

THE DETERMINATION OF HYDROGEN, NITROGEN AND METHANE IN GAS BY COMBUSTION IN A QUARTZ TUBE.

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The purpose of this research was to devise a more convenient and a more accurate method for the determination of hydrogen, nitrogen and methane in gas. Many different methods¹ have been advocated for making this analysis. The Drehschmidt method² of burning the gas residue mixed with oxygen, by passing it through a hot platinum capillary tube is perhaps the best scheme. However, the high cost of the platinum capillary tube together with the rapid deterioration of the apparatus makes a modification desirable. The experiments described in this paper show that a quartz tube filled with pieces of scrap platinum is an entirely satisfactory substitute for the platinum capillary tube in the Drehschmidt apparatus.

The quartz tube was 30.5 cm. long, 7.25 mm. outside and 3.38 mm. inside diameter. Its volume, determined by the weight of mercury required to fill it, was 3.317 cc. The platinum scrap which was used as a contact substance in the quartz tube was prepared by cutting pieces of ordinary scrap platinum wire, which every laboratory has in quantity, into as short pieces as possible with a shears. These small fragments were then placed upon stiff paper which was passed through a cornet roll mill a number of times. These flattened pieces of platinum presented a large surface to the passing gas and at the same time offered very little resistance to the passage of the gas. Two pieces of scrap platinum gauze were used, one in each end of the quartz tube, to keep the small pieces of platinum in position. The platinum weighed 11.189 grams and had a volume of 0.522 cc. The platinum occupied 21.6 cm. of the length of the tube.

The data concerning the many preliminary experiments which merely served to detect the errors, will be omitted. The following form of apparatus and manipulation were found to be satisfactory.

A mercury pipet holding the gas to be burned and the oxygen required for the combustion, was connected to one end of the quartz tube by a

¹"Review of progress in gas analysis," *Chemiker Zeitung*, 32 :801 and 817 (1908).

²Hempel-Dennis, "Gas Analysis," p. 140.

suitable capillary tube with rubber connections. A mercury buret, arranged to receive the gas, was connected to the other end of the quartz tube in a similar manner. Pinch cocks, one on the buret and one on the pipet, controlled the connections with the quartz tube. The buret was provided with a water jacket which was connected at its lower end with a level bottle so arranged that the water could be drawn out and then passed back into the water jacket. This circulation and thorough mixing of the water were necessary to prevent unequal temperatures between the top and bottom of the buret. The water jacket was improvised from the outside of a Liebig condenser. A thermometer, which showed the temperature of the water and gas, was suspended about midway of the buret inside of the water jacket. The quartz tube was heated by a bunsen burner provided with a wing tip which produced a broad flame. An asbestos board was suspended about 5 mm. above the quartz tube, to lessen the radiation of heat. The manipulation was: The temperature of the gas in the pipet, that is the temperature at which it was measured, was carefully read. The pinch-cock connecting the buret to the quartz tube was opened and the burner was lighted for three minutes. The increase in volume of the air in the quartz tube produced by the heat, was cared for in the buret. The pinch-cock connecting the pipet to the quartz tube was opened and the level bottle was raised so that the gas and oxygen passed slowly and regularly over the glowing platinum, generally about three minutes being required. In no case was there any indication of an explosion in the pipet even when the velocity of the gas was greatly increased. The level tube on the buret was raised and the level bottle on the pipet was lowered so that the gas was forced back from the buret into the pipet. The gas was then again passed through the quartz tube over the glowing platinum into the buret. The flame and the asbestos board were removed and water was poured upon the quartz tube to cool it. After the quartz tube had reached room temperature, the pinchcock connecting the buret and quartz tube was closed. The mercury in the buret and level tube was leveled. The water in the water jacket was passed back and forth by means of the level bottle until the thermometer in the water jacket showed constant temperature. The mercury in the buret and level tube was again carefully leveled and the volume of gas was read. The final gas volume was always corrected for variation from the initial temperature.

The process as described above was tried with pure hydrogen gas, which was prepared by the action of boiled dilute sulphuric acid upon

pieces of zinc contained in a gas double pipet for solids. The pipet was filled with boiled distilled water to displace the air. The sulphuric acid was added through a glass tube which entered through the opening for the introduction of solids into the pipet. The hydrogen gas was allowed to escape completely from the apparatus several times before any was saved for analysis. This form of generator very effectively protected the hydrogen gas from the diffusion of air. The results are given in the following table:

Hydrogen Used.	Air Added.	Volume after Combustion.	Time of Experiment.	TOTAL CONTRACTION	
				Experimental	Theory
26.02	90.6	77.6	2.5 minutes	39.03	39.03
21.06	77.9	66.75	2.3	31.6	31.59
20.4	77.9	67.7	3.5	30.6	30.6

The following table shows the results which were obtained in the analysis of gas residues:

Residue cc.	Oxygen cc.	Volume after Combustion.	Time	Total Contraction.	Carbon Dioxide.	Hydrogen	Nitrogen	Methane
51.9	80.4	50.2		82.1	18.8	29.7	3.4	18.8
52.3	71.3	42.4	3	81.4	17.5	29.4	4.25	18.65
52.16	67.18	38.	2	81.34	17.77	29.	3.9	18.9

The result in experiment 1 was obtained with the ordinary combustion pipet. This value was taken as the standard. Experiment 2 in the table shows 17.5 per cent. of carbon dioxide, which was of course obtained by the absorption of the carbon dioxide which was in the buret. This value must be corrected for the amount of carbon dioxide which remained in the quartz tube. The total gas residue after combustion (including the air originally in the quartz tube) was 42.4 plus 2.795 (the volume of the quartz tube which was unoccupied by platinum) which was 45.195. So 93.8, $(42.4 \div 45.195)$, was the per cent. of the gas which was measured in the buret.

All of the results given in the tables show that the quartz tube is as accurate as the combustion pipet. It was found necessary to pass air through the quartz tube to remove the carbon dioxide produced by one experiment if another experiment was to be made at once. If only total contraction was desired the carbon dioxide did not need to be removed. If nitrogen was to be determined the gas remaining in the tube from a previous experiment had to be removed by passing air.

This apparatus gave an excellent method of determining the total nitrogen in gas. The gas was mixed with an excess of oxygen whose nitro-

gen contents was accurately determined. After combustion in the quartz tube, the gas was passed into potassium hydroxide and alkaline pyrogallol pipets. The unabsorbed residue consisted of the nitrogen in the gas and the nitrogen which was in the oxygen. The results are as follows:

Gas	Oxygen.	Nitrogen added in Oxygen	Total Nitrogen	Nitrogen in Gas Taken	Nitrogen per cent.
49.9	76.4	7.10	8.68	1.58	3.17
50.0	74.05	6.95	8.62	1.67	3.34
49.93	78.04	7.19	8.78	1.58	3.20

Other tests showed that under the conditions of the experiment less than 67.7 cc. of the oxygen (63.4 cc. of pure oxygen) did not give complete combustion with 50 cc. of the gas. This was 12 cc. of pure oxygen in excess.

SUMMARY.

Gas residues after the addition of oxygen gas were burned by passing them through a heated quartz tube which contained pieces of scrap platinum. The results are very accurate.

The advantages of this apparatus over the standard combustion pipet are:

1. The quartz tube and pieces of platinum are not easily broken or damaged during use. The quartz tube, however, is brittle and will break if struck a blow. The combustion pipet is very easily broken and the small platinum wire often burns out even when great care is exercised by the operator.

2. No metal or other substance which can be oxidized or acted upon by any of the gases is present in the quartz tube during the burning. In the combustion pipet, mercury, an oxidizable metal, is always present. In some of the experiments during this research, the conditions were such that very serious errors were made by the absorption of gases by the mercury. Everyone is familiar with the formation of oxides upon the mercury and upon the sides of the combustion pipet.

3. Small cracks in the glass tubes, or leaks around the rubber stopper or places where glass tubes enter, in the combustion pipets cause serious errors. There is very little chance for leaks in the quartz tube apparatus.

4. Platinum scrap such as short lengths of wire which is generally plentiful in laboratories, is used in this apparatus. The quartz tubes are cheap.

The disadvantages of this new process are:

1. The gas becomes heated during the combustion, so care must be taken to determine the final temperature at which the gas is measured. Corrections must be made for all temperature changes.

2. A correction must be made for the carbon dioxide which remains in the quartz tube after the combustion. This disadvantage can be overcome perhaps by the use of a smaller bore capillary quartz tube in which the volume is so small that a correction is unnecessary.

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