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ON A SOURCE OF ERROR IN THE ESTIMATION OF UREA BY THE HYPOBROMITE METHOD, WITH APPARATUS OF THE RUSSELL AND WEST TYPE.

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Of the many forms of apparatus employed for estimating the amount of urea contained in urine by means of akaline hypobromite or hypochlorite solutions, probably the one most used by physicians is that devised by Russell and West. These experimenters, by using an alkaline solution of sodium hypobromite, and measuring the nitrogen evolved from the decomposition of the urea in urine, found that with their apparatus 94 or 95 per cent. of the urea present could be estimated. The reaction may be expressed as follows:

$$(NH_2)_2CO + 3NaBrO = 2H_2O + CO_2 + 3NaBr + N_2.$$

According to Knop,[1] the solution of sodium hypobromite should be prepared as follows: Dissolve 100 grams of sodium hydroxide in 250 cc. of water. Allow this solution to cool, and then add 25 cc. of bromine. Upon cooling, the reagent is ready for use. Thus prepared, the solution contains 62.5 grams free sodium hydroxide. Hitherto it has been thought that all the carbon dioxide evolved during the decomposition of the urea was absorbed by the free sodium hydroxide in the hypobromite solution to form sodium carbonate, and in employing this method with the Russell and West apparatus, the percentage of urea has been found to be equal to that originally present in the urea solution employed, and sometimes rather in excess of the amount really present. This was suspected to be due to the non-absorption of an appreciable quantity of the carbon dioxide evolved during the decomposition of the urea. In order to determine this, the following described apparatus was devised and the accompanying experiments per-

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[1] Chem. Centralbl. 1860, 244.

formed: the object being to ascertain if any carbon dioxide was collected unabsorbed with the nitrogen and was measured as nitrogen, and if so, to what extent this took place. The apparatus consisted of a wide-necked bottle containing a small test-tube, in which the decomposition of the urea was to take place, closely stoppered with a rubber cork through which two glass tubes pass, one of which can be pushed down to within an inch of the bottom of the bottle. Connected with this tube upon one side of the bottle was a drying apparatus, consisting of five cylinders, containing respectively a solution of calcium hydrate, caustic soda in sticks, barium hydrate solution, and caustic soda in sticks. The air being admitted to the first cylinder, passes successively through them and is deprived of its carbon dioxide. A pinch-cock prevents any gas during its evolution in the bottle from passing into the cylinders. Attached to the remaining tube emerging from the bottle was a drying-tube containing calcium chloride in small pieces. Next were the Geissler's bulbs for collecting the carbon dioxide escaping absorption in the bottle. These were followed by another calcium chloride drying-tube to prevent access of any moisture from the atmosphere. A rubber tube attached to this drying-tube and connected with an aspirator, rendered it possible to exhaust the apparatus.

To detect qualitatively the presence of carbon dioxide with the nitrogen, a U-tube containing a strong solution of barium hydrate was inserted in place of the Geissler's bulbs. The urea solution was placed in a small test-tube, and introduced into the bottle into which 30 cc. of the hypobromite solution had been poured, and the pinch-cock between it and the drying-cylinders closed. Then upon inclining the bottle containing the reagent with the urea solution in the test-tube, immediate decomposition ensued with the evolution of gas. Ten minutes after the completion of the decomposition in the bottle, the first described tube passing through the cork was pushed down to within half an inch of the surface of the liquid in the bottle, and the pinch-cocks having been opened, aspiration was begun, and air free from carbon dioxide was slowly drawn through the apparatus for about half an hour.

The presence of carbon dioxide was demonstrated several times without doubt by the turbidity of the barium hydrate solution in the U-tube, upon drawing pure air through the bottle in which the decomposition occurred. To determine the actual amount of carbon dioxide passing over with the nitrogen, a weighed set of Geissler's bulbs, containing a strong solution of potassium hydrate, was placed in the position previously occupied by the U-tube after the calcium chloride tube, and connected as before. The method of procedure as to aspiration, etc., was the same as previously described. The bulbs were weighed both before each experiment and at its close, being at these times and as soon as detached from the apparatus tightly corked with rubber, so as to exclude admission of carbon dioxide and moisture from the air. The increase in weight after the passage of the gas is equal to the amount of carbon dioxide absorbed, which in the use of the Russell and West apparatus and of apparatus of that general design is measured as nitrogen. The accompanying table shows the results of fourteen quantitative experiments made with varying quantities of a 5 per cent. urea solution:

No. of Experiment.	No. cc. urea used.	Increase in weight of Geissler bulbs.	Equivalent volume of CO_2 in cc.
1	1	0.001	0.508
2	1	0.0003	0.152
3	1	0.0003	0.152
4	1	0.0007	0.355
5	2	0.001	0.507
6	1	0.0002	0.1015
7	2	0.0011	0.558
8	2	0.0017	0.862
9	2	0.0007	0.355
10	3	0.0004	0.202
11	3	0.0026	1.318
12	3	0.0011	0.558
13	4	0.0012	0.608
14	4	0.0049	2.485

Upon examination of the foregoing results it will be observed that an appreciable quantity of carbon dioxide escapes absorption by the free sodium hydrate contained in the sodium hypobromite solution, and passing out along with the nitrogen, is measured as such, thus increasing the apparent amount of urea in the solution undergoing analysis. The objection to the employment of the Russell and West type of apparatus is this non-absorption of all the carbon dioxide, which is most likely due to the immediate decomposition of the urea coming into contact with *only the surface* of the hypobromite solution in the bottle. This decomposition takes place so rapidly that sufficient time is not allowed for absorption of the carbon dioxide by the caustic soda, and possibly too the caustic soda in the immediate vicinity of the place of decomposition becomes saturated with carbon dioxide.

In the apparatus of Hüfner,[1] and that lately devised by Dr. Wm. H. Greene,[2] in which the evolved gases are obliged to pass through a long column of the sodium hyprobromite solution, the conditions exist for the complete absorption of the carbon dioxide with the least possible likelihood of error. But, even in employing these apparatus, the theoretical quantity of nitrogen (372 cc. from 1.0 gram of urea) is not obtained, but according to Hüfner only 354.33 cc. at 0° C. and 760 mm. pressure.

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[1] Zeitschr. f. physiol. Chem. **1**, 350.

[2] Comptes Rendus **97**, 1141.