ERRORS AND LIMITATIONS IN ANALYZING GASES CONTAINING HYDROCARBONS USING THE BURRELL-OBERFELL APPARATUS

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PREFACE

The analyses of gases have been of primary industrial importance for many years. A fairly accurate analysis is a necessity since the design of new equipment, the control and operation of present equipment, meeting specifications required by law or competition, and the safeguarding of health depends many times upon the composition of a gas. Industry has relied upon the present methods of gas analysis for the lack of better apparatus and procedures.

Gas analyses differ from other chemical analyses in the relative importance of the apparatus as compared to the procedure used in the analysis. A gas analysis unit must necessarily be comparatively extensive and complicated in order to perform a simple analysis that can be relied upon, however, the apparatus does not constitute entirely the present generally unsatisfactory state of gas analysis.

Gases are usually analyzed in the gaseous state since liquefaction and distillation does not always give greater accuracy, and is much less convenient. This requires that gases be selectively absorbed directly on or in some substance, the corresponding contraction in volume giving a direct measure of the amount of a specific gas present, or the gas is burned and the products of combustion when absorbed give a direct relation to the amount of the specific gas present in the original mixture. Methods using conductivity are not reliable under all conditions, consequently, are little used where consistently accurate determinations are required. However, conductivity measurements are applicable in many instances where differences are to be noted in gaseous mixtures, and the actual composition is not necessary. Using absorption alone or combustion and absorption together, chemical reactions usually occur. These reactions may or may not remove completely a specific portion because of the slow rate of reaction, chemical equilibrium or physical hinderance to the absorption.

At the present, many types of apparatus and procedures are used for specific purposes with several applicable to general gas analysis. In view of the advantages over other types there exists errors in the absorption procedures that are subject to wide controversy. This controversy is so general it is hard for one to arrive at a conclusion as to the accuracy of any gas analysis regardless of apparatus or procedure used.

It is upon this condition that the author deemed it necessary to attempt to determine some of the sources of error, and their magnitude in one of the general types of apparatus and procedures, and to place some limitations upon the apparatus in determining the proportion of constituents in mixtures containing hydrocarbons mixed with other gases.

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INTRODUCTION

Lavoisier is recognized as one of the first workers to start gas analysis on its slow journey to what is now the modern gas analysis apparatus. He devoted two chapters in his book, "Traite Elementaire de Chemie" written in 1879, to methods of measuring gas weights, volumes, and the separation of gases by absorption and explosion.

It wasn't until 1845, however, that Bunsen and Playfair presented the first serious attempt to develop methods of gas analysis for technical investigation. These methods formed the background for Bunsen's book, "Gasometrische Methoden", published in 1857.

Doyere, in 1848, devised an apparatus for exact analysis using a separate pipette for each reagent, and this was the basis for W. Hempel's modification and the subsequent publication of his book in 1869. The apparatus devised by each investigator was complicated and inaccurate. Stopcocks that did not leak were a rarity, this alone hindering advancement to a large extent.

Perhaps the earliest successful attempt to devise an apparatus for rapid analysis of industrial gases was that of Schlosing and Rolland, in 1868, whose simple apparatus foreshadows closely the modern type. This was soon set aside in favor of an apparatus devised by Orsat in 1875 which is practically the same as that used today. Many modifications of this apparatus have been proposed since it was first described, but the principle has not been altered.

Toward the end of the nineteenth century many investigations were directed toward the analysis of gases. At this time and in the few years following, most of the procedures and reagents that are used today were developed. Few changes have been made in reagents; most of the changes occur in the design of the more common apparatus for greater accuracy and convenience.

The accuracy of any gas analysis depends upon a number of factors that must be eliminated or corrected to make an accurate determination. The following factors are most important:

1. Change of temperature and pressure during the analysis.
2. Change of water vapor content of the gas.
3. Graduation of the burette.
4. Capillary error of the apparatus used.
5. The type of pipette for gas absorption.
6. The method of securing connections to eliminate leaks, and preventing stopcock leaks.
7. Solubility of the gases in the confining liquid.
8. Choice of a suitable reagent.
9. The method of calculation of results.

The first five factors are solved entirely by the apparatus. The apparatus chosen should be suitable as to accuracy and convenience for which it is to be used. The choice of a suitable reagent and the method of calculating the results present a more difficult problem and is the basis for this paper.

The Change of Temperature and Pressure During the Analysis

When the temperature or pressure of a gas is varied a change occurs in the volume according to the gas laws. The magnitude of the volume change is one percent of the volume at 0°C. for every 2.7 degrees centigrade change in temperature, if the pressure remains constant. In the transfer of a gas from one vessel to another the pressure must be increased, raising the temperature, and when the gas is brought back to the original pressure its volume is increased. The Burrell-Oberfell appartus corrects this change in volume by an auxiliary compensating tube inclosed in a water jacket that also contains the burette, so that any change of temperature or pressure during the analysis affects both the gas in the burette and the air in the tube to the same extent. All readings should be obtained after making connection to the compensating tube, and bringing a mercury manometer to an arbitrary mark that is used for all readings.

Change of Water Vapor Content

A change in the water vapor tension of a gas will make a corresponding change in volume. The compensating tube cannot correct this unless both the burette and tube are brought to the same vapor tension. This is accomplished by having water (1 or 2 ml.) in the compensating tube and water in the burette or water over the confining liquid at all times. This corrects the error that would occur when water is removed by the absorbing reagents or when the vapor tension is changed by temperature. Also, if the volume readings are always made with the gas saturated with water vapor proportionate parts of water are absorbed at each step in the analysis and it can be assumed to be an analysis of the dry gas. (61)

Graduation of the Burette

Accurate results cannot be obtained unless the burette is calibrated properly. This error can be eliminated by purchasing a good burette or checking the calibration on a less expensive burette.

Capillary Error of the Apparatus

The pipettes and burette are connected with capillary glass tubing that should be filled with an inert gas such as nitrogen before an analysis is started. This largely eliminates the error with the exception of the space below the stopcock and liquid level in the pipettes, which is compensated for by making one or two determinations on the gas before a determination is taken as final analysis. The inert gas may be air from which the oxygen and carbon dioxide has been removed in the absorption pipettes.

Type of Pipette for Gas Absorption

A number of gas analysis pipettes have been designed to bring the gas and the reagent into intimate contact. The lowest priced and most generally applicable is the plain pipette filled with glass capillary tubes, and probably is just as efficient and convenient for all solutions as many of the specifically designed pipettes.

The Method of Securing Connections to Eliminate Leaks, and Preventing Stopcock Leaks

The burette and pipettes are usually joined to a common manifold to make the apparatus more versatile by permitting the pipettes to be interchangeable, and allowing the gas to be transferred to any pipette without outside connections. The method used to make the connections gas tight under pressure and vacuum is to join the glass capillaries by sections of high quality, red rubber, pressure tubing approximately one to one and one-quarter inches long with the ends of the glass together. The final seal is made by applying a bead of cellulose cement, preferably Testors cement, around the ends of the rubber tubing after connection has been made. By test this joint did not leak under twelve inches of mercury pressure for twelve hours which means that this error is completely eliminated.

The stopcocks should be of the highest quality to insure a good register of key and barrel. These may be sealed by a good lubricant whose viscosity approximates that of vaseline. Care should be taken to insure exclusion of air and an even film of lubricant in the joint.

Solubility of Gas in the Confining Liquid

All gases are soluble to some extent in water. This is especially true of carbon dioxide and some hydrocarbons. To eliminate this error of solubility, mercury is used as the confining liquid in both the burette and the combustion pipette, if highest precision is desired. The small error is negligible due to solubility of gases in the one or two milliliters of water over the mercury, used to saturate the gas with water vapor, after two or more samples have been run before the results are taken as final analysis.

Choice of a Suitable Reagent

The choice of reagent is difficult, and presents more controversy than all of the other factors in gas analysis. The choice of a specific reagent for absorption depends upon its ease of manipulation, reproducibility of results, ability to absorb the specific gas completely from the wide possibility of mixtures of gases, operator experience required, solubility for gases other than the one for which it is used, formation of foreign by-products, rate of reaction, completion of reaction, life of the reagent, and the comparative cost. A discussion of the more common specific absorbents and designs of apparatus follows to aid in the selection of reagents and apparatus.

Determination of Carbon Dioxide

The determination of carbon dioxide is the least uncertain of all absorbents by using potassium hydroxide solution. It is recommended in nearly all procedures. This alkali absorbs carbon dioxide readily and completely without the formation of much precipitate in the pipette. Burrell and Seibert (18), and Fieldner, Jones and Holbrook (29) recommend it using 33 and 30 grams, respectively, in 100 milliliters of water. Anderson (1) recommends it using one part of potassium hydroxide in one and one-half to two and one-half parts of water, and Shephard (66) recommends fifty grams in 100 milliliters of solution. Stronger solutions may be used, but Bunte and Wunsch (13) recommend not over one part of potassium hydroxide to one part of water because of the removal of more water from the gas by the stronger solutions. Burrell (15) claims paraffin hydrocarbons are completely insoluble in potassium hydroxide solution so its use is suitable for gases containing hydrocarbons.

Sodium hydroxide may also be used and is recommended by Fieldner, Jones and Holbrook (29) using 20 grams of the alkali in 100 milliliters of water, but it precipitates a white deposit of bicarbonate on the capillary tubes. This is sometimes undesirable.

Determination of Oxygen

Oxygen is more commonly determined by absorption in an alkaline pyrogallol solution although there is much controversy over this reagent. The other methods used, absorption in sodium hyposulfite solution and combination with phosphorous, are less satisfactory than the alkaline pyrogallol solution and are seldom used.

Anderson (1) recommends 142 grams of potassium hydroxide to 168 grams of pyrogallol in 690 grams of water, Anderson (2) 15 grams of pyrogallol in 100 milliliters of potassium hydroxide solution of specific gravity 1.55, Anderson (5) 21.2 grams of pyrogallol to 66.6 grams of potassium hydroxide in 100 milliliters of solution, Burrell (16) 120 grams of potassium hydroxide to 5 grams of pyrogallol in 95 grams of water, Hoffman (35) one part of pyrogallol to one part of potassium hydroxide in three parts of water, Haldane and Makgill (32) 10 grams of pyrogallol in 100 milliliters of an 80 percent solution of potassium hydroxide, Bruckner and Bloch (12) uses a 1 to 1.5 ratio of pyrogallol to potassium hydroxide, and Burrell and Seibert (18) recommends for a Hempel pipette a solution of 5 grams of pyrogallol to 120 grams of potassium hydroxide in 95 grams of water.

Potassium hydroxide is generally used for the alkali, but the use of sodium hydroxide has some distinct advantages. Shipley (67) recommends 7.36 grams of sodium hydroxide to 10 grams of pyrogallol in 11.62 grams of water, and Burrell (16) one gram of pyrogallol to 2.5 grams of sodium hydroxide in 5.5 grams of water.

From these it is difficult to choose the best as each worker presents good features for each solution.

Haldane and Makgill (32) and Drakely and Nicol (26) indicate that carbon monoxide evolution will likely give low results for oxygen when determined in alkaline pyrogallol, and have found carbon monoxide evolved from alkaline pyrogallol solutions on absorbing oxygen of 98 percent purity, with the quantity of carbon monoxide evolved increasing as the concentration of the pyrogallol decreases in the solution. Others have found indications of the same evolution, but limit the formation. Bruckner and Bloch (12) have found that carbon monoxide will be evolved when analyzing gases containing over 20 to 25 percent of oxygen, and Shipley (67) finds that no carbon monoxide is formed in either potassium hydroxide or sodium hydroxide pyrogallol if the oxygen content of the gas is below 28 percent. Anderson (1) has found that no carbon monoxide is formed from any concentration of alkaline pyrogallol, and Anderson (2) reports no carbon monoxide is formed in appreciable amounts, and none usually formed even in old solutions. This indicates the unsettled state of gas analysis procedures.

The solutions vary considerably, and Anderson (3) states that the alkaline pyrogallol solutions decrease greatly in specific absorption as the potassium hydroxide density decreases slightly below 1.55. This is in agreement with Drakeley and Nicol (26). Anderson (4) also reports that stronger and more viscous solutions of pyrogallol can be used in the Orsat type than in the Hempel type of pipette resulting in greater efficiency. This is to say that the sodium hydroxide pyrogallol solutions are unsuitable for use in Hempel pipettes since the sodium reagent is good only in viscous solutions (2). Anderson (2) cautions that pyrogallol solutions will deteriorate above 24 degrees centigrade, and Burrell (16) indicates that the pyrogallol solution will last indefinitely if kept in the absence of oxygen. This is a good feature since a supply of solution may be kept on hand.

There is disagreement as to which of the alkaline pyrogallol solutions is superior. Shipley (67) is in favor of sodium hydroxide pyrogallol since it will absorb five times as much oxygen as the corresponding potassium hydroxide pyrogallol solution. The total absorption for the sodium reagent is three plus atoms of oxygen absorbed per molecule of pyrogallol in the solution. However, Anderson (5) and Bruckner and Bloch (12) show that the absorption is slow for the sodium reagent requiring four minutes for complete absorption as compared to one minute for the potassium reagent. This indicates that the potassium hydroxide pyrogallol solution is superior in the ease of handling.

Anonymous (7) has concluded that alkaline pyrogallol solutions are better than sodium hyposulfite or chromous acetate solutions, and Quiggle (62) in agreement has shown that sodium hyposulfite solutions are not good for determinations on standing a few days after being made.

The presence of seven percent ethylene or benzene in the gas, according to Ott (51), will completely suppress the absorption of oxygen on phosphorous, but White (76) states it requires only a fraction of a tenth of a percent. This makes it unsuitable for gases containing hydrocarbons, and the error as shown by Wing (79) is too large for accurate determinations, being from .05 to .10 percent for ordinary gases, regardless of the hydrocarbons present. Also phosphorous is too inconvenient, and too easily inhibited to reaction with the oxygen.

From the literature it is concluded that the density of the potassium hydroxide pyrogallol solution should be about 1.55 and the pyrogallol content fairly high for greatest efficiency. There is no objection to the use of the sodium reagent except that it is much slower to absorb the oxygen from the gas.

There is little indication in the literature that hydrocarbons are soluble in the alkaline pyrogallol solutions. Burrell (15) states that paraffins are totally insoluble in the solutions, but indicates that when higher hydrocarbons are present in natural gas a slight increase in absorption was noted (18).

Determination of Unsaturated Hydrocarbons

The determination of unsaturated hydrocarbons is difficult since a reagent of proper selectivity is not available without many objections from a number of workers. The reagents more commonly used are sulfuric acid or oleum, and bromine water. The latter is not much used since it is difficult to handle, and the errors are much greater than the absorption in sulfuric acid.

The primary objection to the acid is that paraffin hydrocarbons are soluble in various concentrations, and it may introduce an error in the hydrogen determination. Worstall (80) has shown that pure methane is soluble in oleum to the extent of .12 percent in thirty minutes, and natural gas methane solubility is 1.5 percent in sixteen hours. It was also found that the ethane loss was 0.6 milliliters per hour. This indicates that the methane loss is negligible for a short time contact and is in agreement with Burrell and Seibert (18). Schenck and Dingmann (64) recommend the acid, but place a three to five minute time limit of contact to prevent absorption of methane and hydrogen.

Many workers, however, consider the error to be quite large in dissolving paraffins. Burrell and Seibert (18) reported a two percent loss in pure ethane in five minutes when contacting oleum, Niederer (48) and Mulcahy (47) also find appreciable solubility when absorbing methane and ethane in oleum. Considerable amounts of the heavier hydrocarbons are soluble as the concentration of the acid increases and is reported by Anderson and Engelder (6). Orndorff and Young (50) also has reported evidence of propane being quite soluble in oleum.

Ethylene is difficult to remove and to prevent its removal from gases by absorption. Morton (46) findsthat benzene is removed easily in sulfuric acid of specific gravity 1.84, and ethylene is not soluble in it if the benzene concentration is above 0.1 percent. This will lower the absorption error to less than 0.2 percent in any case due to ethylene. Morton also has found that the higher olefins present cause the benzene content to be high by analysis. Ethylene is shown to be insoluble in 87 percent acid if the concentration is not over 20 percent in the gas by Tropsch and Mattox (72), and is in agreement with Dubois (27). To effect the removal of ethylene, acid stronger than 100 percent must be used.

With these difficulties present Ott (51) recommends the acid over bromine water, and Dubois (27), Dennis (23), and Ott (52) find fairly good accuracy and good removal of all unsaturates using 20, 24 and 25 percent oleum.

The exact mechanism or reaction when the olefins are dissolved in oleum is not entirely settled, but Ormandy and Craven (49) has found the reaction, with the exception of ethylene, to form saturated hydrocarbons and highly unsaturated substances that remain in the acid.

The use of catalysts or additives in the acid has not been entirely proven to be advantageous to accuracy. One-half percent of vanadic acid is recommended by Wellers (75) for separating ethylene series hydrocarbons from paraffins, and finds it impossible to separate them in sulfuric acid alone in any concentration at room temperatures. The use of mixed sulfates of nickel and silver is reported as good by Tropsch and Mattox (72), but Davis and Quiggle (22) find that the addition decreases the effectiveness of separation of ethylene and propane. Thorburn (71) reported that 20 to 35 percent oleum plus 0.05 percent iodine is good for absorbing unsaturates, but will absorb also any carbon monoxide that is present. Silver sulfate alone is recommended by Gluud and Schneider (31) in the strengths from 0.5 to 1.0 percent, and an acceleration of absorption is reported by Pigulevskii (60) when using the sulfate.

For the absorption of both the methane and ethylene series a solution of 25 grams of mercuric iodide and 30 grams of potassium iodide in 100 milliliters of water is recommended by Wellers (75), but no other recommendations were found as to the effectiveness or accuracy of this solution.

Determination of Carbon Monoxide and Hydrogen

The removal of carbon monoxide by absorption in solution has been criticised extensively, and its use in exact analysis is very limited at the present time. The common absorbent is a solution of cuprous chloride, but iodine pentoxide, copper ammonium formate and lactate have been used.

Dennis and Hopkins (24) and Berger and Schrenk (41) report that cuprous chloride is effective in complete removal of the carbon monoxide only if used in two pipettes. Ott (52) (53) recommends a small amount of solution, only two milliliters to minimize other errors. Dubois (28) finds that an acid solution of cuprous chloride is rapid but incomplete, and an alkaline solution is complete but slow. He recommends two passes of two minutes each into ten milliliters of solution for the acid absorbent, and three passes of two minutes each into five milliliters of solution for the alkaline absorbent to obtain nearly complete removal of the carbon monoxide. Others such as Yakovlev (81) give longer contact time to obtain the desired results.

The completeness and rapidity of absorption of the carbon monoxide is not the main objection, but the absorption of gaseous hydrocarbons is high which is very undesirable. Niederer (48) has reported methane is soluble in the alkaline solution of cuprous chloride, and Burrell and Seibert (18) find that ethane is quite soluble. Several others including Anonymous (8) and Burrell (15) have found the error due to absorption of higher hydrocarbons may be as high as three percent. Since the errors are so high, Hoffmann (36) recommends the cuprous chloride solution omitted.

However, if the absorption of the hydrocarbons is not important they will not affect the carbon monoxide absorption in the cuprous chloride reagent according to Dittrich (25).

The use of oleum-iodine pentoxide mixtures is too limited for general use. Pieters (59) finds a solution of 25 percent oleum with the iodine pentoxide will absorb all of the carbon monoxide, but less than ten percent of excess sulfur trioxide can be tolerated if any hydrogen or methane is present in the sample. Dittrich (25) agrees with this and also states no higher paraffins can be present. Thorburn (71) states that a solution of oleum-iodine pentoxide will oxidize traces of hydrogen, but the methane present is unaffected. Nevertheless, for good results the hydrocarbon content must be below 1 part in 1000 according to Gautier (30).

Carbon monoxide absorption in copper ammonium formate and lactate is good, and both better than the chloride or acetate according to Zhavoronkov and Reshchikov (82), and the removal of carbon monoxide in copper ammonium hydroxide, carbonate, acetate, chloride, sulfate, and nitrate may be used for technical analyses, but not for exact analyses according to Moller (45).

Hydrogen is sometimes determined by combustion over palladium asbestos, but this is reported unsatisfactory by Hempel (33) and Watase (74) if any hydrocarbons are present. This is also true in the absorption of hydrogen by a solution of or solid palladous chloride or colloidal palladium reports White (77) and Dennis (23).

Carbon monoxide and hydrogen are more commonly determined together over heated copper oxide. This method is much more satisfactory than other methods, and presents much less controversy as to the accuracy of the determination. However, there are quite a number of different temperatures that are optimum among workers for complete combustion.

Methane may also be determined by the same method, and will be discussed along with the carbon monoxide and hydrogen determination.

The procedure for determining carbon monoxide and hydrogen is to pass the gas slowly through a heated tube containing copper oxide where the hydrogen and carbon monoxide are oxidized to water and carbon dioxide respectively. From the contraction after cooling and after absorption in the alkali pipette the amount of the two can be calculated. When methane is determined by this method the carbon dioxide from the combustion is a measure of the methane in the original mixture.

The conditions for optimum results are reported to be according to Tapley (69) as carbon monoxide and hydrogen over copper oxide at 280°C., and with hydrogen and methane over copper oxide at a red heat, Broom (11) reports carbon monoxide and hydrogen over copper oxide at 200° to 300°C., Rassfeld (63) carbon monoxide and hydrogen at 250° to 300°C., and methane at 700° to 800°C., Ott (54) hydrogen at 270° to 290°C., Keller and Klempt (40) hydrogen and carbon monoxide at 500° to 520°C. and methane at 850°C., Bahr (10) hydrogen at 300°C., and methane at 900° to 1000°C., Pauschardt (57) hydrogen at 380°C. for 10 minutes and methane at 900°C. for 10 minutes, and to reoxidize the copper oxide after five to six determinations, Campbell and Gray (21) methane at 700°C. in seven minutes, Ott (55) hydrogen at 300°C., and methane at a red heat and Yakovlev (81) methane at 1050°C. for seven to ten minutes.

Many workers use a catalyst with the copper oxide, and find it satisfactory. Wibaut (78) recommends the addition of ceric oxide to aid in the combustion and to obtain better results. With this addition hydrogen is determined at 270°C. and methane at a red heat. Herrmann (34) states with pure copper oxide the combustion of methane is incomplete, only 70 to 75 percent, even at 900°C., and suggests the addition of a platinum group oxide then determine hydrogen at 350°C. and methane at 825°C. Arneil (9) found that one percent ferric oxide reduces the methane combustion temperature by 200°C. Maly (44) agrees with these workers, and that the addition of cobaltous oxide, ceric oxide or ferric oxide will eliminate many errors.

The reduction of copper oxide by hydrogen has been found to begin at 140°C. by St. John (68), and carbon monoxide oxidation begins at 150°C. using copper oxide on asbestos is reported by Pieters (58). If cobaltous oxide is used as a catalyst, hydrocarbons may be determined over copper oxide at elevated temperatures King and Edgcombe (42) reports.

Dissociation of the copper oxide at elevated temperatures has been noted by Terres and Maguin (70). Bunte and Wunsch (14), and Maly (44), but Maly states the oxygen is reabsorbed on cooling introducing no error. There is also indications of the carbon dioxide being absorbed by the copper oxide introducing an error, King and Edgcombe (42) and Bunte and Wunsch (14) report this. Although there is no reaction between nitrogen and the copper oxide an error is introduced when burning methane that cannot be eliminated according to Ott (56) amounting to 0.5 percent. The largest error, however, is introduced when burning gases containing hydrocarbons. Terres and Maguin (70) have noted that ethylene will deposit carbon on copper oxide, and that methane and carbon monoxide cannot be quantitatively separated. Burning of hydrocarbons over copper oxide at only 280°C. is reported by King and Edgcombe (42) who have found that ethane, propane and butane are burned to the extent of 0.8, 1.0, and 1.4 percent respectively.

Campbell (20) presents data that unsaturates are easily burned over copper oxide at about 300°C., and Jaeger (37) in his procedure specifies that unsaturates be removed before the combustion of hydrogen and carbon monoxide.

Regardless of the errors introduced this method should be far more accurate than other procedures, especially for carbon monoxide, and is recommended by Fieldner, Jones and Holbrook (29), Burrell and Oberfell (17), and Jones and Neumeister (38) for exact gas analyses.

Determination of Hydrocarbons

In the modern apparatus only one method is used to any extent to determine gaseous hydrocarbons. This is by slow combustion of the hydrocarbons with oxygen or air. The sample is placed in a heavy walled pipette after the removal of other gases in the sample, especially oxygen, and a small platinum spiral is heated near the capillary inlet. Oxygen is then introduced slowly. The hydrocarbons burn, and usually methane and ethane are determined from the contraction and the carbon dioxide formed. Using the old explosion method of hydrocarbon combustion the main objection was to the formation of oxides of nitrogen. The volume of oxides of nitrogen formed during slow combustion never exceeds 0.005 milliliters and is usually lower according to Jones and Parker (39). This error is negligible. Schenck and Dingmann (64) report that the methane content of the gas must be below 40 percent to prevent the formation of methanol and formaldehyde, and van Dam (73) agrees with Schenck and Dingmann in that carbon dioxide must be removed after each pass since methane will not burn completely in the presence of carbon dioxide. This is also recommended by many other workers.

If air is used for combustion a smaller sample of gas must be taken which will multiply any error. To minimize this error Burrell (15) recommends the use of pure oxygen with a larger sample.

It can be seen that if a worker is careful to obtain complete combustion other errors are at a minimum, consequently this method is used almost exclusively.

Calculation of Results

When a hydrocarbon is burned carbon dioxide is formed. There is a small difference in the molecular volume of the hydrocarbon and of the carbon dioxide. Burrell and Seibert (19) state there is an error as high as two percent due to this if the volume of the carbon dioxide is taken as the same volume of the original hydrocarbon. Schuster (65) and other workers agree there is a difference, but it is small and can be neglected, contrary to Kobe (43) and Burrell and Seibert (19) who say it should be corrected.

Burrell (18) (16) in other articles presents calculations showing only small differences in the molecular volumes. He states that the deviations from the gas laws are small since methane is nearly a perfect gas, and ethane differs only by 0.01 from 0 to 760 millimeters pressure. Propane and butane differences are but slightly higher and usually are in very small percentages in most gas samples.

This error is of far less magnitude than other errors in gas analyses, and it is concluded that it is negligible.

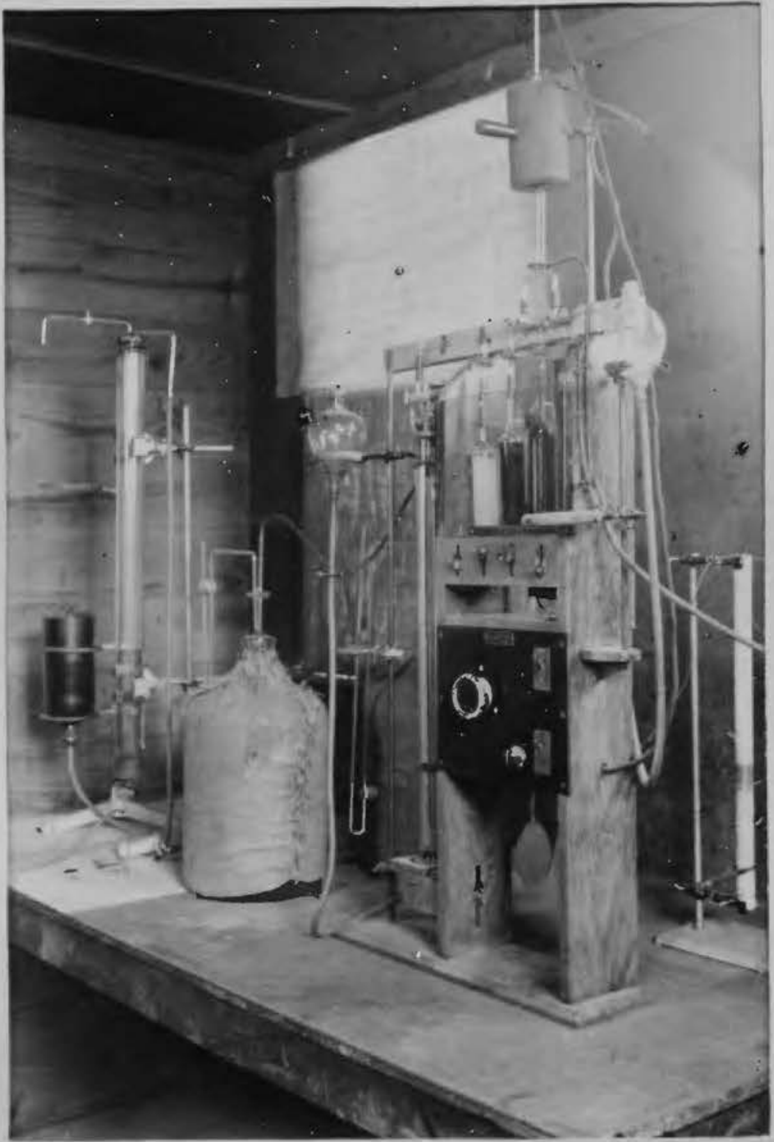

PLATE I

EXPERIMENTAL

Description of the Apparatus

The gas analyzer used was a Burrell-Oberfell gas analysis apparatus sold by E. H. Sargent and Co. Plate 1 shows the apparatus arranged for complete gas analysis. The apparatus consists of a 100 milliliter burette with a compensating tube inclosed in a glass water jacket for correcting changes of temperature and pressure during the analysis, four pipettes, and a copper oxide tube with an electric heater. Mercury was used as the confining liquid in both the burette and the slow combustion pipette.

Three of the four pipettes were common absorption pipettes filled with glass tubes three millimeters in diameter for increasing the area of contact between the gas and the liquid. The first pipette, next to the burette, was filled with alkali for the determination of carbon dioxide, the second was filled with fuming sulfuric acid for the determination of illuminants, and the third with alkaline pyrogallol for the determination of oxygen. The fourth was a slow combustion pipette containing the platinum spiral atop two glass tubes filled with mercury for a conductor, these extend to the opening at the top of the pipette.

The burette was connected at the bottom with a leveling bulb containing mercury sufficient to fill the burette. On the mercury was riding one to two milliliters of water to keep the gas saturated with water vapor. The compensating tube also contained two to three milliliters of water to take care of changes of temperature affecting the vapor tension of the gas inside the tube. The burette and compensating tube were connected by a mercury filled manometer which was leveled before each burette reading to insure a reading of the gas sample at a standard pressure.

All of the apparatus was connected to a common manifold so that a gas sample could be transferred to any pipette or to the copper oxide tube. The common pipettes were filled with solution sufficient to form a seal at the bottom when the capillary side was filled to the mark. To the rear branches of the pipettes were attached rubber bags to prevent access of air to the reagents.

The copper oxide tube was purchased ready filled from E. H. Sargent and Co. It was heated by a 220 volt electric heater capable of raising the temperature to 300°C. in about 15 minutes. A rheostat for accurately controlling the temperature was located on the front panel.

The combustion pipette was connected at the bottom with a leveling bulb containing mercury sufficient to fill the pipette to the mark. Through the stopper at the bottom extended the conductor tubes with platinum lead wires sealed in the glass for heating the spiral at the top. The current was regulated roughly from 110 volts by a sliding contact on the external resistance shown at the extreme right of Plate 1. The fine adjustment was made by a small rheostat on the front panel. The spiral was two and one-quarter inches of No. 30 (B&S gauge) platinum wire forming five loops. Two switches are also on the front panel for the heater and the spiral circuits.

The apparatus was used to detect differences in results when analyzing standard samples. These standard samples were held in five gallon glass bottles under pressure so that a sample could be withdrawn without using a displacing liquid thereby eliminating possibilities of errors from absorption or reaction with the confining liquid. The samples taken from these bottles were assumed to be of the same composition.

Through the stopper in the bottle was a stopcock and a twenty inch mercury manometer. The stopper was held firmly in place by wire, and made gas tight by a bead of Testors cement. To fill the bottle approximately twelve inches of vacuum was pulled on it by a water pump, and the gases were added to the bottle by opening the stopcock. After additions had been made approximately eighteen inches of mercury pressure was applied by compressed air. After several days to insure complete diffusion, the sample was ready for analysis. To withdraw a sample a short section of rubber tubing was attached to the bottle and apparatus, and after opening the sample bottle stopcock slightly and lowering the mercury in the burette a sample could be drawn for analysis. See Plate 1.

The oxygen for the slow combustion was stored in a section of glass pipe fitted with stoppers at each end, and by water displacement from a reservoir and lowering of the mercury in the burette oxygen could be drawn into the burette for the combustion. See Plate 1.

Method of Analysis and Technique of Operation

An "exact" analysis is one in which more than ordinary care has been taken to insure that all existing errors are reduced to a minimum. To perform an "exact" analysis using the apparatus described it is necessary to take utmost care in performing all operations, and to explain the operations in detail would be tiresome to one familiar with gas analysis. However, the general procedure will be given with the understanding that all operations are carefully made, and that good practice in manipulation is closely followed.

1. Preparation of Apparatus

The apparatus must be thoroughly clean before assembly and maintained in that fashion during subsequent analyses. A few milliliters of water are placed over the mercury in the burette and in the compensating tube with readings taken in the burette from the water meniscus after allowing the sample a minute or so to reach equilibrium and become saturated with water vapor.

The rubber bags are slightly inflated first and placed on the rear branches of the pipettes to allow for absorption by the reagents of gases from the air. To test for leaks, approximately fifty milliliters of air are drawn into the burette, and after opening the burette to the manifold ten inches of mercury vacuum and pressure is placed on the apparatus for fifteen minute periods, the volume of gas being noted before and after the test. No loss in volume should occur.

The manifold and copper oxide tube is flushed prior to each analysis with the inert gas residium after absorbing the oxygen from air in the alkaline pyrogallol pipette.

2. Sampling

Before beginning an analysis, the gas in the compensating tube and the manifold is adjusted to atmospheric pressure, and all of the pipette reagents are adjusted to the mark on the capillaries. The heater for the copper oxide tube may be turned on at this time or anytime that is sufficient for the temperature to be at 300°C. when the sample is ready for the combustion of hydrogen and carbon monoxide.

To withdraw a sample from the gas bottle for analysis, connection is made to the gas bottle and six samples of approximately fifty milliliters each are taken and discarded to insure that the tubing and manifold capillary are flushed of air. The seventh sample of fifty to sixty milliliters is retained for analysis. Connection is then made to the compensating tube, the manometer leveled accurately, and the volume read from the burette. The sample is now ready for analysis.

3. Determination of Carbon Dioxide

The reagent used for the determination of carbon dioxide is a potassium hydroxide solution made by adding 30 grams of chemically pure potassium hydroxide to 100 milliliters of water as recommended by Fieldner, Jones and Holbrook (29). This reagent should satisfactorily absorb the carbon dioxide from the sample.

The sample is slowly passed into the alkali pipette, and is allowed to remain in contact for one minute, and then returned to the burette. This is repeated twice and then the reagent is carefully adjusted to the mark. The volume of the sample is taken by connecting to the compensating tube after allowing time for the sample to become saturated with water vapor. To make certain all of the carbon dioxide has been removed it is returned to the caustic pipette for two short passes, and the volume is again read as before. Any further contraction must be added to the first for the volume of carbon dioxide in the sample.

4. Determination of Illuminants

To remove all unsaturated compounds it is necessary to use fuming sulfuric acid. For this purpose, chemically pure sulfuric acid having 15 percent sulfur trioxide was chosen as the reagent.

After the carbon dioxide determination, connections are made and the gas passed six times into the acid allowing 30 seconds for each pass. The gas then contains considerable sulfur trioxide fumes which must be removed in the alkali pipette using the same procedure as for the determination of carbon dioxide. The volume is read and any contraction is recorded as the volume of illuminants in the sample.

5. Determination of Oxygen

Oxygen is determined by the contraction resulting from the absorption of the sample in alkaline pyrogallol.

The reagent used is recommended by Anderson (5), and is made by adding 21.2 grams of pyrogallic acid to 66.6 grams of potassium hydroxide, and making the final volume for the solution 100 milliliters. This reagent is more concentrated than many of the others, and is recommended for greater efficiency and a minimum evolution of carbon monoxide, if any is evolved.

To absorb the oxygen, the sample is passed into the alkaline pyrogallol pipette three times allowing one minute contact for each pass. Then the sample is passed five times into the pipette allowing 30 seconds for a completed pass from the burette and return. The volume is noted, and three more short passes are made. The volume is again read and the total contraction is the volume of oxygen in the sample. If this procedure will not remove all of the oxygen, as noted by still further contraction, the reagent should be discarded and replaced with fresh solution.

6. Determination of Carbon Monoxide and Hydrogen

The heater at 300°C. is lowered over the copper oxide tube, and connection is made between the burette and combustion pipette through the copper oxide tube. The gas is passed slowly (exactly 10 ml. per minute) through the copper oxide tube by raising the mercury level in the burette and lowering the mercury level in the combustion pipette. The rate was found conveniently controlled by a screw clamp on the burette mercury reservoir tube. The gas is passed back at the same rate, and this operation repeated once.

Raise the furnace and cool the copper oxide tube by compressed air to room temperature, and measure the volume. Any contraction is the volume of hydrogen in the sample.

Pass the gas into the caustic pipette and remove the carbon dioxide as in the determination of carbon dioxide. Then pass the gas through the copper oxide tube to flush out residual carbon dioxide remaining in the capillaries and copper oxide tube, and again pass the gas into the caustic pipette. Return the gas to the burette and measure the volume. The contraction is the volume of carbon monoxide in the sample.

7. Determination of the Hydrocarbons as Methane and Ethane

The residual sample is now stored in the alkali pipette, and an excess of oxygen is drawn into the burette, the volume measured, and then passed into the combustion pipette. The sample is then drawn into the burette. Compressed air is directed on the combustion pipette, and the spiral is brought to a bright yellow heat.

Slowly pass the gas into the combustion pipette (10 ml. per minute) by regulating the flow with the screw clamp. When all of the gas has passed out of the burette, open the screw clamp and pass the gas back and forth over the hot spiral several times, and then once through the copper oxide tube to sweep out the remaining hydrocarbons. Measure the volume after cooling.

Pass the gas into the alkali pipette as in the carbon dioxide determination and record the volume. The combustion should be repeated by passing the gas over the heated spiral several times recording again the contraction and absorption in the alkali pipette. If the combustion was properly carried out, the second contraction should be less than 0.5 milliliters.

8. Calculation of Results

The calculations are shown by carrying through an actual sample calculation. For a certain gas assume that the analysis has given the following observed gas volumes and contractions.

Component	Reading	Difference	Percent
Volume of Sample Taken	55.45		
After Absorption of CO_2	50.20	5.25	9.48
After Absorption of Illuminants	49.15	1.05	1.89
After Absorption of Oxygen	38.35	10.80	19.50
Cont. Due to H_2 Over CuO	37.60	0.75	1.35
Cont. Due to CO After Absorption	37.45	0.15	0.27
Oxygen Added for Combustion	48.70		
Total Volume	86.15		
Vol. After First Combustion	69.20	16.95	
Vol. After First CO_2 Absorption	56.60	12.60	
Vol. After Second Combustion	56.25	0.35	
Vol. After Second CO_2 Absorption	55.80	0.45	
Total Contraction		17.20	
Total CO_2 Formed		13.05	
Ethane		5.93	10.17
Methane		2.19	3.95
Nitrogen by Difference			53.39

The percent of carbon dioxide in the gas sample is calculated by the ratio of the contraction after the absorption in the alkali pipette multiplied by 100 to the original volume of the sample.

The percent of illuminants is calculated by the ratio of the contraction after absorption in the oleum multiplied by 100 to the original volume of the sample.

The percent of oxygen is calculated by the ratio of the contraction after absorption in the alkaline pyrogallol multiplied by 100 to the original volume of the sample.

The percent of hydrogen is calculated by the ratio of the contraction after the copper oxide combustion multiplied by 100 to the volume of the original sample.

The percent of carbon monoxide is calculated by the ratio of the carbon dioxide formed after the copper oxide combustion multiplied by 100 to the original volume of the sample.

The percent of ethane is calculated by the ratio of two times the volume of carbon dioxide formed by the slow combustion minus the contraction due to the slow combustion multiplied by 100 to one and one-half times the volume of the original sample.

The percent of methane is calculated by the ratio of the carbon dioxide formed by the slow combustion minus two times the amount of ethane in the sample multiplied by 100 to the original volume of the sample.

9. Preparation of Standard Samples

The samples were prepared by admitting gases to the sample bottles under vacuum. The carbon dioxide was prepared by the reaction of sulfuric acid on calcium carbonate. The light gaseous hydrocarbons were the hydrocarbons present in the natural gas from the Stillwater, Oklahoma city mains. The heavier gaseous hydrocarbons were obtained by removing the vapors from petroleum ether (B.P. 35-65 C.) by vacuum at room temperature. The ethylene used was from a cylinder containing ordinary commercial grade of compressed gas. These gases were mixed as follows:

Sample A contained air, carbon dioxide, and natural gas.

Sample B contained air, carbon dioxide, and the heavier hydrocarbons from petroleum ether.

Sample C contained air, carbon dioxide, natural gas, and ethylene.

Experimantal Data and Discussion of Results

For an exact gas analysis the first two or three analyses made on a new sample are disregarded as inaccurate, and will sometimes show differences in results. After the first two or three analyses all subsequent determinations on the same sample should give constant results. If differences persist indefinitely with the same technique then there are possibilities of errors being introduced other than errors due to faulty manipulation. The following results do not show the first three analyses.

Ordinarily when reporting gas compositions, determined by gas analysis apparatus similar to the apparatus used, the results are reported only to the nearest one-tenth percent. The purpose of this paper is to examine differences in results, and percentages will be reported to hundredths of percent since the gas volumes are read to the nearest five-hundredths of a milliliter.

Sample A.

1. The gas was analyzed by following the generally practiced, standard procedure for determining the composition of a gas containing hydrocarbons or a natural gas. The results are given in Table 1-A.

These results show the presence of hydrogen and carbon monoxide which are not believed to be present.

2. If hydrogen and carbon monoxide were present and knowing the amount from Table 1-A an analysis omitting the copper oxide combustion and burning the hydrocarbons, hydrogen, and carbon monoxide together in the slow combustion pipette from the data obtained the percentage of methane and ethane could be back calculated to obtain the results given in Table 1-A. This would prove the presence of hydrogen and carbon monoxide. The results given in Table 2-A were obtained by omitting the copper oxide combustion, the procedure otherwise being the same as used to obtain the results shown in Table 1-A.

The calculation of methane and ethane percentages from results in Table 2-A deducting for the amount of hydrogen and carbon monoxide shown in Table 1-A are as follows:

Methane $=$ Total $CO_2 - 2 \times$ Ethane

Total CO_2 $=$ Methane $+ 2 \times$ Ethane

Ethane $=$ $2 \times$ Total CO_2 $-$ Total Contraction $\div 1.5$

Total Contraction $=$ $2 \times$ Total $CO_2 - 1.5 \times$ Ethane

Basis 100 milliliters of gas.

Contraction due to Hydrogen $=$ Percentage of Hydrogen

Carbon Dioxide formed from Carbon Monoxide $=$ Percentage of Carbon Monoxide

Total CO_2 $= 10.29 + 2 \times 0.95 = 12.19$ ml.

Total Contraction $= 2 \times 12.19 - 1.5 \times 0.95 = 22.96$ ml.

Contraction due to Hydrogen $= 1.35$ ml. (Table 1-A)

Carbon Dioxide formed from Carbon Monoxide $= 0.17$ ml. (Table 1-A)

Carbon Dioxide from Methane and Ethane $= 12.19 - 0.17 = 12.02$ ml.

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	56.30	59.00	61.50							
CO_2	55.00	57.60	60.05	1.30	1.40	1.45	2.31	2.37	2.36	2.34
Ill	55.00	57.60	60.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O_2	44.60	46.70	48.65	10.40	10.90	11.40	18.50	18.50	18.50	18.50
H_2	43.80	45.90	47.85	.80	.80	.80	1.42	1.35	1.30	1.35
CO	43.65	45.80	47.75	.15	.10	.10	.26	.17	.17	.17
O_2 Added	36.25	32.30	37.10							
Total Volume	79.90	78.10	84.85							
Cont. (1)	67.40	65.30	71.40	12.50	12.80	13.45				
CO_2 (1)	61.60	59.40	64.85	5.80	5.90	6.55				
Cont. (2)	61.40	59.10	64.60	.20	.30	.25				
CO_2 (2)	60.30	57.90	63.70	1.10	1.20	.90				
Total Cont.				12.70	13.10	13.70				
Total CO_2				6.90	7.10	7.45				
Ethane				.733	.733	.800	1.30	1.24	1.30	1.28
Methane				5.43	5.63	5.85	9.64	9.55	9.52	9.57
Total							33.43	33.18	33.15	33.21
Nitrogen							66.47	66.82	66.85	66.79

Table 2-A

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	59.90	57.30	57.30							
CO_2	58.50	55.96	55.95	1.40	1.35	1.35	2.34	2.35	2.35	2.35
Ill	58.50	55.95	55.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O_2	47.45	45.35	45.35	11.05	10.60	10.60	18.50	18.50	18.50	18.50
O_2 Added	36.10	35.20	37.00							
Total Volume	83.55	80.55	82.35							
Cont. (1)	70.00	67.85	69.40	13.55	12.70	12.95				
CO_2 (1)	63.50	61.70	63.00	6.50	6.15	6.40				
Cont. (2)	63.20	61.30	62.80	.30	.40	.20				
CO_2 (2)	62.35	60.50	62.20	.85	.80	.60				
Total Cont.				13.85	13.10	13.15				
Total CO_2				7.35	6.95	7.00				
Ethane				.57	.533	.57	.94	.93	.97	.95
Methane				6.22	5.88	5.88	10.37	10.25	10.25	10.29
Total							32.15	32.03	32.07	32.09
Nitrogen										67.91

Contraction due to Methane and Ethane = 22.96 - 1.35 = 21.61 ml.

Percent of Ethane = 2 x 12.02 - 21.61 - 1.5 = 1.62%

Percent of Methane = 12.02 - 2 x 1.62 = 8.78%

These values do not agree with Table 1-A.

If hydrogen was present it is unlikely that it would not have burned completely over the heated spiral to give the contraction due to burning hydrogen. This indicates from the calculated percentages of methane and ethane from Table 2-A that the carbon dioxide formed by the slow combustion alone is greater than is shown by the slow combustion from the results of Table 1-A.

The average total contraction over the copper oxide tube and slow combustion from Table 1-A is 23.3 percent, and from Table 2-A the average was only 22.9 percent. This indicates that more carbon dioxide should have been formed by combustion over the copper oxide tube in analysis (1) to reduce the contraction apparently due to hydrogen.

It is concluded that some of the hydrocarbons were burned over the copper oxide and deposited carbon accounting for a large contraction with but little carbon dioxide formed. This resulted in an inaccurate determination of the hydrocarbons as well as showing the presence of hydrogen and carbon monoxide when they were absent from the original sample.

3. The recommended temperature for the combustion of hydrogen and carbon monoxide over copper oxide is about 290° or 300°C. Table 3-A shows the effect of elevating the temperature on the probable combustion of the hydrocarbons present. The effect of absorbing the carbon dioxide and oxygen together in the alkaline pyrogallol solution is also shown.

The effect of elevating the temperature of the copper oxide tube in the presence of the light hydrocarbons of sample A is negligible. Only a slight increase is noted between 290° and 340°C. The burning that does take place is probably due to the very small amount of heavy hydrocarbons present which give a constant amount of combustion, while the lighter hydrocarbons are unaffected.

The absorption of the carbon dioxide and the oxygen together in the alkaline pyrogallol solution gives the same total percent as when absorbed separately. This shows that nothing is insoluble in the pyrogallol that is soluble in the potassium hydroxide solution to give any illuminants when run before the carbon dioxide determination in the potassium hydroxide solution; and there is nothing in the gas sample soluble in the fuming sulfuric acid that is also soluble in the potassium hydroxide solution.

4. The results in Table 4-A show the effect of determining the illuminants and carbon dioxide together by passing the sample into the fuming sulfuric acid then into the potassium hydroxide solution. Oxygen is next determined by the usual procedure in the alkaline pyrogallol.

The results indicate that the carbon dioxide neither effects any solubility of the gases in the fuming sulfuric acid, nor is the carbon dioxide soluble in the acid. There is no effect upon the oxygen content when it is determined later.

No differences are noted in the results regardless of the order of absorption, using sample A, consisting of air, carbon dioxide, and the light hydrocarbons from natural gas.

Sample B.

1. The gas was analyzed by the standard procedure, and it was found

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	54.50	61.30	59.90							
$CO_2 + O_2$	43.15	48.50	47.40	11.35	12.80	12.50	20.83	20.85	20.85	20.85
Ill	43.15	48.50	47.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	42.45	47.70	46.60	.70	.80	.80	1.28	1.30	1.33	1.30
CO	42.35	47.60	46.50	.10	.10	.10	.18	.16	.17	.17
Temperature of CuO Tube °C.	290°	310°	340°	290°	310°	340°	290°	310°	340°	

that a constant absorption in the fuming sulfuric acid was not obtainable. The results in Table 1-B show the analysis of sample B omitting the illuminant determination.

The combustion for the determination of hydrogen and carbon monoxide over the copper oxide varied. A constant value was not obtained by a careful time-temperature control due to the non-uniform burning of the heavier hydrocarbons.

The copper oxide was reoxidized with pure oxygen after the determinations in Table 1-B were made, and when the gas was passed into the alkali pipette following the oxidation a contraction was noted. This indicates that carbon was deposited on the copper oxide probably due to cracking of the hydrocarbons during analysis.

2. To find the total hydrocarbon content of the gas the absorption of illuminants and the combustion over the copper oxide must be omitted. The gas was analyzed by burning the hydrocarbons in the slow combustion pipette. The results are given in Table 2-B.

The hydrocarbon content increased from about 19 percent to 21.35 percent by omitting the copper oxide combustion. This means that considerable burning took place over the heated oxide, and that samples containing hydrocarbons heavier than ethane should not be passed over the heated oxide if an accurate analysis is to be made.

3. The carbon dioxide and oxygen were determined together in the alkaline pyrogallol solution to note any difference in absorption or solubility of the hydrocarbons in the reagents. The results are given in Table 3-B.

The absorption of the carbon dioxide and oxygen together in the alkaline pyrogallol solution resulted in the same total percentage as

Table 4-A

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	59.90	57.50	55.30							
Ill $\neq$ CO_2	58.50	56.15	54.00	1.40	1.35	1.30	2.34	2.35	2.35	2.35
O_2	47.40	45.60	43.75	11.10	10.55	10.25	18.50	18.40	18.50	18.50

Table 1-B

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	53.50	53.70	55.50							
CO_2	49.50	49.70	51.35	4.00	4.00	4.15	7.48	7.46	7.46	7.46
O_2	39.65	39.80	41.15	9.85	9.90	10.20	18.40	18.44	18.40	18.40
H_2	39.60	40.10	41.85	.05	+.20	+.70				
CO	38.40	38.20	40.05	1.20	1.90	1.80				
O_2 Added	37.60	34.80	41.30							
Total Volume	76.00	73.00	81.35							
Cont. (1)	64.60	61.60	69.35	11.40	11.40	12.00				
CO_2 (1)	52.30	49.80	56.75	12.30	11.80	12.60				
Cont. (2)	52.10	49.60	56.25	.20	.20	.50				
CO_2 (2)	50.30	47.80	54.85	1.80	1.80	1.40				
Total Cont.				11.60	11.60	12.50				
Total CO_2				14.10	13.60	14.00				
Ethane				11.05	10.40	10.34	20.70	19.40	18.64	
Methane				0.0	0.0	0.0	0.00	0.00	0.00	0.00
Total							46.58	45.26	44.50	
Nitrogen							53.42	54.74	55.50	

Table 2-B

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume Sample	54.10	54.80								
CO_2	50.05	50.70		4.05	4.10		7.48	7.48		7.48
O_2	40.10	40.60		9.95	10.10		18.40	18.42		18.41
O_2 Added	39.80	36.40								
Total Volume	79.90	77.00								
Cont. (1)	66.90	63.80		13.00	13.20					
CO_2 (1)	52.70	49.00		14.20	14.80					
Cont. (2)	52.40	48.80		.30	.20					
CO_2 (2)	51.30	47.60		1.10	1.20					
Total Cont.				13.30	14.40					
Total CO_2				15.30	16.00					
Ethane				11.53	11.74		21.30	21.40		21.35
Methane				0.00	0.00		0.00	0.00		0.00
Total							47.18	47.30		47.24
Nitrogen							52.82	52.70		52.76

Table 3-B

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	59.00	54.50	56.20							
CO_2 + O_2	43.75	40.40	41.70	15.25	14.10	14.50	25.86	25.85	25.80	25.84
CO_2	43.75	40.40	41.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4-B

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	63.40	59.50	58.50							
Ill + CO_2	57.80	54.50	53.50	5.60	5.00	5.00	8.83	8.40	8.54	
O_2	46.10	43.50	42.70	11.70	11.00	10.80	18.47	18.48	18.47	18.47

when absorbed separately, and there was no further absorption afterwards in the potassium hydroxide solution. This indicates that all of the oxygen and carbon dioxide was absorbed in the alkaline pyrogallol, and if any hydrocarbons are soluble in the oxygen reagent no more are soluble in the potassium hydroxide solution after being in contact with the alkaline pyrogallol.

4. A constant value for the carbon dioxide and illuminants when determined together was not obtainable as shown by Table 4-B.

5. The illuminants were determined by carefully controlling the time of contact of the gas with the oleum, and the volume was read after each two passes. The results are given in Table 5-B.

There may be hydrocarbons in the sample that are classed as illuminants, and are absorbed by the fuming sulfuric acid during the first two passes. During subsequent contact periods the contraction is constant for a number of passes which may be due to the dissolving of the heavier saturated hydrocarbons present. The results are uncertain, and the absorption in the oleum should be omitted for an accurate analysis of the hydrocarbons. An approximation of the illuminants could be made from the first two passes by allowing for the constant contraction that occurs in the following passes. However, the results would be questionable.

Sample C.

1. The gas sample containing air, carbon dioxide, natural gas and ethylene was analyzed by following the standard procedure of analysis. The results are given in Table 1-C.

A constant value for the combustion over the copper oxide tube was not obtainable by careful time-temperature control, and as is shown

Table 5-B

COMPONENT	NUMBER OF 30 SECOND PASSES	READING	DIFFERENCE	PERCENT
Volume of Sample		54.45		
CO_2		50.40	4.05	7.45
Ill	2	50.00	.40	
	4	49.80	.20	
	6	49.60	.20	
	8	49.40	.20	
	10	49.20	.20	
	12	49.00	.20	
	14	48.85	.15	
	16	48.75	.10	

more combustion occurred at the higher temperatures. The illuminants show some variation in results. This is probably due to the presence of saturated hydrocarbons heavier than ethane but lighter than the hydrocarbons in sample B where large differences occurred in the illuminant determinations.

2. The results of carefully controlled combustion over the copper oxide tube are shown in Table 2-C.

Inconsistent results over the copper oxide tube indicate that the copper oxide combustion will have to be omitted when the gas sample contains saturated hydrocarbons heavier than ethane.

The carbon dioxide content of the samples analyzed, except those shown in Table 1-C, are considerably higher. When the results of Table 1-C were obtained the higher room temperature may have had a decided effect on the carbon dioxide absorption in the potassium hydroxide solution.

3. A check on the illuminants by controlled time and number of passes gave the results in Table 3-C. The gas samples were given two passes of thirty seconds duration into the fuming sulfuric acid at each reading for the illuminant determination.

The results are similar to those in Table 5-B in that after the first two passes the contraction from each two following passes is a constant. For the lighter hydrocarbons present the constant contraction is 0.05 milliliters for each two passes of thirty seconds while the heavier hydrocarbons gave a 0.20 milliliter contraction under the same conditions.

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	53.00	55.20	54.50							
CO_2	52.50	54.70	54.00	.50	.50	.50	.94	.91	.92	.93
Ill	51.10	53.40	52.50	1.40	1.40	1.50	2.64	2.54	2.75	2.64
O_2	41.50	43.40	42.65	9.60	10.00	9.85	18.10	18.10	18.10	18.10
H_2	40.70	42.40	41.15	.80	1.00	1.50				
CO	40.35	42.30	40.65	.35	.10	.50				
Temp. of CuO Tube °C.	300°	310°	340°	300°	310°	340°	300°	310°	340°	

Table 2-C

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	54.50	54.80								
CO_2	53.85	54.15		.65	.65		1.19	1.19		1.19
Ill	52.35	52.65		1.50	1.50		2.75	2.74		2.74
O_2	42.55	42.75		9.80	9.90		18.00	18.10		18.05
H_2	41.95	42.45		.60	.30					
CO	41.95	42.45		.00	.00					

Table 3-C

COMPONENT	READING			DIFFERENCE			PERCENT			AVERAGE PERCENT
	SAMPLE			SAMPLE			SAMPLE			
	1	2	3	1	2	3	1	2	3	
Volume of Sample	58.20	57.70	58.20							
CO_2	57.50	57.00	57.50	.70	.70	.70	1.20	1.21	1.20	1.20
Ill 2 passes	56.10	55.45	55.95	1.40	1.55	1.55				
Ill 4 passes	55.95	55.40	55.90	.05	.05	.05				
Ill 6 passes	55.90	55.35	55.85	.05	.05	.05				
Ill Total				1.50	1.65	1.65	2.58	2.86	2.84	2.76
O_2	45.30	44.90	45.40	10.60	10.45	10.45	18.20	18.10	18.00	18.10

SUMMARY OF RESULTS

Three gas samples have been analyzed in an attempt to place limitations upon the modern Burrell-Oberfell gas analysis apparatus, and ascertain the magnitude of some errors that accompany an analysis made to determine the exact composition of industrial gases. Gaseous hydrocarbons, due to their complexity, present a difficult problem if they are to be separated by a quick, simple and efficient method. The modern absorption and combustion gas analysis apparatus does not simplify this problem to any great extent.

An analysis of sample A, consisting of air, carbon dioxide, and natural gas, may not be passed over heated copper oxide at the recommended temperature to remove any hydrogen or carbon monoxide that may be present without burning the very small amount of hydrocarbons heavier than ethane. This introduces an error too large to say that the analysis is exact.

Sample B, consisting of air, carbon dioxide, and the hydrocarbon vapors from petroleum ether introduced a large error when passed over heated copper oxide, and the solubility of the heavier hydrocarbons in the fuming sulfuric acid, used to determine illuminants, was too great and gave inconsistent results.

Sample C, consisting of air, carbon dioxide, natural gas, and ethylene likewise burned over the heated copper oxide introducing a large error. The absorption of the sample by fuming sulfuric acid gave approximate results for the determination of illuminants, but the absorption of heavier illuminants in the presence of hydrocarbons heavier than ethane would be questionable.

Since hydrogen and carbon monoxide will burn over the copper oxide at a much lower temperature than 300°C. it may be possible to lower the temperature and increase the time of contact minimizing the error found at the higher temperatures due to the burning of the hydrocarbons. No noticeable effect was introduced by the hydrocarbons in the determination of carbon dioxide and oxygen. However, there is evidence of a decrease in activity of the potassium hydroxide reagent for removing carbon dioxide as the temperature of the reagent increases slightly above ordinary room temperatures.

CONCLUSIONS

The following conclusions may be formed from the experimental work on the gas samples that contain air, carbon dioxide, and saturated and unsaturated gaseous hydrocarbons.

1. The gas samples containing various gaseous hydrocarbons did not affect or introduce an error in the determination of carbon dioxide in the potassium hydroxide reagent.
2. The gaseous hydrocarbons did not affect the determination of oxygen in the alkaline pyrogallol reagent.
3. Oxygen and carbon dioxide were removed completely from the gas samples without introducing an error by determining the two together in the alkaline pyrogallol reagent. This procedure may be used if a saving of time is necessary, but the reagent must be changed more frequently.
4. Carbon dioxide was not soluble nor did it promote the solubility of light hydrocarbons in fuming sulfuric acid when the hydrocarbons are normally soluble in the acid.
5. If any of the gaseous hydrocarbons contained in the samples are soluble in the potassium hydroxide reagent they are equally soluble in the alkaline pyrogallol reagent. The reverse is also true.
6. It is indicated that gases containing saturated hydrocarbons heavier than ethane cannot be placed in contact with fuming sulfuric acid without a portion of the saturated hydrocarbons dissolving in the acid during a determination of illuminants.
7. Gases containing hydrocarbons heavier than ethane cannot be passed over heated copper oxide at 300°C. without some burning or cracking of

the heavier hydrocarbons. The burning of ethane is questionable.

8. An indication was found that carbon dioxide is much less readily absorbed by the potassium hydroxide solution the higher the temperature of the reagent.

9. Increasing the copper oxide combustion temperature increased the error due to the combustion of the hydrocarbons over the copper oxide.

10. At a definite temperature and time of contact, the hydrocarbons heavier than ethane burned non-uniformly over the heated copper oxide.

11. To obtain an exact analysis of a gas containing hydrocarbons with the Burrell-Oberfell apparatus using a complete standard procedure the sample must be limited in its composition by containing only the following gases or combinations of the following gases: carbon dioxide, oxygen, hydrogen, carbon monoxide, methane, ethane, ethylene, and possibly heavier unsaturated hydrocarbons with no heavier saturated hydrocarbons. If the illuminants may be omitted and no hydrogen or carbon monoxide is in the sample, saturated hydrocarbons heavier than ethane may be analyzed by combustion.

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I entered Oklahoma A. and M. College, Stillwater, Oklahoma, January, 1934, and was graduated in May, 1938, receiving a Bachelor of Science degree in Chemical Engineering.

On March 15, 1936, I accepted a part-time position with the Oklahoma Agricultural Chemistry Research under Dr. V. G. Heller where I was employed until September 1, 1938, when I accepted a position as graduate assistant instructor in the Chemistry Department. I entered the Graduate School at Oklahoma Agricultural and Mechanical College at that time. I remained there until June 1, 1939, and on July 1, 1939, I accepted a position with the Phillips Petroleum Company in Kansas City, Kansas.

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