

An Adaptation of Pregl's Microcombustion to a Semi-microcombustion Method for the Determination of Nitrogen.

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During the spring of 1925, DOBROVOLNY and one of us (W. M. L.) devised a semi-micro combustion method for the determination of carbon and hydrogen in organic compounds. Since this method proved to be quite serviceable in the hands of others, it was considered advisable to attempt the development of a similar method for nitrogen. Here again, the admirable work of PREGL served as the foundation upon which this semi-micro method was based. A twenty milligram sample was used and the weighings were performed on a high-grade analytical balance sensitive to $\frac{1}{20}$ the mgm. The procedure here described has been found to yield satisfactory results, and the necessary technique is easily acquired.

Description of Apparatus.

The Source of Carbon Dioxide:

Carbon Dioxide was prepared by means of a Kipp Generator in the manner prescribed by PREGL¹).

The Combustion Tube and Filling:

The combustion tube consisted of a 13 mm. (inside diameter) Pyrex tube, 45 cm. in length, sealed to a 5 mm. (inside diameter) tube 8 cm. long. It was attached to the Kipp Generator by means of a capillary tube (A) fitted with a stop cock (not shown in diagram). The combustion tube was filled as follows: A small plug of ignited asbestos was first passed into place in the neck of the tube. An 8—8.5 cm. layer of wire form copper oxide (E) was then introduced. Another plug of asbestos served to hold this copper oxide in place. A roll of copper gauze (D) 4 cm. in length, which had been reduced by means of methyl alcohol was then put into place, followed by a plug of asbestos. A 7 cm. layer of copper

¹) Quantitative Organic Microanalysis, F. PREGL. — Translated by FYLEMAN; J. & A. CHURCHILL, London, p. 79.

oxide (C) similar to the copper oxide first used, followed by a plug of asbestos, completed the permanent filling of the tube.

A porcelain boat, containing the sample mixed with powdered copper wire oxide and a roll of oxidized copper gauze (B) completes the tube filling.

The use of an oxidized copper spiral simplifies the work of introducing new samples. After heating in air to bring about reoxidation it is ready for use again. The combustion tube was supported by means of an iron trough, 14 inches long, made from angle iron. This trough was sawed into sections from the lower edge to within $\frac{3}{8}$ " of the two upper edges. Two side arms served to fasten the trough to ringstands. A layer of asbestos paper was placed in the trough under the combustion tube. Iron or asbestos covers (2 inches long) were also provided. Three burners, fitted with wing-tops supplied the heat.

The Absorption Apparatus (F).

The absorption apparatus, F, which has a total length of 65 cm. and an internal diameter of 1—2 to 1—4 cm. is similar to a SCHIFF azotometer. Its construction and relation to the remainder of the apparatus is indicated in the figure.

The Measuring Burette (G).

The measuring burette (G) consists of a piece of glass tubing with an internal diameter of about 4 mm. sealed to a capillary tube carrying a stop-cock. The length of this 4 mm. tube should be sufficient to give the burette a capacity of about 5 mm. The measuring burette is surrounded with a waterjacket and connected to a levelling bulb by means of a piece of rubber tubing.

The absorption tube, the measuring burette and the two levelling bulbs are filled with a 33% solution of potassium hydroxide.

A zero mark is etched on the capillary part of the measuring burette and the calibration is carried out using 33% KOH as the calibrating liquid, reading the distance from the zero point to the meniscus on a millimeter scale and weighing the KOH solution removed. A curve is then plotted showing the relationship between these distances and the corresponding volumes.

Detailed Procedure.

After the Kipp generator has been treated as described, the combustion tube filled, all joints made tight, the stop-cocks greased, the absorption tube, and measuring burette, etc., filled

with the 33% potassium hydroxide solution, the 3-way stop-cock closed, the levelling bulb attached to F lowered, the stop-cock between F and E and that between A and the generator are opened so as to sweep the air out of the combustion tube. The air collects above the alkali solution in the absorption tube and is let out by opening the 3-way stop-cock. During the operation the stop-cock between E and F is closed and the levelling bulb attached to F is raised in order to drive out the air. If the residues from the bubbles rising in the potassium hydroxide solution are barely perceptible the carbon dioxide is of sufficient purity to be used, if they are not, the stop-cock between E and F is closed and the plug of the stop-cock, between the generator and A, lifted slightly so as to let most of the carbon dioxide escape. The acid then rises into the middle bulb of the generator, with a resulting rapid evolution of gas. If some of this gas is allowed to escape the air that has collected in the middle bulb will soon be driven out.

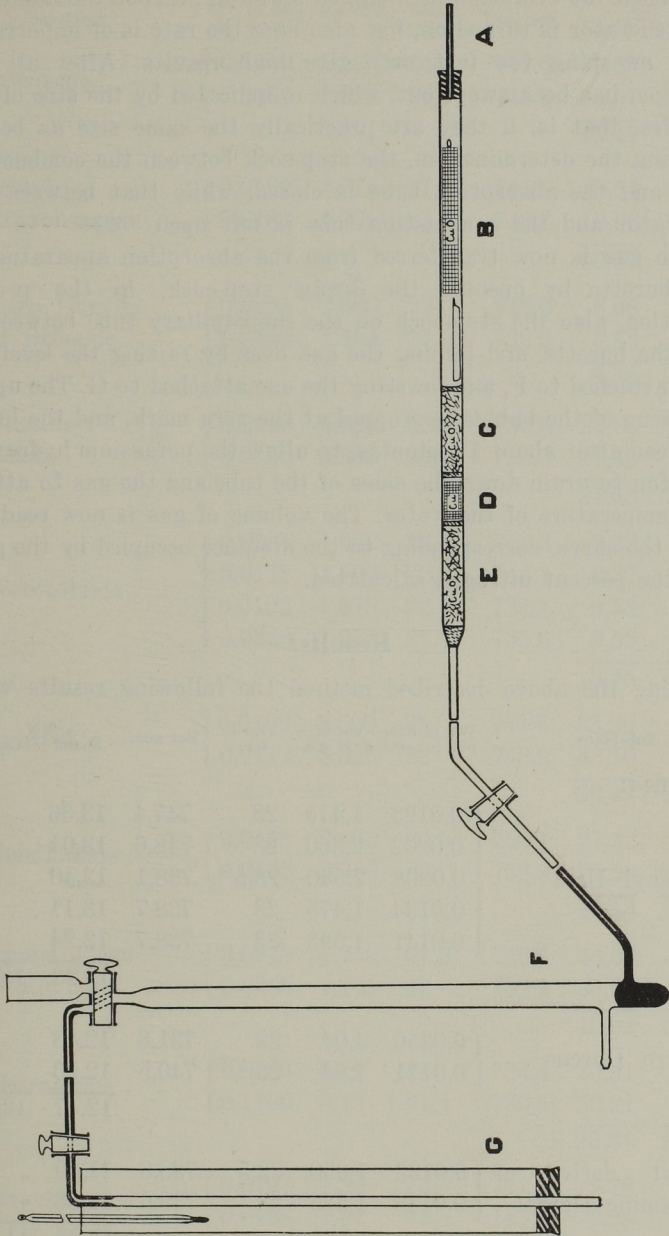
In case the carbon dioxide is found to be of sufficient purity, which is indicated by the minute size of the bubbles and the negligible quantity of gas collected during half an hour or so, while running the gas through at the rate of 8—10 bubbles in 10 seconds, the tube is heated while running carbon dioxide through, to remove absorbed air, and then cooled in the gas. Instead of leaving the oxidized copper spiral (B) in the tube considerable time is saved if 2 extra boats filled with freshly oxidized, powdered copper oxide are put in. The permanent tube filling is good for quite a number of determinations, while for some compounds the powdered copper oxide is so badly reduced on burning one sample that it must be reoxidized and placed in the tube to remove the adsorbed air before it can be used for burning another sample. Thus some time is saved by driving off the absorbed air from three boats full of powdered copper oxide at once.

After the tube filling has cooled in carbon dioxide the tube is opened by taking the stopper which carries the capillary tube (A) out of the combustion tube. Two boats containing copper oxide are set aside for future use, and into the third is placed about 20 milligrams of the substance to be analyzed, covered with powdered copper oxide and placed back into the combustion tube. Then the oxidized roll of copper gauze is put in and the generator connected. During this operation some air will, of course, enter the tube

which must be swept out by carbon dioxide before the tube or any part of it is heated. After the air is removed, which can be determined as above, it is let out through the three-way stop-cock on top of F, and heating of the tube filling is started.

For heating 3 Tirrill burners are used. One fitted with a wing top, under the reduced copper spiral, heating the reduced copper spiral, part of the layer of oxide in front and part of the layer back of it, is started first, then the burner under B, the oxidized copper spiral, is started. In case the substance requires a fairly high temperature for decomposition a wing top is used. The plates used for covering the tube are all taken off, except over the parts to be heated. After these parts have been heated gradually to nearly the full heat of the burner, the third burner under the sample is started, very low at first under the end of the oxidized copper spiral, and gradually raised and moved under the sample. At the same time the covers are gradually put on, but at no time should the bubbles rise faster than 8 per ten seconds, and for some compounds an even slower rate is advisable. During the first part of the heating some gas comes into the absorption tube, due to expansion on heating the tube, so the stop-cock between the generator and A may be left closed during the combustion and only the one between the combustion tube and the absorption tube kept open. If a compound decomposes readily, more care must be used in heating the tube filling and in decomposing the sample. The burner under the reduced copper spiral may, however, always be started with the wing top on. But the burner under the oxidized copper spiral will in some cases have to be started without the wing top and as faraway from the sample as possible. Then after the reduced copper spiral is hot, and also parts of both layers of copper oxide (wire form), the other burner is moved slightly towards the sample, and after a while the wing top may be put on. By this time the sample may have started to decompose and it may not be necessary to start the burner directly under the sample till the sample is practically decomposed. In either case the reduced copper spiral and part of the copper oxide in front of it as well as that in back of it should be hot and the oxidized copper gauze roll as hot as possible. If this is not hot, backward distillation will take place and low results follow.

After the sample is nearly all decomposed, the full heat of the burners will usually be used, and the covers will all have been put



on. When the evolution of nitrogen slows up, carbon dioxide from the generator is turned on, but also here the rate is of importance since sweeping too fast may give high results. After all the nitrogen has been swept out, which is indicated by the size of the bubbles, that is, if they are practically the same size as before starting the determination, the stop-cock between the combustion tube and the absorption tube is closed, while that between the generator and the combustion tube is left open.

The gas is now transferred from the absorption apparatus to the burette by opening the 3-way stop-cock, in the proper direction, also the stop-cock on the the capillary tube between it and the burette, and forcing the gas over by raising the levelling bulb attached to F, and lowering the one attached to G. The upper meniscus of the bubble is stopped at the zero mark, and the lower one read after about 15 minutes, to allow the potassium hydroxide solution to drain down the sides of the tube and the gas to attain the temperature of the water. The volume of gas is now read off from the curve, corresponding to the distance occupied by the gas, and the percent nitrogen calculated.

Results.

Using the above described method the following results were

Substance	Wt. of Sample in gms.	Vo. of N. in c.c.	Tem. °C	Bar mm.	%N Found	%N Calc.
obtained:						
Diphenyl Urea . . .	{ 0,0123	1,475	23	747,4	13,36	
	{ 0,0202	2,360	23	748,6	13,04	
	{ 0,0208	2,540	23,5	738,1	13,40	
	{ 0,0124	1,475	23	738,7	13,11	
	{ 0,0141	1,695	23	738,7	13,24	
					<u>13,23</u>	<u>13,20</u>
Dinitro Durene . . .	{ 0,0356	4,04	22	731,8	12,43	
	{ 0,0171	1,94	23	740,5	12,50	
					<u>12,47</u>	<u>12,50</u>
Acetyl deriv. of Diamino Durene . . .	{ 0,0132	1,350	22,5	738,8	11,30	
	{ 0,0148	1,525	23	739,6	11,36	
					<u>11,33</u>	<u>11,29</u>