XXXI.—*On the Analysis of Organic Bodies containing Nitrogen* (continued).

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IN the short account of my experiments on this subject recently brought before the Society, it will be remembered that it was proposed to absorb the oxide of nitrogen formed during the combustions of nitrogenous organic bodies by potassic chromate, instead of decomposing them by metallic copper as is usually done. In the analysis of uric acid, &c., then referred to, the substances were burnt from a boat with air and cupric oxide, oxygen being employed towards the finish, and the only modification of the ordinary procedure was that potassic chromate occupied the place of reduced copper in the front part of the tube. By this method, however, a considerable quantity of reduced

copper is formed during the combustion, which would decompose more or less of the oxides of nitrogen formed, and it was therefore thought desirable to put the process to a more severe test by using plumbic chromate in place of cupric oxide; and on making combustion of uric acid in this way, it was found that the potassic chromate was not capable of completely absorbing the red fumes formed. This, result being unsatisfactory, fresh experiments were made to obtain a more powerful absorbent for these products.

Several other chromates were experimented with, and of these the most effectual was sodic chromate; this is probably due to the porous nature of the dried salt, but although more active than the potassic salt, it did not act so well as could be desired.

From the observation of a number of experiments, it appeared that some of the oxides of nitrogen present in red fumes were more easily absorbed than others. It was thought therefore that, if they could be more fully oxidised, the chromate would perhaps absorb them more freely. To accomplish this, the use of a peroxide suggested itself, such as that of lead; this, however, has the disadvantage of being easily decomposed when heated. Precipitated manganic oxide was therefore tried. The substance absorbs the oxides of nitrogen freely, but gives them up very easily when heated, and therefore would be useless alone. This, of course, was to be expected, as nitrate of manganese decomposes below 160° C. A quantity of precipitated manganic oxide was therefore made into a paste with a saturated solution of potassic chromate, and then dried and heated somewhat strongly to drive off most of the water of hydration from the manganic oxide.

To test the value of this mixture, it was placed in a short combustion tube, heated in a combustion furnace and dried air passed over it; when dry a weighed Geissler bulb charged with concentrated sulphuric acid was attached to absorb the red fumes; these were generated by igniting weighed quantities of plumbic nitrate in the back part of the tube.

Before testing the absorbing mixture in this manner, experiments were made to determine the quantity of oxides of nitrogen absorbable by sulphuric acid, which nitrate of lead would give off when heated. The following results were obtained:—

I	28.0 p. c.
II	25.8 „
III	26.8 „

In some experiments potash-bulbs were connected with the sulphuric acid bulbs, but they increased in weight only to a very minute extent.

In the following experiments about 0.2 gram of nitrate of lead was used.

The mixture of manganic oxide and potassic chromate was first tried at a temperature approaching dull redness, but in this case a certain amount of the oxides of nitrogen escaped absorption. It was observed, however, that on reducing the temperature this amount diminished, and that if the temperature were sufficiently low, all were absorbed. This will be seen from the following experiments, in which the variations between the weighings of the sulphuric acid bulbs before and after the operation are given.

I	+ 0.0002 gram
II	— 0.0001 „
III	— 0.0001 „

If no absorbing mixture had been used, the difference between the weighings would have amounted to about 0.0540 gram.

Mixtures consisting of different proportions of potassic chromate and manganic oxide have been experimented with, and in I it consisted of one part of potassic chromate and two parts of manganic oxide, and in II and III two parts of potassic chromate and one of manganic oxide.

The above results having been obtained, combustions were made to test this absorbing mixture more fully, chromate of lead being employed so as to get the maximum amount of red fumes; and as bodies containing the group NO_2 are usually supposed to yield these in larger quantities than other nitrogenous substances, dinitrobenzene was selected for analysis. About 40 or 50 grams of a specimen of this substance were fused so that a homogeneous product might be obtained. But before analysing it by the new process, four combustions of it were made by the ordinary method to determine its composition, oxide of copper and reduced copper being used. The average of these gave—

		Theory.
Carbon	42.95	42.85
Hydrogen	2.52	2.38

The slight excess of carbon is supposed to be due to the presence of a little dinitrotoluene.

In the first combustion of this product by the new process only a short length of about four inches of the absorbing mixture was used, and in this case a small quantity of red fumes escaped and was absorbed in the sulphuric acid bulbs; this caused the hydrogen determination to come .33 per cent. too high: the numbers obtained were C 42.74, H 2.71. This slight error is believed to be due to the com-

combustion being conducted too quickly. In the following, however, the length of the absorbing mixture was increased to six inches, and it will be seen that the results agree very closely with the average obtained by the old process.

	I.	II.	Average by old process.
Carbon	42.93	42.81	42.95
Hydrogen	2.54	2.48	2.52

A combustion of a less highly nitrogenised body, chromate of lead, being used as in the above, gave the following numbers. The substance was ethylorthotoluidine.*

		Theory.
Carbon	79.93	80.0
Hydrogen	9.78	9.63

These results, therefore, show that the mixture of potassic chromate and manganic oxide is effectual in absorbing the oxides of nitrogen found in the combustion of nitrogenous organic bodies.

In the preparation of the absorbing mixture, I have used potassic chromate with about ten per cent. of dichromate instead of the pure salt, because precipitated manganic oxide contains potash if this reagent has been used in this preparation, and when purchasing this article one does not know how it has been made. Ordinary powdered pyrolusite washed with dilute nitric acid was not found to answer so well as the precipitated oxide.

In making combustion by this process, a length of from four to six inches of the absorbing mixture placed in the front part of the tube has generally been used. During the preliminary process of drying with air, it has usually been heated as strongly or nearly so as the other parts of the tubes containing the cupric oxide or plumbic chromate, but before commencing the combustion the absorbing mixture must be cooled down, and only about one-fourth of the burners kept lit, and these half-turned down;† by this means a temperature of about 200—250° C. is maintained. Before detaching the bulbs every alternate burner may be used half-turned down for a few minutes, but this is scarcely necessary.

To prepare for a second combustion all the gas is turned up, as for the preliminary drying, and a current of air passed. This will cause any oxides of nitrogen which are not capable of being retained

* This substance was prepared from its acetylic derivative by my assistant, Mr. F. W. Toms, who is investigating the substitution derivatives of orthotoluidine.

† The furnace used in the above experiment was an ordinary one, consisting of a row of Bunsen's burners about three-quarters of an inch apart, the combustion tube being supported in a sheet-iron trough.

by the absorbing mixture at a high temperature to be removed; the gas is then turned down for the combustion.

The absorbing mixture of potassic chromate and manganic oxide can be used many times in succession. It has been used seven times running in my laboratory without apparently losing its power of combining with oxides of nitrogen. It therefore appears to be a very desirable substitute for freshly reduced copper.

Sulphuric and sulphurous acids are also absorbed by this mixture, but a higher temperature is required than that suitable for the absorption of red fumes; in burning, therefore, with oxide of copper, a substance containing both nitrogen and sulphur, it would be advisable to use a greater length of the absorbing mixture than above recommended, and to keep the back part of it somewhat strongly heated for the absorption of sulphurous acid, and the front part cooler for the absorption of the oxides of nitrogen.