XI.—*On the Analysis of Organic Bodies containing Nitrogen, &c.*

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IN the ordinary process for the analysis of nitrogenous organic bodies the use of freshly reduced copper has been found to possess many drawbacks. In the first place the copper is very hygroscopic, and it also appears to occlude hydrogen, so that the hydrogen determinations are always more or less too high, this error being serious when small quantities of substance are under examination. Oxygen also cannot be used freely at the commencement of the combustion. These difficulties have been overcome to a great extent by the use of metallic silver instead of copper, but silver has the great disadvantage of requiring a very high temperature to make it act efficiently, a disadvantage which is very serious if the combustion-tube used be not very infusible.

The method about to be referred to was to some extent the outcome of experiments made some years since in an attempt to obtain not only the determination of the carbon and hydrogen by combustion, but also that of the halogens. To obtain this result it was necessary to burn the substance thoroughly in oxygen, avoiding the use of cupric oxide, lead chromate, &c., the products of combustion being then passed over a weighed quantity of heated metallic silver.

The arrangement actually used consisted of a combustion-tube with about twelve inches of the central part filled with crumpled platinum foil. In the front of this a weighed roll of thick silver foil, supported on platinum rings at each end, was placed for the absorption of the halogens as they came forward as hydrogen-acids or in the free state. The substance was burnt in a boat at the back part of the tube, oxygen being supplied both *before* as well as behind it.

But as most of the substances I wished to burn contained nitrogen, the difficulty arose as to how to get rid of the nitrous fumes produced. It was evident that no process of reduction could be used, as an excess of oxygen was always present. To get over this difficulty, it was thought that perhaps some process of oxidation and absorption might be used, and recourse was had to the process used in the combustion of sulphur compounds, viz., the introduction of a tube filled with

plumbic peroxide between the arrangements for absorbing the water produced and the carbonic anhydride. This succeeded so far as the carbon determinations were concerned, but as the water was absorbed in sulphuric acid, this acid likewise dissolved a large quantity of the nitrous fumes, and the hydrogen determinations were in consequence usually high. Nevertheless, some tolerably good results were obtained, as, for example, in the analysis of the aniline platinum salt, which yielded carbon, hydrogen, chlorine, and platinum determinations in one combustion. The process, however, was found uncertain, and the halogen determinations varied with different specimens of combustion tubing, some being acted on to a considerable extent, especially when substances containing bromine were burnt in them.

Since making these experiments, I have often thought it desirable to do away with the use of copper in the combustion of nitrogenous bodies, especially when I have had to burn small quantities of substance; and, therefore, fresh attempts were made in this direction.

As the use of plumbic peroxide between the sulphuric acid bulb or tube and the potash-bulbs was efficient only so far as the carbon was concerned, experiments were made by placing plumbic peroxide in the combustion-tube itself, in the position usually occupied by the reduced copper. This part of the tube was made to project outside the combustion furnace, so that the plumbic peroxide employed and the plumbic nitrate formed during the combustion might not be decomposed by overheating. But to prevent moisture being retained by its contents, either during the preliminary drying or in the actual combustion, it was made to rest in a thick copper trough, which was heated to a suitable temperature by means of a Bunsen burner. This method, though a great improvement, was not altogether satisfactory, as the plumbic peroxide had to be heated with care, it was difficult to ensure its being thoroughly dry, and thus the hydrogen determinations were uncertain. It is quite likely this difficulty might be overcome by using some more trustworthy method of heating the plumbic peroxide, but the introduction of further precautions was not desirable, as I was seeking for a simple process.

On further consideration it appeared that the thing wanted was some stable oxidising agent containing a metal which would also yield a stable nitrite or nitrate, and it appeared that potassic chromate fulfilled these conditions. Experiments were therefore made with it first to see if it would absorb nitrous fumes diluted with air, and it was found to do so both when cold and when heated, provided of course the stream of gas was not too rapid. It also did not appear to com-

bine with carbonic anhydride, but as this was a most important thing to prove, especially as it is stated in "Watts's Dictionary" that this salt is "decomposed by carbonic acid, yielding the acid potassic chromate," a combustion of sugar was made in the ordinary way, but with a layer of about 6 inches of potassic chromate in the front part of the tube, which was kept at a scarcely dull red heat. The result obtained was exceptionally good, proving that nothing had to be feared on this score. (The statement quoted above is probably intended to refer to solutions of the chromate, and not to the dry salt.)

Combustions of uric acid were then made in the same manner as the above one with sugar, this substance being selected on account of the large percentage of nitrogen it contains, and also because when burnt with cupric oxide and oxygen it yields large quantities of nitrous fumes. Azobenzene was also used. These experiments gave satisfactory results, no oxides of nitrogen appearing.

So far as I have worked with it, this process appears to be both good and simple, and capable of giving much better hydrogen determinations than when copper is used. I have, therefore, thought it best to bring it before the Society in its present state, and without waiting until it is further elaborated. I will, therefore, only add a few remarks, which I hope may be useful to any who may wish to adopt it.

With reference to the potassic chromate, it is of course essential that it should be free from any excess of alkali. The presence of bichromate in small quantities, however, could not be harmful, but bichromate alone does not appear to work so well as chromate. The chromate should be roughly powdered or, better, granulated by evaporating its solution to dryness with constant stirring; it does not then decrepitate so violently when heated. I am now trying pumice-stone coarsely powdered which has been saturated with a solution of potassium chromate and then dried, and it promises to work better than the pure salt.

The length of the combustion-tube to be filled with it will necessarily vary with the amount and nature of the substance to be burnt. For uric acid I have generally filled a length of about 6 or 7 inches, but with most bodies I believe about four or five inches sufficient.

The temperature to which the chromate should be heated appears to be of some importance. This salt is not at all easily fusible, the temperature employed in a combustion furnace not being sufficient for

this purpose, so that during the drying operation it can be heated just in the same manner as the copper oxide. This, however, is unnecessary, as the salt is an anhydrous one, and easily dried, and a high temperature is only a needless expenditure of gas, and it is possible that after the chromate has been used several times, and will then contain nitrate or nitrite, a high temperature might be injurious, as these salts become alkaline from decomposition, though most probably chromate would simply be regenerated. I have not experienced any difficulty in this direction. The temperature used during combustion is worth attention, although I have obtained good results both when using a dull red or only a gentle heat.

The following results will illustrate the importance of this, especially when a short length of potassic chromate is used :—

Three combustions of uric acid were made, to see how short a length of chromate would be sufficient to absorb all the nitrous fumes; about four inches were used, and about 0.15 gram of substance burnt. In the first two experiments the chromate was kept at a very dull red heat; in both of these a small quantity of red fumes passed from the combustion-tube, but not enough to vitiate the results, the hydrogen being a little increased, about 0.2 per cent. The third combustion was made with the chromate only very gently heated at first, but raised to about a dull red at the close of the operation. Not a trace of red fumes appeared, and the results were good.

The cause of this difference I think is not difficult to explain. During the combustion the red fumes are associated with steam, and if the temperature be high, this steam would have but little influence, if any, on the potassic chromate, but if low, it would more or less influence the surfaces of the crystals, and thus the nitrous fumes would be constantly having fresh chromate to act upon.

I cannot say how many times the chromate can be used with safety, but evidently a considerable number of times.

Potassic chromate absorbs not only nitrous fumes, but sulphurous acid, so that it would be useful in the combustion of organic bodies containing sulphur, or both sulphur and nitrogen. It will not absorb iodine vapours perfectly, if at all, but it would be probably useful in the combustion of bodies containing chlorine or bromine. I have not, however, as yet made any experiments in this direction.