	18·248
	<hr/>
∴ CO <sub>2</sub> formed . . .	= 0·576
After second combustion and absorption of CO <sub>2</sub> . . .	18·196
	<hr/>
∴ difference . . .	= 0·052
After oxygen absorbed . . .	15·360
	<hr/>
∴ oxygen which remained after combustion . . .	= 2·836

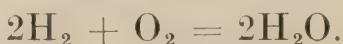
As the contraction was exactly double the CO<sub>2</sub> formed, the combustible gas was evidently pure methane. The total diminution in volume after combustion and absorption of CO<sub>2</sub> was 1·152 + 0·576 + 0·052, or 1·780, and this  $\times \frac{1}{3}$  gives the volume of methane, which is 0·593, or 53·0 per cent. of the volume of gas taken. With the burette used, the oxygen percentage in pure outside air free from CO<sub>2</sub> was 21·01 per cent. Hence the volume of oxygen in the 18·892 c.c. of air taken was 3·969 c.c. But 1·187 c.c. of oxygen were used up

in the combustion, and the excess over at the end was 2.836 c.c.—total 4.023 c.c. Hence  $4.023 - 3.969 = 0.054$  c.c. was present in the sample, or 4.8 per cent. The result of the analysis was therefore as follows :—

	Per cent.
Carbon dioxide . . . . .	3.0
Oxygen . . . . .	4.8
Methane . . . . .	53.0
Nitrogen . . . . .	39.2
	<hr/>
	100.0
	<hr/>

It will be noticed that the percentages are calculated to 0.1 per cent., and not to 0.01 per cent., as in the previous examples. It would be useless to calculate the results further, as the figures would be meaningless, since the graduation of the burette and other experimental errors do not permit of a division of 1.118 c.c. (the volume taken) into smaller parts than one-thousandth. The common practice of putting wholly meaningless figures into the results of an analysis is greatly to be deprecated. If it were of any importance to obtain more accurate results for the carbon dioxide and oxygen, a determination of them could be made with 20 c.c. of the sample ; or a second analysis could be done in the same way as the first, but with double as much of the sample, since only about half the gas was methane.

The foregoing examples will serve to illustrate the general method of determining a combustible gas when one such gas only is present in the sample ; but, of course, the ratio of contraction on combustion to carbon dioxide formed will vary with the kind of combustible gas present. If, for instance, this gas is hydrogen, the combustion will take place in accordance with the equation



The contraction on combustion will thus be  $1\frac{1}{2}$  the volume of hydrogen, and no  $\text{CO}_2$  will be formed. If the gas is carbon monoxide, the equation is

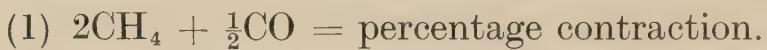


so that the contraction will be half, and the  $\text{CO}_2$  will be equal to, the volume of CO present. Whatever the combustible gas or vapour may be, the relation between volume of gas present, contraction on combustion, and volume of  $\text{CO}_2$  formed, must be kept in mind ; and if the relation between contraction and  $\text{CO}_2$  formed does not correspond to the theoretical value within the limits of error, some other combustible gas must be present.

If more than one combustible gas is present, it is generally known what these gases are, or may be ; and if only two or three can be present, the percentage of each may be determined by means of the apparatus just described. If the possible gases are carbon monoxide and hydrogen (water-gas and various kinds of "producer" gas) it is clear that the carbon monoxide is equal in volume to the carbon dioxide formed on combustion. From this the contraction due to carbon monoxide can be calculated. The rest of the contraction is due to hydrogen, and will be  $1\frac{1}{2}$  times the volume of the hydrogen. If the gases are methane and hydrogen (gases produced in the intestine, by cellulose fermentations outside the body, etc.), a corresponding mode of calculation is applicable.

If only two gases are present, but they both contain carbon, their proportions can still be calculated from the contraction and  $\text{CO}_2$  formed. Let us suppose that the two gases are methane and carbon monoxide. As already explained, one volume of methane gives two volumes of contraction and one volume of  $\text{CO}_2$ , while one volume of carbon monoxide gives half a volume of contraction and one volume

of  $\text{CO}_2$ . Hence, if the symbols  $\text{CH}_4$  and  $\text{CO}$  represent the percentages present of each of these gases, we have the following equations :—



By multiplying both sides of the second equation by two, and subtracting equation (1) from the product, we find that  $1\frac{1}{2} \text{ CO} = \text{twice the percentage of } \text{CO}_2 \text{ formed minus the percentage contraction.}$  From this result, and equation (2), it is easy to calculate the percentages of  $\text{CO}$  and  $\text{CH}_4$ , and also the percentage of oxygen consumed in their combustion.

In most ordinary cases where such gases as methane and carbon monoxide occur together hydrogen is also present, or may be present ; and in many cases where hydrogen and carbon monoxide are present methane may also be present. This is the case, for instance, in mine air vitiated by the after-damp of an explosion of coal-dust or methane, gases from explosives, or from coal which has heated, etc., also in exhaust gases from internal combustion engines, flue-gases, etc., where the combustion has been imperfect. In such cases it is necessary to determine not only the contraction and  $\text{CO}_2$  formed, but also the oxygen consumed. For this purpose it is necessary to make two analyses : the first to determine the carbon dioxide, contraction on combustion,  $\text{CO}_2$  formed on combustion, and residual oxygen ; and the second to determine the oxygen originally present in the sample.

The following is an example of an analysis of a sample of air vitiated by the products of explosion of gelignite, and also to some extent by products of respiration, etc. The sample was taken in a “rise” in a metalliferous mine five minutes after eight bore-holes had been blasted.

*First Analysis.*

	C.c.
Volume of air taken . . . . .	20·298
After CO <sub>2</sub> absorbed . . . . .	19·740
<hr/>	
∴ CO <sub>2</sub> . . . . .	$= 0\cdot558 = 2\cdot75 \text{ per cent.}$
After combustion <sup>1</sup> . . . . .	19·707
<hr/>	
∴ contraction . . . . .	$= 0\cdot033 = 0\cdot16 \text{ per cent.}$
After CO <sub>2</sub> absorbed . . . . .	19·659
<hr/>	
∴ CO <sub>2</sub> formed . . . . .	$= 0\cdot048 = 0\cdot24 \text{ per cent.}$
After residual oxygen absorbed . . . . .	15·668
<hr/>	
∴ residual oxygen . . . . .	$= \underline{\underline{3\cdot991}} = 19\cdot66 \text{ per cent.}$

*Second Analysis.*

	C.c.
Volume of air taken . . . . .	20·294
After CO <sub>2</sub> absorbed . . . . .	19·736
<hr/>	
∴ CO <sub>2</sub> . . . . .	$= 0\cdot558 = 2\cdot75 \text{ per cent.}$
After O <sub>2</sub> absorbed . . . . .	15·719
<hr/>	
∴ O <sub>2</sub> . . . . .	$= \underline{\underline{4\cdot017}} = 19\cdot79 \text{ per cent.}$

From the two oxygen determinations it follows that the oxygen consumed in the combustion of the gas in the sample was  $19\cdot79 - 19\cdot66 = 0\cdot13$  per cent. The contraction on combustion was 0·16 per cent., and the CO<sub>2</sub> formed 0·24 per cent.

<sup>1</sup> To simplify the statement, the very slight differences observed on a second combustion are not separately set down.

In the explosion of gelignite and combustion of the fuses the only gases formed in appreciable quantities are CO, H<sub>2</sub>, and traces of CH<sub>4</sub>. The proportions in which these gases produce contraction on combustion and formation of CO<sub>2</sub> have already been stated, and CO and H<sub>2</sub> each consume half their volume of oxygen, while CH<sub>4</sub> consumes twice its volume of oxygen. Hence if, as before, the symbols CO, H<sub>2</sub> and CH<sub>4</sub> are taken to represent the percentages present of each of these gases, we have the following equations :—

- $$(1) \text{CO} + \text{CH}_4 = 0.24 \text{ per cent.}$$
- $$(2) \frac{1}{2}\text{CO} + 2\text{CH}_4 + 1\frac{1}{2}\text{H}_2 = 0.16 \text{ per cent.}$$
- $$(3) \frac{1}{2}\text{CO} + 2\text{CH}_4 + \frac{1}{2}\text{H}_2 = 0.13 \text{ per cent.}$$

By subtracting (3) from (2) we find that H<sub>2</sub> = 0.03 per cent. ; and from (1) and (2), after eliminating H<sub>2</sub> from (2), we find that CH<sub>4</sub> = 0.00 and CO = 0.24.

The result of the analysis is therefore as follows :—

	Per cent.
Oxygen . . . . .	19.79
Carbon dioxide . . . . .	2.75
Carbon monoxide . . . . .	0.24
Hydrogen . . . . .	0.03
Methane . . . . .	0.00
Nitrogen . . . . .	77.19
<hr/>	
	100.00

When more than three combustible gases or vapours are present they cannot be separately determined by the apparatus described. For instance, in the complete analysis of lighting gas, which contains hydrogen, methane, ethane, carbon monoxide, ethylene, benzene, etc., much more complicated procedures are needed. For some purposes, however, as in determining the percentage of lighting gas in a mixture

of the gas with air, it is quite sufficient to determine the contraction or the CO<sub>2</sub> formed on combustion, provided that it is known what contraction, or formation of CO<sub>2</sub>, a given volume of the original gas gives.

**Management of Apparatus.**—After an analysis the taps should be so turned as to disconnect the burette from the absorption pipettes and open the control tube to the air. Unless this is done a fall of temperature or rise of barometric pressure may cause the potash to be sucked over.

At the end of an analysis the nitrogen left over should be kept. It should be stored in the pyrogallate pipette if, in the next analysis, a determination of oxygen is not needed. It can then be used to wash out the connections before any future determination of oxygen.

If through any accident potash or pyrogallate solution has been sucked over, the taps are sure to stick unless they are carefully cleaned. The burette must, of course, also be cleaned out. For this purpose any potash solution should first be driven out of the burette. Water acidified with a little sulphuric acid is then introduced from a pipette the end of which is pushed into the rubber tubing on the free limb of the three-way tap at the top of the burette. The dilute acid is allowed to run down to the bottom of the burette, and is then cautiously passed along the connecting tubes and down to the marks in the absorption pipettes, so as to remove all alkali. After this operation is complete the acid is driven out of the burette again as completely as possible, but, of course, leaving the glass moist. The taps are then all removed, wiped clean, together with their seatings, and greased with a fresh layer of vaseline. Should a tap jam it should be heated cautiously with a Bunsen flame, which will usually loosen it ; but it may have to be cut out, and a fresh one substituted.

The burette should be cleaned with nitric acid whenever

it begins to look dirty. For this purpose the rubber tubing connecting it with the mercury reservoir is detached, and nitric acid from a small porcelain capsule sucked up cautiously with the help of rubber tubing attached to the free limb of the three-way tap. The nitric acid is afterwards washed out thoroughly with water, and finally dilute sulphuric acid is used.

Alternatively chromic acid, prepared from concentrated sulphuric acid and powdered potassium bichromate, may be employed. The concentrated solution is sucked up into the burette, as described for cleaning with nitric acid, and the burette left filled for some hours, preferably overnight. It is subsequently washed out with water and finally with dilute sulphuric acid.

If the joints in the connecting tubing to the absorption pipettes have been made with soft and thick red rubber tubing they should be perfectly tight from the beginning, and should remain tight. They do not need wiring. The tap should also be tight. A tap that is so badly ground as to leak occasionally should be changed. To test for leakages, heavy pressure should be brought on the different joints in succession. To do this the tap at P should first be turned so as to shut off connection with the control tube or outer air. The connecting tube between the potash pipette and S is then compressed firmly with one hand and squeezed with the other at a point nearer the potash pipette. By this means the pressure in the potash pipette is greatly increased, and any leakage between the potash pipette and the burette is revealed by the potash creeping up from the mark M. The connections of the combustion and pyrogallate pipettes and control tube are all tested by similar methods, and there is no difficulty in rapidly detecting any leakage. The powder used for dusting the inside of the rubber tubing may cause slight and very troublesome leaks.

These do not occur if the rubber is perfectly clean and smooth, or if a little vaseline is used.

A possible source of slight error in the carbon dioxide determinations is the fact that when the potash pipette is first charged the potash may dissolve a little sulphide from sulphur present in the rubber. The potassium sulphide may then absorb an appreciable quantity of oxygen when air is passed into the pipette, so that in successive blank experiments with air the reading is slightly lower each time. If the potash has begun to turn yellow some sulphide is sure to be present, and the pipette should be recharged with fresh solution. If, however, black rubber tubing is used for connecting the potash pipette with the potash reservoir, this source of error can easily be avoided. In the earlier forms of the apparatus the potash pipette was closed below by a red rubber cork, which continued for long to give off sulphide.

To test the efficient working of the apparatus it is an excellent plan to make an analysis of outside air. After the carbon dioxide has been absorbed the reading of the burette should be the same after repeated passage of the air into the potash pipette, or into the combustion pipette, whether or not the spiral has been heated. After the oxygen has been absorbed the reading should also remain steady after repeated passing of the air into the pyrogallate pipette ; and the percentage of oxygen, or at any rate the sum of the percentages of carbon dioxide and oxygen, should be the same for each analysis. If any leakage or other source of accidental error exists anywhere it will be detected by these tests. They are quite indispensable for a beginner, and will soon give him an idea of the great accuracy attainable in gas analysis, and of the degree to which he has mastered the technique of properly adjusting the levels, reading the mercury meniscus, etc. If everything is right the errors of reading and adjusting the pressure ought not to exceed

0.001 c.c., corresponding to 0.005 per cent. of the volume read off.

**Testing the Burette.**—It seldom, if ever, happens that a gas-burette is graduated correctly all the way down to 0.01 c.c. ; and often the error is sufficient to make a very appreciable difference in the results, particularly as regards the oxygen percentage. Unless these errors are corrected, wrong deductions may be drawn, and different analyses are not comparable exactly with one another. As already explained, a burette may be checked by weighing with mercury ; but this method has the disadvantage that the burette has to be inverted unless a tap is fused on at the lower end, so that an error arises on account of the mercury meniscus facing what ought to be the lower end of the burette. This error can only be roughly allowed for. It is also desirable to be able to check the graduation at any time, and under the exact conditions in which it is being used. There is fortunately a very ready and easy means of doing this. In pure outside air Nature has furnished us with a gas mixture of practically constant composition, so that by an analysis of such air we can check the graduations of a burette.

With a gas-burette of which the graduation had been very carefully checked in duplicate in the upright position (a glass tap having been fused on below for the purpose), and with moisture inside the burette just as in an actual analysis, the writer found that the composition of pure outside air was as follows :—

	Per cent.
Oxygen . . . . .	20.93
Carbon dioxide . . . . .	0.03
Nitrogen (including argon) . . . .	79.04
	<hr/>
	100.00

It does not seem probable that there is any variation from these figures by more than 0·005 per cent. By the gravimetric method (see pp. 90-2), the carbon dioxide percentage can be determined easily to the third place of decimals or further, and by this method it can be shown that in summer weather—in consequence of carbon dioxide being absorbed by green plants during the day, and being given off from plants and from the ground during the night—the percentage of carbon dioxide in the lower strata of air may vary from about 0·025 to 0·035. The oxygen doubtless varies correspondingly in the opposite direction, though this has never yet been demonstrated ; but a variation of 0·005 per cent. is within the error of experiment with the apparatus just described. The writer has never observed with this apparatus any sensible variation in the oxygen percentage in the air at Oxford or elsewhere at different times. In large towns the carbon dioxide may rise quite appreciably in the outside air, especially during winter, and it is common to find 0·04 or 0·05 per cent. of carbon dioxide. During a dense black fog as much as 0·14 per cent. was found by Russell in outside air in London. As the excess of carbon dioxide in the air of a large town is due mainly to combustion of coal, the excess of carbon dioxide will be accompanied by a slightly greater deficiency of oxygen. Except in very foggy weather, however, we may assume that the sum of oxygen and carbon dioxide remains the same in all outside air, even in a town. This sum amounts to 20·96 per cent. ; so that if a burette is graduated correctly the oxygen and carbon dioxide of outside air should together give 20·96 per cent.

The following four successive analyses of the same sample of outside air, with the corrected burette just referred to, will give an idea of the limits of accuracy attainable with the apparatus described.

	Oxygen.	Carbon Dioxide.
No. 1	20.930	0.025
,, 2	20.926	0.030
,, 3	20.931	0.035
,, 4	20.924	0.030
Mean	20.928	0.030

If it is found that a burette gives 21.06 for the sum of the oxygen and carbon dioxide the error is 0.1 in 21.06, or almost exactly  $\frac{1}{200}$  of the percentage of oxygen, so that the percentages obtained should always be corrected by deducting  $\frac{1}{200}$ . If the burette has been skilfully graduated, this error is almost certain to be due to error in measuring the volume from the top of the graduation to the tap; and the error usually met with in a burette is caused by this space being under-estimated, owing to the mercury meniscus having been read off with the burette inverted for the purpose of graduation.<sup>1</sup> An error of this kind is easily corrected by deducting  $\frac{1}{200}$  from the percentage of each gas as estimated with the burette. Thus, if the carbon dioxide were given by the burette as 6.06 the corrected result would be 6.03 (provided that the burette had been completely filled with the sample to be analysed).

Errors in a burette might, however, arise from mistakes in the graduation of the graduated part of the burette; and if so this simple method of correction would not be applicable. To test the graduation in the graduated part the following method can be used. The burette is filled with

<sup>1</sup> Burettes graduated in the upright position, with a tap fused on below, are now supplied by Siebe, Gorman & Co.

air to near the bottom of the graduations and carefully read off, with the usual precautions. About 1 c.c. is then shunted into the combustion pipette (which has previously been adjusted accurately to the mark), and the burette again read off, so that the volume of air shunted is accurately known. About 1 c.c. is then expelled to the outside, and the burette again read. The measured volume of air is then returned from the combustion pipette, and another reading made. If the graduation is even, the volume of air returned should read exactly the same as it did when read off on the lower part of the burette. By repeating this process right up the graduated part the whole of the graduations can be tested, and they should show no sensible irregularity. A burette with uneven graduation of the stem should be rejected.

It is evident that when it has been necessary to dilute the sample taken in with 15 c.c. or more of nitrogen or air, as in certain of the examples already quoted, there will be no correction to be made in the percentages found, provided that the graduation of the stem of the burette is even.

If a burette is allowed to get dirty inside, it will be found that the oxygen determinations with it come out very appreciably higher than when it is clean. The difference may amount to as much as 0·10 per cent. if the burette is very dirty. It is therefore desirable to clean the burette pretty frequently, or, failing this, to control the error by occasional analyses of outside air.

**Plain Burette for Measuring Gas.**—In certain cases it is necessary not only to analyse a sample of gas, but also to measure its volume. For instance, the gas exhausted from a given volume of blood or other liquid by the mercury pump has to be measured as well as analysed. For this purpose the form of burette described already will not answer, and a plain straight burette is needed. Fig. 9 shows such a

burette, with its water-jacket and control tube. It is connected with the absorption and combustion pipettes in

exactly the same way as in the case of the burette already described, and the method of using it for an analysis is exactly the same, though the accuracy attainable is, of course, not so great. The gas is collected in the collecting tube shown in fig. 4, and the whole of it is transferred to the burette in the ordinary way. The control tube is opened just before the analysis, so that the gas is measured at the existing atmospheric pressure, which is read off on the barometer. The temperature in the jacket is also read off. The volume of the gas, dry, and at standard pressure and temperature, can then be calculated in the ordinary way, or more conveniently from the table on p. 55.

This type of burette connected to a set of pipettes suitable for the estimation of carbon dioxide, oxygen, unsaturated hydrocarbons and other combustible gases, etc., has been used combined with a similar straight compensating vessel for a number of years in the Mining Research Laboratory for the analysis of complicated gas mixtures such as are evolved during the distillation of coal.

FIG. 9.—  
Plain  
Burette  
for both  
Measuring  
and  
Analysing  
Gas.



**Description of Smaller Apparatus.**—The apparatus just described occupies permanently a good deal of space, and cannot easily be moved about. For this reason a smaller and easily portable apparatus on exactly the same principle was afterwards designed by one of us, and has proved extremely useful, both for laboratory work and for use at any other place where it was required. It was originally

designed for use on shipboard during an investigation of physiological conditions in deep diving,<sup>1</sup> and it has proved very convenient in physiological experiments out of doors, on high mountains, etc. ; also in experiments underground in mines.

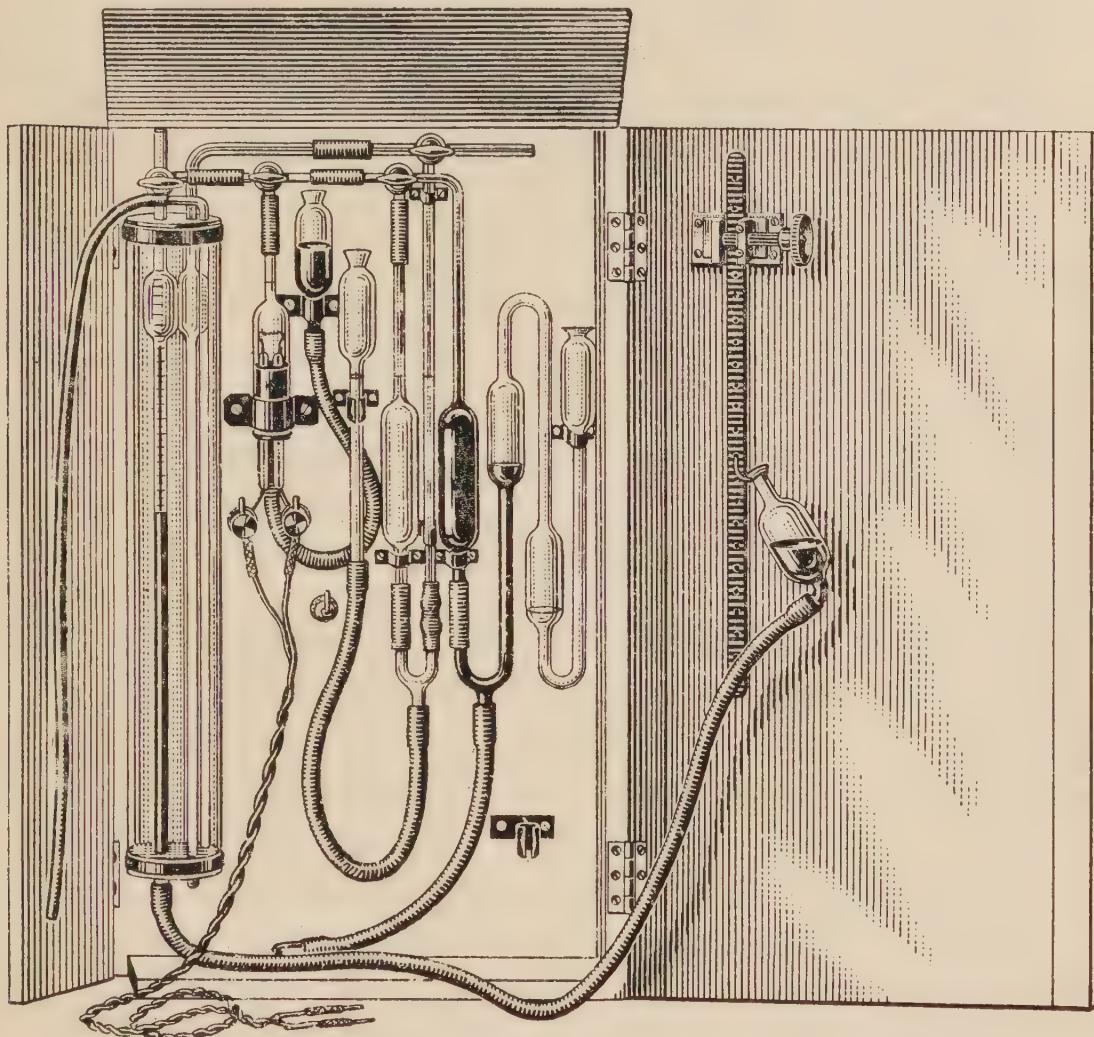


FIG. 10.—Smaller Apparatus for General Air Analysis.

The apparatus is shown in fig. 10. It is contained in a wooden case, of which the internal measurements are  $20 \times 12 \times 2\frac{1}{2}$  inches. This can easily be shut up and transported from place to place without disturbing the

<sup>1</sup> Report of the Admiralty Committee on Deep Diving, Parliamentary Paper [C.N. 1549], 1907.

absorbent solutions, etc., so that the apparatus is always ready for use. It is well, however, to cork up the open tops of the mercury and potash reservoirs when the apparatus has to travel, as it might fall over or be laid flat in ignorance. The front, top and one side are hinged. There must be a clearance of at least an inch between the lower end of the burette and the bottom of the case.

The principle adopted and the method of use are exactly the same as in the larger apparatus, so a detailed description is unnecessary. The only points of difference, apart from the arrangement in a case, are as follows : (1) The capacity of the burette is 10 c.c., instead of 21 c.c., the absorption and combustion pipettes being correspondingly reduced in size, and the weight of mercury, water, etc., thus reduced to within easily manageable proportions. (2) The graduated portion of the burette contains only 3 c.c. instead of 6 c.c., and is thus half the length, though of the same diameter. (3) The arrangement of the combustion and absorption pipettes is slightly different, as shown in the figure. (4) In place of the levelling-tube there is a mercury reservoir. When not in use this is held by the spring clamp close to the bottom of the case, and the rubber tubing connecting the reservoir and burette is kept out of the way by hooking it over a hook, which is shown in the figure, just below the sliding potash reservoir. The case can then be shut up without difficulty. During use the reservoir is hooked into one or other of several holes shown on the rack of the rack and pinion fixed on the door of the case. By raising or lowering the rack the level can be adjusted very exactly. (5) The wires carrying current to the platinum spiral are connected to two binding screws on the back of the case, so that the wires from the rheostat and source of current can be connected with these binding screws. This is a safer arrangement than connecting them directly.

If the apparatus is being used on ship board, and the vessel is not quite steady, it is necessary to place two screw clamps on the rubber tubing connecting the reservoir with the burette. When the level has been roughly adjusted, the clamp farthest from the burette is screwed home : the level can then be adjusted exactly by gradually screwing up or loosening the other clamp. In using the apparatus in mines, etc., it may be supported on an ordinary artist's easel, with pegs long enough to support the case securely. Of course the case is not vertical, but this does not matter.

With care in using the apparatus the limit of error is about 0·01 per cent., so that successive analyses of the same sample should not differ by more than 0·02 per cent. The apparatus should be tested, and the graduation checked, by means of air analyses, as with the larger apparatus. Unless the burette is graduated in the upright position the error of the maker in estimating the volume of the bulb of the burette is apt to be proportionally larger than in the case of the larger apparatus, since the absolute error will be about the same, while the volume of the bulb is only half as great. An error of one-hundredth in the percentages given by the apparatus may thus have to be corrected for, although in other ways the graduation may be perfect.

The graduation may be tested with the burette in its ordinary position, and with moisture inside, by the following method, devised by Dr. C. G. Douglas. A glass tap, with narrow glass tubing, is attached by a joint of stout rubber tubing to the lower end of the burette. The glass tubing dips into a vessel of mercury. Mercury is sucked up from this vessel to the lower level of the graduations by applying suction through the tap at the upper end of the burette. Both this tap and the tap joined on below are then closed, the vessel of mercury weighed, and the burette carefully read off. Mercury is then again sucked up about 1 c.c.

further, the weighing and reading off repeated, and so on up to the top of the burette. The weight of mercury sucked in each time can then be compared with the readings of the burette, due allowance being made for temperature, which is observed in the water of the jacket. By this method the pressure on the rubber joint remains constant, so that there is no error due to the joint giving, and it is unnecessary to fuse on a tap below or otherwise disturb the apparatus. The same method can be applied to the other forms of burette to be described, but of course not to the long burette, which is over 30 inches in length.

The following examples, in which the procedure was the same as with the larger apparatus, will suffice to illustrate the use of the apparatus.

1. *Determination of the Percentage of Coal-gas in the Air of an Experimental Chamber.*

(A) Partial analysis of undiluted coal-gas :—

	C.c.
Air taken . . . .	8.540
+ undiluted coal-gas .	9.486
	<hr/>
∴ coal-gas taken =	0.946
After combustion . . .	8.020
	<hr/>
∴ contraction =	1.466
∴ ratio of contraction to gas taken =	$\frac{1.466}{0.946}$

(B) Partial analysis of the air in the chamber :—

	C.c.
Air taken . . . .	9.996
After combustion . .	9.822
	<hr/>
Contraction	0.174 = 1.74 per cent.

$$\therefore \text{coal-gas present} = 1.74 \times \frac{0.946}{1.466} = 1.12 \text{ per cent.}$$

## 2. Analysis of Alveolar Air from the Lungs.

C.c.

Volume taken . . . 9.588

After CO<sub>2</sub> absorbed . . 9.050

$$\therefore \text{CO}_2 = 0.538 = 5.61 \text{ per cent.} = 5.58 \text{ per cent. corrected.}$$

After O<sub>2</sub> absorbed . . 7.692

$$\therefore \text{O}_2 = 1.358 = 14.16 \text{ per cent.} = 14.09 \text{ per cent. corrected.}$$

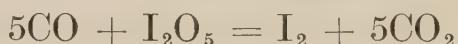
The following results of consecutive uncorrected analyses of outside air illustrate the degree of accuracy attainable, and the correction of the burette.

	CO <sub>2</sub> .	O <sub>2</sub> .
	0.04 per cent.	21.04 per cent.
	0.02	21.03
	0.03	21.04
Mean	<u>0.03</u>	<u>21.037</u>

As atmospheric air contains 20.93 per cent. of oxygen the error in the percentages given by this burette was  $\frac{1}{200}$ , and the results must be corrected by this amount, as shown in analysis (2). As the graduation of the stem was even, there was no correction needed in analysis (1) A, and in (1) B the correction fell within the error of experiment.

In the case of gas mixtures containing physiologically-dangerous amounts of **carbon monoxide** mixed with methane only or methane and hydrogen, the carbon monoxide content may be calculated as shown on p. 34 with a probable accuracy of 0.01 per cent. Gas mixtures, however, are frequently met with, e.g. from the neighbourhood of an underground heating, in which the combustible gases include

a small percentage of higher hydrocarbons as well as methane and hydrogen. For such gas mixtures Graham and Winmill<sup>1</sup> adapted the **iodine pentoxide method** to the larger type (laboratory form) of air-analysis apparatus already described so that determinations could be made with the usual small (20 c.c.) samples of air. The reaction



was made to take place at about 100° C. and by passing the gas mixture from one potash pipette to another, the loss in volume resulting from the absorption of carbon dioxide formed from the carbon monoxide was measured in the usual way. It was found that with mixtures containing less than 20 per cent. of hydrogen and less than 8 per cent. of carbon monoxide an accuracy of within 0·02 per cent. could be obtained. With larger percentages of hydrogen or of carbon monoxide the hydrogen was found to be oxidised appreciably. Methane, on the other hand, is not affected by the pentoxide (see Tables A, B and C, p. 53). A bromine pipette containing 10 per cent. bromine in potassium bromide was used for the estimation of unsaturated hydrocarbons, the removal of which is in any case necessary before the gas mixture is passed over the heated iodine pentoxide. Graham subsequently<sup>2</sup> modified the apparatus to enable the estimation of hydrogen and saturated hydrocarbons to be effected on the one sample.

Fig. 11 illustrates the apparatus. One improvement on the original type is the replacement of the beaker of water used for heating the iodine pentoxide by a small steam-bath of the construction shown in the figure.

The necessity for cooling the iodine pentoxide U-tube to approximately laboratory temperature before the final reading is taken is thus obviated, since all burette readings are

<sup>1</sup> *Trans. Chem. Soc.*, 1914, vol. cv, p. 1996.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1919, vol. xxxviii, pp. 10-14T.

taken with the U-tube at the constant temperature of the steam-bath, and thus a considerable saving of time is effected when carrying out a number of analyses. The steam-bath also holds a second small U-tube containing palladinised asbestos (5 per cent.), connected on the one side to a three-

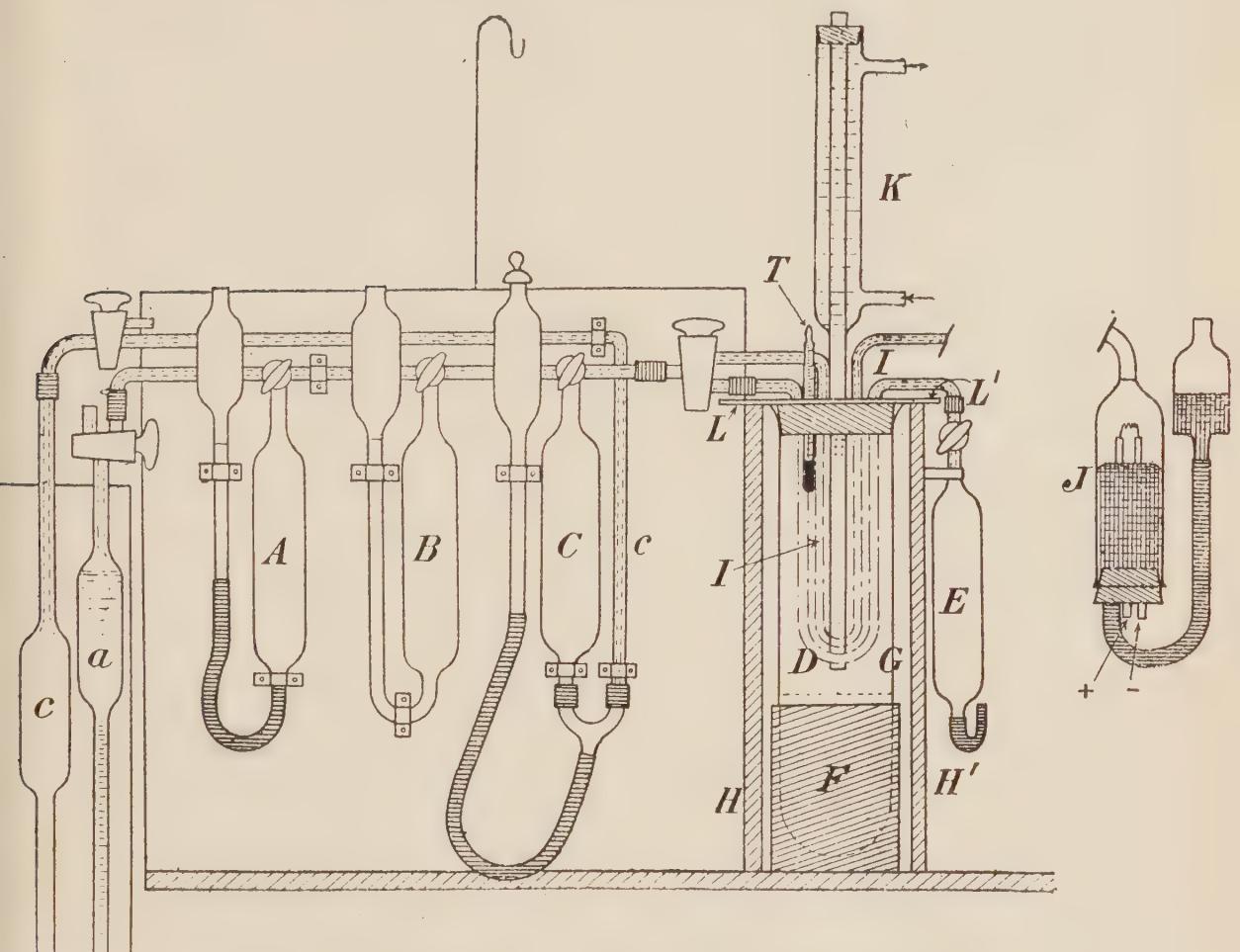


FIG. 11.—Special Apparatus for Carbon Monoxide.

way stop-cock and thence to the burette, etc., and on the other to the ordinary form of Haldane combustion pipette.

The apparatus is mounted on a wooden stand. (a) is a Haldane burette and (c) a Haldane compensator in the usual water jacket. A, B, etc., are pipettes containing approximately (A) 25 per cent. caustic potash, (B) 10 per cent. bromine in potassium bromide solution, (C) 40 per cent.

caustic potash solution. D is a small U-tube containing approximately 2 grammes of iodine pentoxide—the air space over the latter in this tube being less than 1 c.c. E is a pipette containing approximately 40 per cent. caustic potash solution. F<sup>1</sup> is a small electric heater for boiling water in G, which is a wide test-tube (2 inches diam.), fitted with an india-rubber bung through which pass the U-tubes, D ( $I_2O_5$ ) and I (Pd-asbestos), a thermometer T, and K, a small condenser, the inner tube of which reaches below the bend of the U-tubes, and which is pierced with several small holes just below the rubber bung so that the steam from the boiling water passes up to the top of G, and through these holes, the condensed water then dropping straight into the test-tube without coming into contact with the U-tubes. H and H' are two boards covered with asbestos and built out at right-angles to the stand in order to protect the main part of the apparatus from radiation from the electric heater. J is the ordinary form of Haldane combustion pipette (with fine platinum wire) connected to the usual mercury reservoir. Several pieces of asbestos millboard are placed in the position L L' to prevent undue heating of the connecting tubes from D and I. The whole apparatus is sealed together as far as possible ; at certain positions, however, connections by means of india-rubber pressure tubing are desirable in order to facilitate the removal of the iodine pentoxide tube for revivifying purposes. When the apparatus is required for an analysis, the electric heater and the water to condenser are turned on. After about ten minutes, with the heater used by Graham, the water will boil vigorously and after

<sup>1</sup> The small furnace was made from an empty cigarette tin, just over 2 inches in internal diameter and about 3 inches in height. This was covered with a layer of asbestos paper, upon which a suitable length of nichrome resistance wire was wound, and the tin then well covered with more asbestos paper.

half an hour the volume of gas in each U-tube should have become constant. The levels of the liquids in the various pipettes are brought to their respective graduation marks, the sample taken in and analysed for carbon dioxide (sulphur dioxide and hydrogen sulphide), unsaturated hydrocarbons, and carbon monoxide—following the usual procedure. With care, results can readily be obtained agreeing to 0·02 per cent. when the samples are analysed in duplicate. For example, a coal-gas and air mixture on analysis gave carbon dioxide, etc., and unsaturated hydrocarbons, 1·41, 1·40 ; and carbon monoxide 2·16, 2·16 per cent.

The palladium-asbestos U-tube, I, has been found to work satisfactorily for the estimation of hydrogen in gas mixtures, containing of course sufficient oxygen for the reaction. The oxidation of the hydrogen has been found to be rapid and complete even with a gas mixture containing approximately 20 per cent. of hydrogen. The following analysis is illustrative of the accuracy of the method :—By palladium-asbestos tube 6·53, 6·51 per cent. By combustion over red-hot platinum spiral, 6·52 per cent. Carbon monoxide, even when present to the extent of over 6 per cent., was quite unacted upon by the palladium-asbestos at the temperature employed ( $100^{\circ}$  C.).

In analysing mixtures containing a high percentage of hydrogen in addition to saturated hydrocarbons, the gas should be passed through the tube, I, rather slowly at first, otherwise the palladium-asbestos may attain a high temperature locally and as a consequence partial combustion of the hydrocarbons may occur.<sup>1</sup> If this precaution is observed, the method appears to give satisfactory results for the separate determination of hydrogen and methane or other saturated hydrocarbons. In the analysis of a mixture con-

<sup>1</sup> To reduce risk of local superheating fine palladium wire may replace the palladium-asbestos.

taining hydrogen 7·43 per cent., methane 7·17 per cent., no trace of combustion of the latter took place during oxidation of the hydrogen by the palladium-asbestos at 100° C. When analysing samples containing carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen and methane, with sufficient oxygen present for the complete combustion of the last two gases, the carbon dioxide, unsaturated hydrocarbons and carbon monoxide are first estimated. By turning the necessary stop-cocks the gas is then passed to and fro slowly over the palladium-asbestos, a couple of passages having been found sufficient to oxidise all the hydrogen to water. The connections to the remaining pipettes are "washed out" and the residual hydrogen oxidised by passage over the palladium-asbestos, the process being repeated until a constant volume is obtained. Two-thirds of the contraction observed gives, of course, the actual quantity of hydrogen present. The methane may then be estimated in the usual way by burning with the aid of the coil of fine platinum wire heated electrically in the ordinary form of combustion pipette, J, the presence or absence of higher (saturated) hydrocarbons being shown by the ratio of the contraction to the volume of carbon dioxide produced by the combustion. The amount of methane or other hydrocarbon left finally after removal of the other gases mentioned must, of course, be below the quantity necessary to form an explosive mixture, i.e. in the case of methane below 5·6 per cent.

This apparatus is only suitable for the analysis of mixtures containing more than 0·02 per cent. of carbon monoxide and when an accuracy of this figure is sufficient. As will be pointed out later in connection with the detection of spontaneous combustion in coal mines, it is frequently necessary to estimate very much smaller percentages of carbon monoxide. To meet this need Graham designed a portable

apparatus with which it has been found possible to estimate as little as 0·0005 per cent. carbon monoxide provided at least one litre of sample is used. This apparatus and a similar one made for work in the laboratory are in constant use in the Mining Research Laboratory, Birmingham University, and have been found to be thoroughly reliable if the precautions to be described in a later chapter are taken.

The following analyses show that the limit of error with the apparatus described on pp. 48–52 is about 0·02 per cent. :—

#### A. Mixtures of Carbon Monoxide with Air.

Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.	Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.
0·02	0·02	3·06	3·09
0·08	0·10	3·43	3·41
0·11	0·11	8·21	8·20
0·11	0·10	10·22	10·21
0·22	0·22	16·12	16·13
0·39	0·38	24·13	24·14
1·50	1·51		

#### B. Mixtures containing less than 20 per cent. of Hydrogen and less than 8·5 per cent. of Carbon Monoxide.

Hydrogen present, per cent.	Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.
6·38	5·47	5·47
8·30	8·44	8·44
14·00	7·39	7·38
14·00	7·45	7·43
18·80	7·87	7·88
19·58	5·66	5·68

#### C. Mixtures of Natural Fire-damp with Carbon Monoxide and Air.

Fire-damp present, per cent.	Carbon Monoxide present, per cent.	Carbon Monoxide found, per cent.
10·85	0·00	0·00
79·00	0·00	0·00
79·00	0·00	-0·01
10·8	0·18	0·19
10·7	1·12	1·15
74·6	1·98	2·01
70·6	2·60	2·59

## CHAPTER III

### CALCULATION AND STATEMENT OF RESULTS OF ANALYSIS

WHEN numerous analyses have to be calculated out from readings of the burette, and subsequent calculations probably made, as in physiological work, or work on mine air, it saves a good deal of time to use a slide-rule. The ordinary ten-inch slide-rule is not accurate enough, however, for exact work ; and a slide-rule which permits of working accurately to five figures is needed. A Fuller's spiral slide-rule<sup>1</sup> will be found very convenient.

In some cases nothing more is needed than the bare percentages of the gases present ; but often further calculations are required.

**Physiological Analyses.**—We may first take the case of physiological analyses of respiration air. What has been analysed is usually a sample of a large volume which has been measured by an experimental gas-meter, or is contained in a space of known volume ; and it is required to calculate the volume at 0° C. and 760 mm. pressure of the carbon dioxide which has been given off into this volume of air and the oxygen which has been absorbed from it ; also the "respiratory quotient" or ratio by volume of carbon dioxide given off to oxygen absorbed.

The first step is to reduce the volume of the air which has been measured to its volume when measured dry at 0° C. and 760 mm. barometric pressure. This process is so frequent

<sup>1</sup> Made by Stanley & Co., Great Turnstile, Holborn, London.

in work involving air analysis that it saves much trouble to calculate to three figures from the accompanying table, showing for ordinary barometric pressures and indoor temperatures the volume to which 100 volumes of air are reduced. The volume has practically always been measured with the air saturated with moisture, which simplifies the table.

TABLE FOR REDUCTION TO DRY AIR AT 0° C. AND 760 MM. OF 100 VOLUMES OF AIR SATURATED WITH MOISTURE AT DIFFERENT TEMPERATURES AND PRESSURES.

Temperature ° C.	Barometric Pressure in Inches or Millimetres.								
	29.13 740	29.33 745	29.53 750	29.72 755	29.92 760	30.12 765	30.31 770	30.51 775	30.71 780
10	92.77	93.39	94.04	94.66	95.30	95.93	96.57	97.21	97.84
11	92.36	92.98	93.63	94.25	94.89	95.52	96.16	96.79	97.42
12	91.95	92.55	93.18	93.80	94.44	95.07	95.70	96.33	96.96
13	91.54	92.17	92.80	93.41	94.05	94.68	95.31	95.94	96.57
14	91.13	91.76	92.38	93.00	93.62	94.26	94.88	95.51	96.13
15	90.71	91.34	91.96	92.57	93.20	93.82	94.44	95.08	95.70
16	90.29	90.92	91.54	92.15	92.78	93.40	94.01	94.64	95.26
17	89.87	90.50	91.11	91.72	92.35	92.97	93.58	94.21	94.83
18	89.45	89.08	89.68	91.30	91.92	92.54	93.15	93.71	94.39
19	89.02	89.64	90.25	90.86	91.48	92.09	92.71	93.32	93.94
20	88.59	89.21	89.81	90.41	91.04	91.65	92.26	92.88	93.50
21	88.18	88.86	89.40	90.01	90.62	91.23	91.84	92.45	93.07
22	87.71	88.32	88.90	89.53	90.14	90.75	91.36	91.97	92.60
23	87.26	87.87	88.47	89.08	89.69	90.29	90.90	91.51	92.13
24	86.61	87.43	88.01	88.62	89.23	89.83	90.44	91.04	91.65
25	86.35	86.96	87.57	88.17	88.79	89.38	89.98	90.57	91.17

Let us suppose, for instance, that the volume of air expired in exactly ten minutes was 70.4 litres, and that the temperature of the gas-meter was 18.5°, and the barometric pressure 748 millimetres. From the table the factor for correction is evidently about 0.902, and the reduced volume is therefore  $70.4 \times 0.902 = 63.5$  litres.

Let us now suppose that the inspired air was pure, and contained 20.93 per cent of oxygen, 0.03 of carbon dioxide, and 79.04 of nitrogen ; and that the sample of the expired air

contained 16·41 per cent. of oxygen, 3·62 of carbon dioxide, and 79·97 of nitrogen. It is clear that the volume (at 0° and 760 mm., dry) of carbon dioxide given off was

$$\frac{3\cdot62 - 0\cdot03}{100} \times 63\cdot5 = 2\cdot280 \text{ litres.}$$

The volume of oxygen absorbed is less easy to calculate, however, as the volume of dry air has diminished in the process of respiration, because more oxygen has been taken up than carbon dioxide has been given off. Since nitrogen is neither taken up nor given off in respiration it is evident that for every 100 volumes of expired air there corresponded in the inspired air, not 20·93 volumes of oxygen, but

$$20\cdot93 \times \frac{79\cdot97}{79\cdot04} = 21\cdot18 \text{ volumes.}$$

Hence the oxygen which disappeared was

$$\frac{21\cdot18 - 16\cdot41}{100} \times 63\cdot5 = 3\cdot029 \text{ litres ;}$$

and the respiratory quotient was  $\frac{2\cdot280}{3\cdot029} = 0\cdot753$ . Had the

respiratory quotient been incorrectly taken as the ratio between excess of carbon dioxide percentage and deficiency

of oxygen, i.e. as  $\frac{3\cdot62 - 0\cdot03}{20\cdot93 - 16\cdot41} = 0\cdot794$ , and the oxygen

absorption also been calculated in a similar way, the error would have been considerable, and wrong conclusions might have been drawn as to the material being oxidised in the body, the production of heat, etc.

The following table shows the relation between the apparent respiratory quotient (i.e. the ratio of excess in carbon dioxide percentage to deficiency in oxygen) and the real one. With the help of the "difference" column in this table the true respiratory quotient can easily be deduced for any value of the apparent one ; and by dividing the output of carbon dioxide by the true respiratory quotient the intake

TABLE FOR CALCULATING TRUE FROM APPARENT RESPIRATORY  
OR COMBUSTION QUOTIENT.

Apparent Respiratory or Combustion Quotient.	True Respiratory or Combustion Quotient.	Difference.
2.00	2.72	+ 0.72
1.90	2.49	+ 0.59
1.80	2.28	+ 0.48
1.70	2.09	+ 0.39
1.60	1.90	+ 0.30
1.50	1.73	+ 0.23
1.40	1.57	+ 0.17
1.30	1.412	+ 0.112
1.20	1.267	+ 0.067
1.10	1.130	+ 0.030
1.00	1.000	± 0.000
0.95	0.937	- 0.013
0.90	0.877	- 0.023
0.85	0.817	- 0.033
0.80	0.760	- 0.040
0.75	0.704	- 0.046
0.70	0.649	- 0.051
0.60	0.543	- 0.057
0.50	0.441	- 0.059
0.40	0.345	- 0.055
0.30	0.253	- 0.047
0.20	0.165	- 0.035
0.10	0.081	- 0.019
0.00	0.000	± 0.000

of oxygen is at once obtained. Under normal conditions the respiratory quotient lies between 0.7 and 1 ; but under unusual conditions it may temporarily rise or fall much beyond these limits ; and the table is extended accordingly, particularly as it is also of use in connection with analyses of mine air, exhaust gases from internal combustion engines, etc.

**Analyses of Mine Air.**—It will be shown later that the calculation of the "respiratory quotient" may be applied to the results of analysis of mine air samples to give information regarding the composition of the black-damp, and when a similar calculation is made showing the production of carbon monoxide relative to the oxygen absorbed, a valuable indication may be obtained concerning any abnormal

oxidation of coal in underground workings. To facilitate these calculations the figures for the oxygen corresponding to all nitrogen percentages between 0 and 100 in increments of 0·1 per cent. are set out in the table on pp. 170-4.<sup>1</sup>

A complete analysis of mine air should always, of course, be stated in terms of the actual chemical constituents found. It is, however, of advantage to state the results in another form also. In nearly every case a greater or less amount of air is present in the mixture analysed. As atmospheric air is the only source of oxygen in a mine it is clear that the percentage of air in the sample can be calculated from the oxygen percentage by multiplying by  $\frac{100}{20\cdot93}$ . The residue left

after deducting the oxygen, nitrogen and carbon dioxide of the air, consists of nitrogen, carbon dioxide, and possibly methane, carbon monoxide, etc. The methane and any other combustible constituent ought evidently to be stated separately, so that what is left over consists of nitrogen and carbon dioxide. Now, it will be found that in the great majority of cases the composition of this residue corresponds more or less closely to that of the "black-damp" met with in unventilated parts of the mine from which the sample comes. Hence the residue may be set down in the analysis as "black-damp."

By "black-damp" a miner practically understands any sort of gas or air which will extinguish a lamp without at the same time being capable of causing an explosion, and which will not cause symptoms of poisoning or asphyxiation when mixed with just sufficient air to allow a candle to burn. Pure black-damp, free from air, is still very commonly confused with carbon dioxide, but is really a mixture of nitrogen with a relatively small proportion of carbon dioxide, and

<sup>1</sup> From these tables the percentage of "black-damp" in a mine air sample may also be readily calculated.

when resulting from the oxidation of dry coal a still smaller proportion of carbon monoxide. It is simply the gaseous residue resulting from the slow oxidising action of air on oxidisable substances in a mine. Hence it consists chiefly of nitrogen ; and a mixture of black-damp with air has very different physical and physiological properties from a mixture of carbon dioxide with air.

The quantity of carbon monoxide in black-damp is rarely of physiological significance; although cases have arisen in certain mines where it seems that the carbon monoxide in the black-damp formed from dry coal may possibly have been the cause of accident.

The following examples illustrate the mode of statement of an analysis in terms of air, black-damp, etc., and at the same time indicate the justification for this mode of statement. An estimation of carbon monoxide by the blood test (described later) showed less than 0·01 per cent.

1. *Gas issuing into a Return Air-way from Old Workings through a pipe in a brick stopping, Podmore Hall Colliery, North Staffordshire.*

	Per cent.
Oxygen . . . . .	0·72
Carbon dioxide . . . . .	11·03
Methane . . . . .	7·47
Nitrogen . . . . .	80·78
	<hr/>
	100·00
<i>Otherwise expressed.</i>	
Air { Oxygen . . . . .	0·72 }
Nitrogen . . . . .	2·72 }
Methane . . . . .	7·47
Black-damp { Nitrogen . . . . .	78·06 }
Carbon dioxide . . . . .	11·03 }
	<hr/>
	100·00

2. *Air of Main Return of same Colliery.*

	Per cent.
Oxygen . . . . .	20·34
Carbon dioxide . . . . .	0·305
Methane . . . . .	0·65
Nitrogen . . . . .	78·705
	<hr/>
	100·00

*Otherwise expressed.*

Air	Oxygen . . . . .	20·34	97·18
	Nitrogen . . . . .	76·81	
	Carbon dioxide . . . . .	0·03	
Black-damp	Methane . . . . .	0·65	2·17
	Nitrogen . . . . .	1·895	
	Carbon dioxide . . . . .	0·275	<hr/>
			100·00

In these analyses the percentage composition of the black-damp was :—

	No. 1.	No. 2.
Nitrogen . . . . .	87·6	87·3
Carbon dioxide . . . . .	12·4	12·7

From the latter figures it is evident that in this mine about 12·5 per cent. of carbon dioxide appeared in the air for 20·93 per cent. of diminution in the oxygen percentage owing to oxidation. The "apparent" oxidation quotient was therefore  $\frac{12·5}{20·93}$ , or 0·60, and (from the table, p. 57) the true oxidation quotient was 0·54. If 50,000 cubic feet of air per minute were passing along the main return, the production of carbon dioxide (not corrected for temperature, etc.) in the district served by this return would be

$$\frac{0.305 - 0.03}{100} \times 50,000 = 137.5 \text{ cubic feet per minute};$$

the consumption of oxygen  $\frac{137.5}{0.54} = 254$  cubic feet; and the

$$\text{production of methane } \frac{0.65}{100} \times 50,000 = 325 \text{ cubic feet.}$$

It will be of interest to include another more recent analysis in which the specially delicate test for carbon monoxide to be described later showed the presence of a small quantity of this gas. The sample was taken from a badly ventilated working place in a Staffordshire colliery.

	Per cent.
Oxygen . . . . .	16.97
Carbon dioxide . . . . .	1.28
Methane. . . . .	2.26
Nitrogen . . . . .	79.48
Carbon monoxide . . . . .	0.0075
<hr/>	
	<b>100.00</b>

*Otherwise expressed.*

Air	{	Oxygen . . . . .	16.97	}	81.08
		Nitrogen . . . . .	64.09		
		Carbon dioxide . . . . .	0.02		
	{	Methane . . . . .	2.26	}	16.66
Black-damp	{	Nitrogen . . . . .	15.39		
		Carbon dioxide . . . . .	1.26		
		Carbon monoxide . . . . .	0.0075		
	<hr/>			<hr/>	
				<b>100.00</b>	

The composition of the black-damp was in this case nitrogen 92.4 per cent., carbon dioxide 7.55 per cent., carbon monoxide 0.04 per cent., and the oxidation quotients are for  $\text{CO}_2$  0.30 and for CO 0.0018. In practice it has been found

more convenient to express these figures as amounts of carbon dioxide and monoxide produced per 100 per cent. oxygen absorbed. The figures thus become 30 per cent. and 0·18 per cent. respectively. The carbon monoxide figure may be used to indicate the presence of underground heating, and in many cases this indication precedes any evidence given by unusual odour, upon which in practice the miner relies. This will be discussed at greater length in the chapter describing the estimation of small quantities of carbon monoxide.

The composition of the black-damp in different mines varies of course very greatly, and there is consequently a corresponding variation in the value of the oxidation quotient. Unless the oxidation quotients or figures for normal production of carbon dioxide and carbon monoxide are known, incomplete analyses such as the determination of carbon dioxide or carbon monoxide alone may be quite misleading.

## CHAPTER IV

### PORABLE APPARATUS FOR DETERMINING SMALL PERCENTAGES OF CARBON DIOXIDE<sup>1</sup>

THE percentage of carbon dioxide in the air of ordinary rooms, schools, factories, etc., is a convenient index of the degree of vitiation of the air by respiration, and fires. Hence the determination of the small percentages of carbon dioxide present in such air is a matter of considerable practical importance, and the apparatus now to be described was introduced for the purpose of making this determination rapidly and conveniently.

The apparatus is shown in fig. 12. In general principle it is similar to that already described, but with modifications designed to make the process of analysis as rapid and simple as possible. The construction and arrangement will be evident from the figure.

The air-burette A, which is enclosed in a water-jacket with glass face, consists of a wide ungraduated and a very narrow graduated portion. It holds 20 c.c. from the tap to the bottom of the scale. The graduated part, which is 4 inches long, is divided into about one hundred divisions, each of which corresponds to  $\frac{1}{1000}$ th part of the capacity of the burette, when moist, for mercury. The lowest division is marked 0, and the numbering is upwards from this point. Any difference between a reading at or near zero and a

<sup>1</sup> Described in its original form in the *Journal of Hygiene*, 1901, p. 109, and in the *First Report of the Departmental Committee on Factory Ventilation*, Parliamentary Paper [Cd. 1302], 1902.

second reading is thus shown by the scale in volumes per 10,000, there being no calculations or corrections.

In using the apparatus the potash level is first adjusted to the mark at E. The air is then expelled from the burette

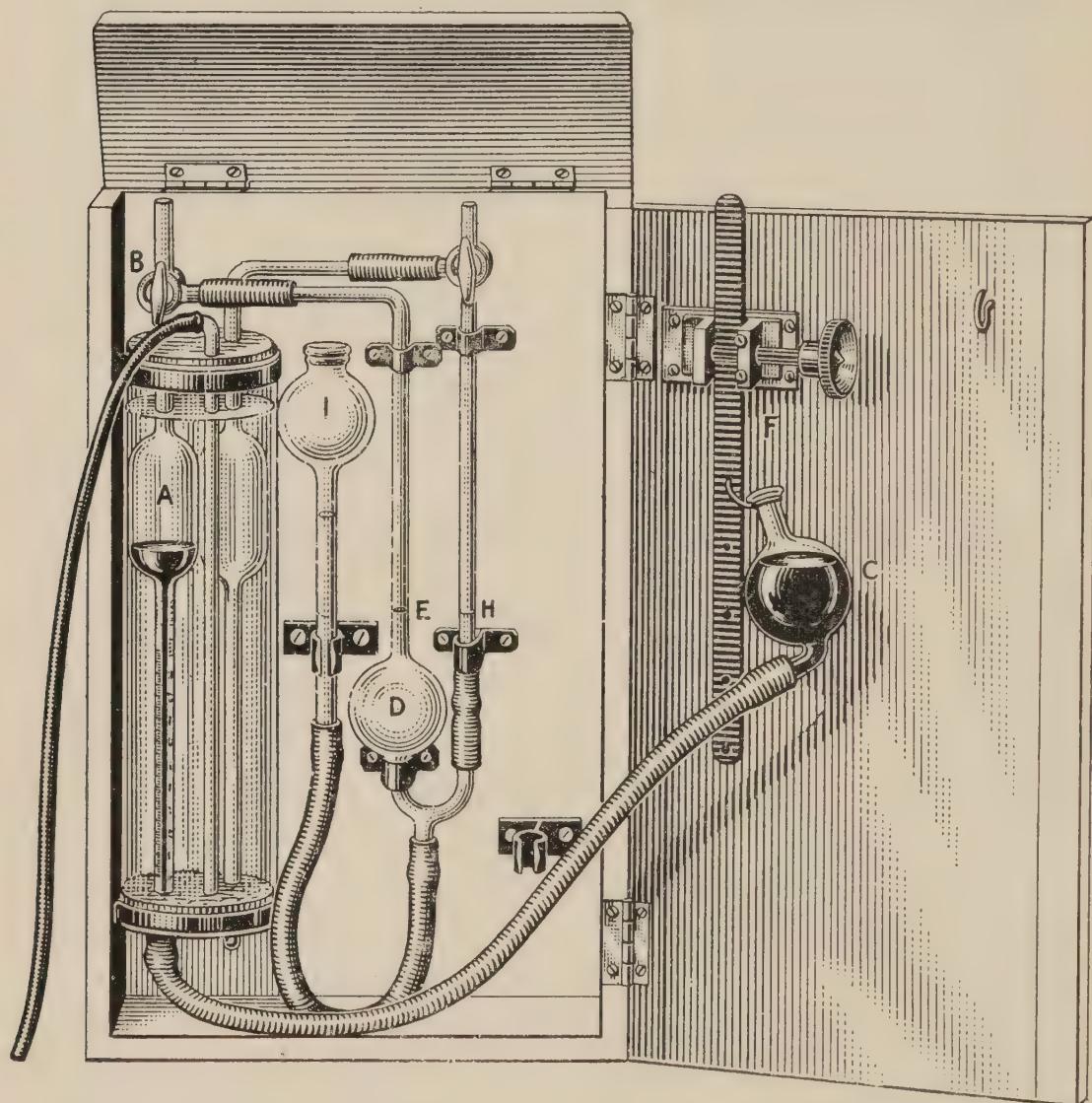


FIG. 12.—Portable Apparatus for Small Percentages of Carbon Dioxide.

by opening the three-way tap B to the outside and raising the mercury bulb C. The tap B is then closed by turning it one-eighth round, and the mercury bulb is lowered and placed on the hook of the rack-and-pinion arrangement F, which is arranged at such a level that on opening the tap to take in a sample the mercury in the burette falls to about the

zero-mark. The sample is taken in at any desired part of a room by carrying the apparatus to the place. If the burette is allowed to fill while the apparatus is carried across the room, a good average sample can be obtained. As it takes some seconds for the mercury to run down, this method of taking the sample can easily be adopted.

The apparatus is now placed on a table, the water in the jacket mixed by blowing through it, the potash level in the tube H adjusted exactly to the mark by raising or lowering the reservoir, I, and the three-way tap at the top of the tube H turned so as to close communication with the outside air and leave H in communication with the control tube. The potash level in E is also brought exactly to the mark by raising or lowering the mercury reservoir, and the mercury level in the burette is then read off. Before doing so it is well to mix the water in the bath again, and to pinch the rubber tube leading to the potash reservoir to make sure that the liquid in the two gauge tubes moves quite freely and returns exactly to the marks. It occasionally happens that a tap is blocked by a drop of mercury, or some vaseline, so that the gauge does not move freely till the obstruction is broken through.

The air is now driven over into the potash pipette (which is filled with caustic potash or soda solution of about 10 per cent. strength) and back at least twice, and a second reading taken with the same precautions, after again thoroughly mixing the water in the jacket. The difference between the two readings gives the proportion of carbon dioxide in volumes per 10,000.

After the analysis the control tube is opened to the air and the burette shut off from the potash pipette. It is most important not to forget this, as potash may otherwise be sucked up, with the result that the apparatus is fouled and the taps possibly jammed.

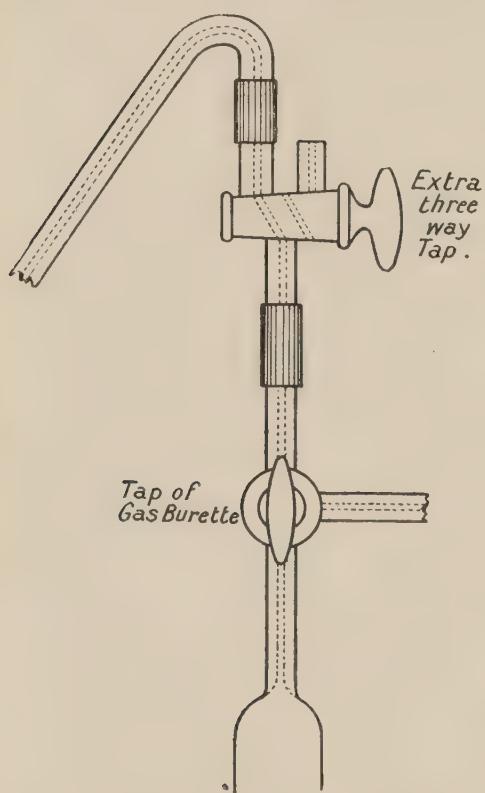
If the samples of air are collected in bottles (fig. 1) and analysed subsequently, they are transferred to the apparatus with the help of the trough and curved tube described already (fig. 7). As, however, the sample is removed at a negative pressure there is difficulty in afterwards equalising the pressure in the very narrow burette, unless provision

is made for the purpose. An extra three-way tap should therefore be attached to the tap of the burette, as shown in fig. 13. In taking in the sample the mercury reservoir is depressed below the level of the table, so that when the extra tap is closed and the reservoir replaced on the hook, the pressure in the burette is positive. On opening the extra tap to the outside the excess of pressure is blown off, and the mercury comes to the zero-point, or a little above it, after which the analysis may be proceeded with in the ordinary way.

FIG. 13.—Arrangement of Extra Three-way Tap.

The efficient working of the apparatus should be checked by making repeated readings with the same sample of air, first freed from  $\text{CO}_2$ . The reading should be the same within one division after repeatedly passing the air into the potash pipette. Any leakage would be shown by this test,<sup>1</sup>

<sup>1</sup> This test would also reveal any absorption of oxygen by sulphide given off by the rubber tubing—an occurrence which must be guarded against in the manner explained in connection with the larger apparatus (p. 37).



and the joints or taps can also be tested by putting pressure on them successively, as explained in connection with the large apparatus (p. 36). It is important to note that the burette must always be kept moist with a very small quantity of water acidified with sulphuric acid, as with the large apparatus. If the burette is dry, a determination will probably give an apparent negative result, due to the air taking up aqueous vapour from the potash. It is also most important to keep the burette clean by occasional washing with nitric acid. Dirt in the stem of the burette may make the results very appreciably too high. If a tap jams and cannot be loosened by heating, it may be cut out and a new one fixed in position by rubber tubing.

To check the calibration of the burette, the mercury which flows out between different points can be weighed with the burette in the inverted position. Another method is to analyse the air in a bottle containing nearly 1 per cent. of carbon dioxide, and compare the results with those given by the large apparatus with the same bottle of air.

The following examples will serve to illustrate the degree of accuracy attainable with the apparatus. The results are in volumes per 10,000.

I. *Six successive samples of outside air (winter).*

(1) 2·8. (2) 3·2. (3) 3·3. (4) 2·7. (5) 3·3. (6) 2·8.  
Mean, 3·0.

II. *Three samples of same outside air, collected in bottles.*

(1) 2·6. (2) 3·3. (3) 2·9. Mean, 2·9.

III. *Six successive analyses of air in same bottle of vitiated air.*

(1) 16·6. (2) 16·0. (3) 16·4. (4) 16·2. (5) 15·6. (6) 15·8.  
Mean, 16·1.

IV. *Three successive analyses of samples from same bottle of vitiated air.*

(1) 51·0. (2) 50·8. (3) 51·4. Mean, 51·1.

These examples show that with ordinary care the analysis may, after some practice, be relied on to within 0·5 volume per 10,000 on either side of the correct result.

The following experiments may be quoted in connection with the reliability of the method of collecting samples of air in bottles in the manner already described and keeping them for some days before analysis.

I. Four samples of outside air collected simultaneously in dry and clean bottles were kept for varying periods and then analysed. The results were as follows in volumes of CO<sub>2</sub> per 10,000 volumes of air :—

Bottle (1), analysed at once . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	3·0 3·0
,, (2) „ „ after 5 days . . .		2·8
,, (3) „ „ „ 9 „ . . .		3·0
,, (4) „ „ „ 19 „ . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	2·8 3·0

II. Five bottles of air collected simultaneously in dry and clean bottles in a room containing vitiated air were similarly kept and analysed.

Bottle (1), analysed at once . . .	$\left\{ \begin{array}{l} (a) \\ (b) \\ (c) \end{array} \right.$	51·0 51·4 50·8
,, (2) „ „ „ . . .		50·8
,, (3) „ „ after 2 days . . .		51·2
,, (4) „ „ „ 6 „ . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	50·7 51·0
,, (5) „ „ „ 14 „ . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	50·6 50·4

III. Four samples of outside air were collected in bottles which were both wet and dirty from dust purposely introduced.

Bottle (1), analysed at once . . . . .	3·0
,, (2) ,,, after 2 days . . . . .	2·8
,, (3) ,,, 6 ,,, . . . . .	{ (a) 8·0 (b) 7·6
,, (4) ,,, 12 ,,, . . . . .	15·0

IV. Five samples of outside air were collected in bottles which were dirty from dust purposely introduced, but dry.

Bottle (1), analysed at once . . . . .	3·0
,, (2) ,,, after 2 days . . . . .	3·2
,, (3) ,,, 6 ,,, . . . . .	{ (a) 3·2 (b) 3·0
,, (4) ,,, 12 ,,, . . . . .	3·0
,, (5) ,,, 17 ,,, . . . . .	2·8

V. Four samples of outside air were collected in bottles which were clean but wet.

Bottle (1), analysed at once . . . . .	3·0
,, (2) ,,, after 3 days . . . . .	{ (a) 2·4 (b) 2·2
,, (3) ,,, 5 ,,, . . . . .	{ (a) 2·0 (b) 2·6
,, (4) ,,, 12 ,,, . . . . .	{ (a) 0·2 (b) 0·0

VI. Four samples of vitiated air were collected simultaneously, two being in clean and dry bottles and two in clean and wet bottles.

*Dry.*

Bottle (1), analysed at once . . . . .	{ (a) 20·6 (b) 20·8
,, (2) ,,, after 9 days . . . . .	{ (a) 21·2 (b) 21·2

*Wet.*

Bottle (3), analysed at once . . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	21.0 20.4
,, (4) ,,, after 9 days . . . .	$\left\{ \begin{array}{l} (a) \\ (b) \end{array} \right.$	18.6 18.8

These experiments show that in clean and dry bottles, with stoppers properly greased with vaseline, samples of air will keep perfectly for long periods, but that in wet bottles, whether clean or not, the percentage of carbon dioxide alters. If the bottle is wet and dirty, the carbon dioxide may increase greatly owing to bacterial action. If the bottle is wet and clean, carbon dioxide may disappear owing to the presence of alkali dissolved from the glass. Samples collected by the old method of emptying a bottleful of water are quite unreliable so far as carbon dioxide is concerned. During the process of emptying the air may either take up carbon dioxide from the water or give it up to the water, and the proportion of carbon dioxide inside the bottle may alter afterwards.

## CHAPTER V

### POR TABLE APPARATUS FOR ROUTINE FIRE-DAMP ESTIMATIONS

IN earlier editions of this book other portable apparatus for the determination of carbon dioxide, carbon monoxide and methane in the air of mines worked with open lights was described in detail. As these apparatuses are manipulated in the same manner as the portable apparatus already described, and since the scope for such special apparatus has proved to be somewhat limited, its description will be omitted from the present volume.

Legislation for British mines enacts that when more than 2·5 per cent. of fire-damp is present in a working place the men must be withdrawn. Numerous devices have been patented which claim to give warning or an indication of a dangerous percentage of fire-damp. A list of these is given in *Memorandum No. 10* of the *Miners Lamps Committee* on the *Testing for Fire-damp (1924)* and their working depends upon such properties as diffusion, density, thermal conductivity and the acoustic properties of gases. In recent years two other gas detectors, the Gulliford and the Ringrose, have been patented and approved for use in safety-lamp mines. These detectors are in each case attached to an electric lamp and give information only concerning one arbitrarily fixed amount, which either causes a platinum wire to fuse, as in the case of the Gulliford lamp, thus cutting off the light (which may, however, be regained by turning another switch), or else, as with the Ringrose, brings a red light into action when a dangerous percentage is reached.

The only satisfactory apparatus approved by the Mines Department for the estimation of fire-damp in safety-lamp pits is that designed by McLuckie. This is based upon

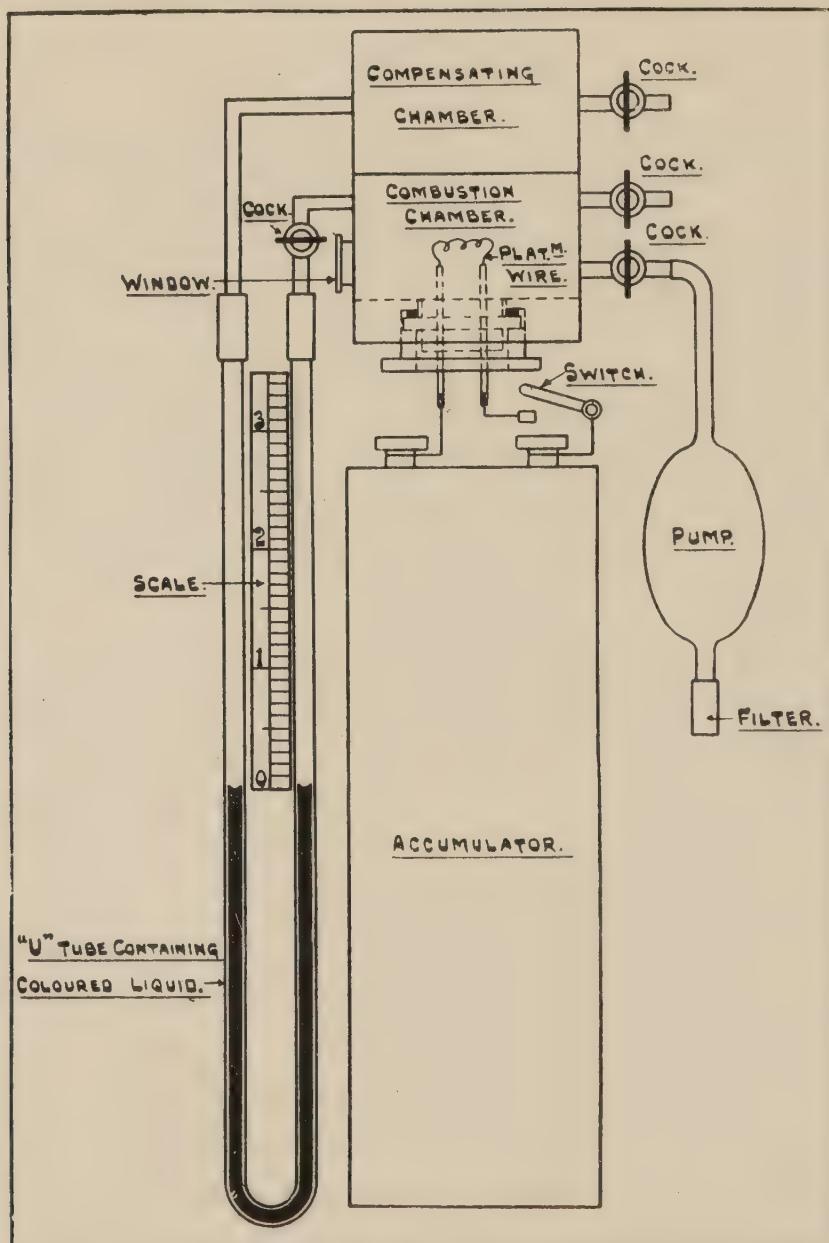


FIG. 14.—“ McLuckie ” Gas Detector (Diagrammatic).

change in volume on combustion, just as in the ordinary routine analysis of combustible gas detailed in the preceding pages. The arrangement of the apparatus is shown in diagrammatic form in fig. 14, and fig. 15 shows the sealed

apparatus. Below is given a description by the designer, Mr. Colin McLuckie, as published in the *Transactions of the Institution of Mining Engineers*, vol. lxxix, pp. 282-7.



FIG. 15.—“McLuckie” Gas Detector.

“The apparatus consists of a metal vessel divided into two equal volumes; the lower part of the vessel is the combustion chamber and the upper part a chamber to compensate for alterations in temperature or pressure. The gas is burnt in the combustion chamber by means of a platinum

wire heated to red heat by an electric current from a 2-volt accumulator, and the liquid in a **U**-tube connected to the two chambers measures the difference in pressure in the two compartments as a result of the combustion of the methane.

"A multi-way cock is used to admit the air into the combustion chamber, to close all passages during the combustion period and to make communication between the two chambers and the **U**-tube. The handle shown in fig. 15 turns the cock between three positions. In the first position all passages are open to the atmosphere, and it is in this position that the sample is forced into the combustion chamber with the aid of a small hand blower, sufficient volume being passed through the chamber to ensure a representative sample of the air under examination. By turning the handle to position 2 the stopcock closes all passages. A short interval (2 mins.) is advisable to permit equalisation of temperature in the two chambers. The handle is then again turned to position 1 to allow the pressure in each chamber to become atmospheric. After again turning to position 2 the electric current is switched on for two minutes. An important feature of the apparatus is that the switch cannot be pulled out when the combustion chamber is open to the air owing to its position. A small window fitted to the combustion chamber enables the platinum wire to be seen from outside. After a further two minutes to allow for cooling and equalisation of temperature in the two chambers the handle is turned to position 3, when the difference in pressure resulting from the condensation of the moisture formed by the combustion of the methane may be read on the scale at the back of the **U**-tube. The scale is graduated in percentages of methane. The apparatus, which is made by Messrs. J. H. Naylor, Ltd., Wigan, is contained, including accumulators, in an aluminium casing approximately 12 inches high by 4 inches square, the total weight being  $8\frac{3}{4}$  lbs."



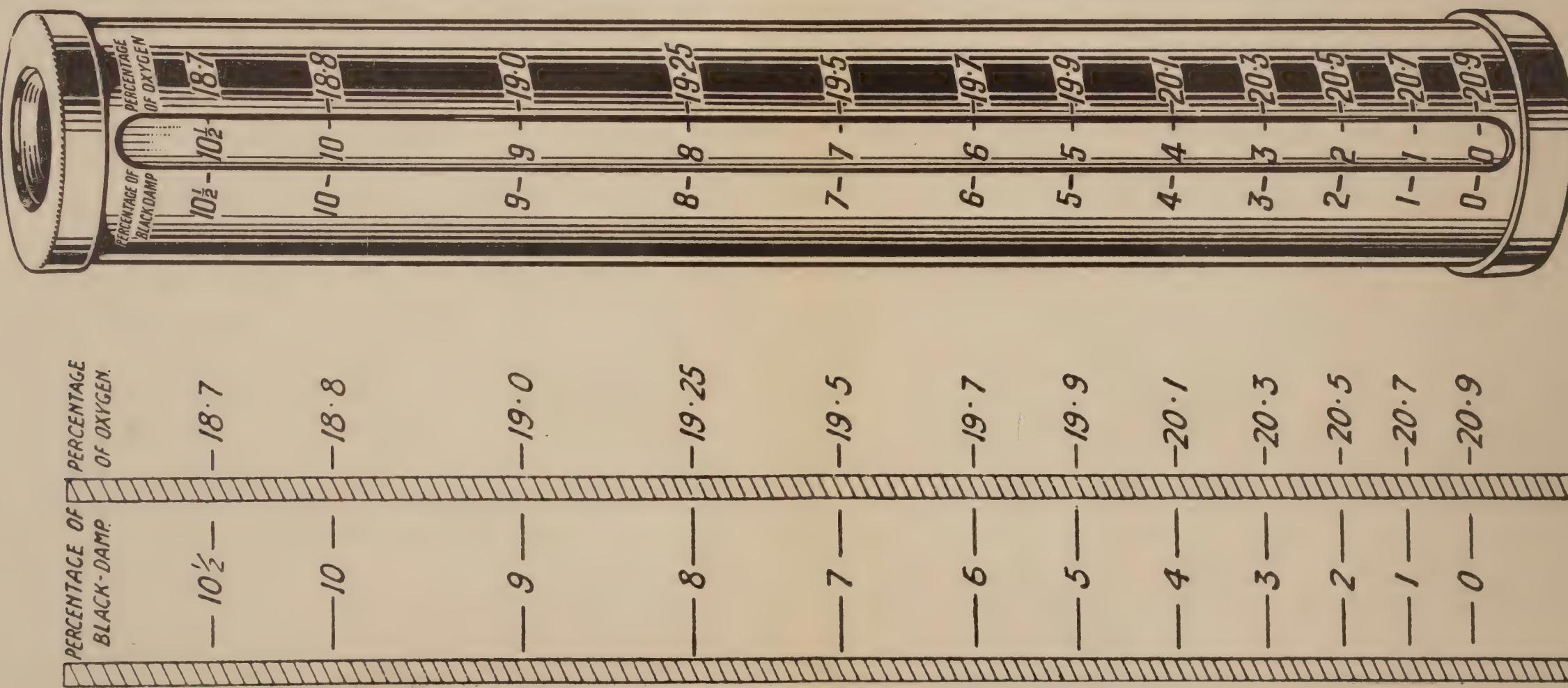


FIG. 16.

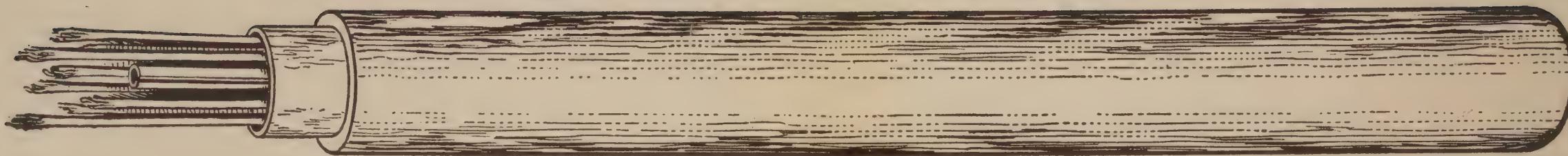
PLATE—Apparatus for Determining Oxygen by Flame Test.

FIG. 16.—Section of Glass Tube, full size.

FIG. 17.—Tube in Aluminium Case.

FIG. 18.—Inner Wooden Tube with Tapers and Brass Holder.

FIG. 18.



## CHAPTER VI

### APPARATUS FOR APPROXIMATE DETERMINATION OF OXYGEN BY FLAME TEST

A FLAME of any kind is extremely sensitive to variations in the percentage of oxygen in air. Both the light given by a flame and the ease with which it can be extinguished by a current of air are greatly affected. Variations in atmospheric pressure (and consequently in the partial pressure of oxygen) have, on the other hand, only a comparatively small influence on the flame. The following method <sup>1</sup> for approximately determining the oxygen percentage in air is based on the fact that as the oxygen percentage in air diminishes the flame is extinguished more and more easily by a current of air.

The apparatus consists of some thin tapers and a stout glass tube 7 inches long and 0·75 inch in internal diameter, graduated as shown in fig. 16. To protect the glass from accident it is enclosed in the aluminium case shown in fig. 17, the scale being marked on the case, in addition to marks on the enclosed glass. The length of the case is exactly 7 inches, and the openings at the top and bottom of the case are 0·75 inch in diameter. The glass itself is slightly less than 7 inches long. Between the case and the glass there is a thin sheet of asbestos cloth, and washers are also provided between the metal caps and the ends of the glass to further protect the glass should the tube be accidentally

<sup>1</sup> Originally described in the *Transactions of the Institution of Mining Engineers*, vol. xli, p. 455, 1911.

dropped. A supply of tapers is carried in a wooden case (fig. 18) which fits inside the tube, and along with the tapers there is a brass holder, with the help of which a lighted taper can, if necessary, be lowered into the tube. The holder also makes it possible to use up quite short pieces of taper. The tube is carried about in an outer case of japanned metal, which keeps the wooden case in position.

When a lighted taper is held vertically inside the tube an upward draught is, of course, produced by the heat ; and this draught varies in strength, according as the taper is held high up or low down in the tube. The draught tends to blow the flame out ; and according to the percentage of oxygen in the air, the flame is extinguished at a point lower down or higher up in the tube. The position of the graduation marks is empirically determined by experiments in a closed chamber, the air of which was vitiated by respiration or by gas burning. One scale gives the oxygen percentage, and the other the percentage of what is familiarly known to miners as "black-damp." The latter is simply the residual gas (a mixture with an average composition of about 92 per cent. of nitrogen and 8 per cent. of carbon dioxide) left by oxidation processes in the mine. It is evident that the percentage of "black-damp" in mine air is determined (provided that methane or other gases are absent) by the percentage of oxygen. Hence the two scales run parallel. The "black-damp" scale is marked on the glass, as being more simple than the oxygen scale ; but the latter scale need alone be considered here.

The lowest oxygen percentage marked on the scale is 18.7. Below about this percentage the taper will no longer burn in the tube, and, when held outside the tube, it will not burn in a vertical position with less than 18.2 per cent. of oxygen ; but when held horizontally it will still burn until the oxygen has fallen to 17.2 per cent. There is thus a wide range

within which the oxygen percentage may be estimated by the taper-and-tube method.

As the flame becomes very small when it is just on the point of extinction, its position with respect to the graduations on the tube can be determined quite easily. The lighted taper should first be pushed up to a point where it burns easily, and then gradually lowered. With a little practice it is easy to find with considerable exactness the point at which it is just extinguished. Care must be taken not to breathe across the lower end of the tube while the observation is being made. If the air is much vitiated, it may be necessary to push the taper (held in the brass holder) through the tube before lighting it, and then to lower it cautiously into the tube.

The tapers used for graduating the tube, and supplied with it by the makers, are white wax tapers  $\frac{1}{16}$ th of an inch in diameter. Other tapers give, however, nearly the same result, though thick ones are less convenient and may crack the glass. An ordinary wax match with the head removed answers well enough when held in the brass holder.

There are several other circumstances, besides the oxygen percentage as revealed by ordinary analysis, which affect the results to some extent. The chief of these is the percentage of aqueous vapour in the air. An ordinary chemical analysis gives the percentage of oxygen in the air when absolutely dry—a condition never met with outside a laboratory. The actual percentage of oxygen by volume in ordinary air is, of course, less than 20·93, because the air is diluted to some extent by aqueous vapour; and on an average outside air in England is mixed with about 1 per cent. of aqueous vapour, which reduces the real oxygen percentage by a hundredth, that is from 20·93 to 20·72. The flame reacts approximately to the real oxygen percentage, and it will thus be understood readily that the

more moisture is present in the air the lower will be the oxygen percentage given by the test. Mine air contains on an average about 2 per cent. of moisture, and about as much moisture is likely to be present in most cases where the tube method would be of use. For this reason the original tube was graduated with air containing 2 per cent. of moisture, which corresponds to saturation with moisture at about 64° F. (see p. 99). Except in warm and moist weather, therefore, the flame will not go out at the zero-point of the graduations when a test is made in pure air.

The indications are not appreciably affected by such variations of atmospheric pressure as occur on the surface in England ; but at depths or altitudes of more than 2,000 feet from sea-level the readings need some correction. Thus at a depth of 3,000 feet, with the barometer at about 33 inches, the indications were found to be about 0·2 per cent. too high ; and with increasing height above sea-level the indications become increasingly too low. At a height of 14,100 feet and a barometric pressure of 18 inches (on the summit of Pike's Peak, Colorado) the indications were about 1·2 per cent. too low.

The experimental results opposite (made in air saturated with moisture at about 64°) illustrate the surprising accuracy with which the oxygen percentage can be determined by means of the tube and taper when there are no disturbing conditions. It must, however, be borne in mind that such conditions (varying air currents, barometric pressures, and percentages of moisture) are usually present to some extent when this method is employed in mines, etc.

This means of testing is not applicable in mines where safety-lamps are required ; but in mines, etc., where the method can be used, and the percentage of aqueous vapour and barometric pressure are not abnormally high or low, the results are reliable to within about 0·2 per cent. The

Percentage of Oxygen.		Percentage of Carbon Dioxide.
Indicated by Tube.	Found by Analysis.	
20.90	20.90	0.06
20.45	20.33	0.49
20.15	20.13	0.65
20.00	20.07	0.71
19.65	19.63	1.07
19.25	19.32	1.33

advantage of the method is that it is very rapid and simple. It does not indicate the carbon dioxide percentage directly, but this can be inferred with tolerable accuracy in a mine if the usual ratio between excess of carbon dioxide and deficiency of oxygen has once been ascertained by analysis. If, for instance, this ratio was known from analyses to be about 3 to 4 (a common ratio in metalliferous mines), and the oxygen percentage indicated by the tube was 19.3, or 1.6 per cent. below the proportion in pure air, the carbon dioxide percentage would be about  $1.6 \times \frac{3}{4} = 1.2$  per cent.

**Briggs' Safety-lamp Method.**—The method just described is of course not applicable in mines where safety lamps have to be used. In order to meet this difficulty Dr. Henry Briggs has devised an arrangement which can be used with a safety-lamp. A full description is given on page 169, vol. li, of the *Transactions of the Institution of Mining Engineers*. The principle of the arrangement is that by means of an adjustable graduated cut-off the air-supply to the lamp is cut down until the flame is just on the point of extinction. The amount to which the cut-off must be adjusted varies with the oxygen percentage of the air, and the cut-off is graduated accordingly.

An accuracy of the same order as that of the tube method

can be reached with the Briggs' lamp method. Moisture and barometric pressure influence the lamp readings in the same way as those of the tube. The presence of fire-damp in the air makes the readings slightly too high. To correct for fire-damp the percentage of the latter must be estimated by the cap method described in the next chapter. A fifth of the percentage of fire-damp is then deducted from the percentage of oxygen which has been indicated by the lamp.

The lamp method is very useful to firemen in ascertaining whether the air contains the minimum percentage of oxygen allowed by the Coal Mines Act (19 per cent.). The cut-off is simply set to 19 per cent.; and if the flame does not threaten to go out, the fireman knows at once that the air complies with the standard.

## CHAPTER VII

### APPROXIMATE ESTIMATION OF METHANE, ETC., BY FLAME TEST

WHEN methane or any other combustible gas or vapour is present in air in proportions not sufficient to form an explosive mixture a zone of combustion extends above the limits of the ordinary flame, manifesting its presence by the appearance, under favourable optical conditions, of a pale "cap" on the flame. With increasing percentages of the combustible gas the cap becomes more and more luminous, and later increases rapidly in height. When the mixture is just inflammable, the cap may be said to have increased to a size only limited by the extent of the inflammable atmosphere.

It must be clearly understood that the cap itself is one thing, and its visibility another. When the flame itself is luminous, the cap may be invisible because the excitation of the retina at the point on which the image of the flame falls diminishes enormously the excitability of the adjoining part on which the image of the cap falls. It is only, therefore, when the cap is long and relatively luminous, and the air nearly inflammable, that a cap is visible on a luminous flame. Nevertheless, it is quite easy to photograph the invisible cap on a luminous flame, as has been shown by Messrs. E. B. Whalley and W. M. Tweedie; and the heating of the gauze in the chimney of a safety-lamp to redness may also furnish unpleasant evidence of the existence of a cap.

It should also be understood that the height of the actual

cap depends on the size, or perhaps rather the height, and the temperature of the flame. There is thus no definite ratio between height of cap and percentage of inflammable gas, unless the flame is of a standard height and temperature. The relatively long and very hot flame of a jet of hydrogen will give a longer cap than a small blue oil flame with fifteen times as much methane in the air.

The presence of the cap on the flame affords an invaluable means of estimating, with an ordinary oil flame, the percentage of methane in the air of a mine, or, more generally, the approach towards inflammability of any mixture of a combustible gas with air. A mixture of methane with air becomes just inflammable when 5·6 per cent. of methane is present, while the cap on the oil flame of a miner's safety-lamp can, with proper care, be observed with all percentages from 1 up to the point of inflammability.

It will be sufficient to describe here the method of testing for methane with an ordinary safety-lamp and the ordinary burner, burning the ordinary mixture of "colza" and paraffin oil. To test for methane, the flame of the lamp is cautiously pulled down until only a very slightly luminous tip is left on the flame, which is about a tenth of an inch high. If 1 per cent. or more of methane is present in the air a cap, or part of one, will be visible above the flame. Fig. 19, which is constructed from a series of plates from observations and sketches made by Sir John Cadman,<sup>1</sup> the percentages of methane being accurately determined by analysis, shows in full size the outlines of the burner, the testing flame, and the visible caps. It will be noticed that with 1 per cent. only the base of the cap can be seen. With 1½ per cent. most of the cap is visible, but the tip fades into invisibility. At

<sup>1</sup> *Reports on Mine Ventilation and on Methods of Determining Firedamp*, by Professor Cadman and Mr. E. B. Whalley, Parliamentary Paper [Cd. 4551], 1909.

2 per cent. the tip is just visible, and with increasing percentages the height of the cap increases in a rapidly increasing ratio. The diagram does not show, however, the fact that the luminosity of the cap increases steadily from the lower percentages upwards. It is by the luminosity and the visibility of the tip, rather than by the height of the cap, that the percentage of methane can best be gauged up to 3 per cent. It is very important to note that the tip is just visible at 2 per cent. Tests for the Miners Lamps

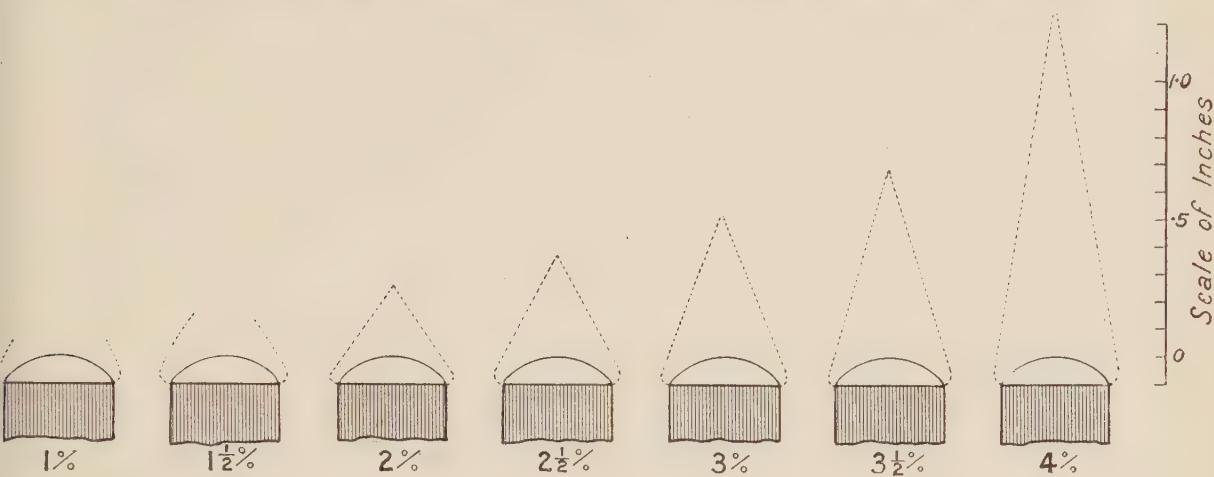


FIG. 19.—Diagram showing Outlines of Caps Visible on an Oil Flame with Different Percentages of Methane.

Committee<sup>1</sup> gave almost identical results with those just described.

In testing for fire-damp by the method just described there is considerable risk of the flame going out ; and to obviate this, and increase the delicacy of the test, Sir Henry Cunynghame and Professor Cadman have introduced a device by which the cap on a full flame can be rendered luminous by sodium vapour, so that the test can be made with a full flame.<sup>2</sup>

A still simpler method of rendering the cap visible on a full flame has been described by Prof. H. Briggs.<sup>3</sup> By intro-

<sup>1</sup> Memorandum No. 10, 1924.

<sup>2</sup> Trans. Inst. of Mining Engineers, vol. xxxix, p. 13.

<sup>3</sup> *Ibid.*

ducing a loop of copper wire into the flame the latter's luminosity is so much diminished that the cap is made easily visible. The same loop can also be employed to indicate whether the oxygen percentage in the air is above or below 19 per cent. The presence of fire-damp interferes with this latter test, however.

The most delicate cap test for fire-damp, etc., is that with the hydrogen flame ; and by means of the Clowes hydrogen testing lamp it is possible to detect as little as 0·2 per cent. of methane. The cap with this percentage is very pale, but can be seen to extend about 0·6 inch above the tip of the standard hydrogen flame.

Spirit lamps usually give larger caps for the same percentage of methane.

## CHAPTER VIII

### GRAVIMETRIC DETERMINATION OF MOISTURE AND CARBON DIOXIDE IN AIR

IN some cases it is necessary to determine with great accuracy the amount of carbon dioxide or aqueous vapour, or of both, in air ; and for this purpose it may be desirable to use the gravimetric method, although usually the moisture can be estimated with sufficient closeness from dry- and wet-bulb thermometer readings, and carbon dioxide by ordinary gas analysis, as already described. The gravimetric method is required more particularly in certain kinds of physiological work, where moisture and carbon dioxide have to be determined together ; and the apparatus <sup>1</sup> now to be described was designed with a special view to physiological investigations, although it is equally suitable for other work in which great accuracy is essential.

**Determination of Moisture.**—The absorption apparatus (together with that for carbon dioxide) is shown in fig. 20. It consists of a pair of thin glass test-tubes, *a*, *a*, containing pumice soaked in sulphuric acid. Each tube measures  $4 \times 1$  inch, and is provided with a double-bored cork about  $\frac{1}{2}$  inch thick, which is fitted with glass tubing of about  $\frac{3}{16}$  inch internal diameter, and in the form shown in the figure. The longer piece of tubing in the first tube should be made shorter than the corresponding piece in the second tube, in order to avoid resistance caused by the accumulation of water. The tubing must fit firmly. The corks are

<sup>1</sup> Haldane and Pembrey, *Philosophical Magazine*, 1890, p. 306.

covered with a layer of paraffin wax inside and out. They are pushed down flush with the tops of the tubes, the end of each tube being first very carefully wiped inside free of acid, and then warmed to soften the paraffin on the cork and so facilitate its entrance. To enable the longer limb of the tubing to be pushed down, a passage should first be cleared in the pumice with a glass rod. A layer of paraffin is spread smoothly over the top of the cork. The apparatus must be absolutely tight, and should allow air to pass quite freely

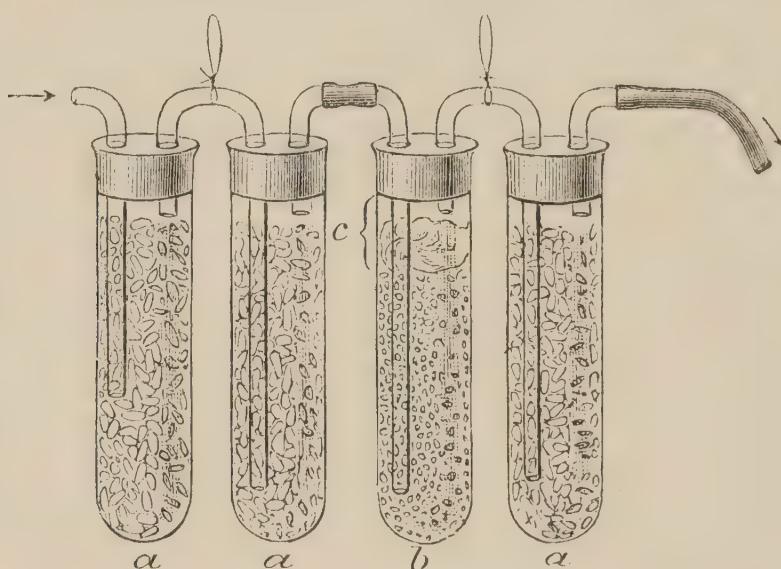


FIG. 20.—Absorption Tubes for Determination of Moisture and Carbon Dioxide in Air.

when suction is applied. It should be carefully cleaned with a wet cloth to remove any trace of acid, and then dried.

The fragments of pumice are sifted through a sieve with about seven meshes to the inch, and shaken on a fine one to remove the powder. They are then heated to redness with a large blow-pipe flame, and thrown, still hot, into pure re-distilled sulphuric acid. The superfluous acid is then poured off, and the pumice preserved in a stoppered bottle, from which the tubes are filled. Before using the tubes they should be washed out with air, to remove traces of sul-

phurous acid. Each pair of tubes weighs, when filled, about 80 grammes.

To diminish to a minimum the errors arising from accidental variations in weight of the tubes, the weighing is always done against a counterpoise consisting of a similar pair of absorption tubes, always kept in the same place. Since, during an experiment, the absorption tubes will have been warmed above the temperature of the counterpoise, the weighing must be deferred for half an hour, so as to allow the temperatures to become equal again. The tubes are provided with stoppers consisting of a short piece of rubber tubing, closed at one end with a piece of glass rod. The weighing is done without stoppers, and if several tubes are to be weighed, the stoppers are removed from the whole of them, including the counterpoise, and not replaced till the last has been weighed. No absorbent for moisture is kept inside the balance case. The tubes should be lifted by the wires attached to them for hanging on the balance.

Numerous experiments have shown that the absorption of moisture by one of these pairs of tubes is complete, even with very rapid currents of air. Thus with two pairs in series and the air passing through at the extremely fast rate of 7 litres per minute, the increase of weight was as follows after 21 litres of air had passed :—

Pair (1) + 0·2142 gramme

Pair (2) + 0·0001      ,,

With a rate of 1 litre per minute the absorption by the first pair was still perfect after 13 grammes of moisture had been absorbed from 2,300 litres of air. The first tube had then become blocked by dilute acid, so that the experiment had to be stopped.

The tubes should be weighed to decimilligrammes, and by using the counterpoise the errors of weighing are reduced

to a maximum of 3 decimilligrammes. Without the counterpoise they are about ten times as great.

The use of paraffined corks for closing the tubes has the disadvantage that after a few weeks the sulphuric acid begins to attack the cork. To overcome this defect, and at the same time facilitate the preparation and re-charging of the tubes, a form in which corks are entirely dispensed with was designed by Mr. W. Blount, and is shown in fig. 21. The stoppers are of glass and are lubricated with vaseline.

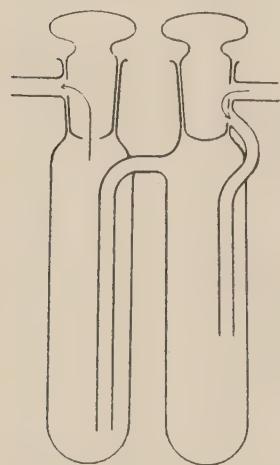


FIG. 21.—Improved Form of Absorption Tubes for Moisture and Carbon Dioxide.

The air passes through them in the direction shown by the arrows. In other respects the dimensions are the same as those of the tubes shown in fig. 20.

In place of the acid tubes described, two glass-stoppered **U**-tubes containing phosphorus pentoxide may be employed. The resistance of these is usually so high as to render them unsuitable for use where a current of more than 8 litres per minute is employed. Where an absorbent having a low resistance is required, "silica-gel" dried at 300° C. in a current of air will be found very useful. A second tube containing a small quantity of phosphorus pentoxide may be used as a check tube.

The drying efficiency of the silica-gel may be recovered by reheating at 300° C. in a current of dry air.

In physiological experiments it is often not necessary to measure exactly the air current passing through the absorption apparatus for moisture and carbon dioxide. When exact measurement is required this can be carried out by means of a wet gas-meter, or still more exactly by using an aspirator of known capacity. For many purposes the following form of aspirator is very convenient. Two bottles

(fig. 22), each holding a little over 5 litres, or 10 litres, or any other convenient amount, up to a mark in the neck, are arranged as shown in the figure, and connected together by a piece of stout, non-collapsible rubber tubing, provided with a screw clip for regulating the flow of water. The burette-clips are for starting or stopping the flow. The bottles are covered outside with a layer of felt, to keep the temperature

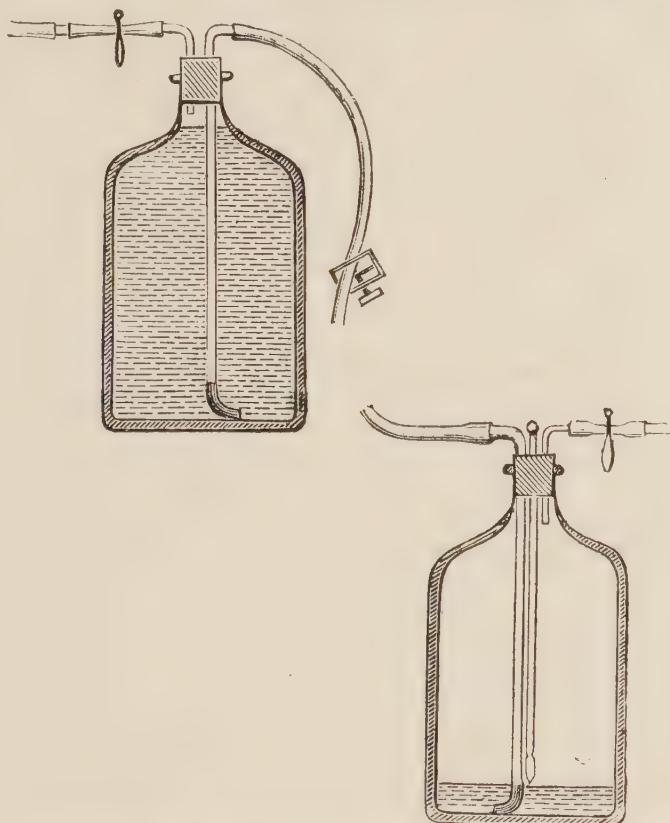


FIG. 22.—Aspirator for Determination of Moisture and Carbon Dioxide in Air.

of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched and the reading of the thermometer taken. The bottles are graduated roughly by fastening strips of paper at intervals of 1 litre up the uncovered strip of glass. It is thus easy to see that the water is running at about the proper rate.

To graduate the aspirator one of the bottles is allowed to drain for a minute, and is then weighed accurately. The two bottles are now connected, and the weighed bottle filled with water to the mark, the tubing also being filled with water. The rubber stopper of the weighed bottle is then removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again ; and by deducting from this weight that of the empty bottle, and making the usual small corrections, as in the graduation of a measuring flask, the volume of water held by the bottle filled to the mark, and with the tubing in position, is obtained. If a suitable balance is not available, this volume can be measured, though less accurately, with a large measuring cylinder. The difference between the capacity of the bottle and some round volume, such as 5,000 c.c., is now measured into the bottle, which has previously been emptied and drained for a minute. The stopper is then replaced, care being taken, as before, not to spill any of the water in the glass tubing. The other bottle is filled with water to the mark, and the aspirator is ready for use. It measures off exactly 5,000 c.c., or whatever other volume has been chosen, each time the bottles are reversed and the lower one allowed to fill to the mark. The air measured is at the temperature shown by the thermometer, and is, of course, saturated with moisture.

In determining very exactly the percentage of carbon dioxide in outside air it may be desirable to use a very large aspirator. For this purpose a pair of large glass carboys, arranged on the same principle as that just described, is very convenient.

**Determination of Carbon Dioxide.**—The absorption apparatus (fig. 20) consists of a pair of test-tubes arranged in the same way as already described for absorption of moisture. The first tube is filled with soda-lime, and the

second with sulphuric acid and pumice for absorbing the moisture given off by the soda-lime. The air must arrive perfectly dry at the absorption tube for carbon dioxide, and is therefore first passed through the absorption apparatus for moisture.

The soda-lime may be made by heating together in a copper vessel 1,200 grammes of caustic soda in saturated solution and the product obtained by slaking to a fine powder 1,000 grammes of quicklime. The heating is continued until the soda-lime can be broken up in a mortar. The fragments are rapidly sifted through a wire sieve of about twelve meshes to the inch, and the product freed from powder by a finer sieve. Commercial soda-lime similarly sifted may answer equally well, but is sometimes unsatisfactory. A piece of cotton-wool is placed between the cork and the soda-lime, as shown in the figure, in order to prevent any soda-lime from being carried over by a rapid air current.

The weight of carbon dioxide in the air aspirated through the apparatus is shown by the increase in weight of the pair of tubes. With good soda-lime, and only a small proportion of carbon dioxide in the air, the absorption is complete until about 500 litres of air have passed through, if the rate does not exceed about 1 litre per minute ; but after this a second pair of tubes will usually begin to increase in weight. The absorption of carbon dioxide is thus not nearly so efficient as that of moisture, and unless the soda-lime is fresh it is well to use a second absorption apparatus for carbon dioxide in case of any appreciable failure of the first one.

The following is an example of results obtained when 90 litres of laboratory air, measured by a meter, were aspirated through two pairs of absorption tubes for carbon dioxide, at a rate of 1 litre per minute.

Increase of first pair . . . .	0·1615 gramme
,, second pair . . . .	0·0001 ,,

If the percentage of carbon dioxide in the air is required, the volume of air aspirated must be corrected to dry air at 0° C. and 760 mm. barometric pressure. The number of c.c. of carbon dioxide in this air can then be calculated by dividing the number of milligrammes by 1·97, since 1 c.c. weighs 1·97 milligrammes.

The following instance of a determination of carbon dioxide in outside air will serve as an example. The volume of air aspirated was 30·0 litres, and the temperature in the aspirator was 11·0° C., while the barometric pressure was 753 mm. This volume of air, reduced to dry air at 0° C. and 760 mm., is 28·20 litres. The increase in weight of the absorption apparatus for carbon dioxide was 0·0162 gramme, corresponding to 0·00821 litre. The proportion by volume of carbon dioxide was therefore 0·0291 per cent. As, however, there might be an error in weighing of three decimal milligrammes, the last decimal figure in the result has little significance.

## CHAPTER IX

### DETERMINATION OF MOISTURE BY DRY- AND WET-BULB THERMOMETERS

FOR most ordinary purposes the moisture in air can be determined with sufficient accuracy from the readings of dry- and wet-bulb thermometers. But apart altogether from the absolute amount of moisture in air, or the "relative humidity," the wet-bulb temperature is of great direct hygienic significance when it is much above 60° F. (15.5° C.). In warm mines, factories, etc., and in warm climates, the wet-bulb temperature is of great importance.

The dry- and wet-bulb temperatures of the air can be determined correctly out of doors (except on still days), or wherever there is a good air-current, from the readings of the ordinary fixed dry- and wet-bulb thermometers, if they are properly protected from the sun. Where, however, there is little or no air-current, as in a room indoors, or where the air is nearly still in a mine, a fixed dry- and wet-bulb thermometer does not give correct readings unless an artificial air-current is produced. Such a current may be produced by means of a small fan driven by clockwork, as in the Assmann hygrometer. To obviate the frequent winding necessary with a clockwork drive for the small fan, the latter may be connected to a small electric motor fitted in place of the clockwork and run off the electric supply mains. This is a somewhat cumbrous and expensive apparatus, however, and it is usually best to use two ordinary chemical thermometers and keep them in brisk motion until the readings

are obtained. It is now easy to obtain suitable thermometers at a very moderate price. They must read together, and correctly, at all parts of the scale, and the scales should be open and very plainly marked if they have to be read by artificial light. The bulbs should be long and narrow, to save waste of time in getting constant readings.

A layer of thin muslin is secured with thread round the bulb of one of them, and just before use this is wetted with water, carried in a small bottle. The thermometers are held in one hand, with the bulbs well separated, and vigorously waved to and fro in the air to be tested, until the readings of both thermometers are perfectly steady. In reading the thermometers care must be taken that they are not affected by the heat of a candle or lamp. A pocket electric lamp is useful for making the readings. Unless the air is saturated with moisture the wet-bulb thermometer will read lower than the dry-bulb, and may often read considerably lower than a stationary wet-bulb thermometer.

To calculate from the readings the weight of moisture in a cubic foot of the air, the dew-point, the relative humidity (i.e. the percentage relation between the amount of moisture present and the amount which air saturated at the same temperature would contain), and the pressure due to the aqueous vapour present, Glaisher's well-known tables<sup>1</sup> may be used. The percentage by volume of the aqueous vapour present in the air is given by reducing to a percentage the ratio of the pressure of aqueous vapour to the existing barometric pressure. Thus if the air is saturated at 64° F., the pressure of aqueous vapour is 0.596 inch of mercury. Hence if the barometric pressure is 30.0 inches the percentage of aqueous vapour by volume is  $\frac{0.596}{30.0} \times 100 = 1.99$ .

<sup>1</sup> *Hygrometrical Tables*, by James Glaisher, F.R.S. Published by Taylor and Francis, Red Lion Court, Fleet Street, London.

To facilitate the readings of the two thermometers and ensure that air at a sufficient velocity (about 600 feet per minute) is passing over the wet bulb, a whirling hygrometer

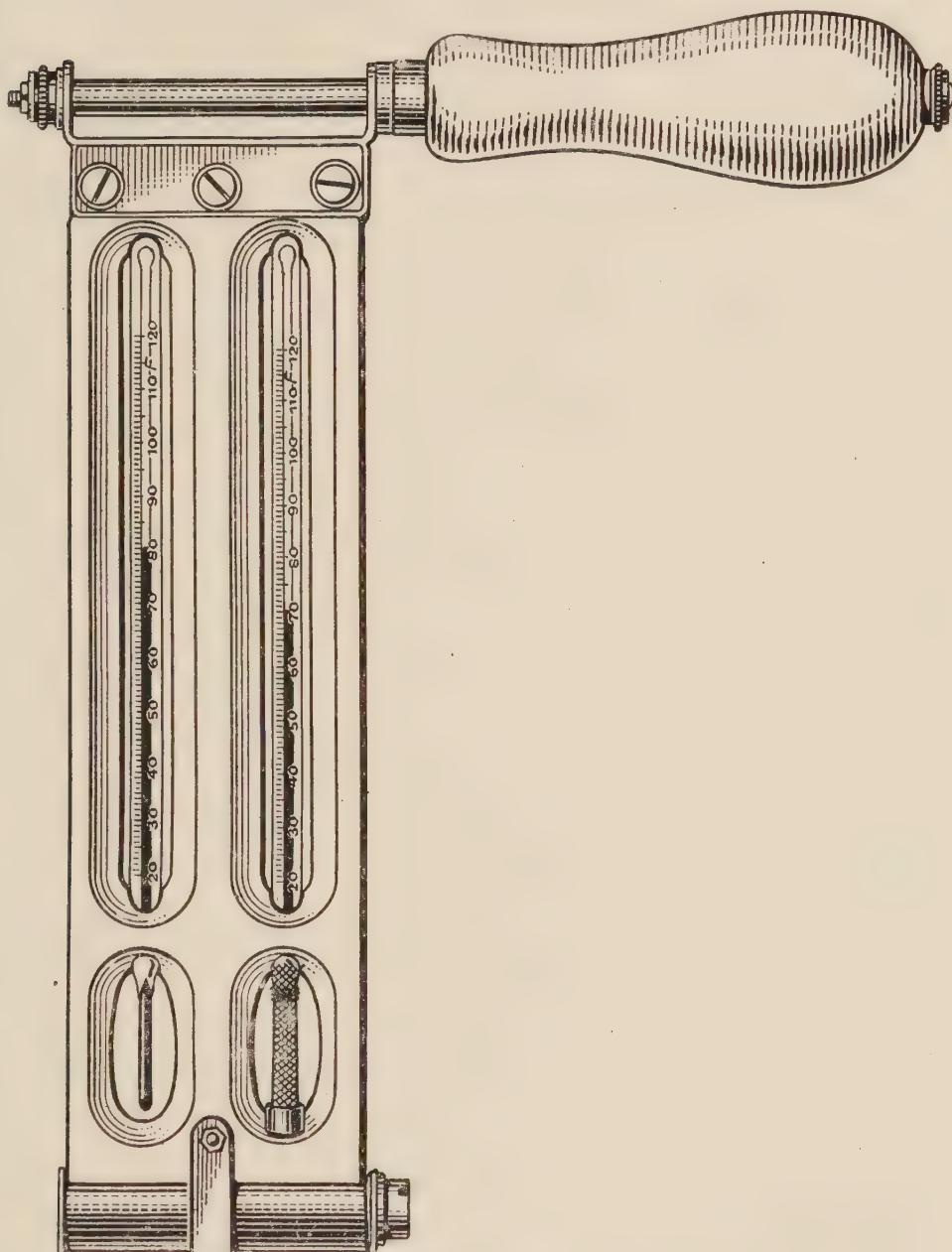


FIG. 23.—Whirling Hygrometer.

may be employed. One form of this, designed by Mr. J. T. Storror for the committee of the Institution of Mining Engineers appointed to investigate the control of atmo-

spheric conditions in hot and deep atmospheres,<sup>1</sup> has proved most useful in making underground observations. This is shown, with minor alterations, in fig. 23. Two sensitive mercury thermometers about 6 inches long are fixed in grooves on cork in a wooden frame. The frame is cut through along the length of the graduated portions and also by oval holes at the positions of the bulbs. The wood should be cut away from the bulbs of the thermometers as far as possible to minimise interchange of heat through radiation.<sup>2</sup> The slots in which the two thermometers are situated enable the position of the mercury in each to be read quickly by holding against a light. Two pieces of metal are let into the sides at the top of the frame with their tops, which are bored to take a spindle, projecting beyond the wooden frame. A wooden handle is fitted to the spindle by means of milled nuts and by movement of the wrist the frame and thermometers can be whirled without appreciable effort. When whirled at about 200 revolutions per minute, the necessary velocity for giving a correct wet-bulb reading will be obtained. A small reservoir is fitted below the wet-bulb thermometer, which is situated on the side on which the handle projects, so that during whirling it may be at the lower level and thus prevent any particles of water being thrown out on to the dry-bulb thermometer. This reservoir may be made of metal, as in fig. 23, or alternatively of glass with a short length of glass tubing sealed into the top, and is fitted with an air hole to facilitate filling. The wet bulb is wrapped with one layer of ordinary gauze bandage which dips into the tube leading into the water reservoir. The most convenient range for either pit or indoor

<sup>1</sup> *Third Report to the Committee*, by J. P. Rees, *Trans. Inst. Min. Eng.*, 1920, vol. Ixi, pt. 3, pp. 101-18.

<sup>2</sup> This precaution is desirable since the temperature of the wooden frame may sometimes be much different from that of the air being tested.

work is 40° to 120° F., but for observations in the open air the range should, of course, extend below freezing-point. Whirling for 30 seconds is usually found to give the correct temperatures. Tables prepared by C. F. Marvin<sup>1</sup> will be found very useful when observations are made with the whirling hygrometer since they have been specially drawn up for use with this type of hygrometer. From these the relative humidity, dew-point and amount of moisture in grains per cubic foot may be ascertained. The tables are arranged for use at high altitudes or decreased atmospheric pressure, and from them the correction for the increased pressure encountered in mine workings may be made.

**The Hancock Hygrometer.** For use in places where it is impossible or inadvisable to use the Storrow whirling hygrometer, Hancock has devised a simple instrument rather similar to the Assmann hygrometer. In this sensitive thermometers, of the same type as are employed in the Storrow hygrometer, are fitted in two vertical glass tubes, which are constricted in the position of the thermometer bulbs and connected to each other by a horizontal T-stopcock. Through the third limb of the T-stopcock air may be drawn by a series of inspirations, until the wet-and dry-bulb thermometers give a constant reading. The area of the annular space surrounding the bulbs is such as to give a velocity of at least 600 feet per minute over the bulbs during inspiration. Full details of this instrument are given in the *Transactions of the Institution of Mining Engineers*, vol. lxxii (1927), 6, pp. 336-41.

It has been pointed out that the wet-bulb temperature is of great importance physiologically. A man's capacity for work in hot places is largely influenced by the wet-bulb

<sup>1</sup> *Psychrometric Tables for Obtaining Vapour Pressure, Relative Humidity and Temperature of Dew-point.* Published by U.S. Dept. of Agriculture Weather Bureau.

temperature, and also by the amount of air passing over him. In other words, the cooling effect of any one set of atmospheric conditions is not given simply by the wet-bulb temperature alone. The actual cooling effect on the human body depends on the rate of air circulation over the skin, etc., and in order to give a ready means of measuring the



FIG 24.—  
Kata  
Thermometer.

maximum cooling effect Dr. Leonard Hill<sup>1</sup> designed the Kata thermometer (fig. 24). This instrument measures the cooling power of the atmosphere on its surface in milli-calories per square centimetre per second. It is essentially an alcohol thermometer, having a sufficiently large bulb to enable a reliable estimate to be made of the time taken for cooling of the alcohol in the instrument from 100° F. to 95° F. This range is taken to give a mean figure coinciding approximately with the body temperature. The bulb is about 4 cm. in length and 2 cm. in diameter and the stem is graduated for 100° F. and 95° F. The top of the stem is enlarged into a small safety reservoir to avoid the danger of bursting when heated to above 100° F. and also to permit of the temperature being raised sufficiently high to allow the cooling to become steady by the time the 100° mark is reached. Either "dry" or "wet" Kata readings may be taken, the bulb of the instrument being exposed quite dry in the former case, whilst in the latter it is covered with a wet silk net finger-stall. The dry Kata gives the cooling power by radiation and convection, while the wet Kata gives the cooling power by radiation, convection and evaporation. In the case of work in hot places underground the wet Kata readings are the more instructive. The bulb

<sup>1</sup> Med. Res. Council Spec. Rep. No. 73, 1923.

of the instrument is immersed in hot water until the alcohol rises well into the top reservoir and then removed. For dry readings the bulb is completely dried and the time in seconds for the meniscus of the alcohol to drop from the 100° to the 95° mark observed with a stopwatch. Three to five readings should be made, the first discarded and the remainder averaged. The procedure is the same for the wet Kata readings except that the silk net finger-stall is fitted before warming the instrument, and on taking from the hot water excess of water is removed from the bottom of the bulb by means of a cloth. Each instrument has engraved on its stem a factor. This, divided by the average time of cooling in seconds, gives the cooling power in millicalories per square centimetre per second. A wet cooling power of less than 11 is very trying to anyone unaccustomed to work in hot places.

It is convenient to remember that between the temperatures of 40° and 70° F. the dew-point is approximately as many degrees below the wet-bulb reading as the wet-bulb reading is below the dry-bulb. The dew-point is the temperature at which, if the air were cooled, it would be just fully saturated with moisture, so that it could not be cooled further without depositing moisture. With the barometer at 30 inches the percentage by volume of the aqueous vapour in air fully saturated with moisture would be as shown in the following table. If the barometer were below or above

Temperature, ° F.	Percentage of Aqueous Vapour by Volume.	Temperature, ° F.	Percentage of Aqueous Vapour by Volume.
12	0·25	76	3·0
27·5	0·5	81	3·5
45	1·0	85	4·0
56	1·5	88·5	4·5
64	2·0	92	5·0
70·5	2·5	95	5·5

30 inches, the percentages would have to be proportionally increased or diminished.

Glaisher's tables and also Marvin's give all the data in English measure (grains and cubic feet). One grain is 0·0648 gramme, one cubic foot 0·0283 cubic metre, and one inch 25·4 millimetres.

## CHAPTER X

### RECOGNITION AND DETERMINATION OF SMALL PROPORTIONS OF CARBON MONOXIDE IN AIR WITH THE AID OF BIRDS OR MICE AND BY THE BLOOD TEST

ON account of the poisonous properties of carbon monoxide, the frequency of its presence in air, and the impossibility of detecting small proportions of it by smell, tests by which it may be detected and estimated in air are of much practical importance. When present in considerable concentration it has a distinct garlic-like odour ; but this is practically of no use in revealing its presence, as the odour is faint and is nearly always concealed by that of other gases or vapours present along with it. Most of the chemical reactions for estimating carbon monoxide are also more or less unreliable in ordinary cases, as they are given by other gases and vapours which may probably be present. Methods by which carbon monoxide may be determined when it is present by itself, or along with other combustible gases, have already been described (pp. 31 and 47-53).

**Testing with a Small Animal.**—This method,<sup>1</sup> which was introduced by one of us as a means of testing for dangerous proportions of carbon monoxide in the air of mines, depends upon the fact that while small warm-blooded animals are about as sensitive in the long run to carbon monoxide

<sup>1</sup> *Report on the Causes of Death in Colliery Explosions and Fires*, Parliamentary Paper [Cd. 8112], 1896 ; also Haldane and Douglas, *Trans. Inst. of Mining Engineers*, vol. xxxviii, p. 267, 1909.

poisoning as large animals, including man, the small animals react far more quickly, and can therefore be used safely as indicators of the presence of carbon monoxide. A mouse, or a small bird, such as a canary or linnet, may be employed for the test. The bird is more sensitive to carbon monoxide ; and it is easier to see whether a bird, sitting on its perch in a cage, is affected, as it becomes unsteady and falls off its perch. A bird is, however, very apt to die suddenly when in a dangerous atmosphere, and thus to become useless as a further guide. Under conditions of rest a bird or mouse is, roughly speaking, affected in less than one-tenth of the time taken to affect a man. The actual time depends upon the percentage of CO and also upon the amount of work being done. When, therefore, work is being done by a man, for example, in walking along an underground roadway (which may be the equivalent of 5,000 ft.-lbs. per minute) and a bird is carried for the purpose of indicating any dangerous percentage of carbon monoxide, the margin for safety is not so great as that given above. Under such conditions of work the man will probably absorb three or four times the amount of carbon monoxide that he would take up during rest. Thus owing to the fact that the bird is at rest and the man working, the man may be affected in some cases in about two or three times the time necessary to affect the bird. It is very necessary therefore that the bird should be kept under constant observation and that when it does collapse or fall off its perch the man should retreat into purer air immediately.<sup>1</sup> The bird should also be carried at the same height as the head of the investigator, since the atmosphere at this level is what is being inhaled and is frequently more vitiated than at lower levels. If the bird or mouse is affected at all, it will show the effects within less than ten minutes. The bird will probably die (unless

<sup>1</sup> Veale, *Trans. Inst. Min. Eng.*, 1922, vol. lxiii, pp. 417-22.

promptly removed) with anything more than about 0·2 per cent. of carbon monoxide in the air, while the mouse will probably be only disabled by this percentage, and may still live with 0·4 or 0·5 per cent. It seems probable that anything more than 0·2 per cent. would, after 15 minutes, when doing work, be very dangerous to a man, while anything more than 0·02 per cent. might produce, after several hours, headache and partial disablement.

A mouse does not show distinctly, by its symptoms, the presence of less than about 0·1 per cent. of carbon monoxide in the air ; but its blood may be used to detect as little as 0·01 per cent. The animal is left in the suspected air for 15 or 20 minutes, and then killed by drowning. If more than about 0·01 per cent. of carbon monoxide was present in the air, the blood, when sufficiently diluted and compared with fresh normal blood similarly diluted, will have a more or less pink tint ; and from the degree of pinkness it is possible to estimate roughly the percentage of carbon monoxide which was present in the air.

The poisonous action of carbon monoxide is due to the fact that this gas combines with hæmoglobin, the coloured blood constituent which normally carries oxygen in loose combination from the lungs to the tissues. As the carbon monoxide takes the place of oxygen, the blood is more or less prevented from carrying oxygen, and the animal dies, if the process has gone far enough, from want of oxygen. The extent to which the hæmoglobin becomes saturated with carbon monoxide depends in the long run on the relative mass influences of the oxygen and carbon monoxide present in the blood as it leaves the lungs. In human blood at the body temperature the affinity of carbon monoxide for hæmoglobin is about 300 times greater than the affinity of oxygen. Hence in air (containing nearly 21 per cent. of oxygen) the hæmoglobin would finally become equally

saturated with carbon monoxide and oxygen if 0·07 per cent. of carbon monoxide was present in the air and the blood were thoroughly saturated till no more gas was taken up or given off. With twice as much carbon monoxide in the air the haemoglobin would be shared in the proportion of 2 to carbon monoxide and 1 to oxygen, and so on (see fig. 26).

It can thus be readily understood that there will be a more or less definite relation between the proportion of carbon monoxide in the air and the extent to which the haemoglobin has combined with carbon monoxide in the blood of an animal which has been sufficiently long exposed for maximum saturation of its blood with carbon monoxide to have been reached. Were this relation a constant one, we could infer the exact percentage of carbon monoxide in the air from a determination of the percentage saturation of the animal's haemoglobin with carbon monoxide. In a living animal, however, the relation is disturbed by several factors, one being the fact that in an animal suffering from want of oxygen, owing to carbon monoxide poisoning, oxygen is actively taken up by the epithelial cells lining the lungs, and passed into the blood at a higher partial pressure than that of the air. In consequence of this the mass influence of the oxygen is increased, and carbon monoxide is correspondingly kept out. The extent to which this is the case varies a good deal in different animals ; and consequently we can only form a rough idea, from examination of the blood, of the percentage of carbon monoxide in the air. Nevertheless, a rough estimate is often quite sufficient for practical purposes, so that the test by means of the blood of a mouse is often very useful.

To make the test, the skin of the drowned mouse should be slit up along the middle line of the abdomen and chest with a pair of scissors. The chest wall is then removed after cutting through the ribs on each side, and the heart exposed.

By holding the heart over the mouth of a test-tube two or three drops of blood are easily obtained. This blood should be diluted at once with a good deal of water, to prevent clotting. For the purpose of comparison a dilute solution of human blood, or any other normal blood, must now be prepared. The human blood solution can be prepared from a drop or two of blood squeezed out from a prick of the finger with a large-sized needle. This blood is diluted with water in a test-tube until its tint becomes yellow. Part of the solution is then taken in another test-tube, into which coal-gas is passed through a piece of rubber tubing. As the tubing is withdrawn, the mouth of the test-tube is closed with the thumb, and the blood solution shaken up vigorously for three or four seconds with the gas. It will now be found that the solution has become pink and contrasts strongly with the yellow solution in the first test-tube. The pink colour is not seen properly unless the blood is sufficiently diluted, but it is easy to judge of the proper dilution after one or two trials.

There are now three test-tubes containing blood solution : one being solution of normal blood, the second being the same solution saturated with carbon monoxide, and the third being the solution of blood from the mouse. The last will be stronger than the two former, and must be diluted with water until its colour is the same in *depth* as that of the other two. If carbon monoxide was present, the mouse blood solution will appear pinker than the normal blood. To make the comparison, the two tubes are held up against the sky and changed from side to side in order to eliminate physiological errors in colour-perception. If the mouse blood is pinker, the degree to which it is saturated with carbon monoxide can be roughly estimated by comparing its degree of pinkness with that of the fully saturated blood. The estimate is, of course, only a very rough one.

The accompanying diagram (fig. 25) shows the average extent to which the blood of mice has been found to become saturated with carbon monoxide in air containing different percentages of the gas. The data are taken from the results of experiments made for other purposes, but in which the composition of the air and percentage saturation of the blood

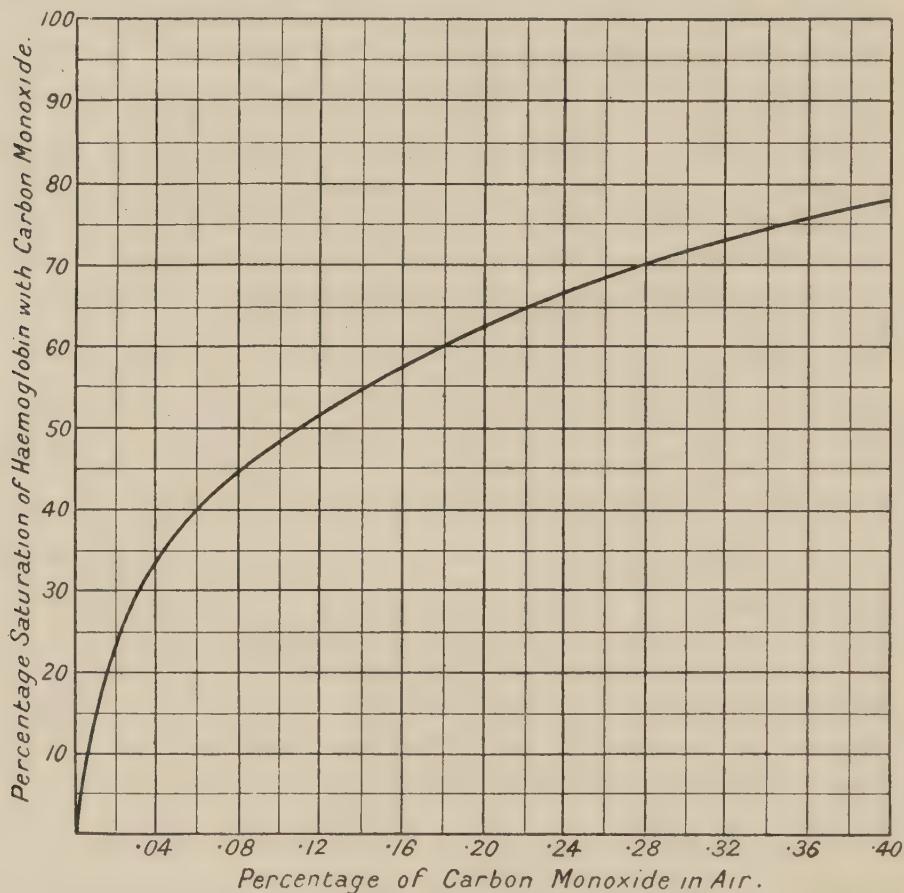


FIG. 25.—Curve showing Average Percentage Saturations of the Blood in Mice with Different Percentages of Carbon Monoxide in the Air.

were accurately determined. The difference in tint can be seen on careful examination when the blood is only 10 per cent. saturated, so that even with as little as 0·007 per cent. this test shows the presence of carbon monoxide.

The blood of a bird is not quite so delicate a test ; and if a bird's blood is used, a drop of ammonia must be added to clear the solution.

**Determination of Carbon Monoxide with Blood Solution.—**

Small percentages of carbon monoxide in air can be determined with considerable accuracy with the help of blood solution, the percentage saturation of the haemoglobin with carbon monoxide being titrated by means of a solution of carmine. In many cases this is the only available method of determining small percentages of carbon monoxide in air ; and in all cases it is a very useful and certain method, particularly as only a small sample of air is needed. The principle of the method is that a few cubic centimetres of normal blood solution are shaken to saturation with the sample of air. A known volume of the normal blood solution is then taken, and standardised carmine added to it from a burette until (1) equality of pinkness with the solution saturated with the air sample is reached, and afterwards (2) until equality with the same blood solution fully saturated with carbon monoxide is reached. From the two results the percentage saturation of the blood solution saturated with the sample of air can be deduced ; and from this the percentage of carbon monoxide can be calculated.

The colorimetric titration is a peculiar one, since quality, and not depth of colour, is being estimated. The carmine has a bluer tint than blood solution saturated with carbon monoxide, and the mixture of the carmine colour with the yellow of normal blood solution reproduces accurately the tint of blood containing carbon monoxide. It must be remembered, however, that the equality of tint is physiological only, since the two solutions are not spectrally identical. The points of identity are not quite the same for different individuals, and are affected by the quality of the light. Nevertheless, the results of the analyses are nearly the same for different individuals, although some persons, on account of defective colour-sense, may get less accurate results than others.

The sample of air is collected in the ordinary way, as described on p. 3, in a bottle holding about 100 c.c. or a little more. The use of vaseline for lubricating the stopper must be avoided, however, since the vaseline is apt to become suspended in the blood solution and render it turbid. The stopper should therefore be lubricated with glycerine. Sufficient ammoniacal blood solution (about 150 c.c.) is prepared to partly fill a small mortar, in which the bottle is inverted and the stopper removed under the blood solution. A curved glass tube of narrow bore is then introduced through the blood solution into the bottle, and sufficient air is allowed to pass out to let about 5 c.c. of the blood solution pass up into the bottle. The stopper is then replaced securely and the bottle removed and wrapped up in a duster to shield it from light. It is then shaken as vigorously as possible for five minutes. It is hardly possible to continue the shaking for more than a minute at a time ; but a rest can be taken for, say, fifteen seconds after each minute of shaking, in which case six minutes in all will be needed until the process is complete.

If the bottle is exposed to bright daylight during the shaking, the saturation will be far too low, and the method as originally described<sup>1</sup> was found to be defective because no precautions were taken to exclude light. The previous addition of ammonia to the blood solution is also essential : otherwise the vigorous shaking will produce a precipitate, particularly if any carbon dioxide is present in the air. With gentle agitation, and no ammonia, the result is the same in the end ; but the gentle agitation has to be continued for half an hour or more, and the insufficiency of the time allowed with gentle agitation was a further source of error in the method as formerly described.

The blood required for making the blood solution is easily

<sup>1</sup> *Journal of Physiology*, vol. xviii, p. 463, and vol. xxii, p. 478.

obtained by pricking a finger with a large needle and squeezing out about 1 c.c. of blood. Unless the finger is warm the blood will not flow readily. By means of a narrow graduated pipette 0·75 c.c. of the blood (before it clots) is measured out into 150 c.c. of distilled water to which about 30 drops of strong ammonia solution have been added. The solution is well mixed, and is now ready for use. It will be found that this strength of solution, when looked at in an ordinary test-tube, shows very satisfactorily the contrast in tint between normal blood and blood containing carbon monoxide.

For the titrations two test-tubes of equal bore (about 0·6 inch) are selected and marked as No. 1 and No. 2, the carmine being always added to No. 1 in the titrations. The carmine solution is prepared as follows. A comparatively strong stock carmine solution is first made by dissolving about half a gramme of carmine in strong ammonia and diluting to about 100 c.c. with distilled water. This solution should be preserved in a cool and dark place. The standard carmine solution is prepared fresh by adding a few drops of the stock solution to 100 c.c. of distilled water in a measuring cylinder of about the same diameter as the cylinder containing the blood solution ; and sufficient of the stock carmine is added to make the depth of colour of the diluted carmine solution slightly greater than the depth of colour of the blood solution. A 20 c.c. burette is then filled with the diluted carmine, and another similar burette with distilled water.

The next step is to measure out 5 c.c. of blood solution into test-tube No. 1 with a pipette, and also pour about the same quantity into test-tube No. 2 and saturate it with coal-gas in the manner already described. Carmine is now added from the burette to test-tube No. 1 until its tint is about equal to that of No. 2. The depth of colour in No. 1 will,

however, be too great, as the carmine was purposely made of a rather deeper tint than the blood solution. Distilled water is therefore added till the depths are the same, and more carmine if necessary, until complete equality of tint and depth are attained. In making the comparisons the test-tubes should be held up against the sky, and it is absolutely essential to transpose them from one side to another at each observation. It will nearly always be found that the right-hand tube looks slightly pinker or yellower, or slightly deeper or less deep in tint, than the left-hand tube. This is in reality of great assistance in determining the exact point of equality.

When the point of equality is reached, the volumes of carmine solution and water added are read off on the two burettes. Distilled water is now added to the carmine in the cylinder in the same proportion as it had to be added to the carmine in test-tube No. 1. Let us suppose, for instance, that 6·0 c.c. of carmine and 1·2 c.c. of water had to be added to test-tube No. 1. The carmine in the cylinder would then have to be diluted in the proportion of 6·0 to  $6\cdot0 + 1\cdot2$ , or 5 to 6; and if 80 c.c. of carmine solution were left in the cylinder, 16 c.c. of water would have to be added. The carmine solution is now ready for use, and the burette is filled with it.

To determine the percentage saturation of the hæmoglobin in the solution which has been shaken in the bottle, this solution is poured out into test-tube No. 2 (after both test-tubes have been thoroughly washed out and as much adherent water as possible shaken out of them), and 5 c.c. measured from the pipette into No. 1. Carmine is now added from the burette until the two tubes appear equal in tint. If the saturation is low, not more than 0·1 c.c. is added at a time when the point of equality is near, and in observing the tint the test-tubes are frequently transposed,

the addition of carmine being continued until the tints again become unequal. It will probably be found that two readings of the burette give sensible equality of tint, and the mean of the two readings is taken as the correct one. If the saturation is over about 30 per cent., 0·2 c.c. is added at a time. The solution in No. 2 is now saturated with coal-gas, and a second determination made of the quantity of carmine required to produce equality. In this titration about 0·4 c.c. of carmine may be added at a time, since the higher the saturation the less effect has the carmine in altering the tint.

The following example will illustrate the method of calculating the result :—

*Determination of First Point of Equality.*

$$\left. \begin{array}{l} 1\cdot0 \text{ c.c. right} \\ 1\cdot1 \text{ , , } \end{array} \right\} \text{Mean, } 1\cdot05.$$

*Determination of Second Point of Equality.*

$$\left. \begin{array}{l} 6\cdot8 \text{ c.c. right} \\ 7\cdot2 \text{ , , } \end{array} \right\} \text{Mean, } 7\cdot0.$$

Thus, to produce the tint of complete saturation 7·0 c.c. of carmine had to be present in  $7 + 5 = 12$  c.c. of the mixture ; while to produce the tint of the solution from the bottle 1·05 c.c. of carmine had to be present in  $1\cdot05 + 5 = 6\cdot05$  c.c. of the mixture. The percentage saturation  $x$  is therefore given by the proportion sum

$$\frac{7}{12} : \frac{1\cdot05}{6\cdot05} :: 100 : x.$$

Hence  $x = 29\cdot8$ .

Test experiments with solutions made by diluting known mixtures of normal and fully saturated blood have shown that the results of the titrations can, with a little previous experience, be relied on to within 2 per cent. of the correct result. In the above example, for instance, the correct

percentage saturation might be either 2 per cent. higher or lower.

It is unfortunate that neither the blood solution nor the carmine will keep. It is therefore necessary to prepare them fresh every day. The titrations must also be performed in daylight. In ordinary artificial light the difference in tint between the normal and the saturated blood solution is almost invisible. In working with blood solution the vessels used must be perfectly clean : otherwise the blood solution may begin to decompose within three or four hours, and will no longer give the full pink tint when it is saturated with carbon monoxide.

To calculate the percentage of carbon monoxide in the air from the percentage saturation of the blood solution with carbon monoxide, advantage is taken of the fact that the percentage saturation is proportional to the relative percentages of carbon monoxide and oxygen present, according to the law already explained. As the percentage of oxygen in ordinary air is practically constant, the calculation becomes a very simple one, for the curve representing graphically the relation between percentage of carbon monoxide and percentage saturation is evidently a simple rectangular hyperbola ; and the percentage of carbon monoxide in the air can be read off at once from this curve.<sup>1</sup> The actual curve for human blood solution at the ordinary room temperature of about 60° F. (15.5° C.) is shown in fig. 26. It will be seen that the blood becomes half saturated in presence of 0.055 per cent. of carbon monoxide, a third saturated with 0.027 per cent., a fourth saturated with

<sup>1</sup> If the percentage of oxygen in the air is considerably below normal, the percentage of carbon monoxide as read off from the curve must be correspondingly diminished. Thus, if there were only 10 per cent. of oxygen in the air in the bottle, the percentage of carbon monoxide would have to be multiplied by  $\frac{1}{2}\frac{1}{1}$ . In other words, the test would be doubled in delicacy, though longer shaking would probably be needed.

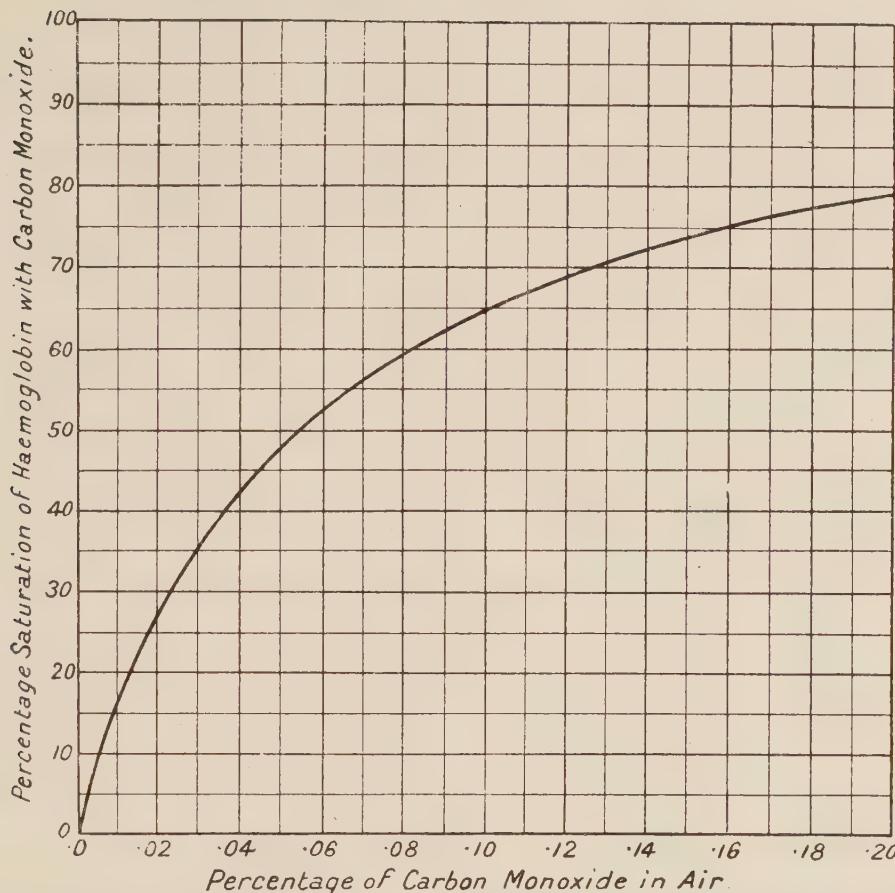


FIG. 26.—Curve showing Percentage Saturations of Human Blood Solution with Different Percentages of Carbon Monoxide in the Air.

0.018 per cent., etc. The percentage of carbon monoxide may also be calculated from the formula

$$P = \frac{S \times 0.055}{100 - S}.$$

P = percentage of carbon monoxide.

S = percentage saturation of the haemoglobin.

The following are examples of determinations made with known mixtures of pure carbon monoxide and air.

Percentage Saturation of Hæmoglobin.	Percentage of Carbon Monoxide in Air.	
	Calculated from Saturation.	Actually present.
50.3	0.056	0.052
48.0	0.051	0.052
30.0	0.024	0.026
19.8	0.014	0.013

This method of determination is only suitable for air con-

taining less than about 0·2 per cent. of carbon monoxide. It may, however, be desirable to use it for higher percentages, in which case the sample must be diluted to a suitable extent with air. The bottle used for the saturation may be partly filled with water and inverted in a basin of water. A suitable volume of the sample is then measured off in a very small measuring cylinder and introduced under the water into the bottle, which is then allowed to fill up with air, transferred to a small basin of the blood solution, and the rest of the process carried out in the manner already described. To calculate the dilution, the capacity of the bottle must, of course, be known. The blood solution in the bottle will, of course, be diluted a little by water which adhered to the inside of the bottle ; but this does not affect the titration. It is only necessary to tilt the test-tube No. 1 a little in order to make the depth of tint in the contained solution appear equal to that in No. 2 test-tube.

For detecting carbon monoxide this reaction is about five times as delicate as the older spectroscopic test.

The only other gas which will give the colour reaction with blood solution is nitric oxide which forms NO-hæmoglobin. It is, however, practically impossible for nitric oxide to be inhaled as such, since in presence of any oxygen it will be immediately converted to nitrogen dioxide,  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$  (see p. 146). The latter on being inhaled is converted to nitrates and nitrites. The former have no harmful effect but the latter produce the same action as when sodium nitrite is swallowed. The nitrite first produces methæmoglobin and after death NO-hæmoglobin which imparts a cherry red colour to the blood very similar to that produced by the formation of carboxy-hæmoglobin in carbon monoxide poisoning. There seems little doubt that the pathogenic organism responsible for certain types of pneumonia is sometimes accompanied by a nitrifying organism which is capable

of producing nitrite, and consequently NO-hæmoglobin. This gives many of the distinctive reactions shown by carboxy-hæmoglobin but may be distinguished very readily from the latter by boiling dilute solution of the blood. The NO-hæmoglobin gives a pink coagulum whereas that left on boiling a solution of blood saturated with carbon monoxide is a dull grey<sup>1</sup> as with ordinary blood.

### The Hartridge Reversion Spectroscope

The sensitivity of the spectroscopic method for estimating the percentage saturation of blood by carbon monoxide is immensely increased if the instrument designed by Hartridge is used.<sup>2</sup> The absorption spectrum given by a solution of carboxy-hæmoglobin is very similar to that of oxy-hæmoglobin, a distinctive band being shown in each case in the yellow; but the mean position of this band for carboxy-hæmoglobin is distinctly nearer the violet end of the spectrum, and consequently when carboxy-hæmoglobin replaces oxy-hæmoglobin a shifting of the band takes place in that direction. In the Hartridge spectroscope the movement of this band is measured and the accuracy of measurement doubled by the formation of a second but reversed spectrum, which can be moved by means of a micrometer screw until the respective bands in each spectrum are brought into the same vertical line. The position of the bands may be different for different observers and at different times, so the zero position must be determined for each test. Under favourable circumstances the measurements are correct to one Ångström unit, and as complete saturation of a blood solution with carbon monoxide gives a movement of 50 Å units, the accuracy of the instrument is about 2 per cent.

<sup>1</sup> "The Presence Post-mortem of Nitric Oxide-Hæmoglobin," H. A. L. Banham, J. S. Haldane and Thos. Savage, *Br. Med. Journ.*, 1925, Aug. 1, pp. 187-9.

<sup>2</sup> The instrument is made by W. H. Grayling, Instrument Maker, Cambridge.

## CHAPTER XI

### THE ACCURATE ESTIMATION OF VERY SMALL QUANTITIES OF CARBON MONOXIDE

THE estimation of carbon monoxide when in sufficient concentration to be of physiological importance has been described in the previous chapter. Either the blood test or the iodine pentoxide modification of the gas analysis apparatus may give results to 0·02 per cent. It is, however, frequently desirable to make an accurate determination of carbon monoxide when present in concentration much lower than 0·02 per cent. and this is particularly so in the case of the analysis of mine air. In order to obtain more exact information regarding the production of carbon monoxide in coal mines one of us designed, in 1918, a portable apparatus for the determination of the gas in quantity varying from about 0·0005 per cent. to 0·2 per cent. by volume. Iodine pentoxide is employed as the reagent for the determination of the carbon monoxide, but instead of the measurement being made by absorption of  $\text{CO}_2$ , the iodine produced in the reaction  $\text{I}_2\text{O}_5 + 5\text{CO} = 5\text{CO}_2 + \text{I}_2$  is absorbed in 10 per cent. potassium iodide solution and subsequently titrated with N/500 sodium thiosulphate solution. With starch as indicator this titration is extremely sensitive, the iodine produced by as little as 0·0005 c.c. of carbon monoxide being easily detected. The most satisfactory temperature range found for the  $\text{I}_2\text{O}_5$  reaction was 90° to 130° C. In the portable apparatus now to be described the pentoxide is kept within this temperature range by immersion in hot oil contained in

a thermos flask. The oil, which should be of high boiling- and flash-point, such as transformer oil, is heated to a temperature of 135° C. or thereabouts prior to use, and to facilitate the heating the glass tube containing the iodine pentoxide is covered with a couple of layers of asbestos paper around which is wound nichrome wire of such a length as to permit the passage of a current of approximately 1 ampère when connected directly to a 220-volt mains supply. The oil in the thermos flask may in this way be heated to a temperature of 135° C. in about 5 minutes, after which the apparatus is ready for a preliminary test with fresh air to ensure that no coloration is given by starch to the iodide solution in the absence of carbon monoxide. With a good thermos flask the temperature of the oil should not fall below 90° C. within 6 hours. Ample time is thus allowed for a considerable number of analyses.

The apparatus consists essentially of the following, contained in a portable wooden case with hinged front, side and top (fig. 27). (A) Gas-sampling vessel, capacity 200 c.c. (or other known volume<sup>1</sup>), fitted with a three-way stop-cock (*a*). (B) Reservoir connected to (A), containing slightly more than 200 c.c. of water, or glycerine and water, by means of which the sample is taken into (A) and passed through the apparatus during the subsequent analytical process. The reservoir is fixed and the passage of the gas sample brought about by blowing through the india-rubber tube fitted with a pinch-clip. Alternatively, a blowing bulb may be connected to (B) through a three-way stop-cock. (C) Set of absorption tubes for purifying and drying the gas sample; the first contains a strong solution of bromine in potassium bromide,

<sup>1</sup> A burette having the upper portion graduated in cubic centimetres up to 50 c.c. and enlarged below to give a total of 200 c.c. is useful when samples containing a high percentage of CO have to be tested but first diluted with CO-free air before estimation.

the second saturated caustic soda solution, and the third solid caustic soda or askerite or similar alkaline absorbent for  $\text{CO}_2$  and other acid gases, a little charcoal, and finally phosphorus pentoxide. In more recent apparatus a specially designed U-tube is employed, the two 4-inch limbs being

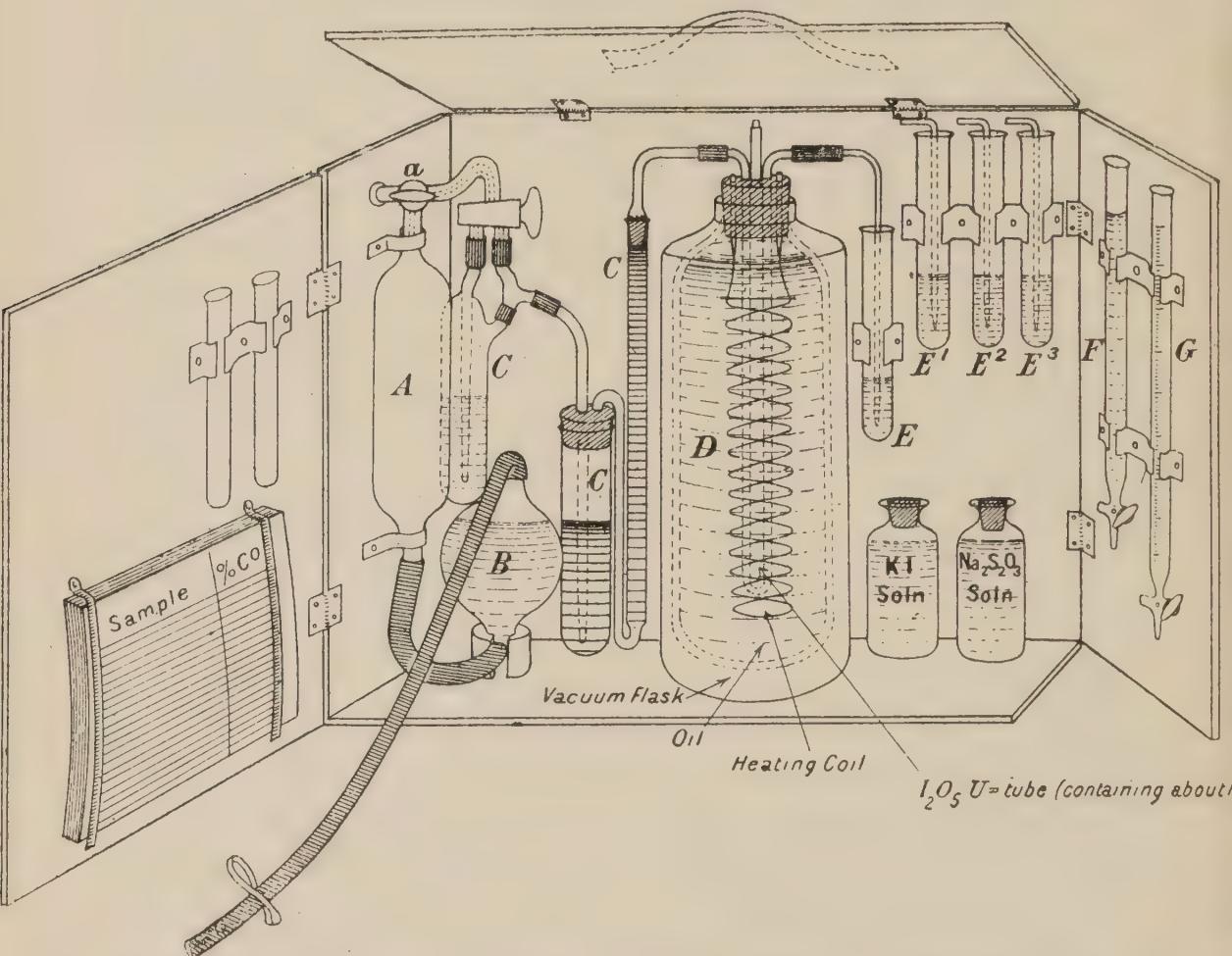


FIG. 27.—Portable Apparatus for Determining Small Amounts of Carbon Monoxide.

connected by 2 inches of 5 mm. bore tubing in which is placed 0.5 gramme of respirator charcoal. The bromine vessel is fitted with a small tap which can be closed when the apparatus is standing so that practically no bromine vapour will diffuse through into the strong caustic soda solution. Since mine air contains practically no trace of unsaturated hydrocarbons under ordinary conditions, it has been found

useful to have a second three-way tap so that the gases can be passed either directly through the caustic soda solution, if unsaturated compounds (which interfere with the action of iodine pentoxide on carbon monoxide) are known to be absent, or, if the contrary is the case, bubbled by turning the tap the other way in a fine stream through the bromine solution, and then passed on through the concentrated soda solution. (D) A vacuum flask, containing oil and fitted with a bung holding the U-tube containing about 10 grammes of iodine pentoxide, a thermometer, and two narrow tubes containing a small quantity of mercury into the bottom of which are sealed copper leads connected to the heater. The latter is made of nichrome or other high-resistance wire. It has a resistance of approximately 220 ohms when required for use where the electric supply is 220 volts. In order to raise the oil to the necessary temperature two leads from the mains are placed in the mercury cups and the current passed until the requisite temperature is attained. (E) Right-angled delivery tube connected at one end by an india-rubber connection to the iodine pentoxide tube, the other end being so drawn out and dipping into approximately 2 c.c. of potassium iodide solution in a test-tube that the gas passing through the apparatus comes out of E in a series of very small bubbles. Complete absorption of the iodine is thus ensured. (E<sup>1</sup>), (E<sup>2</sup>), etc., are spare test-tubes containing 10 per cent. potassium (or sodium) iodide solution. (F) Ungraduated burette containing starch solution (approximately 1 per cent.). (G) 5- or 10-c.c. burette graduated to 0·1 c.c. and containing N/500 sodium thiosulphate solution.

The 1-c.c. burette shown in fig. 28 was designed by one of us for more accurate work and should be employed where it is desired to titrate to within 0·02 c.c. of thiosulphate. The burette is graduated to 0·01 c.c. and by estimation the level

of the thiosulphate may be read to nearly 0·002 c.c. It

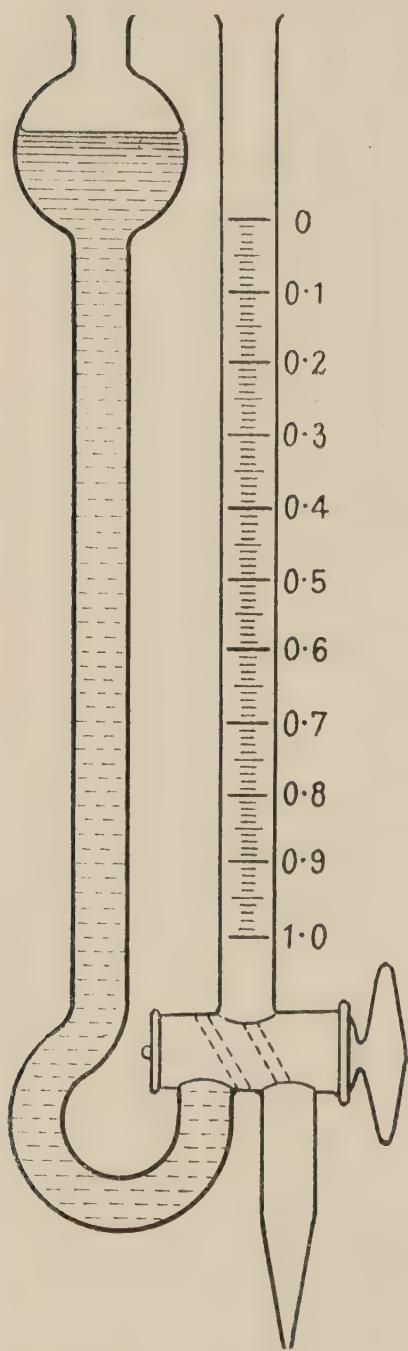


FIG. 28.—Special Burette for use in the Estimation of Small Quantities of Carbon Monoxide.

will be seen from the illustration that the usual single-way stop-cock has been replaced by a three-way stop-cock, one branch of which is bent round to connect with a 25-c.c. reservoir. The latter is sufficiently above the zero graduation mark on the burette to enable the burette to be filled rapidly by gravity. The burette nozzle is drawn out to a fine point so that the end-point in the titration can be determined very exactly.

To carry out an analysis, the tap (*a*) (fig. 27) is turned to the outside atmosphere, and by opening the pinch-clip and blowing through the tubing connected to (B), (A) is filled to the tap with water from (B). The pressure in (B) is then released and the water allowed to flow back from (A) to (B) until the 200-c.c. mark is reached [the quantity of water in (A) and (B) is just such that the levels are approximately the same at the 200-c.c. mark]. The final adjustment of the level of the liquid in (A) to the graduation mark may be effected either by blowing or sucking through the

rubber tube connected to (B). This is done with the stop-cock still open to the atmosphere under test.

The tap is then turned to connect to the purifiers (C) and the sample forced rapidly through the apparatus, the tube (E) not yet being connected. This preliminary "washing out" process fills the purifying tubes, etc., with the sample to be analysed. A second 200-c.c. sample is then taken in as before, the tube E (dipping into the potassium iodide solution in the test-tube) is connected to the iodine pentoxide tube and the sample then passed through the apparatus at such a speed as to complete the passage in approximately three minutes. The tap (*a*) is then turned to the horizontal position, thus shutting off (A) from both air and purifier.

(E) is then disconnected and the test-tube containing the potassium iodide solution removed from the spring-clip ; a little of the solution is drawn up into (E) by suction in order to rinse out the inside of this tube, and a few drops of starch solution are added to the test-tube, the characteristic bluish-violet colour of starch-iodide being produced if any appreciable quantity of carbon monoxide was present in the sample. Standard thiosulphate solution is then added drop by drop, and the mixture well shaken, until the blue coloration completely disappears.

When more than 0·3 per cent. of carbon monoxide is present in the sample under investigation a portion of the iodine liberated may condense in the upper part of the iodine pentoxide tube or in the delivery tube (E). To obtain accurate results in such a case, 100 c.c. of the sample may be passed through the apparatus and the iodine liberated absorbed (without the preliminary "washing out" of the purifiers, etc.), followed by the passage of 200 c.c. of fresh air, or air of small known carbon monoxide content. Any condensed iodine will then be volatilised completely and carried through into the potassium iodide absorption tube. The amount of carbon monoxide present in the air used for "washing out" the sample is then deducted from the actual

amount found. The accuracy of any determination can be increased by passing several lots of sample through the apparatus without changing the tube (E) or the potassium iodide solution.

Before commencing any series of tests, i.e. just after heating the contents of the vacuum flask to 140° C., it is advisable to do a blank test on two 200-c.c. lots of fresh air. The potassium iodide solution should give no appreciable colour on the addition of a couple of drops of starch solution.

A number of spare test-tubes with delivery tubes are fitted by means of spring-clips into the case. The same solution and tube can, however, be used over and over again provided decolorisation has been very carefully effected each time.

The complete apparatus in case weighs about nine pounds.

The following results give an idea of the accuracy obtainable with careful working of the apparatus and indicate the effect of temperature of the reagent upon the accuracy.

#### *Analysis of Mixtures of Carbon Monoxide and Air.*

Volume of Sample.	Temp. of I <sub>2</sub> O <sub>5</sub> .	Time of Passage of Sample.	Per cent. CO by Titration.	Actual Quantity CO present.
(1) 200 c.c.	83	2½	0·056	0·061
(2) "	84	5	0·058	0·061
(3) "	115	8	0·061	0·061
(4) "	120	3	0·060	0·061
(5) "	136	4½	0·061	0·061
(6) "	137	4½	0·060	0·061
(7) "	161	5	0·066	0·061
(8) "	165	8	0·070	0·061
(9) "	170	4	0·067	0·061

Similar agreement with theoretical values has been obtained with other mixtures containing a lower concentration of carbon monoxide. The apparatus has been employed

very successfully underground, and even under such conditions the estimation may be carried out speedily and with no difficulty due to artificial light.

Instead of using N/500 thiosulphate, 1 c.c. of which corresponds to 0·112 c.c. CO measured at 0° C. and 760 mm., the thiosulphate solution may be standardised so that 1 c.c. is equivalent to 0·1 c.c. of CO measured at 15° C. or any other temperature. Any variation in temperature can then be allowed for—for example, if the thiosulphate solution is standardised for use at 15° C. and the apparatus is being employed in an atmosphere at 20° C., the correction to be added to the titration result will equal 1·5 per cent. Correction should also be made for pressure when this differs considerably from normal.

#### **Apparatus for Use in "Naked-Light" Pits or Other Places**

This is essentially the same as that described for safety-lamp pits, with the exception that the iodine pentoxide tube is heated in a hot-air bath produced by passing a current of approximately 2 ampères from a 2-volt accumulator cell through a coil of wire surrounding the iodine pentoxide U-tube, the whole being contained in a vacuum flask as before. In this way an air bath remaining more or less constant at 110° C. can be obtained. The 2-volt accumulator should last for about six hours under these conditions. The air bath and iodine pentoxide tube take one-half to three-quarters of an hour to attain the requisite temperature (approx. 100°–110° C.) from the time of first switching on the current. By using two 2-volt cells, and with suitable switch connections, the time taken to heat the iodine pentoxide tube in the first instance may be considerably reduced by connecting the cells in series until the requisite temperature is reached, and then switching over to put them in parallel. Under these conditions the

apparatus will remain for a much longer period at the necessary temperature. A small electric bulb, with short pieces of flexible connection, can be fixed to the case and used to illuminate the apparatus.

If the apparatus is required for use in places where the temperature approximates to the freezing-point of water, certain modifications are necessary owing to the very slight volatility of iodine vapour at low temperatures. For example, at 0° C. a sample containing more than 0·02 per cent. of carbon monoxide would deposit crystals of iodine after leaving the iodine pentoxide tube and becoming cooled to the atmospheric temperature. To overcome this difficulty the iodine vapour may be prevented from condensing before reaching the potassium iodide absorption tube by continuing the heating wire round the exit end of the pentoxide tube and as near as possible to the connection to (E). This portion of the pentoxide tube is then covered with asbestos paper in order to retain a maximum quantity of heat. It is advisable to have the bung, fitting the vacuum flask, made of asbestos.

It is important that the N/500 thiosulphate solution should not be kept for more than 24 hours, since after this period appreciable decomposition will have set in. On the other hand, the N/10 solution is relatively stable and may therefore be used as a stock solution, from which the N/500 solution can be made by diluting 1 c.c. (accurately measured from a pipette or a burette similar to that shown in fig. 28) to 50 c.c. with distilled water in a graduated flask kept specially for the purpose.

In the earlier tubes used by Graham and his colleagues between 7 and 10 grammes of iodine pentoxide were employed and the air under examination could be passed through at a rate of about 100 c.c. per minute. More recently, tubes containing about 4 grammes have been

employed, and even with these the flow may be nearly as great without introducing any error.

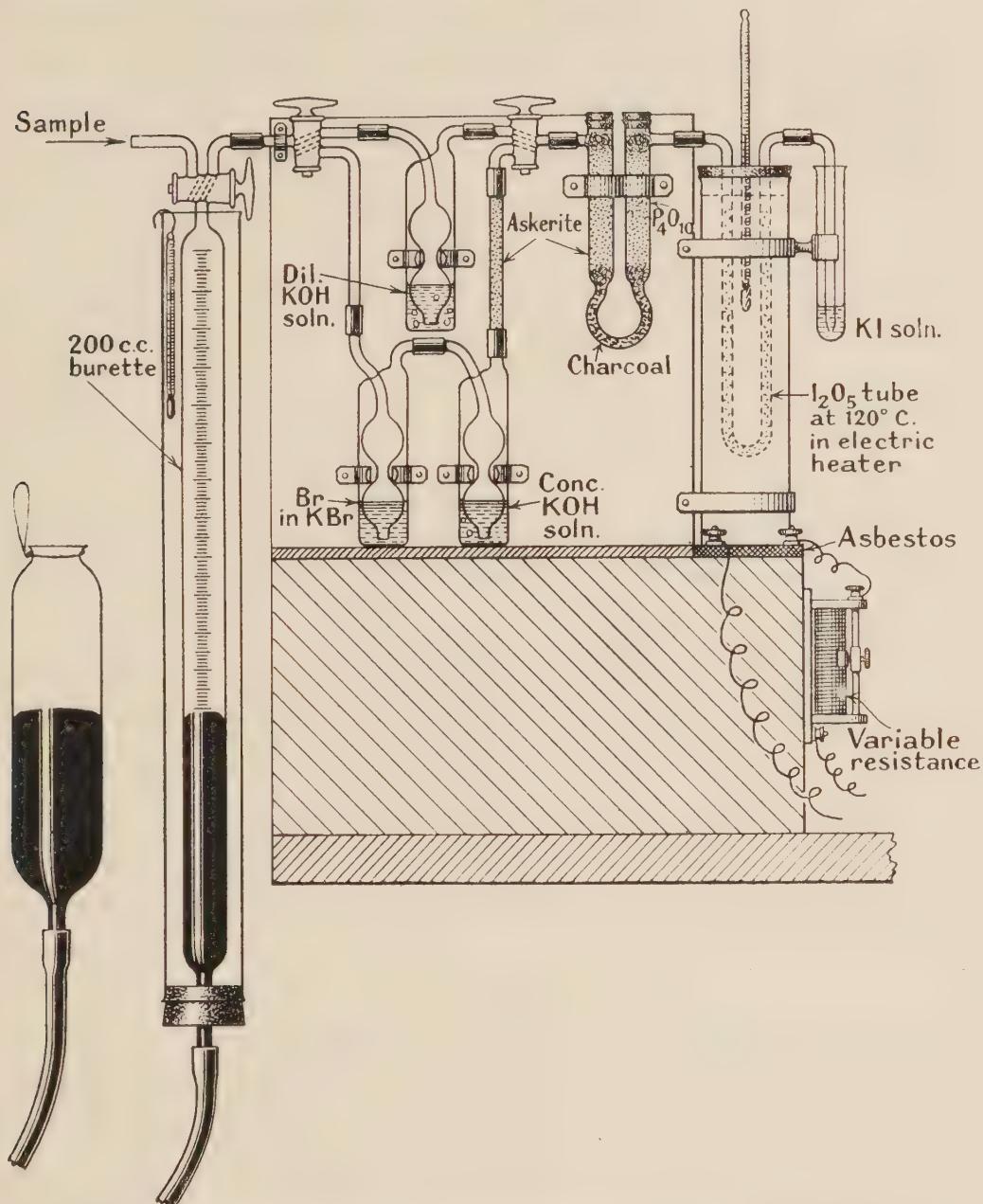


FIG. 29.—Laboratory Apparatus for the Determination of Small Quantities of Carbon Monoxide.

The laboratory form of apparatus is shown in fig. 29. The thermos flask is replaced by an electrically-heated air bath the heater of which may be made by winding the requisite amount of nichrome wire upon a short length of steel tubing

covered with asbestos paper, the whole subsequently being well lagged with asbestos paper and millboard. A long 200-c.c. burette graduated to 1 c.c. is surrounded by a water-jacket, the temperature of which is read whenever the sample of gas under test is taken into the burette. Mixtures containing high concentrations of carbon monoxide can be diluted with CO-free air in known proportion in the burette before passing through the apparatus.

Where it is necessary to pass the air under test through the bromine solution care should be taken that the concentrated potash (40 per cent.) in the subsequent absorption bulb has not become strongly yellow, otherwise traces of some bromine compound (probably HOBr) may be carried through the subsequent purifying train. The introduction of the small quantity of charcoal between the soda-lime and the phosphorus pentoxide prevents any error which would otherwise result from the interaction of this bromine compound with the iodine pentoxide, but it is nevertheless wise to replace the concentrated potash solution as soon as it becomes slightly yellow. The charcoal also serves the purpose of removing traces of any higher hydrocarbons such as pentane, the vapour of which is appreciably attacked by iodine pentoxide.

The iodine pentoxide method has got into a certain amount of disrepute, probably owing to the employment of material sold as  $I_2O_5$ , but which is not so actually. It has been found<sup>1</sup> that the composition of the material labelled iodine pentoxide, obtained from various sources, may vary greatly, sometimes approximating to that of iodic acid, whilst on the other hand specimens of iodic acid have been found to

<sup>1</sup> "The Use of Dehydrated Iodic Acid in the Estimation of Carbon Monoxide," J. Ivon Graham and F. Lawrence, *Chemistry and Industry*, 1925, p. 165.

differ in iodine content, including even the material sold as A.R., owing, no doubt, to partial dehydration. The manner of preparation of iodine pentoxide to be used for the estimation of carbon monoxide is very important, the most satisfactory method being that of Stas as described and modified by Nicloux.<sup>1</sup> This consists in adding iodine in small quantities at a time to pure fuming nitric acid in a flask immersed in a water-bath at about 73° C. Copious evolution of red nitrous fumes takes place and the iodic acid finally separates out as a white granular powder. Most of the nitric acid is driven off by heating to 180° C. The iodic acid is then dissolved in a small quantity of distilled water, the solution filtered and evaporated to dryness. The residue is then broken up, placed in the U-tube and heated at a temperature of 200–210° C. in a current of dry air for several hours. On testing with 1 litre of air the coloration given with the starch potassium iodide solution should not require more than 0·02 c.c. N/500 sodium thiosulphate for complete decolorisation. The iodine pentoxide prepared in this way has been found to retain its activity for years if the tube is kept sealed and absorption of moisture prevented. Nevertheless it is advisable to check the accuracy fairly frequently by means of a standard quantity of pure carbon monoxide or with a monoxide-air mixture of known composition. A convenient method of testing is to have a small length (about 7 cm.) of 2-mm. bore capillary tubing fitted with two three-way (parallel type) stop-cocks so that it can be filled readily with pure carbon monoxide from a generator in which the gas is made by adding, from a dropping funnel, concentrated solution of formic acid to concentrated sulphuric acid heated to 100° C. The gas should be evolved dry and may be passed directly to the monoxide testing tube which is connected horizontally, and the taps turned, so that

<sup>1</sup> *Compt. Rend.*, vol. 154, part 1, pp. 1166–8.

the gas flows through the upper branches of the stop-cocks. Sufficient monoxide is passed through to secure complete replacement of all air previously contained in the tube. As the outlet is to air the gas in the tube is at atmospheric pressure. When the tube is filled the taps are turned off and the atmospheric temperature and pressure noted. The tube is then connected by one of the lower tubes to the carbon monoxide apparatus the burette of which has previously been filled from the reservoir with mercury or salt solution as the case may be, the reservoir lowered and burette tap opened. The testing tube taps are then turned so that all the monoxide may be sucked into the burette through the lower branches of the stop-cocks and complete washing out of the gas contained between the two taps ensured by the passage of air into the burette. The length of capillary tube (volume approximately 0·2 c.c.) should be accurately calibrated by filling with mercury and weighing the latter. The monoxide-air mixture in the burette is then passed through the apparatus and the residual monoxide in the purifying train of the latter washed out with 200 c.c. of fresh air in the usual manner. The titration of the carbon monoxide should correspond to at least 99 per cent. of the theoretical. Unless sufficient time is allowed for the removal of all air originally in the generator, a low result may be obtained.

To facilitate the rapid testing of the portable apparatus sodium formate tablets may be used, each of which will yield sufficient carbon monoxide to be equivalent to 1·0 c.c. of standard sodium thiosulphate solution. One of these is dropped into a small vessel containing concentrated sulphuric acid and fitted with a bung through which pass inlet and outlet tubes, the former dipping beneath the acid. The outlet tube is connected directly to the burette previously filled with its usual containing liquid. Immediately the sodium formate pellet is added and the bung placed in the

small generator, the tap of the burette is turned so that air plus evolved monoxide is drawn into the burette.

Since pure carbon monoxide may now be obtained in the compressed condition, a small cylinder of the gas and a testing-tube of known volume as just described are undoubtedly the most convenient means of checking the accuracy of the iodine pentoxide apparatus.

## CHAPTER XII

### THE APPLICATION OF GAS ANALYSIS TO THE DETECTION OF SPONTANEOUS COMBUSTION IN COAL MINES

SPONTANEOUS heating and fires in coal mines have caused the loss of many lives and been of very great expense and anxiety to numerous collieries. The usual method of detection of a heating has been by noting a change of smell of the return air coming from the affected area. The unusual odour is known as "gob-stink" and is due partly to products of oxidation of coal at a relatively high temperature and in part to distillation with production of hydrocarbons such as pentane and higher homologues of the saturated or paraffin series of hydrocarbons along with a certain amount of unsaturated hydrocarbons. The term "fire-stink" is usually applied when the odour resembles that of a burning fire and includes tar products and benzene. It has been well recognised for many years that in dealing with underground fires there is great danger of poisoning from carbon monoxide and that during the high temperature oxidation of coal this gas is produced in relatively large quantity. The production of carbon monoxide during the oxidation of coal at ordinary temperatures was first shown by Haldane<sup>1</sup> in 1898, but reliable information concerning the extent of its formation in underground workings was difficult to obtain until a method, more sensitive than those usually employed, was available. Investigations in the Doncaster Coal Owners'

<sup>1</sup> Haldane, *Trans. Inst. Min. Eng.*, vol. xvi, 1898-9.

Laboratory<sup>1</sup> and later in the Mining Research Laboratory, Birmingham University, have shown that the production of the oxides of carbon relative to oxygen absorption increases in a marked manner with rise of temperature. Underground investigations<sup>2</sup> have further shown that an analysis of the vitiated air will frequently indicate heating of coal some time before this can be detected by the smell of any product of destructive distillation. Black-damp has already (p. 58) been described as the gaseous mixture found underground which will extinguish a lamp without causing an explosion and which will not cause asphyxiation when mixed with sufficient air to allow a candle to burn. It is the residual gaseous mixture found after absorption of oxygen from the air through oxidation of coal, timber or mineral matter such as pyrites. In a well-ventilated pit the vitiation by the breathing of men or animals and by the burning of lamps is negligible.

When formed by the oxidation of dry coal underground black-damp will usually have the composition—

Nitrogen . . . . .	94·8
Carbon dioxide . . . . .	5·0
Carbon monoxide (about) . . . . .	0·15

When the black-damp results from the oxidation of old dry coal-dust, the monoxide content may rise to 0·5 per cent.

<sup>1</sup> "The Absorption of Oxygen by Coal," T. F. Winmill and J. Ivon Graham, *Trans. Inst. Min. Eng.*, vol. xlvi, 559–91; xlviii, 503–49; xlix, 35–43; li, 494–547.

<sup>2</sup> "The Normal Production of Carbon Monoxide in Coal Mines," J. Ivon Graham, *ibid.*, lx, 222–34.

"The Gaseous Products Resulting from Fires and Underground Heatings," J. Ivon Graham, *ibid.*, lxxix, 92–111.

"The Application of Gas Analysis to the Detection of Gob Fires," J. T. Storrow and J. Ivon Graham, *ibid.*, lxviii, 408–29.

Also Graham and Jones, *ibid.*, lxix, 413–27; lxxii, 334–48; Morgan, *ibid.*, lxxi, 1–29; lxxv, 346–55; lxxviii, 181–99.

And other papers.

The quantity of carbon monoxide in the black-damp formed by the oxidation of coal depends partly upon the chemical nature of the coal and partly upon whether the coal is wet or dry. Moreover, it has been shown recently by Haldane and Makgill<sup>1</sup> that in the presence of thoroughly wet coal the carbon monoxide becomes oxidised, so that black-damp formed as a result of the oxidation of wet coal will contain no carbon monoxide. The following is a typical analysis of a return air sample taken in a Yorkshire pit working the readily oxidisable Barnsley seam, the workings being deep.

	Per cent.		Per cent.		Composition of	
$\text{CO}_2$	0.15	$\text{CO}_2$	0.03	$\text{O}_2$	Air	Black-damp.
$\text{CH}_4$	1.31	$\text{O}_2$	20.18	$\text{N}_2$		
$\text{O}_2$	20.18	$\text{N}_2$	76.20	$\text{CH}_4$	Black-damp	Per cent.
$\text{N}_2$	78.36	$\text{N}_2$	2.16	$\text{CO}$		
$\text{CO}$	0.0041	$\text{CO}$	0.0041	$\text{CO}_2$	0.12	94.6

Alternatively the oxides of carbon may be expressed as percentages of the oxygen that has disappeared giving figures which are 100 times the respiratory quotients of the oxidation processes taking place underground. In order to obtain the real oxygen absorption the assumption is made that nitrogen is not evolved from the coal to an appreciable extent, and that found is simply the nitrogen present in the air descending the pit. This assumption is based upon analytical evidence obtained from samples taken from many boreholes in different coal seams. The oxygen corresponding to the nitrogen percentage found by analysis is calculated from the relation in which these two gases occur in fresh air. Thus taking the analysis just quoted, 78.36 parts of nitrogen were originally mixed with 20.75 parts of oxygen by volume. The oxygen absorbed therefore equals 20.75

<sup>1</sup> "The Formation of Blackdamp and of Carbon Monoxide from Coal at Ordinary Temperatures," *Trans. Inst. Min. Eng.*, lxxxv, 172-85.

less 20·18 parts or 0·57 part. The carbon dioxide formed equals  $0\cdot15 - 0\cdot03$  (the amount present in fresh air) = 0·12 part, and the carbon dioxide production is therefore  $0\cdot12 \times 100/0\cdot57$  or 21 per cent. of the oxygen absorbed. Similarly the carbon monoxide produced is 0·0041 part for an oxygen absorption of 0·57 part or  $0\cdot0041 \times 100/0\cdot57 = 0\cdot72$  per cent. of the oxygen absorbed. To facilitate these calculations the oxygen corresponding to all nitrogen percentages between 0 and 100 in increments of 0·1 per cent. is given in the tables on pp. 170–74.

The following figures, which are the results of tests carried out on a readily oxidisable coal from the Barnsley seam, South Yorkshire, will give some idea of the influence of temperature upon the absorption of oxygen and the production of the oxides of carbon. At 30° C. (a common pit temperature) the oxygen absorption in 96 hours was approximately 500 c.c. per 100 grammes, the carbon dioxide production after 12 hours being about 2·5 per cent. and the carbon monoxide production 0·5 per cent. At 50° C. the absorption in 96 hours was about 900 c.c. and the carbon dioxide and carbon monoxide productions about 3 and 1·0 per cent. respectively after 12 hours. At 100° C. the absorption was increased considerably, being 4,500 c.c. for 96 hours, while the carbon dioxide production after 12 hours had jumped up to 8 per cent. and the carbon monoxide production to 2 per cent. of the oxygen absorbed. Another 20° C. rise in temperature caused the absorption in 96 hours to increase to over 8,000 c.c. and the dioxide and monoxide productions after 12 hours to 12 and 3 per cent. respectively, whilst at 140° C. the oxygen absorption was over 15,000 c.c., the carbon dioxide 15 per cent. and the carbon monoxide 4 per cent. of the oxygen absorbed. Figures higher than those quoted above for the production of the oxides of carbon are obtained after exposure of the coal to air for 96 hours, but

since the *rate* of oxidation is then very much reduced the values after 12 hours have been taken as representative of the average for each temperature. It is clear that where rapid oxidation of coal is taking place at a continually increasing temperature the production of carbon dioxide and particularly of carbon monoxide relative to the oxygen absorbed, or in other words the respiratory quotients for these gases, will increase markedly. Since, however, as already pointed out, carbon dioxide is frequently met with in considerable proportion in air samples obtained underground it is difficult to base any conclusions as to heating on variation in carbon dioxide production, although a certain amount of helpful information has been obtained by careful comparison of this figure obtained from frequent samples taken at carefully chosen sampling places<sup>1</sup> where normally the black-damp contained a relatively small proportion of carbon dioxide. Where "heatings" have occurred the carbon dioxide production tends to drop at first, reach a minimum and then rise, passing the original figure. On the other hand, the carbon monoxide production usually shows a steady increase as the "heating" progresses. The investigations referred to have made it clear that the normal production of carbon monoxide varies in different pits and that this figure must be known in order to be able to detect a heating from the analysis of one or two isolated samples. Thus a carbon monoxide production of 0·6 per cent. of the oxygen absorption may be perfectly normal for one pit, but if found by analysis of a sample from another pit which normally showed practically no carbon monoxide, would indicate a heating.

Although it cannot be denied that the olfactory nerve is extremely sensitive and that "gob-stink" may be very readily detected by a trained observer, a reliable analysis

<sup>1</sup> Storrow and Graham, *loc. cit.*

with an accurate determination of the carbon monoxide content may give warning before any trace of unusual odour can be detected. This will be the case if heating of a large mass of coal is taking place, since a greatly increased oxygen absorption will occur with production of carbon monoxide in larger quantity than normal and with consequent marked vitiation of the return air. As an example two return airways from different sections of the same seam in North Staffordshire gave the following analyses :—

I.	Per cent.	II.	Per cent.
CO <sub>2</sub> . . .	0·72	CO <sub>2</sub> . . .	0·25
Gas . . .	0·40	Gas . . .	0·18
O <sub>2</sub> . . .	19·78	O <sub>2</sub> . . .	20·57
N <sub>2</sub> . . .	79·10	N <sub>2</sub> . . .	79·00
CO . . .	0·005	CO . . .	0·0045
CO <sub>2</sub> production =	60 per cent. of	CO <sub>2</sub> production =	63 per cent. of
oxygen absorbed.		oxygen absorbed.	
CO production =	0·4 per cent. of	CO production =	1·2 per cent. of
oxygen absorbed.		oxygen absorbed.	

The first sample was normal, the second contaminated by a heating. A sample of the return air from another seam in the same colliery gave the following analysis, although nothing could be detected by the odour :—

Per cent.	
CO <sub>2</sub>	0·21
Gas	0·95
O <sub>2</sub>	20·21
N <sub>2</sub>	78·63
CO	0·0124

CO<sub>2</sub> production = 29·5 per cent. of oxygen absorbed.  
CO , , , = 2·0 , , ,

A few months after this sample was taken this district had to be sealed off owing to a serious fire.

The drawback to the application of gas analysis in this way to the detection of a heating lies in the time taken before a result may be obtained. It will be obvious from the results quoted that the analyses must be carried out with extreme care and that there must be the complete analysis

(preferably carried out with the large apparatus described on pp. 8-42) as well as the independent determination of carbon monoxide.

#### Apparatus for Combined Estimation of Carbon Dioxide and Carbon Monoxide

In some cases considerable help may be obtained more rapidly simply from an accurate determination of carbon dioxide and carbon monoxide alone, and for this purpose an apparatus has been designed (see fig. 30) somewhat similar to the laboratory gas analysis apparatus. This is fitted with a 100-c.c. burette composed of a bulb of nearly 98 c.c. capacity and a stem graduated from 98 c.c. to 100 c.c. in 0·01 c.c. divisions and capable of being read by estimation with the aid of a lens to 0·001 c.c. The bulb of the compensator must be at the same level in the water-jacket as that of the burette, and care must be taken that the water is stirred very efficiently. A mechanical stirrer driven at high speed by an electric motor was found to be effective. This is not shown in the illustration. A suitable-sized potash pipette with reservoir, the usual connecting tubes and graduation marks, is connected to the burette and compensator, a three-way parallel type stop-cock being used between the burette and potash pipette. The third arm of this is connected, as in the laboratory form of iodine pentoxide apparatus shown in fig. 29, to a U-tube containing askerite, charcoal and phosphorus pentoxide, and thence to an iodine pentoxide tube maintained at about 120° C. in an electrically-heated air bath. The outlet of the iodine pentoxide tube is fitted with the usual right-angle tube dipping under about 2 c.c. of potassium iodide solution contained in a test-tube. In order to overcome error from solubility of any constituents of the gas sample under test, approximately 100 c.c. are first taken into the burette and

passed several times to and from the potash pipette. The levels in the potash tubes are then carefully adjusted and the

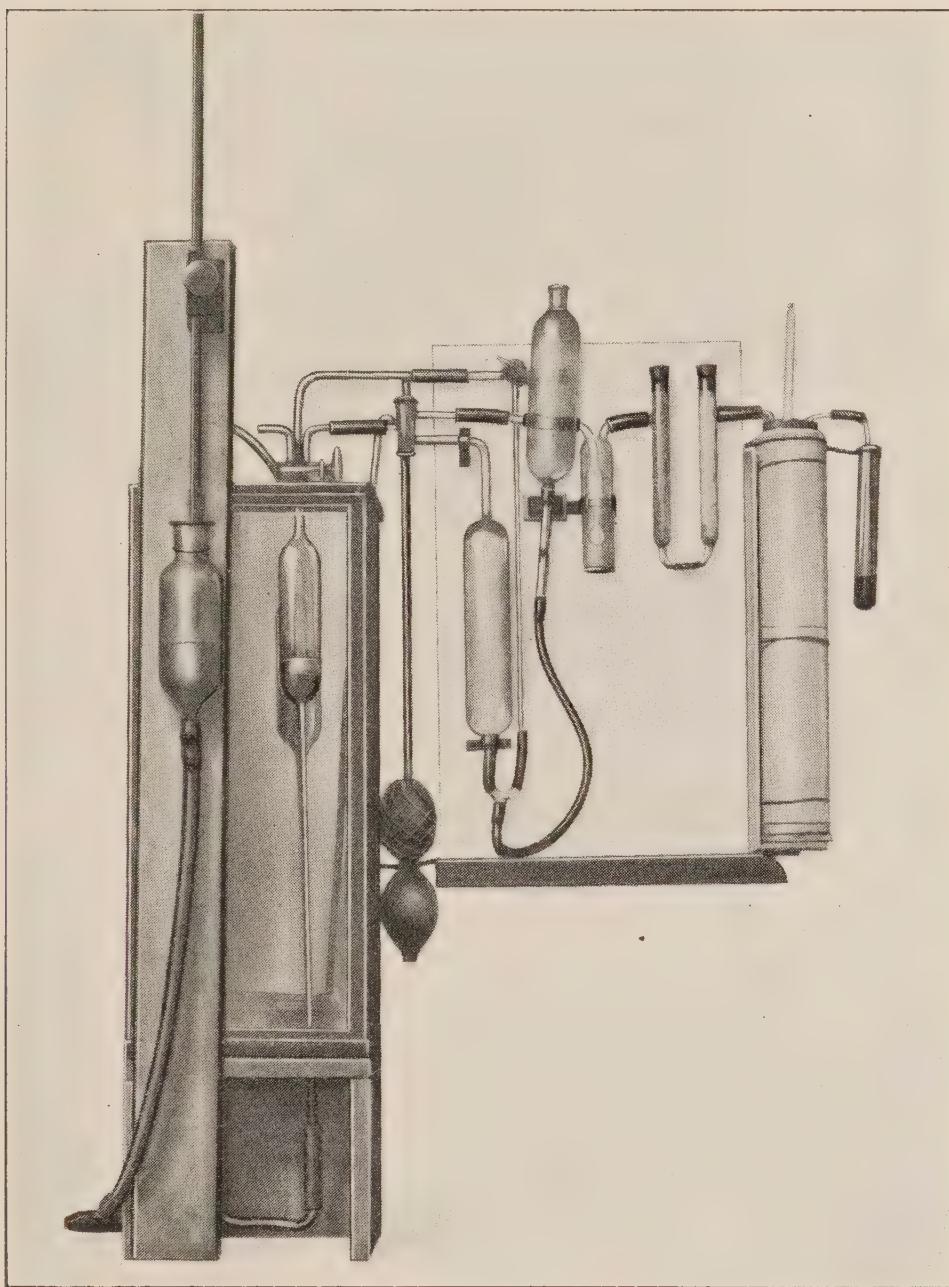


FIG. 30.—Apparatus for the Combined Estimation of Carbon Dioxide and Carbon Monoxide.

three-way stop-cock is turned so as to enable passage of the gas from the burette through the iodine pentoxide tube, the

burette stop-cock being turned to the air just before all the gas is expelled. The burette is then filled in the usual way with a completely new sample and the volume measured exactly after levelling in the usual way. This volume is then passed to and fro between the burette and potash pipette until a constant reading is obtained. The tests carried out have shown that this apparatus is capable of giving results for carbon dioxide accurate to 0·003 per cent. The second 100-c.c. sample is then passed through the iodine pentoxide tube, the connections and U-tube containing purifying agents being washed out with two 100-c.c. lots of fresh air and the liberated iodine estimated in the usual way by titration with N/500 thiosulphate solution.

## CHAPTER XIII

### DETECTORS AND RECORDING APPARATUS FOR CARBON MONOXIDE

SEVERAL carbon monoxide detectors have recently been put on the market, but none of these seems capable of giving results of accuracy sufficient to distinguish clearly between quantities differing in physiological significance. One of these, using " hoolamite " (iodine pentoxide soaked in sulphuric acid), was tested some years ago by the authors. The reagent is contained in a small glass tube, the sealed ends of which are broken for a test, and the tube is connected to the detector which consists essentially of a blowing-bulb and purifying-tube containing cotton wool and respirator charcoal. Carbon monoxide changes the original white colour of the material to a bluish-green shading into violet-brown or black according to the concentration in the gaseous mixture. The results of tests carried out by Katz and Bloomfield<sup>1</sup> indicate that the instrument is only of practical value with comparatively gross amounts of carbon monoxide, and with this the present authors are in agreement. One great drawback is that the colour produced is only transient, disappearing rapidly. It would therefore appear absolutely necessary to carry out a test under standard conditions, particularly in regard to time between commencement and completion of test (i.e. comparison of the colour produced with the colour scale).

What appears (from tests so far carried out by the authors)

<sup>1</sup> *J. Ind. & Eng. Chem.*, **14**, No. 4, p. 304.

to be a useful and convenient detector is that invented by Ljumggren (Br. Pat. Nos. 341269, 379304). Specially prepared palladium chloride test-papers are used, being moistened immediately prior to a test, and give a grey ring when more than 0·02 per cent. of carbon monoxide is present. The time taken for the ring to equal in intensity a standard ring gives a rough but not very reliable measure of the monoxide concentration. For 0·03 per cent. this is about 60 seconds, whereas for 0·12 per cent. it is only about 30 seconds.

### The Automatic Recording of Carbon Monoxide

It is now well known that the exhaust gases from spark ignition internal combustion engines using petrol as fuel contain, as a rule, a high percentage of carbon monoxide. The amount of this is frequently about 7 per cent., but varies greatly with the setting of the carburettor, speed and temperature of the engine. Where motor-car engines are running in enclosed areas there is considerable danger of the accumulation of a poisonous quantity of carbon monoxide unless provision is made for ample ventilation. Extensive tests were carried out a few years ago by the United States Bureau of Mines in connection with the problem of dealing with the exhaust fumes from motor traffic passing through the Holland Tunnel, which passing under the Hudson River connects New York and New Jersey and is approximately 2,000 yards long. These tests showed that the average carbon monoxide content of the exhaust was 6·5 per cent. Tunnels used for motor traffic have, therefore, to be very efficiently ventilated in order that the exhaust gases may be diluted to such an extent that the carbon monoxide content does not exceed a definite amount, usually 0·02 per cent., i.e. a quantity having little physiological significance.

An ingenious apparatus for recording small percentages

of carbon monoxide was designed by Katz and others and first put on the market by the Mines Safety Appliance Company of Pittsburg, whilst more recently the Cambridge Instrument Company has acquired the rights for the manufacture of this apparatus in England. The M.S.A. apparatus is shown in fig. 31. Its *modus operandi* is the measurement of the heat produced during the oxidation of the carbon monoxide by "hopcalite"<sup>1</sup> when the air containing the former is passed through the apparatus at a constant speed. A number of thermocouples (sometimes as many as 48) are arranged differentially to give the increase in air temperature resulting from the oxidation of the carbon monoxide. The increase in temperature may be recorded by a recording potentiometer. For satisfactory working of the catalyst the air passing to the "hopcalite" must be thoroughly dried and for this purpose concentrated sulphuric acid has been used by the designers. The air under test is forced through the apparatus by means of a rotary blower, passing from the pump to an oil filter, thence through two bottles each containing approximately 2 lbs. of concentrated sulphuric acid, a glass wool filter to remove acid spray and thence through a canister containing soda-lime or similar material and activated charcoal. The latter removes any easily condensable vapours not previously taken out by the acid or alkali. A stop-cock is fitted in the circulating system near the pump, by means of which the air flow through the apparatus can be controlled. After leaving the canister the air is forced through an orifice on either side of which connections are made to a long U-tube filled with coloured liquid which serves as a flow-meter. Connected through a T-tube to the air circuit before the orifice is a wide-bore tube which dips into

<sup>1</sup> A mixture of CuO and MnO<sub>2</sub>. This is the material used in box respirators for protection against carbon monoxide.

a 2-inch glass tube containing water, the bottom of this tube being connected to a second closed vessel containing water.

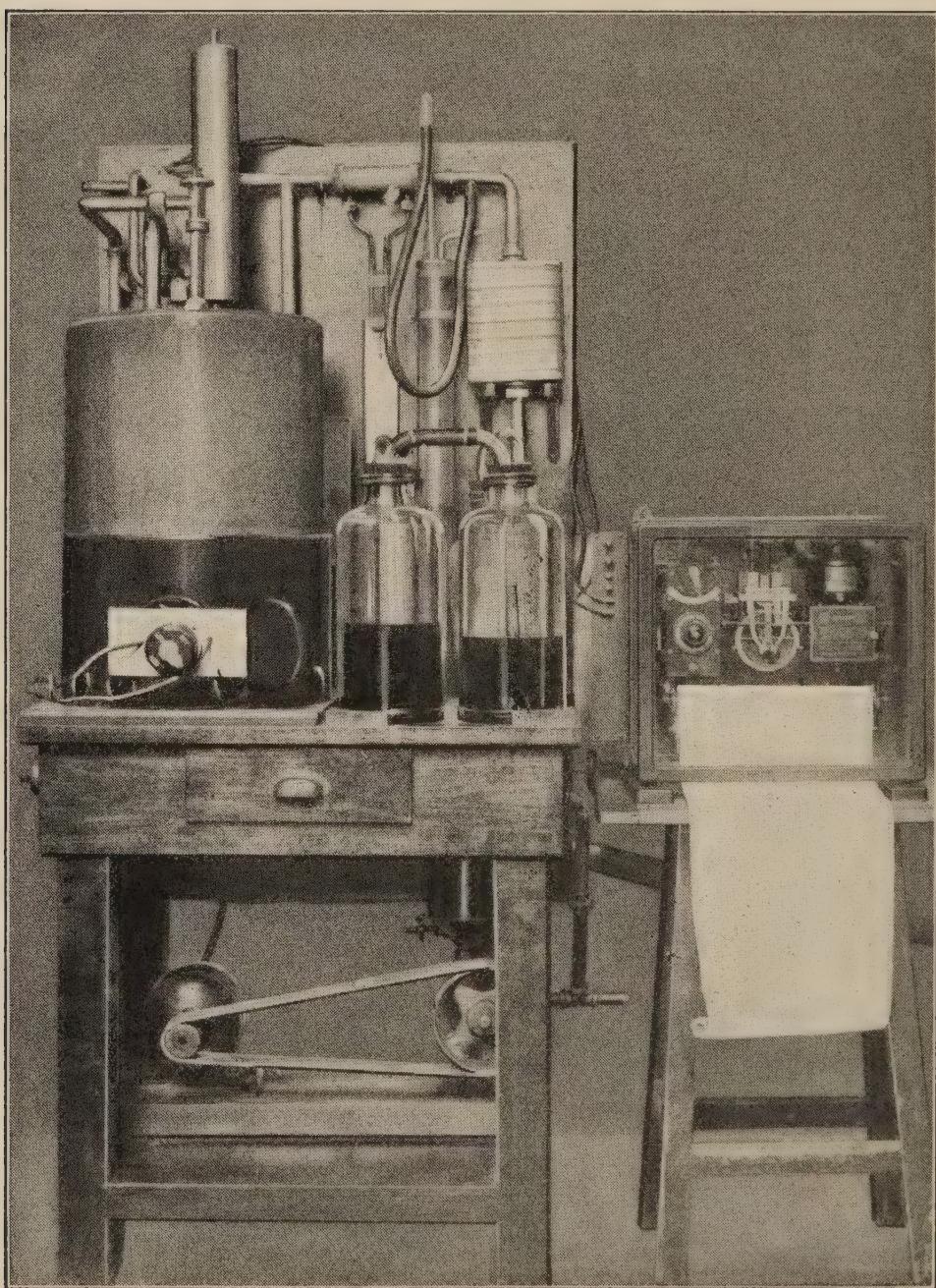


FIG. 31.—Automatic Carbon Monoxide Recorder.

The air space above the water in this vessel is connected to the outflow side of the orifice. Normally air is blowing out to the atmosphere through the wide-bore tube

and the depth to which this is immersed controls the flow through the orifice and the remaining portion of the apparatus. The arrangement just described ensures that a constant flow is obtained irrespective of any alteration of resistance to the air flow after leaving the orifice. The air passes through a calcium chloride drier and then to the catalyst chamber containing the sensitive differential thermocouple equipment arranged so that one series of couples is embedded in pumice and the other in "hopcalite." The whole metal chamber is contained in a large steam-bath which is electrically heated and which ensures that the air is at a constant temperature when it reaches the catalyst. The latter oxidises any carbon monoxide present and the heat of reaction is recorded as already mentioned by a recording potentiometer. The apparatus is somewhat bulky, occupying, apart from the potentiometers, approximately 4 feet by 3 feet of floor space and standing 5 feet high, and it is of course expensive, costing approximately £300. It is, however, exceedingly sensitive and for a total range of 0·0 to 0·04 per cent., or four parts per ten thousand by volume, would seem to be accurate to 0·0005 per cent. when working at the correct rate of flow. These recorders are of great value in the control of the ventilation required for modern tunnels made for vehicular traffic. The ventilation of the Holland tunnel connecting New York and New Jersey is controlled by fourteen of these carbon monoxide recorders, and should the carbon monoxide content of any ventilation section reach 2·5 parts per ten thousand, additional fans are automatically brought into action.

The new Mersey Tunnel is equipped with twelve carbon monoxide recorders. On these the acid drying bottles, which have to be replenished frequently with fresh acid, and have other drawbacks, have been replaced at the suggestion

of the present authors by a regenerative system, employing silica-gel, which has been thoroughly tested for the Mersey Tunnel Engineers in the Mining Research Laboratory. Carbon monoxide recorders have also been installed in the recently opened vehicular tunnel at Antwerp running under the River Scheldt. The need for artificial ventilation of large subterranean garages which are now being built in many cities is obvious, and since ventilation costs money a large financial saving may be secured by control of the ventilation by means of an accurate carbon monoxide recorder or indicator similar to the one described. There seems no reason, however, why an apparatus much smaller in size and price should not be put on the market.

Reference has been made to the high percentage of carbon monoxide in the exhaust from internal combustion engines. A carbon monoxide content of 6·5 per cent. in the exhaust gases indicates a wastage of 30 per cent. of fuel, whilst 13·2 per cent. (the highest amount found in any of the Bureau of Mines tests) is equivalent to 50 per cent. loss. An analysis of the exhaust and especially a determination of the carbon monoxide content gives, therefore, valuable information regarding the satisfactory working or otherwise of the engine. It may be mentioned in passing that in the exhaust of a properly working Diesel engine a comparatively low percentage of carbon monoxide is usually found, particularly when the engine is working under load. It is also claimed that with internal combustion engines running on coal gas, either compressed in cylinders or from gas mains, the combustion is much more complete and in consequence no appreciable amount of carbon monoxide appears in the exhaust.

## CHAPTER XIV

### RECOGNITION OF OTHER POISONOUS GASES

THE recognition or determination in air by chemical tests of commonly occurring poisonous gases and vapours other than carbon monoxide is usually of minor practical importance, as these usually may be recognised by smell or by their irritant action on the nose, eyes, and air-passages. This is the case, for instance, with chlorine, sulphurous acid, ammonia, acid fumes, sulphuretted hydrogen, phosphor-  
retted hydrogen, nitrous fumes, and practically all the gases and vapours used in warfare. The test with a mouse or bird may also be employed. The smell of a poisonous gas is, however, often difficult to detect on account of the presence of other odorous but possibly harmless substances, or because after a time the smell becomes scarcely noticeable.

Nitrous fumes, sulphuretted hydrogen, phosgene and other lung-irritant gases or vapours used in warfare are of special importance on account of their treacherous action. They have this in common, that a person exposed to them in sufficient concentration to produce comparatively slight irritation of the eyes and air-passages may die within the next day or two from acute inflammation of the lungs and air-passages. With other ordinary irritant gases there seems to be no such danger from a slight exposure, as any symptoms of irritation decline steadily after leaving the irritant atmosphere.

### Nitrous Fumes

These are frequently evolved in harmful amount during blasting when the explosive contains nitro-compounds as is now usually the case. Their formation is indicative of the burning rather than exploding of the explosive. They consist of nitrogen tetroxide which at ordinary temperatures contains molecules having either the formula  $N_2O_4$  or  $NO_2$ . The former are readily condensed to an almost colourless liquid boiling at  $21\cdot6^{\circ}C.$  but are converted by heating into the simpler molecules, giving a dark reddish-brown gas.

The other common oxides of nitrogen are nitrous oxide or nitrogen monoxide,  $N_2O$ , and nitric oxide or nitrogen dioxide,<sup>1</sup>  $NO$  (or  $N_2O_2$ ). The latter in the presence of oxygen is immediately transformed into the tetroxide, so that inhalation of nitric oxide as such is impossible. Nitrous oxide is without irritant action and is used as an anæsthetic. It has proved especially useful when administered along with oxygen in operations requiring prolonged anæsthesia. Occasional complaints have been made of the occurrence of small quantities of carbon monoxide in compressed nitrous oxide. The estimation of a small percentage of this gas by the iodine pentoxide method becomes somewhat complicated owing to the fact that the nitrous oxide is itself attacked to a small extent with liberation of iodine when the pure or almost pure gas is passed over the iodine pentoxide at  $120^{\circ}C.$  The amount of decomposition is constant however when the gas is passed through the apparatus at the same rate, and the authors have found the following procedure to be satisfactory. In place of the usual test-tube containing potassium iodide solution for trapping the iodine, one is used which is fitted with side-tube and rubber bung through which passes the

<sup>1</sup> The compounds  $NO_2$  and  $N_2O_4$  have for many years been incorrectly called nitrogen dioxide.

tube leading from the iodine pentoxide. The side-tube is connected to a sample tube (fitted with three-way stop-cocks and of capacity about 150 c.c.) either filled with mercury and connected in its turn to a mercury reservoir or else evacuated. 100 c.c. of the nitrous oxide sample are passed through the apparatus, the stop-cock of the sample tube being turned to air. When approximately 50 c.c. (or whatever may be the volume of the connections, etc., of the carbon monoxide apparatus) have passed through, the tap is turned to collect the issuing gas in the sample tube. The apparatus is then washed out with two lots of 100 c.c. of pure air, 50 c.c. of the first washings being collected in the sample tube, which then contains practically all the nitrous oxide in an almost pure condition. The free iodine in the iodide solution is titrated and the contents of the sample tube are then passed through the monoxide apparatus, the latter washed out with 200 c.c. of air and a second titration carried out ; the result of this is deducted from the first, giving the amount of iodine liberated by the carbon monoxide alone.

Nitrous fumes ( $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ) are readily detected by the production of a blue colour with a test paper soaked in potassium iodide and starch solution. A quantitative estimation may be made by absorption in alkali, oxidation to nitrate and colorimetric comparison, with the aid of phenoldisulphonic acid, with solutions containing known amounts of nitrates. It will be seen from the table on p. 154 that the quantity producing harmful effects is very small, being anything over 40 parts per million.

### Sulphuretted Hydrogen, $\text{H}_2\text{S}$

This gas is colourless and is usually the product of decomposition of sulphur compounds. It possesses a characteristic odour usually described as a "smell of rotten eggs," but if encountered in quantity sufficient to produce harmful

physiological effect this smell is not noticeable, but instead the gas has a pleasant odour. In sewer gas or smoke the smell of sulphuretted hydrogen is often masked. A frequent source of sulphuretted hydrogen in mines is the burning of black powder. It is often found in highly toxic quantity in sewers, and since the gas is roughly five times as poisonous as carbon monoxide and much more rapid in causing death on the spot or dangerous after-effects, great care should be taken where its presence is suspected. It will be seen from the table, p. 156, that 0·1 per cent. is sufficient to cause serious symptoms after a few minutes. In low concentration the gas causes irritation of the eye, causing this organ to feel as if irritated by grains of sand. Sulphuretted hydrogen can easily be recognised by the blackening of a test paper dipped into a solution of lead acetate. Any air in which this blackening occurs within a minute should be regarded as very dangerous. Tests carried out by the authors and Mr. F. Lawrence in the experimental chamber of the Mining Research Laboratory have shown that the test is much more sensitive if the air be blown on to the test paper, as little as 0·0005 per cent. by volume being capable of detection in this way. The concentrations of this gas causing serious symptoms are shown in the table, p. 156.

### Sulphur Dioxide, $\text{SO}_2$

This gas, although extremely unpleasant to breathe, having a strong sulphurous smell, is less dangerous than the others so far considered. Owing to its irritating action it is practically intolerable to breathe a concentration that will have dangerous physiological effects. It will be present at fires where there is free burning of sulphur-containing bodies. It may be detected by means of papers soaked in potassium iodate solution to which a little starch has been added. An excess of sulphur dioxide reduces the iodine first formed in

the reaction, so that the blue (starch-iodide) colour may first be produced and subsequently disappear. The gas may be estimated quantitatively by passing a known volume of sample through a standard iodine solution, the subsequent titration of the latter giving the quantity of sulphur dioxide. Care should be taken, however, to employ a second absorption vessel containing potassium iodide solution to trap any iodine vapour carried over by the air current.

#### **Hydrogen Phosphide (*Phosphoretted Hydrogen*), $\text{PH}_3$**

This gas is also extremely poisonous and treacherous in its action. It may be recognised chemically by the fact that it blackens paper dipped in silver nitrate solution but not paper dipped in lead acetate. It is evolved when water acts on calcium phosphide, which is frequently an impurity in calcium carbide, and also when ferro-silicon containing phosphide is moistened with water. The maximum amount that can be breathed for an hour without harmful result appears to be between 100 and 200 parts per million.

#### **Hydrogen Arsenide (*Arsine or Arseniuretted Hydrogen*), $\text{AsH}_3$**

This is formed whenever an acid acts upon a metal containing arsenic or when the acid itself contains arsenic. Poisoning by arsine sometimes occurs during the filling of balloons with hydrogen made from zinc and hydrochloric acid if either of these reagents contained arsenic. Arsine may also be formed in charging electric storage batteries and has sometimes been produced in this way in dangerous amount in submarines. The table on p. 156 shows the effect of inhalation of various concentrations. Hydrogen arsenide acts cumulatively when in great dilution. It may be detected by its action (yellow coloration) on a strip of filter paper soaked in mercuric chloride and allowed to dry (Gutzeit test).

**Hydrogen Cyanide (*Hydrocyanic Acid*), HCN**

This is frequently used for the fumigation of ships and buildings and is highly poisonous, anything over 100 parts per million, or 0·01 per cent. being considered unsafe. It has been suggested that this gas is produced during the incomplete combustion of coal. We have not been able to verify this, but it is well known, of course, that it is formed in the destructive distillation of coal and consequently occurs in unpurified coal gas as well as in blast furnace gas. It boils at 26° C. Cyanogen,  $(CN)_2$ , is also used as a disinfectant. The cyanogen compounds exert an inhibiting action upon oxidation in the tissues and their poisoning action is a form of asphyxia caused by the arrest of internal respiration.<sup>1</sup> Hydrogen cyanide and cyanogen may be detected by the prussian blue reaction. A quantity of the gas under test is passed through 10 per cent. potassium hydroxide solution. A portion of this is then treated with a small amount of 10 per cent. ferrous sulphide solution and heated. Ferric chloride is then added in excess, and if hydrogen cyanide or cyanogen is present in the gas under test a prussian blue colour is produced by acidifying with sulphuric acid.

**Chlorine, Cl<sub>2</sub>**

This gas is yellowish-green at ordinary temperatures, and has a specific gravity 2·47 times that of air. It was used in large amount in the Great War and is employed extensively for the disinfection of water and sewage of cities and in various manufacturing processes. It is stored in the liquid form in cylinders and contamination of the air may occur during the storage of these and particularly where a fire occurs. Chlorine is nearly 20 times as toxic as

<sup>1</sup> Henderson and Haggard, *Noxious Gases*, Chem. Catalog. Co., 1927.

hydrochloric acid. Its toxic action, which is shown in the table, p. 157, is probably due to the rapid oxidation of moist tissues by nascent oxygen formed as a result of the reaction of the chlorine with water to form hydrochloric acid. It may be estimated by passing a known volume through 10 per cent. potassium iodide solution and titration of the liberated iodine using starch as indicator.

### **Phosgene, COCl<sub>2</sub>**

This is a colourless gas which fumes in moist air owing to partial conversion to hydrochloric acid. It is used in the dyestuffs industry and is usually transported in cylinders. Like nitrous fumes, a small concentration of phosgene may be inhaled with little immediate discomfort but very serious after-effects. One of the chief sources of contamination of air by this gas is the use of carbon tetrachloride as a fire extinguisher in a confined atmosphere, for example in a mine or inside a building. A number of fatalities have occurred from such use. The carbon tetrachloride is converted by the action of heat into phosgene and a highly dangerous atmosphere may be produced unless efficient ventilation is available. Any fire extinguisher containing carbon tetrachloride should therefore not be used for mine fires. In experiments conducted by the U.S.A. Bureau of Mines <sup>1</sup> in a gas-tight room of 1,000 cubic feet capacity, the use of 1·0 litre of carbon tetrachloride produced approximately 170 parts per million of phosgene by volume or 0·017 per cent. It will be seen from the table, p. 156, that this concentration is more than sufficient to give an atmosphere which would be rapidly fatal.

### **Ammonia, NH<sub>3</sub>**

Ammonia is a gas at ordinary temperatures and pressures, having a density slightly more than half that of air. It is

<sup>1</sup> *Bureau of Mines Tech. Paper 248, 1921.*

transported either as dissolved gas or in the liquefied form in cylinders. The liquid is used extensively for refrigeration and a small leak of the gas from plant in a confined space, such as a basement, may soon produce a dangerous atmosphere. It will be seen from the table, p. 155, that any quantity over 0·2 per cent will produce severe irritation and may have dangerous effects. When present in very small concentration it may be estimated by passing a known volume of the air under test through water in an effective absorption vessel with subsequent comparative colorimetric tests with standard solutions of ammonia and Nessler reagent. For higher concentrations, of the order of 0·2 per cent. by volume, about 20 litres of the gas may be passed through the absorption vessel and the resulting solution titrated with standard acid using methyl red as indicator.

Where it is necessary to enter an atmosphere where any of the foregoing gases may be present or suspected, e.g. for the purpose of sampling the air, it is always desirable to wear an efficient respirator. One of the "box" type containing highly adsorbent charcoal as well as alkali, e.g. soda-lime, will protect the wearer against any of these gases and various vapours not mentioned, with the exception of carbon monoxide. To protect against the latter either a box respirator containing, in addition to the charcoal and soda-lime, "hopcalite," which, as already mentioned, is a mixture of copper oxide and manganese dioxide, or a self-contained oxygen apparatus must be worn. If a moderately high concentration of ammonia is anticipated the box respirator should contain a layer of pumice coated with copper sulphate, in addition to charcoal. A cotton wool filter-pad should be included in all respirators for the removal of particulate matter present as solid or as a mist.

**Physiological Effect of Lack of Oxygen and Presence of Various Noxious Gases**

Gas.	Per cent. by Volume in Air.	Effect.
Oxygen (O <sub>2</sub> )	20·93	Normal air supply.
	17·5	Flame lamp extinguished. Can be breathed and work done without ill-effect for several hours.
	13·0	Acetylene flame extinguished. Work trying. Considerably increased rate of breathing if work done. Lips distinctly blue; nausea and headache develop gradually, and may become very severe.
	11·8	Loss of consciousness on exertion. Individual differences.
	Below 6	Unconsciousness and death if not quickly removed.
Carbon Dioxide (CO <sub>2</sub> )	0·5	Lung ventilation increased slightly.
	2·0	Lung ventilation increased 50 per cent. and rather laboured on exertion.
	3·0	Lung ventilation increased 100 per cent. and very laboured on exertion.
	5·0	Lung ventilation increased 300 per cent., breathing laboured and only very slight exertion possible.
	10·0	Intolerable panting.
	Above 10·0	Narcotic effect upon system.
		When, as is commonly the case, deficiency of oxygen in the air is accompanied by some excess of carbon dioxide, a lower percentage of oxygen can be breathed with impunity. This is due to the effect of the carbon dioxide in increasing the rate of breathing and circulation.

Gas.	Per cent. by Volume in Air.	Effect.
Carbon Monoxide (CO)	0·02	Slight headache in some persons after about 7 hours during rest or 2 hours during exertion.
	0·04	After 2 or 3 hours during rest, or 45 minutes during exertion, headache and discomfort, with possibility of collapse.
	0·12	Palpitation after 30 minutes during rest, or 10 minutes during exertion. Weakness in legs after 1 hour during rest, or 20 minutes during exertion, headache and nausea following. Complete disablement after 2 hours during rest or $\frac{3}{4}$ hour during work.
	0·20	Unconsciousness after 30 minutes during rest or 10 minutes during exertion.
	0·30	Unconsciousness after 15 minutes during rest or 5 minutes during exertion.
	1·00	Unconsciousness after 3 minutes during rest or 1 minute during exertion.
		The above figures are for unacclimatised persons. It appears that with acclimatisation, which is very easily induced, the figures for low concentrations would need to be about doubled.
Nitrous Fumes (NO <sub>2</sub> , N <sub>2</sub> O <sub>4</sub> )	0·004	Can be detected by smell, and tolerated for several hours.
	0·01	Seriously affects respiratory passages.

Gas.	Per cent. by Volume in Air.	Effect.
	0·012 to 0·015	May cause dangerous illness if breathed for short time (e.g. 20 minutes). Patient may not be affected at time, but collapse several hours later with symptoms of acute broncho-pneumonia.
	0·024	Rapidly fatal for short exposure. <sup>1</sup>
Hydrogen Cyanide (Hydrocyanic Acid) (HCN)	0·002	Slight symptoms after several hours. <sup>2</sup>
	0·005	Maximum quantity safe to inhale for 1 hour. <sup>3</sup>
	0·012 to 0·015	Dangerous in 30 minutes to 1 hour. <sup>3</sup>
	0·07	Fatal if breathed for more than a few minutes.
	0·25	Rapidly fatal. <sup>4</sup>
Ammonia (NH <sub>3</sub> )	0·005	Least amount detectable by odour. <sup>5</sup>
	0·04	Causes immediate irritation to throat. <sup>5</sup>
	0·25–0·5	Dangerous to breathe for 30 minutes. <sup>6</sup> Great irritation of respiratory passages.
	1·00	Causes irritation of the skin and is rapidly fatal.

<sup>1</sup> Lehmann and Hasegawa, *Arch. für Hygiene*, 1913, **77**, p. 323. Henderson and Haggard, *Noxious Gases*, Chem. Catalog. Co., New York, 1927.

<sup>2</sup> Lehmann, quoted by Kobert in *Kompend. der Prakt. Toxicol.*, Stuttgart, 1912. Henderson and Haggard, *loc. cit.*

<sup>3</sup> Kobert, R., *loc. cit.* Henderson and Haggard, *loc. cit.*, p. 111.

<sup>4</sup> Kohn-Abrest, *Annales des Falsifications*, 1915, **8**, pp. 215–39.

<sup>5</sup> U.S.A. Bureau of Mines, *Tech. Paper 248* (Table).

<sup>6</sup> Lehmann, *Arch. für Hygiene*, 1886, **5**, p. 1. Henderson and Haggard, *loc. cit.*

Gas.	Per cent. by Volume in Air.	Effect.
Hydrogen Sulphide (Sulphuretted Hydrogen) (H <sub>2</sub> S)	Below 0·005	Not poisonous, and scarcely any irritation of eyes.
	0·010	Irritation to eyes and respiratory tract, with inflammation of eyes developing later. Headache.
	0·060	Serious symptoms within few minutes, followed by conjunctivitis and bronchitis.
	0·100	Very dangerous almost at once.
Hydrogen Phosphide (PH <sub>3</sub> )	0·01	Can be inhaled for 1 hour without serious effect. <sup>1</sup>
	0·04	Dangerous in 30 minutes to 1 hour.
	0·2	Rapidly fatal. <sup>2</sup>
Hydrogen Arsenide (AsH <sub>3</sub> )	0·003	Slight symptoms after several hours. <sup>3</sup>
	0·005	Dangerous symptoms after exposure for several hours. <sup>3</sup>
	0·025	Fatal after exposure for 30 minutes. <sup>3</sup>
Sulphur Dioxide (SO <sub>2</sub> )	0·0003	Least detectable by odour. <sup>4</sup>
	0·01	Unpleasant to breathe.
	0·1	Very irritating and causes serious bronchitis if breathed for more than $\frac{1}{2}$ hour.
Phosgene (COCl <sub>2</sub> )	0·0004	Causes irritation to eyes and throat. <sup>5</sup>
	0·0025	Dangerous for even short exposure. <sup>5</sup> Death may occur some time after, although apparently little effect at time of exposure.
	Over 0·025	Rapidly fatal.

<sup>1</sup> Kobert, R., *loc. cit.*

<sup>2</sup> Rambousek, *Industrial Poisoning*, London, 1913, p. 191.

<sup>3</sup> References, Henderson and Haggard, *loc. cit.*

<sup>4</sup> U.S.A. Bureau of Mines, Bull. 98, 1915, p. 36.

<sup>5</sup> U.S.A. Bureau of Mines, Tech. Paper 248, 1921 (Table).

Gas.	Per cent. by Volume in Air.	Effect.
Chlorine (Cl <sub>2</sub> )	0·00035	Least detectable by odour. <sup>1</sup>
	0·005	Very irritating.
	0·01	Causes severe irritation to lungs, with bronchitis following.
	0·1	Rapidly fatal for short exposure.

<sup>1</sup> Kober, R., *loc. cit.*

## CHAPTER XV

### DETERMINATION OF DUST IN AIR

IT is now well recognised that the inhalation of free silica in the form of particles of size less than  $10\mu$  ( $1\mu = 0.001$  mm.) is the cause of the disease of the lungs known as silicosis, or miner's phthisis. This disease, in which tubercular infection plays an essential part, occurs not only among miners and workers in siliceous stone but also in various other industrial employments where persons are exposed to dust containing more than about 60 per cent. of free silica, for example amongst pottery workers and grinders and polishers in certain trades. In the driving of rock headings in coal-mines rocks having a dangerously high percentage of free silica are sometimes encountered. The Various Industries (Silicosis) Scheme, 1931, under the Workmen's Compensation Act, specifies that a workman becomes entitled to compensation if he is certified as suffering from silicosis and has been engaged on the drilling or blasting of stone in any sinking pit or staple pit or cross measure drift, or in the handling or moving of stone where these processes are carried on. In view of the disastrous effects produced by the habitual inhalation of certain kinds of dust from hard stone, or of metallic dust, it is therefore often important to determine the quantity of the dust in order to judge of the efficacy of means taken to prevent its inhalation. The method of estimation depends upon whether it is desired to know the weight and composition of the dust or the number of particles suspended in the air.

For the gravimetric estimation of dust in air, a measured volume of the air is passed through a suitable filter and the weight of deposited dust obtained either by weighing the filter before and after the test or else by the use of a soluble filtering material such as fine crystalline sugar, the dust being obtained by dissolving this and filtering through a weighed filter paper.

Apart from the danger of silicosis, many occupations are exceptionally dusty and considerable discomfort, if not eventually lung or bronchial trouble, may be incurred even though the dust may contain a low percentage of free silica.

For relatively high concentration, and where only the quantity of suspended dust is required, the following simple method described in earlier editions of this book may be employed.

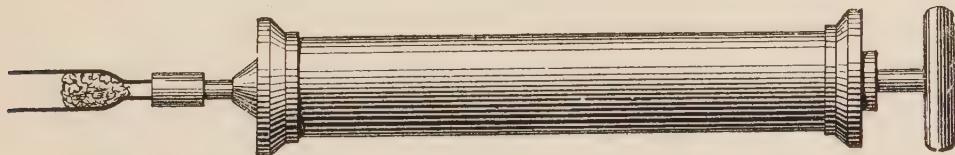


FIG. 32.—Apparatus for Dust Determination.

A piece of glass tube about  $2\frac{1}{2}$  inches long and  $\frac{1}{2}$  inch in diameter is prepared in the form shown in fig. 32. A small plug of cotton-wool is pushed firmly down to the constricted part. This filters off any dust in the air drawn through the tube. An additional guard plug, or a cork at the wide end of the tube, serves to prevent accidental contamination, or loss of dust. At the place where it is desired to determine the dust (usually as near as possible to the place where it is given off into the surrounding air) the cork or guard plug is removed, and the glass tube attached by a piece of rubber tubing, about an inch long, to the nozzle of a brass exhausting syringe taking about 200 c.c. or more of air at each stroke, and provided with thoroughly efficient valves. The glass tube should touch the nozzle of the syringe, so as not to

require any support. The syringe is then held so that the tube points horizontally, and a sufficient quantity of air drawn through. The quantity is measured by counting the strokes of the syringe, the capacity of which has been measured beforehand by sucking air through a tube from a measuring cylinder inverted over water, or by attaching the syringe, with the tube and plug in position, to an experimental gas-meter. Care must be taken that at the end of each stroke time is given for the full charge of air to enter, as the resistance of the cotton-wool causes a slight delay.

After the air has been drawn through the tube the guard plug is replaced. If any dust was present in the air it will now be seen on the plug of cotton-wool. The further steps will depend on the nature of the dust and the object of the determination.

**Inorganic or Stone Dust.**—If the dust is from stone the plug of cotton-wool is ignited in a platinum crucible, carefully weighed to decimilligrammes, with the usual precautions as regards cooling. The difference in the weight of the crucible and the weight after ignition gives the weight of dust in the air. The weight of the ash from the cotton-wool is not appreciable. The quantity of air needed for the analysis depends, of course, on the amount of dust present. In the air of an "end" or "rise" in a mine, with a rock-drill boring dry holes, 10 litres of air would usually be sufficient to give 50 to 100 decimilligrammes of dust. With an efficient jet of water to prevent dust no appreciable quantity of dust should be yielded by 20 litres of air.

**Organic Dust.**—The weight of the tube + cotton-wool is first ascertained after a few litres of air, dried by passing through a calcium chloride or sulphuric acid absorption tube, have been run through to dry the cotton-wool thoroughly. The same process is gone through after the

dust has been collected, and the difference in weight gives the weight of dust in the air.

**Lead Dust.**—On account of the poisonous properties of lead it may be necessary to determine lead in the dust collected from the air of factories, etc., where lead is used. The following method, recommended by Vernon Harcourt,<sup>1</sup> may be employed :—Dilute nitric acid (10 per cent.) is poured, a few drops at a time, through the tube containing the plug into a beaker of about 50 c.c. capacity. The plug is then transferred to the beaker, the tube washed out, and the plug stirred and pressed with a glass tube sealed at the end, while the liquid is gently heated. Hydrofluoric acid, a few drops at a time, is then added directly (not down the glass) in order to dissolve lead silicate. The very dilute hydrofluoric acid has little action on the glass, but dissolves the particles of silicate suspended in the liquid. The liquid, amounting to about 20 c.c., is now passed through a small filter into a 50-c.c. measuring flask, and the beaker, plug of cotton-wool and filter washed with successive small portions of water till the flask is filled to the mark. After thorough mixing, a few cubic centimetres of the liquid are then taken out in a pipette, and tested colorimetrically for lead after addition of sulphuretted hydrogen, etc., as described in a paper by Vernon Harcourt in the *Journal of the Chemical Society*, vol. xcvi, p. 841. If the colour is as pale as, or less pale than, that due to half a centimilligramme of lead, a larger proportion of the remaining liquid is used for a second testing, and the amount of lead calculated in the manner described in the paper.

Other metals, such as copper, etc., may be determined in the collected dust by similar methods when this is necessary.

If it is of importance to know the composition of rock dust suspended in the air, a relatively large quantity of air is

<sup>1</sup> Report of the Departmental Committee on Lead Poisoning, Etc., Parliamentary Paper [Cd. 5278], 1910, vol. ii, p. 120.

usually required in order to obtain sufficient material for analysis.

Tests carried out by one of the present authors and F. Lawrence have shown the "sugar-tube" method to be satisfactory for an accurate determination of concentration and also for obtaining a sample sufficiently large for analysis. Instead of using sugar, however, crystallised potassium nitrate, A.R., was employed for trapping the dust, since it was found that in humid atmospheres sugar soon became partially dissolved and thereby increased the resistance of the apparatus enormously. The apparatus used was designed for estimating the dust in mine atmospheres containing concentrations of the order of one grain or less per cubic foot, the quantity of air which it is necessary to draw through the apparatus depending upon the dust concentration. Since a volume of several hundred cubic feet of air may be required for a test, either a pump driven by a small compressed air engine or an air ejector is used for passing the necessary quantity of air through the filtering apparatus and through a meter. Where compressed air has not been available the pump has been fitted to a portable pedal cycle by means of which 2 cubic feet per minute could be drawn through the apparatus. The filtering apparatus is shown in fig. 33, from which it will be noted that two tubes are placed side by side, in order to diminish the resistance—an important matter if an air ejector is used for obtaining the required air flow. To differentiate between fine and coarse dust a fine mesh gauze, having holes approximately  $40\mu$  in size (325 mesh I.M.M. standard), may be attached to the inlet, or alternatively a settling bottle may be employed (as shown in fig. 33), in which the larger particles settle out, this being in turn connected to the potassium nitrate tube. The upper portion of the latter is made with 60-mm. bore tubing, sealed

to short lengths of 20-mm. tubing (external), which pass through bungs to fit Gooch crucibles. The bottom ends of the 20-mm. tubes are ground and are seated on small filter papers lying on the bottoms of the crucibles. The rubber bungs keep the nitrate tubes in position in the Gooch crucibles, which in turn are fixed into the outlet tube

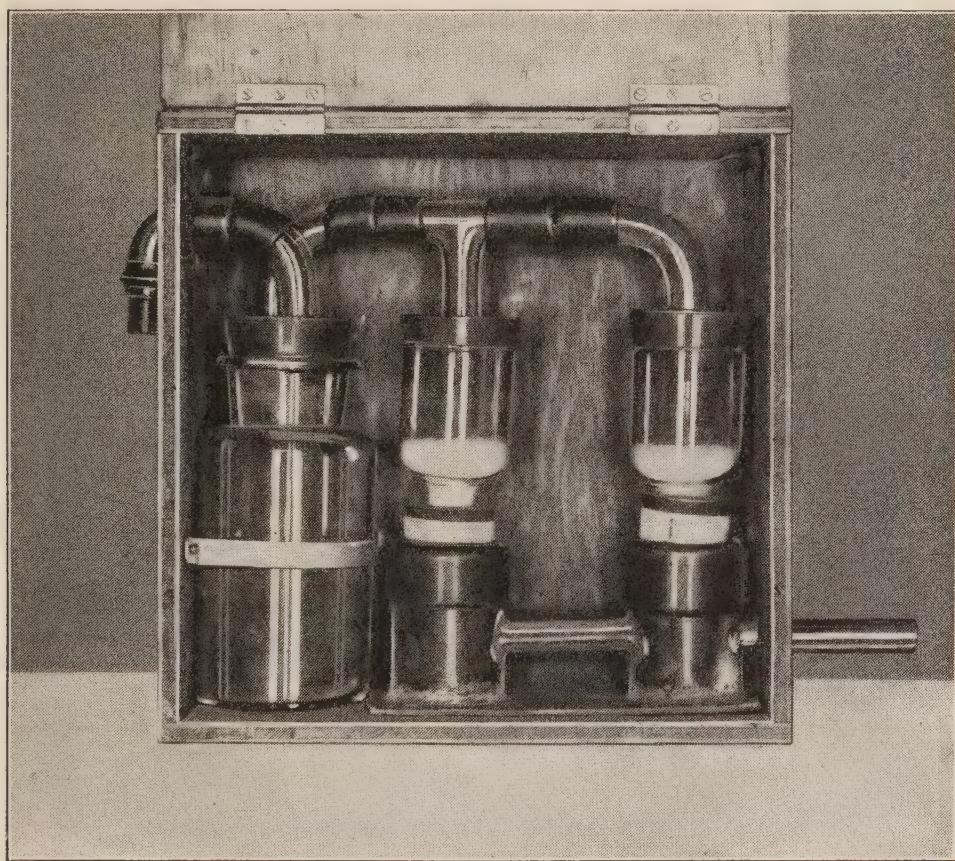


FIG. 33.—Apparatus for Collecting Dust from Air for Analysis.

connected to a dry gas-meter, which is in turn connected to the pump or ejector. Each nitrate tube is filled with approximately 30 grammes of pure (A.R.) potassium nitrate (through 20 lying on 60 I.M.M. mesh) to a depth of 1 cm. in the wide upper portion. Tests with very fine coal-dust have shown that all the dust is trapped within the top half centimetre of nitrate. The dust filter should be hung in the position of test, whilst the meter and pump are housed

in a separate box which may be placed in any convenient spot, connection with the filter being made by means of half-inch hose piping. When a test sample is ready the filter box is brought to the laboratory or the nitrate tubes are replaced by fresh tubes and carefully sealed with clean bungs. The nitrate and dust are carefully transferred to a beaker (800-c.c. capacity), the nitrate dissolved and the dust thoroughly wetted with hot distilled water, care being taken that no dust escapes into the atmosphere. The transference is best accomplished by placing the nitrate tube (after removal of bungs and careful wiping of the external part of the tube) wide end innermost inside a beaker containing a small amount of distilled water, each being held as nearly horizontal as the water will allow. The tube is pressed against the bottom of the beaker and both are then turned over carefully until the beaker is in its normal position, when a water seal is obtained around the tube and escape of dust prevented. The Gooch crucibles are removed and about 200 c.c. of distilled water added to the beaker, penetrating into the nitrate tube, wetting the dust and dissolving the nitrate. The tube is finally lifted out and all adhering particles washed off. The contents of the beaker are washed on to a dried and weighed filter paper, washed free from nitrate and finally dried under the same conditions as the filter paper, cooled in a desiccator and weighed. If the amount of free silica is required, about 0·15 gramme of the dust is carefully removed from the filter paper, accurately weighed and then subjected to a rational analysis<sup>1</sup> modified so as to be suitable for the small quantity of dust employed. The results may be taken as

<sup>1</sup> A. Shaw's investigations in the Mining Research Laboratory have shown that the method of rational analysis is as accurate as any known method for the estimation of "free" silica in coal-measure rocks, the error usually being within  $\pm 1\cdot 5$  per cent.

accurate to  $\pm$  2 per cent. As an example the results of a test in a North Staffordshire "crut" during heading operations may be quoted :—

Weight of dust obtained . . .	0·988 gramme.
Volume of air passed through apparatus during $46\frac{1}{2}$ hours . . .	448·7 cu. ft.
Dust concentration . . .	0·034 grain or 2·2 milligrammes per cu. ft.
Free silica in dust (1) 28·8 (2) 27·6	mean 28·2 per cent.

**The Konimeter.**—It is evident that the gravimetric estimation of suspended dust is a somewhat lengthy operation, and where dust of more or less constant composition is encountered, valuable information may be obtained with the konimeter, designed by Sir R. N. Kotzé for use in the South African Gold Mines. By means of a small pump worked by spring and trigger 5 c.c. of air can be projected at a high velocity through a fine nozzle against a glass slide smeared with vaseline. The dust particles are trapped in the vaseline, forming a circular spot, and can subsequently be examined with a microscope under a magnification of, say, 200. By means of a special eye-piece two opposite sectors each having an angle of  $9^\circ$  are counted and the count multiplied by four gives the number of particles per cubic centimetre.

As a result of practical experience a figure of 300 particles per cubic centimetre has been taken as the maximum number of particles of free silica for a safe atmosphere. The Kotzé konimeter is usually fitted with a rotating slide on which it is possible to take 29 "spots." It may also be fitted with a

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*Note.*—An improved form of dust collector, in which resistance to air flow has been greatly diminished, has been designed in the Mining Research Laboratory during recent months.

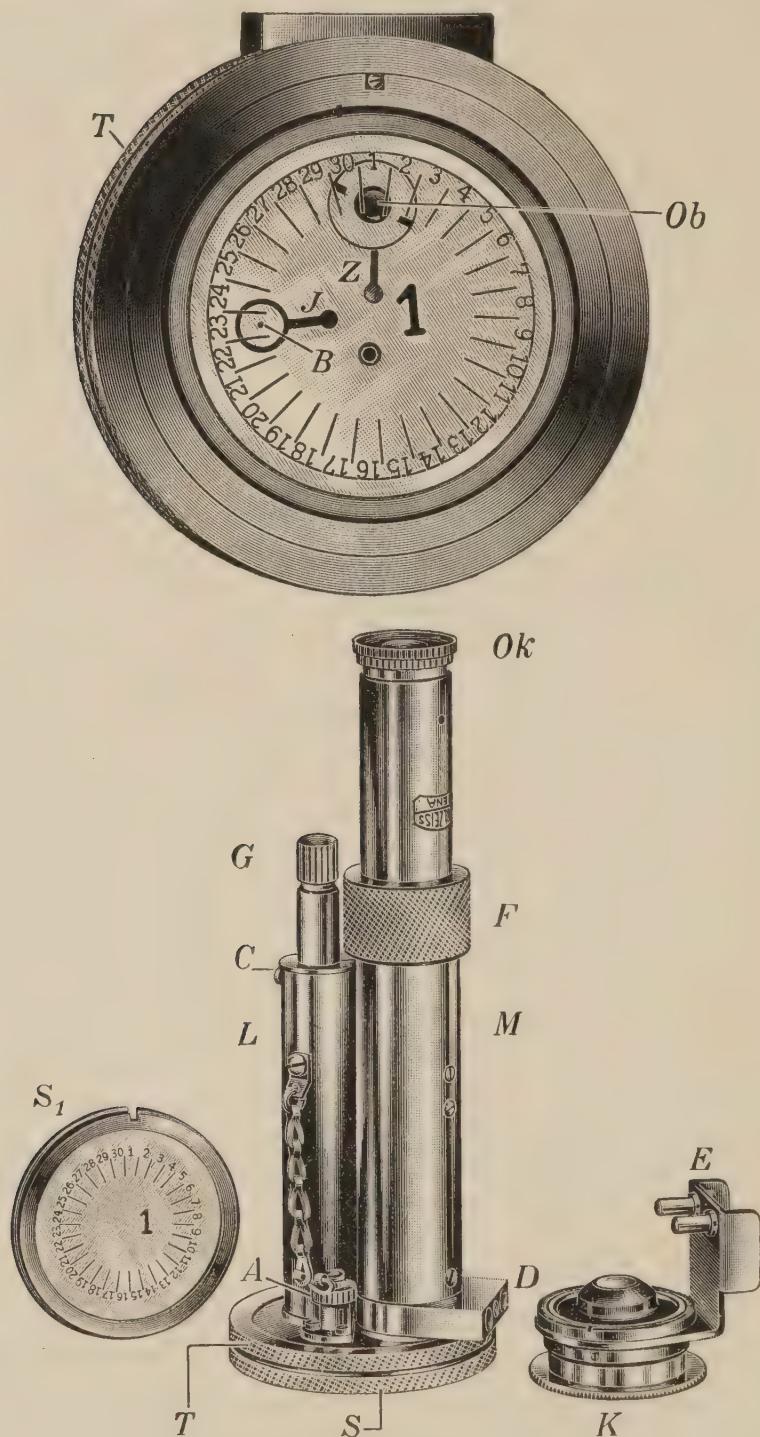


FIG. 34.—Zeiss Konimeter.

small microscope so that these "spots" may be examined and counted without opening the instrument.

A similar instrument made by Carl Zeiss is illustrated in

fig. 34. The glass sampling disc  $S_1$ , shown on the left of the illustration, rests on a ring mount  $S$ , which screws on to the holder  $T$ , pressing the disc tight against a rubber ring. Before assembling,  $S_1$  is smeared with the thinnest possible layer of a suitable adhesive such as "Kaloderma." The holder  $T$  forms the base of the pump  $L$  and microscope  $M$ , and is fitted with the mounted orifice  $A$  (shown in figure with covering cap), for entry of the air sample. The movable piston can be pushed in, against the tension of a strong spring, by means of the handle  $G$ , until it is held by the catch under the knob  $C$ . By pressing the latter the piston flies back, sucking, as in the Kotzé instrument, 5 c.c. of the air under test through the fine jet  $B$ , and causing deposition of dust on the slide  $S_1$ . The position of the jet is indicated on the end view of the instrument shown in the upper portion of fig. 34 by the black line  $J$ . To examine the "spot," the disc  $S$  is turned until the desired field number comes beneath the microscope objective  $Ob$ , indicated by a red line  $Z$ . The microscope may be fitted with an eyepiece,  $Ok$ , containing a squared micrometer, or the latter together with a sector, or simply a sector alone, having an angle of  $18^\circ$ . The two opposite sectors have a total angle of  $36^\circ$ , and together make one-tenth of the total area of the spot formed from the 5 c.c. of air drawn in by the pump. The dust particles are brought into focus by means of the milled ring, and the number on the two sectors counted and taken as representative of 0.5 c.c. If the particles are not distributed regularly around the centre of the spot, counts should be made for the two sectors in several positions by rotation of the eyepiece, and the mean of the figures taken and multiplied by two to give the average number of particles per c.c. At a distance of 0.05 millimetre from one of the sector lines runs a parallel line, which provides a measure of  $5\mu$ , since the magnification of the objective is  $\times 10$ . The total magnifica-

tion of the microscope is  $\times 200$ . Should the number of particles in 5 c.c. of air prove too great for counting, 2·5 c.c. only may be sampled by pushing the piston just beyond the catch and turning it around its axis until the mark on the side is opposite the figure 2·5 c.c. On the piston being released by pressing C, only half the full stroke is made.

On the right-hand side of fig. 34 is shown the dark field condenser K, with a vertical arm fitted with two holding pins E, which may be slipped into the holes D on the projection at the bottom of the microscope. The count of particles is much increased by the use of this condenser over that obtained by examination with a light background.

The South African technique for the examination of dust spots now includes treatment of the slide to eliminate all carbon and particles of matter soluble in water and hydrochloric acid. For satisfactory results the count of the remaining particles must be under 300.

H. L. Green and H. H. Watson<sup>1</sup> have found that the counts obtained with a circular konimeter, similar to the Kotzé or Zeiss instruments, are much lower than the true figures as determined by settlement on microscopic slides fitted in the bottom of cylindrical brass vessels in which samples are taken (three hours being desirable for settlement of all the particles). Thus under favourable conditions this instrument gave only 35 per cent. of the true counts with a light background and about 55 per cent. with a dark background. The Owens instrument (described below) gives 41 per cent. of the number of mineral dust particles obtained by settlement.

**The Owens Dust Collector.**—This instrument, designed

<sup>1</sup> An account of their work is being published in the Special Report Series of the Medical Research Council under the title "Physical Method for the Estimation of the Dust Hazard in Industry (with Special Reference to the Occupation of the Stonemason)."

by Dr. J. S. Owens for the Advisory Committee on Atmospheric Pollution first formed in 1912 and now attached to the Department of Scientific and Industrial Research, differs from the konimeter in that 50 c.c. of the air under examination are taken in by means of a pump, saturated with moisture by passage through a humidifying chamber and then projected through a slit upon an ungreased slide. The velocity of the air through the slit is such that a drop in pressure takes place, with resultant condensation of moisture upon the dust particles, and the "fog" adheres to the glass slide. As the velocity of the air falls off, the pressure and temperature rise and the deposited water particles evaporate from the slide, leaving the dust particles behind. The latest model permits rotation of the cover slip so that several records may be taken on the same slide, the dust deposits showing as lines of uniform width about 1 cm. in length, and crossing each other at the middle of each record. Ample length is available at either end of each record for the microscopic examination of the particles, and for obtaining a number of "counts" over known lengths of the deposit, from which the number of particles per c.c. of air may be calculated. For fuller details of this instrument the reader is referred to the descriptive pamphlets issued by the makers, Messrs. C. F. Casella & Co., London.

Although agreement is not shown by these instruments, any one of them is in reality suitable for comparative tests, since an arbitrary standard may be fixed for each.

*Note.*—Just before going to press H. L. Green has described to the Institution of Mining and Metallurgy a hot-wire precipitator by means of which it is claimed 100 per cent. of the dust particles can be deposited on a cover slip in a thin line which is capable of ready examination under the microscope.

## OXYGEN CORRESPONDING TO VARIOUS PERCENTAGES OF NITROGEN IN THE PROPORTION EXISTING IN FRESH AIR

N <sub>2</sub>	O <sub>2</sub>								
0·0	0·00	4·0	1·06	8·0	2·12	12·0	3·18	16·0	4·24
·1	·02	·1	·08	·1	·14	·1	·20	·1	·26
·2	·03	·2	·11	·2	·17	·2	·23	·2	·29
·3	·08	·3	·14	·3	·20	·3	·26	·3	·31
·4	·10	·4	·16	·4	·22	·4	·28	·4	·34
·5	·13	·5	·19	·5	·25	·5	·31	·5	·36
·6	·16	·6	·22	·6	·28	·6	·34	·6	·39
·7	·18	·7	·24	·7	·30	·7	·36	·7	·42
·8	·21	·8	·27	·8	·33	·8	·39	·8	·45
·9	·24	·9	·30	·9	·36	·9	·41	·9	·47
1·0	·26	5·0	·32	9·0	·38	13·0	·44	17·0	·50
·1	·29	·1	·35	·1	·41	·1	·47	·1	·52
·2	·32	·2	·37	·2	·44	·2	·49	·2	·55
·3	·34	·3	·40	·3	·46	·3	·52	·3	·58
·4	·37	·4	·43	·4	·49	·4	·55	·4	·61
·5	·40	·5	·45	·5	·52	·5	·57	·5	·63
·6	·42	·6	·48	·6	·54	·6	·60	·6	·66
·7	·45	·7	·51	·7	·57	·7	·62	·7	·68
·8	·48	·8	·54	·8	·59	·8	·65	·8	·71
·9	·50	·9	·56	·9	·62	·9	·68	·9	·74
2·0	·53	6·0	·59	10·0	·65	14·0	·71	18·0	·77
·1	·55	·1	·62	·1	·67	·1	·73	·1	·79
·2	·58	·2	·64	·2	·70	·2	·76	·2	·82
·3	·61	·3	·67	·3	·73	·3	·78	·3	·84
·4	·63	·4	·69	·4	·75	·4	·81	·4	·87
·5	·66	·5	·72	·5	·78	·5	·84	·5	·90
·6	·69	·6	·75	·6	·81	·6	·87	·6	·93
·7	·71	·7	·77	·7	·83	·7	·89	·7	·95
·8	·74	·8	·80	·8	·86	·8	·92	·8	·98
·9	·77	·9	·83	·9	·89	·9	·94	·9	·00
3·0	·79	7·0	·85	11·0	·91	15·0	·97	19·0	·03
·1	·82	·1	·88	·1	·94	·1	·00	·1	·05
·2	·85	·2	·91	·2	·97	·2	·02	·2	·08
·3	·87	·3	·93	·3	·99	·3	·05	·3	·11
·4	·90	·4	·96	·4	3·02	·4	·08	·4	·14
·5	·93	·5	·98	·5	·04	·5	·10	·5	·16
·6	·95	·6	2·01	·6	·07	·6	·13	·6	·19
·7	·98	·7	·04	·7	·09	·7	·15	·7	·21
·8	1·01	·8	·06	·8	·12	·8	·18	·8	·24
·9	·03	·9	·09	·9	·15	·9	·21	·9	·27
4·0	·06	8·0	·12	12·0	·18	16·0	·24	20·0	·30

OXYGEN CORRESPONDING TO VARIOUS PERCENTAGES OF NITROGEN IN THE  
 PROPORTION EXISTING IN FRESH AIR (*continued*)

N <sub>2</sub>	O <sub>2</sub>								
20·0	5·30	24·0	6·35	28·0	7·41	32·0	8·47	36·0	9·53
·1	·32	·1	·38	·1	·44	·1	·50	·1	·56
·2	·35	·2	·41	·2	·47	·2	·53	·2	·59
·3	·37	·3	·43	·3	·49	·3	·55	·3	·61
·4	·40	·4	·46	·4	·52	·4	·58	·4	·64
·5	·43	·5	·49	·5	·55	·5	·61	·5	·66
·6	·45	·6	·51	·6	·57	·6	·63	·6	·69
·7	·48	·7	·54	·7	·60	·7	·66	·7	·72
·8	·51	·8	·57	·8	·63	·8	·69	·8	·74
·9	·53	·9	·59	·9	·65	·9	·71	·9	·77
21·0	·56	25·0	·62	29·0	·68	33·0	·74	37·0	·80
·1	·59	·1	·65	·1	·70	·1	·77	·1	·82
·2	·61	·2	·67	·2	·73	·2	·79	·2	·85
·3	·64	·3	·70	·3	·76	·3	·82	·3	·87
·4	·67	·4	·73	·4	·78	·4	·84	·4	·90
·5	·69	·5	·75	·5	·81	·5	·87	·5	·93
·6	·72	·6	·78	·6	·84	·6	·90	·6	·95
·7	·75	·7	·80	·7	·86	·7	·92	·7	·98
·8	·77	·8	·83	·8	·89	·8	·95	·8	10·01
·9	·80	·9	·86	·9	·92	·9	·98	·9	·03
22·0	·82	26·0	·88	30·0	·94	34·0	·900	38·0	·06
·1	·85	·1	·91	·1	·97	·1	·03	·1	·09
·2	·88	·2	·94	·2	·8·00	·2	·06	·2	·11
·3	·90	·3	·96	·3	·02	·3	·08	·3	·14
·4	·93	·4	·99	·4	·05	·4	·11	·4	·16
·5	·96	·5	7·02	·5	·08	·5	·14	·5	·19
·6	·98	·6	·04	·6	·10	·6	·16	·6	·22
·7	6·01	·7	·07	·7	·13	·7	·19	·7	·24
·8	·04	·8	·10	·8	·16	·8	·21	·8	·27
·9	·06	·9	·12	·9	·18	·9	·24	·9	·30
23·0	·09	27·0	·15	31·0	·21	35·0	·27	39·0	·32
·1	·12	·1	·17	·1	·23	·1	·29	·1	·35
·2	·14	·2	·20	·2	·26	·2	·32	·2	·38
·3	·17	·3	·23	·3	·29	·3	·35	·3	·40
·4	·20	·4	·26	·4	·32	·4	·37	·4	·43
·5	·22	·5	·28	·5	·34	·5	·40	·5	·46
·6	·25	·6	·31	·6	·37	·6	·43	·6	·48
·7	·27	·7	·34	·7	·40	·7	·45	·7	·51
·8	·30	·8	·36	·8	·42	·8	·48	·8	·54
·9	·33	·9	·39	·9	·45	·9	·51	·9	·56
24·0	·35	28·0	·41	32·0	·47	36·0	·53	40·0	·59

OXYGEN CORRESPONDING TO VARIOUS PERCENTAGES OF NITROGEN IN THE  
 PROPORTION EXISTING IN FRESH AIR (*continued*)

N <sub>2</sub>	O <sub>2</sub>								
40·0	10·59	44·0	11·65	48·0	12·71	52·0	13·77	56·0	14·83
·1	·61	·1	·67	·1	·73	·1	·79	·1	·85
·2	·64	·2	·70	·2	·76	·2	·82	·2	·88
·3	·67	·3	·73	·3	·79	·3	·84	·3	·90
·4	·69	·4	·75	·4	·81	·4	·87	·4	·93
·5	·72	·5	·78	·5	·84	·5	·90	·5	·96
·6	·75	·6	·81	·6	·87	·6	·93	·6	·99
·7	·77	·7	·83	·7	·89	·7	·95	·7	15·01
·8	·80	·8	·86	·8	·92	·8	·98	·8	·04
·9	·83	·9	·88	·9	·95	·9	14·01	·9	·07
41·0	·85	45·0	·91	49·0	·97	53·0	·04	57·0	·10
·1	·88	·1	·94	·1	13·00	·1	·06	·1	·12
·2	·91	·2	·97	·2	·03	·2	·09	·2	·15
·3	·93	·3	·99	·3	·05	·3	·11	·3	·17
·4	·96	·4	12·02	·4	·08	·4	·14	·4	·20
·5	·99	·5	·05	·5	·11	·5	·17	·5	·22
·6	11·01	·6	·07	·6	·13	·6	·20	·6	·25
·7	·04	·7	·10	·7	·16	·7	·22	·7	·27
·8	·07	·8	·13	·8	·19	·8	·25	·8	·30
·9	·09	·9	·15	·9	·21	·9	·27	·9	·33
42·0	·12	46·0	·18	50·0	·24	54·0	·30	58·0	·36
·1	·15	·1	·21	·1	·26	·1	·32	·1	·38
·2	·17	·2	·23	·2	·29	·2	·35	·2	·41
·3	·20	·3	·26	·3	·31	·3	·37	·3	·43
·4	·23	·4	·28	·4	·34	·4	·40	·4	·46
·5	·25	·5	·31	·5	·37	·5	·43	·5	·49
·6	·28	·6	·34	·6	·40	·6	·46	·6	·52
·7	·31	·7	·36	·7	·42	·7	·48	·7	·54
·8	·33	·8	·39	·8	·45	·8	·51	·8	·57
·9	·36	·9	·42	·9	·48	·9	·53	·9	·59
43·0	·38	47·0	·44	51·0	·51	55·0	·56	59·0	·62
·1	·41	·1	·47	·1	·53	·1	·58	·1	·64
·2	·44	·2	·50	·2	·56	·2	·61	·2	·67
·3	·46	·3	·52	·3	·58	·3	·64	·3	·70
·4	·49	·4	·55	·4	·61	·4	·67	·4	·73
·5	·52	·5	·58	·5	·63	·5	·69	·5	·75
·6	·54	·6	·61	·6	·66	·6	·72	·6	·78
·7	·57	·7	·63	·7	·69	·7	·74	·7	·80
·8	·59	·8	·66	·8	·72	·8	·77	·8	·83
·9	·62	·9	·68	·9	·74	·9	·80	·9	·86
44·0	·65	48·0	·71	52·0	·77	56·0	·83	60·0	·89

OXYGEN CORRESPONDING TO VARIOUS PERCENTAGES OF NITROGEN IN THE  
PROPORTION EXISTING IN FRESH AIR (*continued*)

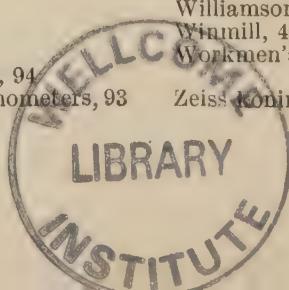
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60·0	15·89	64·0	16·95	68·0	18·01	72·0	19·07	76·0	20·12
·1	·91	·1	·98	·1	·04	·1	·10	·1	·15
·2	·94	·2	17·00	·2	·06	·2	·12	·2	·18
·3	·96	·3	·03	·3	·09	·3	·15	·3	·20
·4	·99	·4	·05	·4	·12	·4	·18	·4	·23
·5	16·02	·5	·08	·5	·14	·5	·20	·5	·25
·6	·05	·6	·10	·6	·17	·6	·23	·6	·28
·7	·08	·7	·13	·7	·20	·7	·26	·7	·31
·8	·10	·8	·16	·8	·22	·8	·28	·8	·33
·9	·13	·9	·18	·9	·25	·9	·31	·9	·36
61·0	·16	65·0	·21	69·0	·28	73·0	·33	77·0	·39
·1	·19	·1	·24	·1	·30	·1	·36	·1	·41
·2	·21	·2	·26	·2	·33	·2	·39	·2	·44
·3	·24	·3	·29	·3	·35	·3	·41	·3	·47
·4	·26	·4	·32	·4	·38	·4	·44	·4	·49
·5	·29	·5	·35	·5	·41	·5	·47	·5	·52
·6	·31	·6	·37	·6	·43	·6	·49	·6	·55
·7	·34	·7	·40	·7	·46	·7	·52	·7	·57
·8	·37	·8	·43	·8	·49	·8	·54	·8	·60
·9	·39	·9	·45	·9	·51	·9	·57	·9	·63
62·0	·42	66·0	·48	70·0	·54	74·0	·60	78·0	·65
·1	·45	·1	·50	·1	·57	·1	·62	·1	·68
·2	·47	·2	·53	·2	·59	·2	·65	·2	·71
·3	·50	·3	·56	·3	·62	·3	·67	·3	·73
·4	·52	·4	·59	·4	·64	·4	·70	·4	·76
·5	·55	·5	·62	·5	·67	·5	·73	·5	·79
·6	·58	·6	·64	·6	·70	·6	·75	·6	·81
·7	·60	·7	·67	·7	·72	·7	·78	·7	·84
·8	·63	·8	·69	·8	·75	·8	·81	·8	·87
·9	·66	·9	·72	·9	·78	·9	·83	·9	·89
63·0	·68	67·0	·74	71·0	·80	75·0	·86	79·0	·92
·1	·71	·1	·77	·1	·83	·1	·88	·1	·94
·2	·74	·2	·80	·2	·86	·2	·91	·2	·97
·3	·77	·3	·82	·3	·88	·3	·94	·3	21·00
·4	·79	·4	·85	·4	·91	·4	·96	·4	·02
·5	·82	·5	·87	·5	·94	·5	·99	·5	·05
·6	·84	·6	·90	·6	·96	·6	20·02	·6	·08
·7	·87	·7	·93	·7	·99	·7	·04	·7	·10
·8	·90	·8	·95	·8	19·02	·8	·07	·8	·13
·9	·93	·9	·98	·9	·04	·9	·09	·9	·15
64·0	·95	68·0	18·01	72·0	·07	76·0	·12	80·0	·18

OXYGEN CORRESPONDING TO VARIOUS PERCENTAGES OF NITROGEN IN THE PROPORTION EXISTING IN FRESH AIR (*continued*)

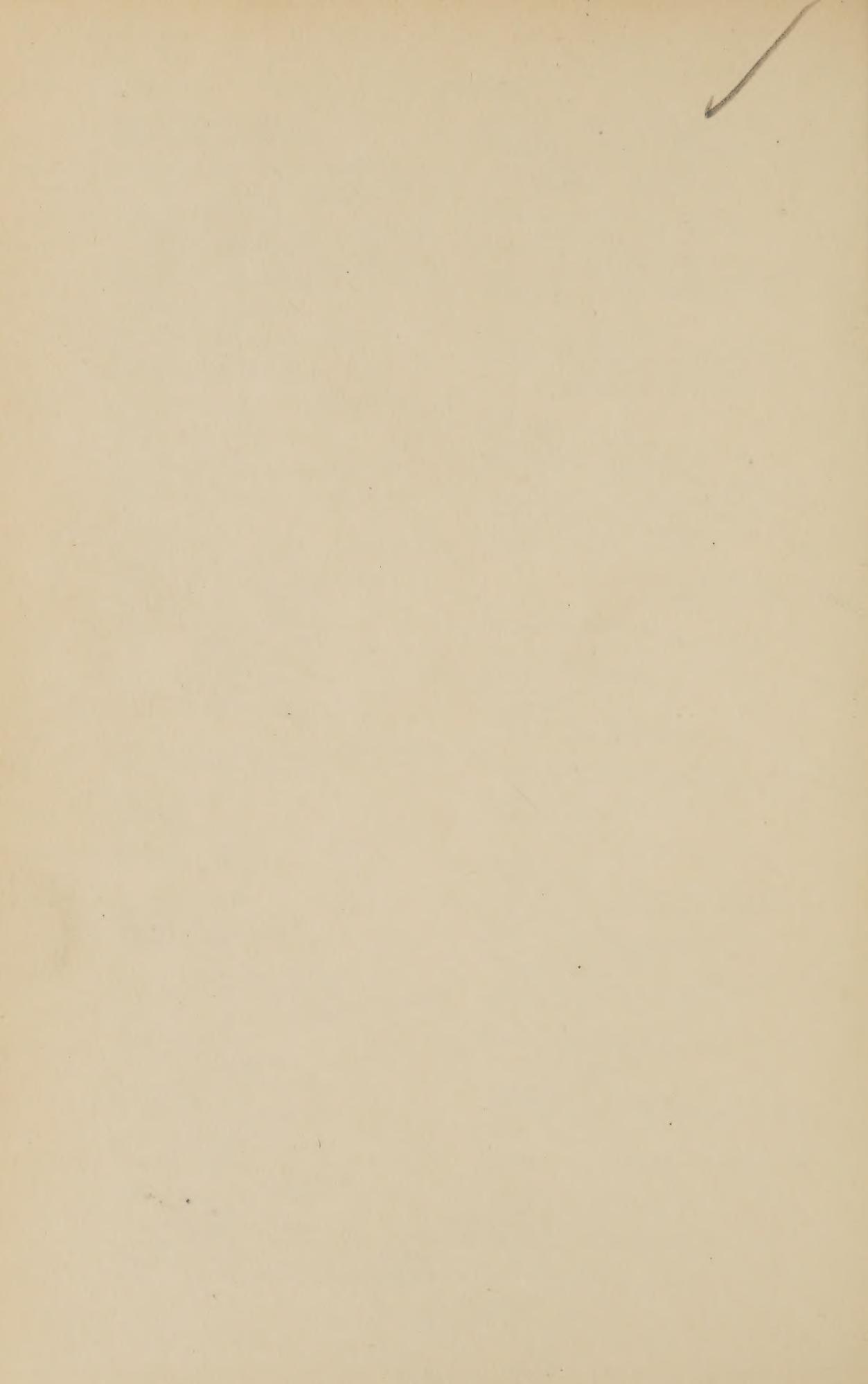
N <sub>2</sub>	O <sub>2</sub>								
80·0	21·18	84·0	22·24	88·0	23·30	92·0	24·36	96·0	25·42
·1	·20	·1	·27	·1	·33	·1	·39	·1	·45
·2	·23	·2	·30	·2	·35	·2	·42	·2	·47
·3	·26	·3	·32	·3	·38	·3	·44	·3	·50
·4	·29	·4	·35	·4	·41	·4	·47	·4	·53
·5	·31	·5	·38	·5	·43	·5	·49	·5	·55
·6	·34	·6	·40	·6	·46	·6	·52	·6	·58
·7	·37	·7	·43	·7	·49	·7	·55	·7	·61
·8	·39	·8	·46	·8	·51	·8	·57	·8	·63
·9	·42	·9	·48	·9	·54	·9	·60	·9	·66
81·0	·45	85·0	·51	89·0	·56	93·0	·63	97·0	·69
·1	·47	·1	·53	·1	·59	·1	·65	·1	·71
·2	·50	·2	·56	·2	·62	·2	·68	·2	·74
·3	·52	·3	·59	·3	·64	·3	·70	·3	·77
·4	·55	·4	·62	·4	·67	·4	·73	·4	·79
·5	·58	·5	·64	·5	·70	·5	·76	·5	·82
·6	·61	·6	·67	·6	·72	·6	·79	·6	·85
·7	·63	·7	·69	·7	·75	·7	·81	·7	·87
·8	·66	·8	·72	·8	·77	·8	·84	·8	·90
·9	·69	·9	·75	·9	·80	·9	·87	·9	·93
82·0	·71	86·0	·77	90·0	·83	94·0	·89	98·0	·95
·1	·74	·1	·80	·1	·86	·1	·92	·1	·98
·2	·77	·2	·83	·2	·88	·2	·95	·2	26·01
·3	·79	·3	·85	·3	·91	·3	·97	·3	·03
·4	·82	·4	·88	·4	·94	·4	25·00	·4	·06
·5	·85	·5	·90	·5	·96	·5	·02	·5	·09
·6	·87	·6	·93	·6	·99	·6	·05	·6	·11
·7	·90	·7	·96	·7	24·02	·7	·08	·7	·14
·8	·93	·8	·99	·8	·04	·8	·10	·8	·17
·9	·95	·9	23·01	·9	·07	·9	·13	·9	·19
83·0	·98	87·0	·04	91·0	·10	95·0	·16	99·0	·22
·1	22·01	·1	·06	·1	·12	·1	·19	·1	·25
·2	·03	·2	·09	·2	·15	·2	·22	·2	·27
·3	·06	·3	·11	·3	·18	·3	·24	·3	·30
·4	·08	·4	·14	·4	·20	·4	·27	·4	·32
·5	·11	·5	·17	·5	·23	·5	·29	·5	·35
·6	·14	·6	·19	·6	·26	·6	·32	·6	·38
·7	·16	·7	·22	·7	·28	·7	·34	·7	·40
·8	·19	·8	·25	·8	·31	·8	·37	·8	·43
·9	·22	·9	·27	·9	·34	·9	·40	·9	·46
84·0	·24	88·0	·30	92·0	·36	96·0	·42	100·0	·48

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