CXIV.—*A Method for the Rapid Ultimate Analysis of Certain Organic Compounds.*

By JOHN NORMAN COLLIE.

THE method described in the following communication is not a new one, but a modification of that first suggested by Saussure and Prout. In 1827, Prout published a paper on organic analysis in the *Philosophical Transactions*, in which he described an apparatus for estimating the amount of carbon and hydrogen in an organic compound by the combustion of a known weight of the substance in a known volume of oxygen. Considering the difficulty of obtaining apparatus in those days, many of his results were marvellously accurate.

Nowadays, with mercury pumps, glass taps, and all the appliances of a modern laboratory, the method should at least not be less accurate, and at the same time should be far easier to carry out. It seemed therefore worth while to use this method again with such modifications as were possible, for the following reasons: (1) as it depends on measurements of volumes of gases, it is extremely accurate; (2) the amount of substance used can be reduced to nearly one-tenth of that ordinarily employed; (3) the time taken in an analysis ought to be very materially shortened.

At present, however, the method has its limitations, as it can only be used for the combustion of compounds containing carbon and hydrogen, or carbon, hydrogen, and oxygen, moreover, only for those which are not appreciably volatile in a vacuum.

An accurately weighed amount of the substance is introduced into a hard glass combustion tube, which can be heated in a furnace. The tube is filled with oxygen, the volume of which is obtained by exhausting the apparatus by means of a mercury pump and delivering the oxygen into a measuring tube. The oxygen is then allowed to re-enter the combustion tube, which is forthwith rapidly heated to redness, and even if complete combustion of the compound does not occur at once, the gases can be passed backwards and forwards through the tube by means of two mercury reservoirs, and any carbon monoxide is completely and rapidly burnt to carbon dioxide. The whole of the gases are pumped out again, measured, and passed into a separate vessel containing strong caustic potash solution to absorb the carbon dioxide, and finally back again into the measuring vessel. From the data obtained, the percentage of carbon and hydrogen in the compound can be calculated.

Description of the Apparatus.

A carefully weighed quantity of the substance to be analysed is introduced in a boat, *S*, into the combustion tube at *O*. The mercury pump, *T*, is cleared of air by closing the tap 4 and delivering all the air

through the tap 11 into *B*. The mercury in *B* is then raised until all the air has been expelled; the tap 6 is then closed. Oxygen is passed into the combustion tube through the taps 3 and 4, and the displaced air allowed to escape by removing the core of tap 10, the mercury in the

reservoir, *C*, being brought to the level of tap 10. As soon as oxygen issues from the combustion tube, the core of tap 10 is replaced. Tap 3 is now closed, and the whole of the oxygen is allowed to enter the mercury pump by opening the tap 4. The volume is then read under atmospheric pressure, and the temperature of the water in the outer jacket surrounding the measuring tube, *B*, is noted on the thermometer, *F*. The height of the barometer is also taken. Tap 4 is now closed, and tap 6 is opened so that the oxygen may again enter the combustion tube.

The combustion tube may now be heated at *A* and *A'*, where asbestos, covered with copper oxide made from pure copper nitrate,* is placed. As soon as both ends of the tube are red hot, all the burners under the combustion tube may be lighted, and the substance in the boat, *S*, volatilised as rapidly as possible. When this occurs, the tap 6 is slightly opened so as to draw the vapour of the substance mixed with oxygen over the red hot asbestos and copper oxides. Taps 6 and 10 are then fully opened, and the mercury in *B* and *C* rapidly raised and lowered alternately for two or three minutes. Most of the water produced by the combustion of the compound is absorbed in tube *D*, which is filled with pumice moistened with sulphuric acid. This sulphuric acid can be renewed by allowing it to run out through tap 1 and afterwards sucking up a fresh supply.

The actual combustion of the substance should take less than five minutes, and from the results obtained seems to be very complete.

The mercury in *B* is now raised to tap 6, which is closed. Tap 4 is slowly opened, so that the gas before entering the pump may be dried by passing, not too quickly, over the phosphoric anhydride. As soon as the mercury in *C* has risen to the tap 10, this should be closed, otherwise mercury will run into the combustion tube. The whole of the gas in the apparatus can now be pumped into the measuring tube, *B*. It is safest, perhaps, to allow the gas again to stream slowly into the pump by closing tap 4 and opening tap 6, the reason for this being that even a small amount of moisture makes a considerable difference in the volume. After delivering the gas again into *B*, its volume can be read.

To absorb the carbon dioxide, the gas is now transferred to the vessel *E*, through the tube *P*, which should be of capillary bore. By raising and lowering the reservoir in connection with *E*, the carbon dioxide is very soon absorbed and the residual gas is then returned to *B*. At this point also it is best to send the gas once through the pump, over

* An attempt was made to produce pure copper oxide by heating a spiral of very thin copper gauze. First it was heated for five hours in a current of air, then for over two days in oxygen gas; even after this treatment it still slowly absorbed oxygen.

the phosphoric anhydride, in order to remove traces of moisture. The volume of the gas is now measured for the last time.

The author has completed such a combustion in thirty-five minutes, but as a rule the time employed should be about one hour, for too much haste may easily ruin, not only the analysis, but also the apparatus. For instance, if the gas be allowed suddenly to enter the mercury pump through the tap 4, while mercury is in the head of the pump, it will drive the liquid before it with such violence that the top of the pump is certain to be broken.

Results of Analyses.

The first substance employed to test the apparatus was β -naphthol.

β -Naphthol taken, 0.0163 gram; oxygen in apparatus, 107.3 c.c.; gas after combustion, 103.5 c.c.; gas after absorbing CO_2 , 78.4 c.c. In every case the volume is reduced to N.T.P. From these results, the following data can be obtained: diminution due to the production of water by the oxygen, 3.8 c.c.; diminution due to the production of carbon dioxide, 25.1 c.c. Amount of carbon = 0.013554 gram, whence C = 83.2 per cent.

The percentage of hydrogen can be determined indirectly, inasmuch as part of the hydrogen *a* in the substance is oxidised by means of the oxygen in the tube, and part *b* is oxidised to water by means of the oxygen already in the compound.

The weight of part *a* can be calculated as follows: the diminution in volume after combustion = 3.8 c.c. This is due entirely to oxygen consumed to form water (for the oxygen employed in forming carbon dioxide produces its own volume of carbon dioxide). Therefore 3.8 c.c. will have combined with 7.6 c.c. of hydrogen.

a = weight of 7.6 c.c. of hydrogen = 0.000684 gram.

The weight of part *b* is found in the following manner: weight of substance taken = weight of carbon and hydrogen found + weight of water produced by the combined oxygen in the substance. $0.0163 - (0.013554 + 0.000684) = 0.002062$ (weight of water), which is equivalent to 0.000229 gram of hydrogen. Hence the total hydrogen is $0.000229 + 0.000684 = 0.000913$ gram, the percentage being 5.6.

Two more combustions were made.

	Found.		Calculated.
			$\text{C}_{10}\text{H}_8\text{O}$.
C	83.3	83.0	83.3
H	5.3	5.2	5.5

Several other substances were analysed; the amounts taken were never more than 0.04 or less than 0.012 gram.

Dimethylpyrone, C₇H₈O₂.

	I.	II.	III.	Calculated.
C.....	67.7	67.4	67.9	67.8
H	6.4	6.9	6.7	6.4

Cane Sugar, C₁₂H₂₂O₁₁.

	I.	II.	III.	IV.	Calculated.
C	42.3	42.4	42.0	42.3	42.1
H	6.7	6.2	6.5	6.1	6.4

Diacetyldimethylpyrone, C₁₁H₁₂O₄.

	I.	II.	Calculated.
C.....	63.1	63.2	63.5
H	6.1	5.5	5.8

Anthracene, C₁₄H₁₀.

	I.	II.	III.	Calculated.
C.....	94.1	94.4	93.9	94.4
H	5.6	5.5	5.8	5.6

Phthalic Anhydride, C₈H₄O₃.

	I.	II.	Calculated.
C.....	65.1	64.7	64.8
H	3.1	2.4	2.7

The errors of experiment in this method for the ultimate analysis of organic compounds are not great. The substance can be accurately weighed to tenths of a milligram, an error therefore of one-tenth of a milligram in 0.030 gram of substance is only one in three hundred. In reading the volume of carbon dioxide (as a rule, the amount produced is from 40—50 c.c.), the error is probably not more than a tenth of a c.c.; here again the error would only be about one in four hundred. Of course, however, any error in the amount of carbon also affects the hydrogen, and should the percentage of carbon be too high, then the hydrogen would probably be too low, and *vice versa*. Incomplete combustion of the substance, as a rule, only occurs in one way, namely, by the partial burning and subsequent condensation of difficultly volatile compounds on the tubes between the combustion tube and the rest of the apparatus. This, however, does not occur

1116 PATTERSON: THE INFLUENCE OF SOLVENTS ON THE

when asbestos mixed with copper oxide is present in the combustion tube.

When once the apparatus has been fitted up, it is merely necessary to weigh out the substance in a boat, take out the india-rubber cork at *O*, and put the boat into the combustion tube. As it does not matter whether the tube is moist or not, the india-rubber cork can be wetted before it is replaced, and by that means a perfectly tight joint results. Three combustions can be easily made in an afternoon, and the total amount of substance used need only be 0.10 of a gram.

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE,
LONDON.