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Standard methods of gas analysis involve the use of a slow combustion pipette. There are several objections to this type of unit. Many modifications have been proposed although few have been incorporated into standard apparatus.

A capillary combustion unit has been made and tested in a Burrell Bureau of Mines type gas analyzer. Results indicate that the device compares favorably in efficiency with standard methods. It provides a faster and more convenient method of analysis. The danger of explosion seems to be eleminated. The unit may be readily incorporated into standard apparatus.

A MODIFIED COMBUSTION CAPILLARY FOR USE IN GAS ANALYSIS

by

ROBERT NELSON CARLTON

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APPROVED:

Assistant Professor of Chemistry
In Charge of Major

Head of Department of Chemistry

Chairman of School Graduate Committee

Chairman of College Graduate Council

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INTRODUCTION

A MODIFIED COMBUSTION CAPILLARY FOR USE IN GAS ANALYSIS

INTRODUCTION

Gases are usually analyzed by application of one of three general methods: Titration, gravimetric, and volumetric. Of these the volumetric method is by far the most important. This method which was worked out by Cavendish and later by Bunsen (7) involves the removal by successive absorbtion in suitable reagents of the several constituents of a measured volume of a gas. The amounts of these constituents absorbed are determined from the loss in volume. The residue is generally analyzed by combustion. The amounts of oxidizable materials are calculated from the loss in volume, (the water is condensed) the amounts of the various products of combustion absorbed, or the amount of oxygen used by the reaction.

The standard method for combustion of gases involves the use of a slow combustion pipette. This method was first described by Winkler (12) in 1889. Present day apparatus has been modified but very slightly. This slow combustion pipette consists essentially of a pyrex glass pipette connected by capillary glass tubing to the manifold of a gas analysis apparatus. It contains a coil made of platinum wire mounted on glass tubes projecting through a stopper in the bottom. Leads to the platinum coil are

sealed with wax into the glass tubes supporting the coil. Another glass tube projects through the stopper and is connected with rubber tubing to a leveling bulb filled with mercury.

In use the pipette is filled with mercury by means of the leveling bulb. A measured quantity of oxygen is transferred from the gas Burette to the pipette forcing out mercury and exposing the platinum coil. Current sufficient to make the platinum wire glow brightly is then passed through the coil. The gas or gas residue is then carefully measured in the gas burette and slowly transferred to the combustion pipette. Two minutes or longer is generally required to complete combustion. The residue is then withdrawn to the gas burette and its volume measured. It is then passed into an absorbent for carbon dioxide. After absorbtion its volume is again measured. Often the above procedure is reversed in that oxygen is added to the gas.

This type of combustion unit presents many difficulties. Among them are the following:

1. Unless the flow of gas into the unit is very carefully regulated there is danger of explosion.

2. Mercury must be used as a confining liquid. Because of the great density of mercury, the levels in the combustion unit and leveling bulb must remain very nearly equal. Otherwise the gases will be under increased or

diminished pressure which makes for leakage. This manipulation of the leveling bulb makes the procedure tedious and inconvenient.

3. It is difficult to get tight joints when using a stopper carrying leads to the coil.

Many attempts have been made to modify or dispense with this combustion unit.

Catalytic oxidation has been sucessfully demonstrated at Oregon State College by Walker and Christensen (10) but is objected to on the ground that the catalyst is difficult to prepare and that the resulting apparatus is more complex.

Among the modifications to the slow combustion unit are those of Weaver and Ledig (11) who introduced leads to the coil through side arms. Soft glass caps are sealed with cement over the side arms.

In a modification of this unit by Shepherd (8) the leads are folded under metal caps which are sealed over the side arms with cement. Connection to the electrical circuit is made through these metal caps.

In Amblers Bubbling Combustion Pipette (7) the gases are introduced through a side arm and bubbled through the mercury. This makes possible a finer control of the incoming gases.

Other modifications have been introduced by Steacie

(9), Kobe (5), Kaleta (4), and Evans and Davenport (3). In that by Evans and Davenport electrical connections are made by means of tungsten wires sealed into tubes projecting from the pipette. This modification was used in a special apparatus for the analysis of flue gases but was not adapted to standard gas analysis apparatus.

Another general method for effecting combustion consists of passing the gas mixed with oxygen through a small tube containing heated platinum or an electrically heated platinum coil. Of these the Drehschmidt Capillary (7), the Levy Platinum-Silica Capillary (6), and one described by Weaver and Ledig (11) are representative.

The Drehschmidt Capillary consists of a small platinum tube packed with small pieces of platinum wire. The ends of the tube are soldered to pieces of brass tubing provided with water jackets for cooling. Heat is supplied by a gas flame. The chief objections to this device are the expense of the platinum and the complicated set-up necessary.

The Levy Platinum-Silica Capillary consists of a coil mounted in a silica tube with molybdenum leads fused into the silica and joined to lumps of lead which in turn are soldered to the external wires. This device is not in common use due to the difficulties of making the unit and replacing the combustion coil.

The capillary described by Weaver and Ledig has leads connected by metal caps through side arms as in their slow combustion unit mentioned above. The mechanical instability of cemented joints is its most objectional feature.

DESCRIPTION OF APPARATUS

DESCRIPTION OF THE APPARATUS

The capillary unit (see Figure 1) was made of pyrex glass. The platinum spiral was made of 36 guage wire mounted on 20 guage tungsten wire leads which were sealed through the glass. The temperature of the spiral was maintained by placing a variable resistance (rheostat 94 ohms 2.2 amperes in series) using a 110 volt alternating current.

In the initial experiments a safety valve was incorporated in the intake capillary of the unit. This valve consisted of a bulb, blown into the capillary, in which was placed a mercury bead. Due to the difficulty of maintaining the mercury in the bulb this method was abandoned. Further investigation revealed the fact that no additional safety device was required when the intake capillary was less than .5 mm in diameter. Using such a capillary effectively prevented the explosion from passing through to the burette, an occurrence which was not prevented by the usual tubing.

This unit when incorporated into a standard Burrell, Bureau of Mines type, gas analyzer (1) is placed with its intake (3 way stopcock) to the left of the potassium hydroxide pipette and its exit between the first and second pipettes of the gas train.

A further simplification of the gas analyzer can be

effected if the combustion unit is incorporated in one arm of a standard copper oxide tube as shown in Figure 2. This permits the use of a simple manifold.

The platinum coil may be readily replaced by cutting the combustion tube immediately below and above the tungsten leads. The new coil can then be mounted in place and the tube resealed.

EXPERIMENTAL

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Because it is the most difficult of gases to oxidize methane was chosen to test the efficiency and practicability of the coil.

Procedure for analysis with the capillary unit differs from that with the slow combustion pipette in that the gas and oxygen are mixed before entering the combustion chamber. To a measured quantity of gas in the gas burette is added sufficient oxygen to insure a 2½ to 1 oxygen-methane ratio. The total volume is then read after which the mixture is slowly passed over the glowing coil. Two passages through the unit were found sufficient to insure complete combustion.

In order to check the range and limitations of the unit, test runs were made with varying concentrations of methane and oxygen at different space velocities. Both the .4 mm and 1.5 mm intake capillary were tested in the unit.

These results which are shown in Table I indicated that it was safe to pass methane and oxygen even in theoretical proportions over the heated coil when the smaller intake capillary was used. When the larger intake was used the higher concentrations of methane caused flashing explosions which traveled back through the manifold and on one occassion exploded the mixture in the gas

burette.

The rate at which the gas was introduced depended on the concentration of methane in the mixture. When the content was low the methane burned noiselessly regardless of the rate. At the higher concentrations, (1 part methane to 2½ parts oxygen) as the space velocities were increased, the reaction in the combustion chamber became audible. The rate of delivery for these mixtures was adjusted so that the sound was just perceptible.

A series of analyses were made using mixtures of methane and air. Check determinations were made using a standard slow combustion pipette. Results are shown in Table II. Satisfactory agreement was noted at all concentrations.

The fuel gas regularly supplied in the laboratories at Oregon State College was used to check the operation of the combined copper oxide and combustion unit. Since this gas contains a number of constituents a more involved procedure was necessary. First carbon dioxide and oxygen were removed with potassium hydroxide and alkaline pyrogallal solution respectively. The gas was then passed over the combined unit with a furnace heating the copper oxide portion. Hydrogen and carbon monoxide reacted with the copper oxide forming carbon dioxide and water. From the total loss in volume and the amount of carbon dioxide absorbed the carbon monoxide and hydrogen contents were

calculated. The residue was then passed through the unit again with the combustion coil heated and the methane determined as before. Results for four consecutive determinations on a sample of gas are shown in Table III.

SUMMARY

SUMMARY

1. Standard methods of effecting combustion of gases and several modifications to these methods are discussed.

2. A capillary combustion pipette employing a platinum spiral mounted on tungsten leads sealed through the glass is described.

3. Evidence that this combustion unit affords a safe, precise and convenient method for the analysis of combustible gases is included.

4. This unit can be easily incorporated into a standard gas analysis apparatus.

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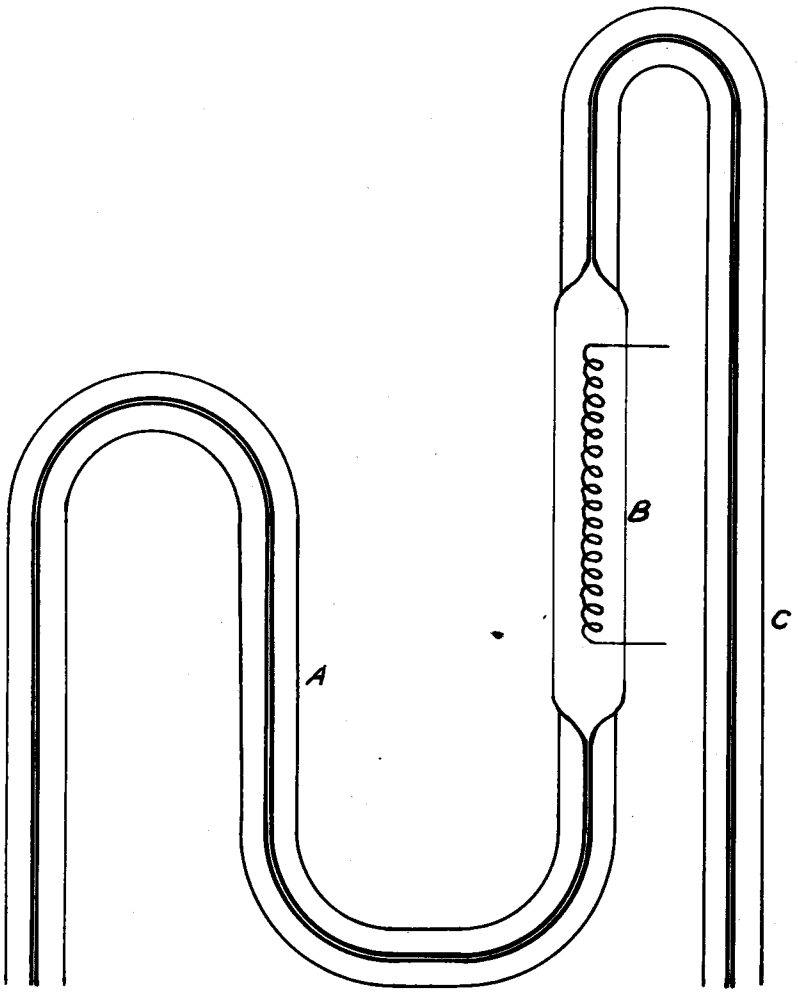
Fig. 1



A - Intake capillary
B - 8x50 mm combustion unit
C - Outlet capillary

Fig. 2

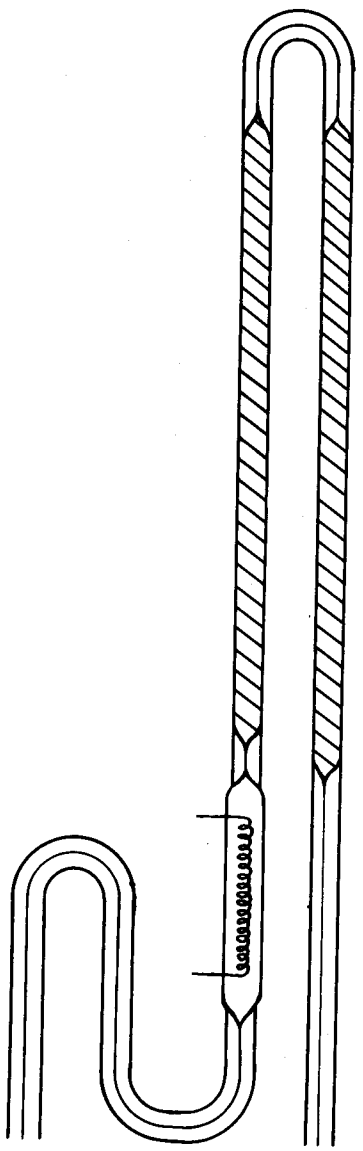


TABLE I

EFFECTIVENESS OF 1.5 and .4 mm INTAKE CAPILLARY

IN PREVENTING FLASHBACK OF EXPLOSIONS

Sample	Methane cc.	Total with added oxygen	Methane %	Rate of Delivery	Diameter of Intake	Result
1	4.68	66.6	7.0	15 cc min	1.5 mm	Burns quietly
2	7.94	75.8	10.5	15 cc min	1.5 mm	Explosive No Flashback
3	10.7	74.9	14.2	15 cc min	1.5 mm	Explosive Some Flashback
4	12.3	76.4	16.2	15 cc min	1.5 mm	Explosive Some Flashback
5	10.1	73.7	13.7	30 cc min	1.5 mm	Explodes No Flashback
6	10.3	74.2	13.9	15 cc min	.4 mm	Explodes No Flashback
7	13.6	79.6	17.0	15 cc min	.4 mm	Explodes No Flashback
8	20.1	72.6	27.7	15 cc min	.4 mm	Explodes No Flashback
9	19.6	60.6	32.3	15 cc min	.4 mm	Explodes No Flashback
10	29.8	90.0	33.1	15 cc min	.4 mm	Explodes No Flashback

TABLE II

COMPARISON OF RESULTS OF ANALYSIS WITH CAPILLARY UNIT AND STANDARD SLOW COMBUSTION PIPETTE

	% Methane	
Sample No.	Capillary Unit	Slow Combustion Pipette
1	94.3	94.3
2	91.8	91.9
3	90.3	90.3
4	89.7	89.5
5	82.9	82.6
6	82.2	82.1
7	59.8	60.1
8	40.9	41.1
9	37.6	36.8
10	24.2	23.9
11	19.5	19.5
12	12.5	12.3
13	7.6	8.2

TABLE III

RESULTS USING COMBINED COMBUSTION AND COPPER OXIDE TUBE

No.	1	2	3	4
% CO	8.3	8.1	7.9	8.2
% H_2	42.2	42.0	42.2	42.0
% CH_4	35.9	36.0	35.8	36.1

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