

XVI.—COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

No. V.--*Note on some Trials of Frankland and Armstrong's
Combustion Process in vacuo.*

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WHEN Frankland and Armstrong (*Chem. Soc. Journ.*, xxi (1868), 89) described their process of combustion *in vacuo* as a means of estimating organic carbon and nitrogen contained in water-residues, they incidentally expressed their belief that it would be found generally useful in the analysis of all organic compounds containing nitrogen, which are not volatile at ordinary temperatures. With the exception of a few determinations of carbon and nitrogen in residues from the evaporation of solutions containing known quantities of urea and hippuric acid, together with sodic carbonate, they gave no analyses to support this anticipation, and we are not aware of any experiments made by others to test its correctness. From its nature the process seemed particularly adapted to the exigencies of physiological and pathological researches, where the quantities of material at the disposal of the investigator are not rarely so small as to exclude the possibility of determining the elements by the ordinary processes of analysis, or of verifying the results of a single analysis by repetition. In order to test this surmise we have made the following experiments, which, although small in number, seem to be sufficiently precise to serve as materials for the formation of some definite conclusions on the subject.

Relating to the materials to be employed in the analysis, Frankland and Armstrong state (*loc. cit.*, p. 93) that cupric oxide prepared from the nitrate should on no account be used, since, even after being actually fused, it evolves considerable quantities both of carbonic anhydride and nitrogen when ignited *in vacuo*. Our experience has in a measure corroborated this statement, so far as relates to carbonic anhydride (or rather gas absorbed by caustic potash), but not as regards nitrogen. This is shown by the following experiments:—

Exp. I. A tube of the usual size was charged with cupric oxide made from the nitrate, and of the same kind as that which we employ in our ordinary combustions, with a roll of metallic copper in front. This was rendered vacuum, heated to bright redness, and the pump set working and maintained so for about half an hour. By the time the second vacuum was obtained there was collected 1·5 c.c. gas,

which, after the ordinary corrections, became 1.0 c.c. normal. It was almost entirely absorbed by potash.

Exp. II. In this experiment the procedure was identical with that described under experiment I, except that, after the tube had been rendered vacuum and heated to redness, the pump was not set working till the fire had been put out. In this way the cupric oxide gave off gas which when normal measured 0.5 c.c. On the introduction of some potash only a trace of gas remained unabsorbed. These experiments prove therefore that while the error involved in the use of cupric oxide as ordinarily prepared for combustion is great enough to destroy the accuracy of the determination of carbon, it does not seriously affect that of the nitrogen. But they also show that the error in the carbon is dependent upon variations in the vacuum in this manner, that it becomes less (by one-half in the above experiment) if the vacuum be not actively maintained at the time that the combustion-tube is at its highest temperature; or the experiments seem to indicate that cupric oxide retains carbonic anhydride at temperatures below glowing heat even in a vacuum, while the same cupric oxide does not retain it in a vacuum at bright red heat. This recalls the relations of hydrogen to metallic copper *in vacuo*, under ordinary pressure, which has been treated of before this Society on a former occasion. We incline to the belief that the small amount of carbon found in cupric oxide by the vacuum method is introduced, during the heating of the oxide, by diffusion of the products of combustion into the covered crucibles. The error may be entirely avoided, either by the precaution adopted by Frankland and Armstrong of using cupric oxide prepared from metal by oxidation in air, or by using cupric oxide heated to redness in a glass tube in which the vacuum has been actively maintained during the entire period of ignition.

We here take note of the fact that Frankland no longer uses plumbic chromate in the combustion of water-residues, as originally recommended by him and Armstrong, but conducts the entire operation with cupric oxide only.

Exp. III. In this experiment a combustion was made with the oxide of copper which had been used in experiment I, that is, which had given up *in vacuo* at a red heat its occluded carbon as carbonic anhydride. With it there was burned 0.0242 grm. of hematine, which by combustion with PbCrO_4 had furnished 61.81 per cent. C. In the present combustion it gave 28.1 c.c. CO_2 , and 1.7 c.c. N, both normal, equal to 62.25 per cent. C. and 8.78 per cent. N, or a relation of $\text{N} : \text{C} = 1 : 8.2$. From a number of ordinary elementary analyses we had fixed the formula of this hematine as $\text{C}_{32}\text{H}_{32}\text{FeN}_4\text{O}_6$, in which the nitrogen stands to the carbon as 1 : 8, and which requires 61.53 per cent. C and 8.97 per cent. N.

We next made combustions *in vacuo*, with similar precautions, of the following substances:—

Exp. IV. Uric acid. 0·0845 grm. gave 57·7 c.c. CO₂, and 22·3 N.

Exp. V. Urea. 0·0350 grm. gave 15·6 CO₂, and 13·2 c.c. N.

Exp. VI. Leucine. 0·0408 grm. gave 41·3 c.c. CO₂, and 3·6 c.c. N.

Exp. VII. Bromobiliverdin. 0·0282 grm. gave 22·4 c.c. CO₂, and 1·38 c.c. N, = 6·12 per cent. N.

Exp. VIII. Bilirubin. 0·0483 grm. gave 9·96 per cent. N.

Exp. IX. (Choline, HCl)₂PtCl₄. 0·0536 grm. gave 4·20 per cent. N.

Exp. X. Myeline (from blood corpuscles). 0·0246 grm. gave 2·54 per cent. N.

If we consider these experiments as tests simply of the composition of substances which have not been specially prepared as test objects, although the composition of some was known from previous analysis, while others had been prepared according to the best rules and answered the current tests of purity, they are not very satisfactory. The carbon varies in a manner so as to be either deficient or in excess.

Table showing Atoms of Carbon found if N = 1.

Substance.	Formula.	Atoms of Carbon.
Hematin	C ₃₂ H ₃₂ FeN ₄ O ₆	8·2
Uric acid	C ₅ H ₄ N ₄ O ₃	1·27
Urea	CH ₄ N ₂ O	0·561
Leucine	C ₆ H ₁₃ NO ₂	5·7
Bromobiliverdin.	C ₈ H ₈ BrNO ₂	8·1
Bilirubin	C ₈ H ₉ NO ₂	8·4
Choline, PtCl ₄ ..	(C ₅ H ₁₃ NO.HCl) ₂ PtCl ₄ ..	5·7
Myeline	C ₇₂ H ₁₆₄ N ₃ P ₂ O ₁₄ (CdCl ₂) ₂ ..	26·0

The actual percentage of carbon in organic substances of a composition controllable by the atomic theory seems at present better determinable by combustion in the ordinary way. For many substances this may be explained at once by the well-known difficulty of burning carbon entirely without the aid of gaseous oxygen. The carbon determination seems, however, the least important part of the process and can be made useful, its faults notwithstanding, as an approximative measure of the proportion between carbon and nitrogen. For as the vacuum-method cannot be used for determining the hydrogen, a combustion must be made in the ordinary way in order to determine the percentage of this element, when a trustworthy carbon determination can always be effected simultaneously.

Considered only as a method for determining the quantity of nitrogen in any organic substance, the vacuum process seems excellent, and less

troublesome than the ordinary process in which air is displaced by CO_2 . This is evident from the comparison of the results of some of the analyses already given with the relative numbers required by theory.

	N per cent.	
	Theory.	Found.
Hematine, Exp. III	8.97	8.78
Uric acid, Exp. IV	33.33	33.06
Urea, Exp. V.....	46.66	47.18
Leucine, Exp. VI.....	10.68	11.03
Bromobiliverdin, Exp. VII..	6.08	6.12
Bilirubin, Exp. VIII	8.58	9.06
Choline plat. chl., Exp. IX..	4.52	4.20
Myeline, Exp. X	2.24	2.54

If, however, the experimentalist will take the trouble of combining the vacuum method with the displacement method in which bichromate of potash and carbonate of soda is employed as the source of CO_2 (Thudichum and Wanklyn, *Chem. Soc. Journ.*, xxii [1869], 293), and if he will subject his caustic potash and mercury to the vacuum for some time, we believe that nitrogen analyses can be made which will surpass all others in accuracy, and in which not even that obstinate bubble in the gas-tube will be perceived which has puzzled so many of the best experimentalists.

The following examples are illustrative of the value of this combustion method as a test for the presence of nitrogen:—

Exp. XI was conducted with a body obtained in the chemolysis of myeline, which itself contains N. 0.0238 grm. gave 33.1 c.c. normal CO_2 , and 0.39 c.c. normal N.

Exp. XII related to a similar substance. 0.0288 grm. gave 32 c.c. CO_2 , and 0.3 c.c. N; both normal.

That is to say, both these substances contained, as was expected, traces of nitrogen, from non-completion of the chemolysis.

Exp. XIII was conducted on a red product from urine, termed urrhodine, and commonly believed to be identical with indigo-red.

0.0178 grm. gave 26 c.c. CO_2 normal, and 0.1 c.c. N normal, showing that the substance was non-nitrogenous, and therefore disproving the stated identity.

The vacuum-process seems also to admit of a new application for the determination of the nitrogen in some ammonium salts.

Exp. XIV. During an investigation, to which we need not more particularly refer here, there was obtained a volatile base, which was converted into sulphate, once recrystallised from boiling absolute alcohol and analysed.

0.0218, burnt as ordinarily *in vacuo*, gave 4.91 c.c. N normal = 21.23 per cent. nitrogen. Sulphate of ammonium $(\text{NH}_4)_2\text{SO}_4$ should contain 21.21 per cent. N. Further analysis showed the substance to be this salt.

Exp. XV. Ammonic chloride was now subjected to combustion *in vacuo*.

0.0210 grm. gave 4.5 c.c. N normal = to 26.80 per cent. N. Theory requires 26.16 per cent. N.

Exp. XVI. Next ammonic nitrate was burnt in the same way.

0.0190 grm. gave 5.38 c.c. N normal = to 35.42 per cent. N. Theory requires 35.00 per cent. N, if both atoms of N be given up, which proved, as is seen, to be the case.

These experiments indicate therefore a method of estimating nitrogen in ammonium salts, which possesses some decided advantages over the soda-lime process.
