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Gas Analysis by Absorption

Albert D. McMahon

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Mc Mahon, A.

GAS ANALYSIS BY ABSORPTION

A Thesis

Presented to

the Faculty of the Metallurgical Department
the Montana State School of Mines

In Partial Fulfillment

of the Requirements for the Degree
Bachelor of Science in Metallurgical Engineering

by

Albert D. McMahon

May 1941

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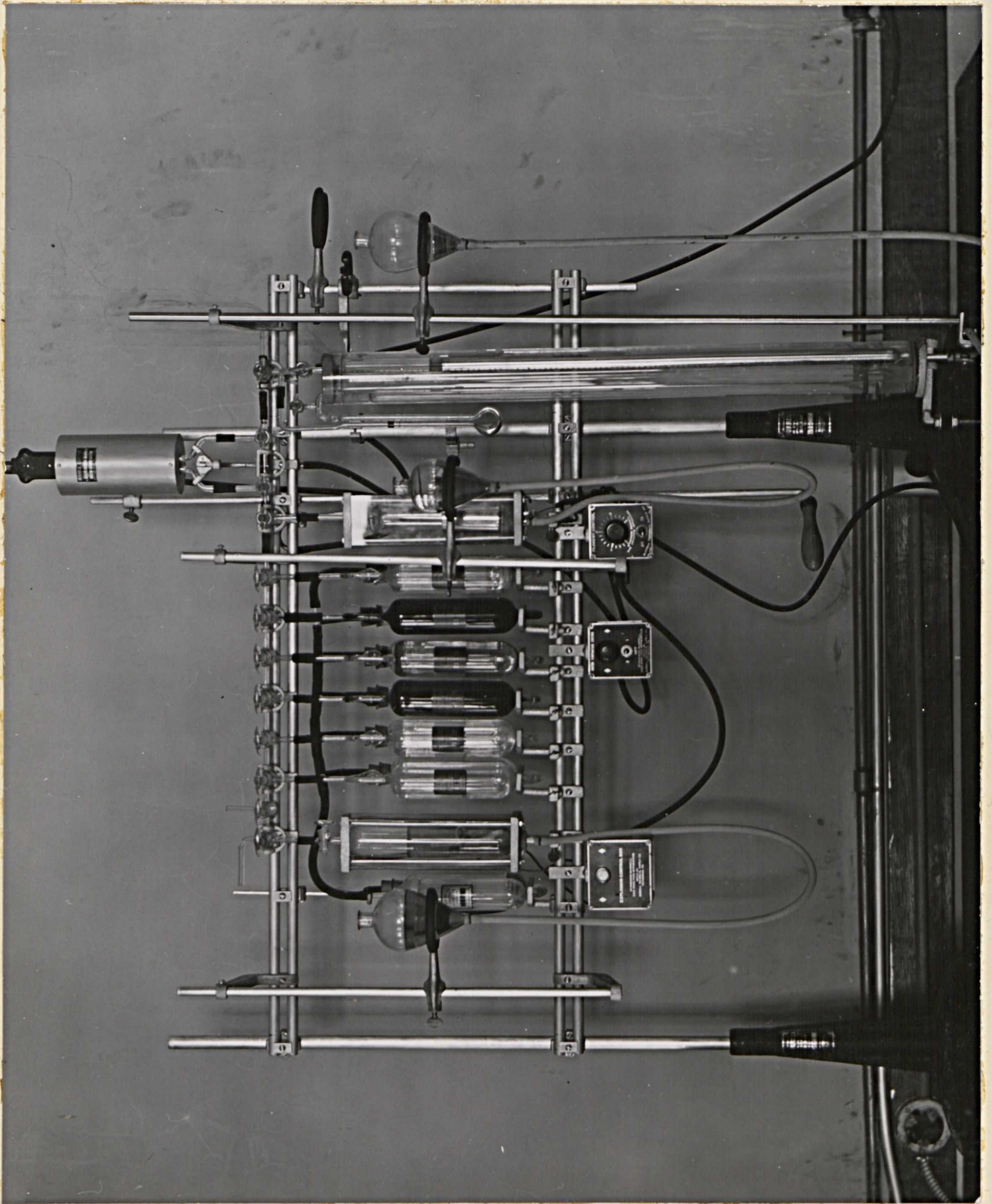
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CHAPTER I

INTRODUCTION

The object of work done for the preparation of this thesis was to become familiar with the operation and manipulation of the Burrell "Build Up" Premier Model B gas analysis apparatus used at the School of Mines. Although the manipulation of the apparatus is routine, it is precise, and a thorough knowledge of the function of each part of the machine should be gained before a complete analysis of any gaseous mixture is attempted.

References:

- "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases" 1927
- "Burrell Manual for Gas Analysts" 1937
- "Fuel and Flue Gases" A. G. A. 1940
- "The Analysis of Natural Gas" Curtis L. Wilson
Glück Auf December 1937
- "Standard Methods of Chemical Analysis"
Wilfred W. Scott 1927

Much information is available in the references mentioned pertaining to the principle, action, operation, and reactions of the apparatus. Under manipulation I shall try to stress the different operations which caused me trouble and the helpful suggestions I received from Mr. Harrity and Mr. Willis, chemists at the A. C. M. Company laboratory.

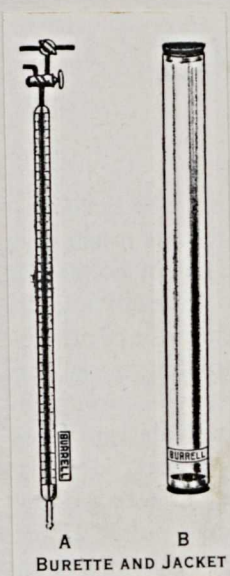
Many different gaseous mixtures are not available at the School of Mines, meaning of course the different commercial gases, such as: blast furnace gas, coal gas, coke oven gas, carburetted water gas, etc. Nevertheless from the natural gas, the flue gas of the boiler furnace and a few prepared gases, samples can be obtained which will contain all of the constituents that the gas analysis apparatus is capable of determining. There may be a large difference in the composition of gaseous mixtures, but those produced or consumed in the ordinary industrial processes are made up principally of the components which may be determined quantitatively by the Burrell model.

There is practically only one method of gas analysis. This was worked out many years ago by Bunsen, Hempel, and Winkler and consists in the successive absorption with different chemicals of the various constituents of the gas. The only improvement to this method is the oxidation and combustion of different components of a mixture followed by absorption.

CHAPTER II

DESCRIPTION OF THE APPARATUS

Frame.--This consists of two metal standards upon which are mounted four cross-bars that support the pipettes and electrical control boxes. The water jacket for the burette is fastened at the bottom to the stand of the right hand standard.



Burette.--The burette is of the Schellbach type graduated downward from the top stopcock. It was calibrated by the maker at 20°C and has a standard tolerance of 0.2 ml. The burette is surrounded by a water jacket which makes temperature corrections unnecessary by maintaining the gas sample at the same temperature throughout the period of analysis.

Mercury is used as the confining liquid and is raised or lowered in the burette by a leveling bulb which is connected to the bottom of the burette by a rubber tube.

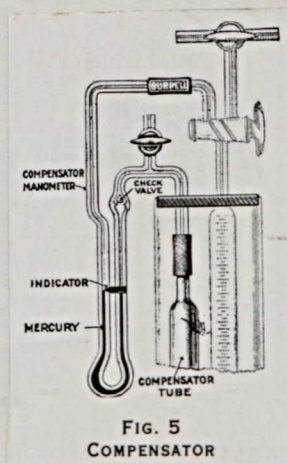


FIG. 5
COMPENSATOR

Compensator.--This device is a U-tube manometer, one leg communicating with the burette and the other being connected to a closed glass tube, approximately the same size as the burette, which is also contained in the water jacket. The air inside the closed end tube is maintained in a saturated condition by a small amount of water in the tube and the pressure responds to any changes in temperature of the jacket water as does the gas in the burette. The measurement

of gas volumes in the burette is made by balancing the pressure of the gas in the burette against that of the saturated air in the closed tube. This compensator allows the measuring of gases under pressures independent of atmospheric pressure.

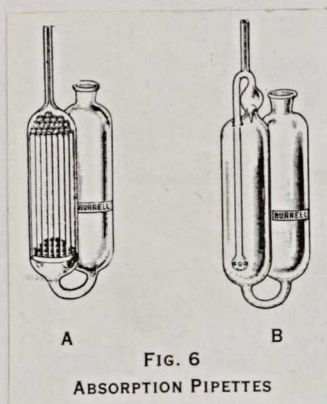


FIG. 6
ABSORPTION PIPETTES

Absorption Pipettes.--These pipettes are of the Francis Automatic Bubbling type which bring the gas in contact with the solution in the form of small bubbles. This is desirable for two reasons. First, the gas comes into better contact with the absorbing solution. Second, the bubbling action keeps the solution well mixed increasing its life.

The bulb on the end of the bubbling tube also prevents the bubbles from being carried into the reservoir chamber.

The rear chambers of the pipettes are connected to a common manifold which terminates in a contact pipette filled with caustic solution. This prevents air from coming in contact with the absorbing solutions and eliminates the use of individual rubber bags.

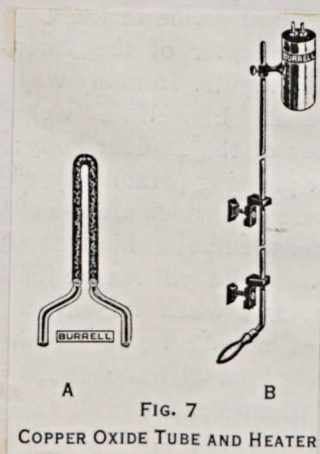
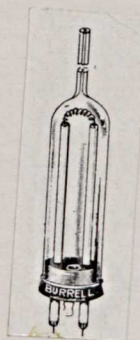


FIG. 7
COPPER OXIDE TUBE AND HEATER

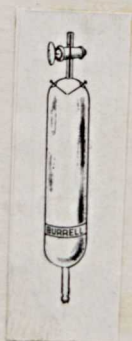
Copper Oxide Tube.--The copper oxide tube is made of pyrex shell tubing having an outside diameter of 7 mm. and an inside diameter of 5 mm. It is mounted above the manifold to provide proper drainage, minimize the possibility of mercury or reagents entering and spoiling the copper oxide, and because it must be heated, to keep it away from the pipettes so that the absorbing solutions

will not be heated. The U part of the tube is filled to the first bend in each of the legs with fine wire copper oxide containing some particles of metallic copper. The copper acts as a catalyst in the oxidation of hydrogen and carbon monoxide.

The electric heater for the copper oxide tube consists of a heating element coiled around an alundum tube which is insulated from the jacket with silicojel or magnesium oxide, sodium silicate and fiber asbestos. The heater is fastened to a rod provided with a wooden handle and clamp support so that it can be raised and lowered over the tube.



Slow Combustion Pipette.--The slow combustion pipette is a 180 ml. pyrex glass shell having a rubber stopper in the bottom which supports two small mercury filled pyrex glass tubes. A piece of copper wire is sealed in the bottom of each tube for connection to the slow combustion control box. The heating element is a piece of platinum wire about five inches long, bent and coiled so that it will stay in the tubes when the mercury is raised over it. A rubber tube connects a leveling bottle to the bottom of the pipette. Mercury is also used here to draw in and force out gas. A blower tube with holes in the bottom encircles the top of the pipette and cools it after a gas has been burned.



Explosion Pipette.--The explosion pipette is a pyrex glass shell having glass tubes at both ends, the upper one fitted with a stopcock and the lower one connected to a leveling bulb. Two platinum electrodes are fused through the walls of the upper portion of the shell and the outer ends are connected to the explosion control box. The ends of the

electrodes inside the pipette are set about one sixteenth of an inch apart and when a spark is caused to jump between the two, the explosive mixture of gases in the pipette is ignited. This pipette is also used for flushing, using a five per cent solution of sulphuric acid or a five per cent solution of sodium sulphate colored with methyl orange as a flushing solution. For this reason it is located farthest away from the burette.

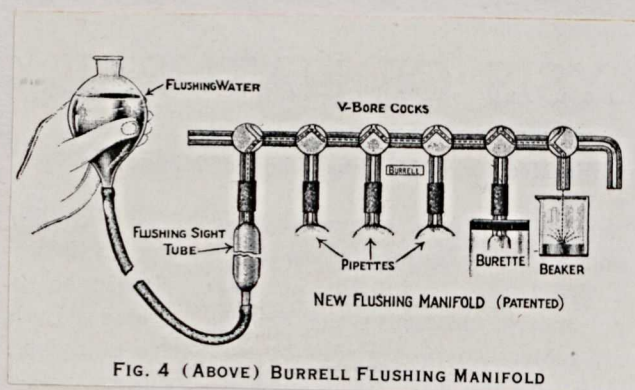


FIG. 4 (ABOVE) BURRELL FLUSHING MANIFOLD

The Manifold.--The

manifold is made of one fourth inch outside diameter capillary tubing. It is divided into two sections, one short one and a long one. This allows substitution and elimination of parts

and also the divided manifold is easier and cheaper to make. The stopcocks are all in the horizontal header and have a three way V bore which allows the filling of all capillary space in the apparatus which is essential in avoiding small errors.

CHAPTER III

ABSORBING SOLUTIONS

For Carbon Dioxide, CO₂.

Sodium and Potassium Hydroxides.--For the determination of carbon dioxide, solutions of both sodium and potassium hydroxides are used. The concentration of the solutions recommended in "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases".

Potassium Hydroxide Solution:

Potassium Hydroxide (pure electrolytic)	360 gms.
Water to make	1000 ml.

Sodium Hydroxide Solution:

Sodium Hydroxide (pure electrolytic)	315 gms.
Water to make	1000 ml.

These solutions are equally good for the absorption of carbon dioxide. The potassium hydroxide is said to have the greater capacity for the gas and to be more rapid than sodium hydroxide, but the caustic soda solution is cheaper than the potash and does not have a tendency to foam when gas is bubbled through it, as potassium hydroxide does. In either case, that purified by electrolysis is specified, because the same alkalis are generally used in preparing alkaline pyrogallol solutions for the determination of oxygen, and the hydroxides purified with alcohol causes these solutions to give off carbon monoxide gas.

If the gas contains components of an acid character, such as:

sulphur dioxide, hydrogen sulphide, hydrocy anic acid or cyanogen, these components should be removed before the carbon dioxide, otherwise they will be absorbed by the caustic solutions and measured as carbon dioxide. The caustic solutions also absorb some of the illuminants, especially benzene, until they become saturated with these gases.

Barium Hydroxide:--This reagent is used for determining small amounts of carbon dioxide, as in air.

Barium Hydroxide Solution.

Barium Hydroxide	14 gms.
Barium Chloride	1 gm.
Water to make	1000 ml.

One ml. of this solution is equal to approximately one ml. of CO₂ measured at standard conditions. With this reagent a liter or more of gas may be collected in a flask, an accurately measured portion of barium hydroxide shaken well with the gas and the excess hydroxide titrated with oxalic acid. The oxalic acid solution is prepared by dissolving 5.3653 gms. of pure crystallized oxalic acid in one liter of freshly boiled water. The barium chloride is added to secure a better end point and phenolphthelein is the indicator used.

For Illuminants.--(Ethylene, propylene, acetylene, butylene, benzene and the higher paraffins.)

Fuming Sulphuric Acid.--When separation of the illuminants is not desired, fuming sulphuric acid, containing an excess of 15 per cent to 20 per cent SO₃ is used.

This reagent absorbs the higher paraffin hydrocarbons, such as:

pentane, C_5H_{12} , and hexane, C_6H_{14} , probably by solution. But the olefins, such as, ethylene, C_2H_4 , propylene, C_3H_6 , and butylene C_4H_8 ; the aromatic hydrocarbons, such as, benzene, C_6H_6 ; and acetylene, C_2H_2 , are absorbed by direct chemical action. Passage of a gas through a fuming sulphuric acid pipette always carries some fumes with it, so that it is necessary to pass the gas through the caustic pipette after each treatment.

Bromine Water.--This reagent has been used by some chemists for absorbing illuminants, but because of its properties it is not suitable for use in pipettes.

For Oxygen:

The reagents most commonly used for the absorption of oxygen are a strongly alkaline solution of sodium or potassium pyrogallate, and yellow phosphorous in stick form. But chromous chloride is the most rapid and for some purposes the most accurate.

Potassium Pyrogallate Solution.--A stock solution of potassium hydroxide is prepared by dissolving 600 gms. of electrolytic potassium hydroxide in water and diluting to 1000 ml. with water. A stock solution of pyrogallic acid in 800 ml. of water and diluting to one liter. To prepare the pyrogallate solution for use, 50 ml. of the pyrogallic acid solution is put into the pipette and to this is added 175 ml. of the potassium hydroxide solution. The pipette is then closed with a rubber stopper to protect the solution from the air, and the two solutions are thoroughly mixed.

Sodium Pyrogallate Solution.--This solution is made up by

dissolving one part of pure sodium hydroxide in one part of water. 160 ml. of this solution is then mixed in the pipette with 65 ml. of the pyrogallic acid solution described above.

These solutions absorb oxygen fairly rapidly when fresh, but after they have absorbed eight to ten volumes of the gas, they gradually become slower in action. Their absorbing power is also affected by temperature, the rate becoming very slow at 0°C. The use of potash or caustic soda purified by alcohol is prohibited as the solutions made from them give off carbon monoxide. Being strongly alkaline, these solutions will absorb any or all the gases absorbed by the potassium or sodium hydroxide solutions.

Yellow Phosphorous has been extensively used for the absorption of oxygen in some gases. It is prepared by casting it into small sticks about four to six mm. in diameter. To prepare the sticks the phosphorous is placed under water in a test tube and heated in a bath to about 50°C. A glass tube of the proper internal diameter is pushed down into the molten phosphorous and by means of suction is filled to a desired height when the tube is withdrawn and immediately dipped into cold water. The solidified phosphorous is then pushed out with a glass rod into the reagent pipette, also filled with water. When in use, the water in the pipette should be changed occasionally to remove the oxides of phosphorous in solution. Also the chamber of the pipette containing the phosphorous should be covered with a piece of black paper to protect it from light which converts it into red phosphorous.

This reagent cannot be used on a gas rich in oxygen, such as air, because the reaction of the phosphorous with the oxygen generates so much heat that the phosphorous is fused into a solid mass. Also it cannot be used on gases containing small amounts of ethylene, benzene, alcohol, petroleum vapors or ammonia, as these substances prevent its action on oxygen.

Chromous Chloride.--Though it is the most rapid absorbent for oxygen it is not much used because of its strong reducing properties and the difficulty of preparing and keeping it in a reduced state. It can be obtained from the Burrell Technical Supply Company under the name of Ox-sorbent.

Managanous Hydroxide.--When freshly formed, this compound, which is a white precipitate in a water solution, absorbs oxygen strongly, being oxidized to manganic hydroxide, which is brown. When the manganic hydroxide is treated with potassium iodide and sulphuric acid, iodine is liberated giving the solution a pink tint. The test is made quantitative by titrating the liberated iodine with sodium thiosulphate.

For Carbon Monoxide.

The reagents used for the absorption of carbon monoxide are ammoniacal cuprous chloride, acid cuprous chloride and cuprous sulphate-beta naphthol mixture.

Ammonical Cuprous Chloride Solution--Stock Solution

Ammonium Chloride

300 gms.

Cuprous Chloride	270 gms.
Water to make	1000 ml.

To prepare the solution for use, one volume of ammonium hydroxide is required to three of the stock solution. On account of the excess ammonia used, ammonia fumes are liable to be carried out with the gas after each absorption, therefore it is necessary to pass the gas through an acid pipette after absorbing the carbon monoxide. For this reason, acid cuprous chloride is preferable. It is prepared as follows:

Acid Cuprous Chloride Solution

Cuprous chloride	75 gms.
Hydrochloric Acid	600 ml.
Water to make	1000 ml.

As a precaution against hydrochloric acid fumes being carried out of the pipette, the gas should always be passed through the caustic pipette after treatment with it.

Both these solutions absorb oxygen and therefore must be protected from the air.

In the acid and ammoniacal solutions, the cuprous chloride has a strong tendency to oxidize and it is necessary that the solution be kept in a reduced condition. A few pieces of fine copper wire or a strip of copper gauze kept in the stock solution and in the reservoir arm of the pipette keeps the cuprous chloride from oxidizing. The color of the acid solution should be a yellowish green or straw color and a few drops added to water should give a white precipitate.

Stannous chloride solution may also be used to reduce the acid solution. Having a straw colored solution is an important point, for if it has a greenish color it will absorb other gases.

The action of these solutions depends upon the formations of an unstable compound having the formula $\text{Cu}_2 \text{Cl}_2 \cdot 2\text{CO}$. Fresh solutions, therefore, absorb all the carbon monoxide in the gas, but after the solution has absorbed a certain amount it becomes very unstable and will give up carbon monoxide to a gas carrying a small amount of this constituent. This drawback is overcome by passing the gas through two or three pipettes in series keeping the last one charged with a fresh solution. Also one pipette of the cuprous chloride solution may be used with one of cuprous sulphate-beta naphthol mixture the gas being passed first into the cuprous chloride pipette to remove most of the carbon monoxide and then into the cuprous sulphate mixture which is prepared as follows:

Cuprous Sulphate-Beta Naphthol Mixture (pipette charge)

Cuprous Oxide (Prepared by wet process)	20 gms.
Sulphuric Acid	200 ml.
Water (Distilled)	25 ml.
Beta Naphthol	25 gms.

The acid is added to the water and allowed to cool. The cuprous oxide is placed in a porcelain mortar, the dilute acid is added a little at a time, and these ingredients are quickly and thoroughly mixed by rubbing, or grinding, with a pestle until all the oxide is in suspension. Then the beta naphthol is added and mixed

with the suspension in the same way. After filtering through glass wool to remove unmixed particles of beta naphthol, the mixture is ready for use and should be put into the pipette at once as it slowly absorbs oxygen from the air.

The cupric oxide forms cuprous sulphate, which is slightly soluble and very stable in the sulphuric acid used. With carbon monoxide the sulphate forms $\text{Cu}_2 \text{SO}_4 \cdot 2\text{CO}$, which is a stable compound and the mixture does not liberate CO, as does the cuprous chloride solution. This mixture will absorb about eighteen times its own volume of carbon monoxide. The cuprous sulphate mixture absorbs ethylene, propylene, butylene, some acetylene, and a little oxygen, but does not absorb methane, other saturated hydrocarbons, hydrogen or nitrogen.

Carbon monoxide is also determined indirectly by combustion with oxygen in the explosion pipette or the slow combustion pipette. It is burned to CO_2 which is absorbed by potassium hydroxide. The volume of CO_2 absorbed is the same as the amount of CO burned. The copper oxide tube offers another method of determining carbon monoxide. The CuO gives up its oxygen to form CO_2 which is absorbed and the contraction is measured as CO.

For Hydrogen.

There is no absorbent for hydrogen that can be used in a pipette. It is determined by combustion with oxygen in the explosion or slow combustion pipettes or by oxidation in the copper oxide tube.

For Ethane and Methane.

The ethane and methane are determined by burning the gas with

an excess of oxygen preferably by the slow combustion method. The contractions due to the formation of water and absorption of the CO_2 formed are the basis for the calculations of the amount of these two components present. These calculations appear under "Operation of the Apparatus".

The components of a gaseous mixture are determined in a definite order, namely; carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, ethane and methane. If they are not removed from the gas in this order, the results will be wrong, because the determination of one will interfere with the determination of the other. In the case of the absorbing solutions, that used to remove any given constituent will also absorb some of the gases preceding it in the list.

CHAPTER IV

OPERATION OF THE APPARATUS

Importance of Sampling.--Here it is only necessary to point out that if the sample does not truly represent the gas to be analyzed, the analysis will mean nothing no matter how accurately it is made. Methods of sampling, therefore, should receive the same careful attention as the methods of analysis.

The factors to be considered in obtaining a representative gas sample are the possibility of variations in the composition of the gas, the location of the sampling point, types of sample containers, suitability of displacing liquids, selection of sampling tubes and connections between the sampling tube and the sample container.

Care of Stopcocks.--To keep the stopcocks in good condition they must be kept well lubricated. For the gas analysis apparatus ordinary vaseline is not suitable being too light to give a seal against high pressures. A good stopcock grease is made by melting one part rubber and adding one part beeswax. This is then thinned down to the consistency desired with vaseline. Unless a good stopcock lubricant is obtained the apparatus is liable to develop a leak in the midst of an analysis.

Testing for Leaks.--Draw fifty ml. or more into the burette. Then turn the stopcocks so that the manifold is open from the burette to the flushing pipette. Now close the stopcock at the top of the flushing pipette and raise the burette leveling bulb so as to put the

air in the burette under about ten inches of pressure. If the level of the mercury in the burette does not rise within fifteen or twenty minutes the manifold connections and stopcocks may be considered gas tight. A rise indicates a leak, which must be located by testing each stopcock and connection in succession.

Eliminating Dead Capillary Space.--One important advantage of the Flushing Manifold on the laboratory model is that the dead capillary space in the manifold can be entirely eliminated. To do this, level all pipette solutions at the stopcocks in the header and set all manifold stopcocks so as to seal off the pipettes and to establish a clear path across the manifold. Fill the capillary of the manifold with acidified colored solution by raising the flushing leveling bulb until the liquid runs out of the opposite end. Turn the burette stopcock toward the source of the sample and draw the gas into the burette. After the sample has been obtained and measured raise the burette leveling bulb a little to put the gas in the burette under pressure and open burette cock to the manifold. Lower the flushing bulb until the colored liquid is drawn back just past the potassium hydroxide pipette which is the first pipette ordinarily used.

After the carbon dioxide is absorbed draw the potassium hydroxide solution up to the manifold and allow the colored liquid to follow the gas back towards the burette stopping the liquid just at the burette stopcock.

If this procedure is followed throughout the analysis, there will be no gas remaining in the manifold at any time.

Measuring the Sample.--To avoid calculations as far as possible all analyses are made on 100 ml. of sample, so that the difference in burette readings give per cent by volume.

The sample is trapped in the burette by turning the lower stopcock in the burette a half turn. The manifold is filled, with liquid from the flushing pipette, to the top stopcock of the burette. The sample is allowed to stand for three minutes to let the burette drain. The burette is now connected to the compensator and the indicator set at the top of the mercury in one of the legs of the monometer, when the gas is at the 100 ml. mark in the burette. All subsequent readings are made with the same level of mercury in the monometer.

The burette is connected to the manifold and the flushing liquid drawn back just past the pipette in which the first absorption is to take place.

Manipulation of Absorption Pipettes.--With the manifold open as far as the first absorption pipette, the stopcock in the header is turned so that the burette communicates with the pipette. Then, by merely raising and lowering the leveling bulb, the gas may be passed through the pipette as often as desired. After the last pass, the levelling bottle is carefully lowered until the solution in the pipette just reaches the stopcock in the header. This cock is then turned and the flushing liquid is forced back to the top stopcock of the burette. The lower stopcock is then turned to connect

the burette with the compensator and after letting the burette drain for three minutes the leveling bottle is raised or lowered so that the mercury level in the monometer coincides with the indicator and a reading is taken. The difference between this reading and the previous reading is the percentage of the constituent, just absorbed in the gas.

Manipulation of the Copper Oxide Tube.--The current is switched on the heater for the copper oxide tube at the beginning of the analysis, and the rheostat is adjusted so that by the time the tube is needed the temperature of the heater will be between 290° and 310°C . Then, after the gas has been drawn from the oxygen pipette and measured, it is driven in the manifold as far as the first stopcock leading to the copper oxide tube. The heater is placed over the tube, and the stopcock nearest the burette is turned to connect the burette with the copper oxide tube. The leveling bottle on the burette is raised, and the one connected to the slow combustion pipette is lowered slightly. Then the stopcock above the slow combustion pipette is turned to connect this vessel with the copper oxide tube, and the second cock leading to the tube is turned slowly until the gas is flowing into the slow combustion pipette at the rate of about fifteen ml. per minute. When the liquid in the burette has reached the tube, the leveling bottle on the burette is lowered, and the gas is drawn back at the same rate. This operation should be repeated four or five times. The heater is next raised and the cooler connected to the

compressed air line. After about three minutes, the remaining gas in the slow combustion tube is drawn into the burette. The manifold is flushed and a reading is taken with the use of the compensator as previously described. The contraction is due to the hydrogen combining with oxygen to form water and if a 100 ml. sample was taken at the beginning of the analysis, this contraction is the per cent of hydrogen in the gas.

The flushing fluid is now drawn back past the potassium hydroxide pipette and the rest of the gas is bubbled through the potash solution to remove the carbon dioxide formed by the oxidation of the carbon monoxide in the copper oxide tube. The amount of carbon dioxide formed is equal to the volume of carbon monoxide in the sample, therefore, after absorption, the contraction gives the percentage of CO in the gas.

The copper oxide becomes exhausted in time. To restore its usefulness it is heated to 350°C and oxygen or air passed through a number of times.

Manipulation of the Slow Combustion Pipette.--Carbon monoxide and hydrogen can be determined by slow combustion, but this method is rather slow and they are usually determined by one of the methods previously mentioned. The slow combustion method is used mostly for the combustion of methane and ethane.

Methane requires 2 volumes of oxygen or 9.56 volumes of air for combustion and ethane requires 3.5 volumes of oxygen or 16.73 volumes of air. An excess of ten to fifteen per cent over these figures must be present for complete combustion. It is therefore

evident that oxygen should be used and that if it is known that the sample of gas contains a large amount of methane or ethane, such as natural gas, only a portion of the sample can be used for combustion.

To burn gas in the slow combustion pipette the following procedure is recommended:

The gas remaining, after the determination of absorbable components and hydrogen, is stored in the explosion pipette. Then about 100 ml. of oxygen is drawn into the burette, measured, and transferred to the slow combustion pipette. About 20 ml. of the gas is drawn back into the burette (assuming it is mostly methane with some ethane) and carefully measured. The rest of the sample is ejected from the apparatus. Then the switch is turned on, heating the filament in the slow combustion pipette to a bright yellow. A clamp is put on the leveling bottle tube and the bottle is raised opposite the top of the burette. The stopcock above the pipette is then turned to connect the pipette with the burette. The clamp is loosened so that the gas flows into the slow combustion pipette at the rate of 10 ml. per minute until the gas is all burned. The gas is then drawn back into the burette at the same rate. This operation is repeated three or four times at a little faster rate to make sure that the gas has all burned. Then with the gas in the pipette, the electric current is turned off, and the gas is allowed to cool for three minutes when it is drawn into the burette for measurement.

The difference between this measurement and the preceding

one is due to the hydrogen of the methane and ethane combining with the oxygen to form water and is called "Contraction I". The rest of the gas is then passed into the potash solution several times to absorb the CO_2 formed. After absorption the gas is again measured and the contraction is noted as "Contraction II". The methane and ethane content of the sample are calculated as follows:

Volume of ethane in sample

$$\frac{2x \text{ Contraction II} - \text{Contraction I}}{1.5}$$

Per cent ethane

$$\frac{\text{Volume of ethane} \times 100}{\text{Original sample volume}}$$

Volume of Methane

$$\text{Contraction II} - 2 \times \text{volume of ethane}$$

Per cent methane

$$\frac{\text{Volume of methane} \times 100}{\text{Original sample volume}}$$

Precaution in this operation must be taken so as not to mix the gas and oxygen in moving them back and forth. The filament must be hot enough to burn the gas, otherwise some of the gas passing by the wire without burning will create an explosive mixture in the pipette. Also the filament must not be too hot because the heat of combination of water and of carbon dioxide will raise the temperature of the filament and there is a possibility of it fusing.

Manipulation of the Explosion Pipette.--The explosion method for determining combustibles is more rapid, but has more disadvantages

and errors are more likely than with slow combustion. In this method the sample is purposely made explosive by the addition of an air-oxygen mixture, confined over an aqueous solution in the explosion pipette and ignited by means of an electric spark.

Air as a source of oxygen is unsatisfactory because of the low oxygen content. If pure oxygen is used, oxides of nitrogen are apt to be formed by the explosion and too, the explosion may break the pipette. The best plan is to use a mixture of equal parts of pure oxygen and air. The proportioning of the mixture for explosion is very important. If it is near the lower explosive limit, incomplete combustion may result, and if near the upper limit, the oxygen content is inadequate for complete combustion of all the combustible components.

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

Mix the gases thoroughly by passing back and forth between the burette and explosion pipette cock and lower the leveling bulb to create negative pressure in the pipette. Press the spark button to explode the mixture. Do not permit the spark to vibrate between the electrodes. If the mixture does not explode with the several sparks the proportions

are probably wrong. Pass the gas back into the burette and measure carefully noting any contraction in volume. Then determining the amount of CO_2 formed. Calculations from combustion data are the same as those applying to the slow combustion method.

Determination of Nitrogen.--In the usual gas analysis the percentage of nitrogen is obtained by subtracting the sum of the percentages of all the other components from 100, the difference being the percentage of nitrogen.

CHAPTER V

APPLICATION OF GAS ANALYSES

The most obvious application of gas analysis is for the purpose of identifying a sample of gas. For example, if the analysis of a gas showed a high percentage of illuminants, carbon monoxide and hydrogen, it would indicate a carburetted water gas. Natural gas would be identified by the very high methane content. Producer gas has considerable amounts of CO and H₂ and a high nitrogen content. Blast furnace gas is high in nitrogen and carbon monoxide, has considerable CO₂ and a very small amount of hydrogen. The value of correct identification becomes apparent in territories in which several kinds of gas are used interchangeably either with or without mixing.

One of the major uses of gas analysis is for the control of plant operation. Like every other product, the quality of gas can be controlled within certain limits and this requires considerable attention both from the standpoint of delivering satisfactory gas to the consumer and from the standpoint of efficiency and economy of operation. A lack of air in boiler firing will result in the incomplete burning of fuel to carbon monoxide and the production of 4500 heat units to the pound instead of to carbon dioxide and the production of 14500. An excess of air will dilute and chill the flue gases and cause needless heating of large quantities of air which escape up the stack. An analysis of the chimney or flue gas will tell definitely and accurately the conditions as to air supply of a boiler.

In gas works, iron and steel plants, in all forms of furnaces

and for ventilating purposes, an analysis of the gas will give information upon the condition of the apparatus, will detect leaks of air, or gas, and will serve as an index to the character of the changes taking place inside the apparatus. This knowledge can be used in bettering the economy of the operation.

The problem of atmospheres other than those from combustion involves investigations for three purposes: safe entry, explosion hazards, and identification of source of contaminant. Various combustible gas indicators and instruments for the detection of explosive conditions, safe entry, etc., have taken the place of regular gas analyses in mine air and other working atmospheres that become contaminated with noxious gases.

Absorption methods are used to analyze furnace atmospheres when they are not surrounding sensitive materials. This is because small amounts of oxygen exert marked effects on certain materials and the absorption method is not accurate enough to determine less than 0.2 per cent oxygen.

The importance of an analysis of many forms of gas either produced or consumed is being more appreciated because of its economic value in many industrial processes.

CHAPTER VI
DETERMINATIONS

Prepared Gas.--Carbon monoxide was prepared by warming a solution of oxalic acid and sulphuric acid and collecting it over water in a flask. Carbon dioxide was made by adding hydrochloric acid to calcium carbonate and run into the same flask. Oxygen and nitrogen were admitted to the flask from the air. The mixture was forced into the apparatus by displacement with acidulated water and determination of the components were made by absorption.

Vol. of ml. Sample	Reading Minus CO ₂	% CO ₂	Reading Minus O ₂	% O ₂	Reading Minus CO	% CO	% N ₂	Total %
100	48.0	52.0	39.7	8.3	33.2	6.5	33.2	100
100	48.6	51.4	39.9	8.6	33.8	6.1	33.8	100
100	48.4	51.6	40.0	8.4	32.7	6.3	32.7	100

Five such mixtures were prepared and determinations of each made until at least two checks were obtained. Differences of from 0.8 to 2.1 per cent in CO₂ content of the same sample were noted when water instead of acidulated water was used to force the gas into the apparatus. This was due to the fact that water absorbs its own volume of CO₂. Solubilities of oxygen and carbon monoxide in terms of volumes of water are 0.031 and 0.023 respectively, therefore, differences due to their solubility would be below the standard tolerance of the apparatus.

Flue Gas.--Six samples of the flue gas from the boiler room were analyzed and three checked. The gas was drawn into a winchester bottle

which had two tubes through the stopper. The bottle was filled with acidulate water and one of the tubes was inserted in the flue then by running the water out of the bottle the flue gas was drawn in.

Vol. of Sample	Reading Minus CO ₂	% CO ₂	Reading Minus O ₂	% O ₂	Reading Minus CO	% CO	% N ₂
10	95.8	4.2	87.7	8.1	86.8	0.9	86.8
10	95.7	4.3	87.6	8.1	86.6	1.0	86.6
10	96.1	3.9	88.1	8.0	87.1	1.0	87.1

For all six samples two of the three furnaces were burning with just about half of the gas turned on.

ANALYSES OF NATURAL GAS

Sample	Vol. of Gas	Vol. of Gas -CO ₂	Per Cent CO ₂	Vol. of Gas -O ₂	Per Cent O ₂	O ₂ Used for Combustion	Gas Used for Combustion	Com-bined Volume Before Combustion	Com-bined Volume After Combustion	Con-traction in Com-bined	Com-bined Volume After Combustion -CO ₂ formed	CO ₂ formed from Combustion
1	99.06	96.67	2.43	96.55	0.12	99.17	19.80	118.97	80.80	38.17	60.80	20.0
2	99.58	97.30	2.29	97.00	0.30	98.47	20.00	118.47	80.10	38.37	60.00	20.1

CALCULATIONS

(1)
$$\text{ETHANE} = \frac{2 \text{ CO}_2 - \text{contraction}}{1.5} \times K = \frac{(2 \times 20) - 38.17}{1.5} \times \frac{26.55}{19.8} = 5.95\%$$

$$\text{METHANE} = \text{CO}_2 - 2 \times \text{Ethane} \times K = 20 - (2 \times 1.22) \times \frac{26.55}{19.8} = 85.63\%$$

(2)
$$\text{ETHANE} = \frac{(2 \times 20.1) - 38.37}{1.5} \times \frac{27}{20} = 5.92\%$$

$$\text{METHANE} = 20.1 - (\times 1.22) \times \frac{27}{20} = 85.65\%$$

CHAPTER VII

CONCLUSIONS

The Burrell Laboratory Gas Analysis Apparatus was designed to determine the components of various fuel gases and their products of combustion, namely; carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen. Other constituents, such as, hydrogen sulphide, ammonia, tar vapor, cyanogen, hydrocyanic acid, and sulphur dioxide are removed from a gaseous mixture before an analysis is made and they are determined in separate samples by suitable methods.

The methods used for the determination of the different gases by the apparatus are as follows:

Absorption

CO₂ by KOH solution

Illuminants by fuming sulphuric acid

O₂ by Alkaline pyrogallate solution

CO by Acid cuprous chloride solution

Oxidation with copper oxide

H₂

CO

Slow Combustion

H₂

CO

CH₄ and C₂H₆

Explosion

 H_2

CO

 CH_4 and C_2H_6

This shows three ways for determining hydrogen, four ways for carbon monoxide, and two ways for methane and ethane. Hydrogen is preferably determined by oxidation with copper oxide or by explosion; carbon monoxide by absorption or oxidation with copper oxide, methane and ethane by slow combustion.

No determinations of methane and ethane were made by the laboratory apparatus because the slow combustion control box was burned out and difficulty was encountered in replacing it. I spent several afternoons in the Moonlight Laboratory while Mr. Willard Willis ran a number of analyses on natural gas. The apparatus there operates on exactly the same principle as the one in the School of Mines laboratory although it is of somewhat different design.

The sources of trouble I encountered in the manipulation of the apparatus and those observed at the Moonlight Laboratory are as follows:

1. Vaseline is not a good stopcock grease for it leaks under pressure and caustic or potash solutions attack it. A preparation of melted rubber, beeswax and vaseline as previously described was found to be satisfactory.
2. The explosion control box is designed for 7.5 volts and the jumper cord from it should be connected to the 7.5 volt plug on the side of the slow combustion control box. The electrical control box for the copper oxide tube operates on 110 volts

and its jumper cord is connected to one of the outlets at the rear of the slow combustion control box; the other plug is for connection to the 110 volt circuit.

3. After a reading has been taken, the burette leveling bulb must not be raised until the monometer stopcock is turned so that the burette communicates with the header manifold, otherwise the mercury in the monometer will be forced into the compensating tube.
4. In storing the combustible gases, drawing in oxygen and confining it to the slow combustion pipette, care must be exercised so as not to mix the two gases which may form an explosive mixture. Also the oxygen in the slow combustion pipette should not be under a negative pressure for fear there may be a leak in the stopcock above the pipette which would allow some of the combustible gas to be drawn in with the oxygen.
5. Patience is a virtue in operating the apparatus. To get upset will only increase the personal errors. When some error is made in manipulation, the remaining portion of the sample should be forced out of the apparatus and a new sample of the gas taken in for analysis.

The operation of the Burrell Gas Analysis Apparatus is not simple and a good deal of practice is required to acquire the technique for correct manipulation. After a knowledge of the workings of the

apparatus is gained, the analysis of a gaseous mixture is an interesting experiment. Also, the information obtained in its operation is knowledge which may be applied in the future.

The Montana State School of Mines is fortunate in having this piece of equipment in its laboratory.