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An Application of the Oxidation Reaction between Ammonia and Bromate, Permanganate or Dichromate for the Determination of Ammonia Nitrogen in the Kjeldahl Digests without Distillation

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Nitrogen in organic compounds, agricultural and animal products is converted into ammonium sulphate by Kjeldahl digestion. The ammonium sulphate is reacted quantitatively with hypobromite produced *in situ* by the addition of an excess of potassium bromate and bromide. The unutilized potassium bromate is determined iodometrically and the amount of ammonia nitrogen can be calculated from the consumed potassium bromate. Accurate results are also obtained when potassium bromate is replaced with potassium permanganate or dichromate for the determination of ammonia nitrogen in Kjeldahl digests. However, the present method is not applicable to the determination of ammonia nitrogen in undigested sample.

It has already been reported by various workers that the distillation step in the Kjeldahl method can be effectively replaced by a bromometric titration. Thus a hypobromite method,[1] employing brominating mixture and potassium tetraborate has been proposed. A similar method in which potassium tetraborate is replaced with an alkali has been applied to the determination of non-protein nitrogen in serum.[2] Recently such a method has been modified and used for the determination of organic nitrogen on both the micro as well as the semi micro scales.[3]

During the present investigations, it has been shown that potassium permanganate and potassium dichromate work as well as potassium bromate in the brominating mixture in this method. In addition, these oxidants have been shown to be successfully applicable to all types and scales of Kjeldahl nitrogen. Both potassium permanganate and potassium dichromate solutions are already employed as analytical reagents whose stability is, at any rate, better than that of hypobromite or even hypochlorite solutions prepared in the laboratory.

Potassium permanganate or dichromate and potassium bromide in the acidic medium generate bromine which on the addition of an alkali, can be coverted into hypobromite *in situ.* Although hypohalite solutions have been previously extensively used for the determination of nitrogen in organic compounds,[4] soil,[5] biological material and agricultural products,[6] yet they are not ordinarily stable. In the matter of stability, hypobromite solutions are hopelessly inferior to hypochlorite solutions.[7] Difficulties encountered in their preparation and application are known too well to be enumerated here. Such difficulties do not arise when bromate, permanganate or dichromate is used as oxidant in the presence of potassium bromide.

Experimental

Apparatus. A 500 m*l* round bottom flask, with B 19 neck fitted with a 15 cm tube attached to B 19 cone, is used for digestion on the macro scale. After digestion the cone is replaced with an *N*-shaped tube[3] having the following dimensions. Tube bore 1.8 cm, the B 19 cone limb 4 cm, the middle limb 16.5 cm, and stoppered (with B 19 joint) limb 14 cm long.

Reagents. Sulphuric acid (d, 1.84), G.R.; Potassium sulphate, G.R.; Mercuric sulphate, G.R.; Glucose, G.R.; Potassium bromate solution, 0.5 N Potassium permanganate solution, 0.5 N; Potassium dichro-

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mate solution, 0.5 N; Sodium hydroxide solution, 60% W/V; Potassium iodide, G.R.; Hydrochloric or sulphuric acid, 10 N; Sodium thiosulphate solution, 0.25 N; Starch solution (aqueous), 1%.

Procedure. Weigh accurately 0.1 to 0.2 g of the organic sample (dried blood=0.1—0.2 g, cereal, tea leaves and meat=1 g, fresh vegetables=2 g, etc) into the flask. Add 5.6 g of the catalyst (5.0 g potassium sulphate and 0.6 g mercuric sulphate) and use 12 m*l* concentrated sulphuric acid for organic compounds and 15 m*l* for commercial materials. Add 1—2 g of glucose and 16 m*l* of sulphuric acid in case of compounds which require reduction prior to digestion. Digest the sample for 1—2 hr. Cool and dilute the digest by rinsing the cone with about 50 m*l* of distilled water. Place the flask in cold water and add 20 m*l* of the potassium bromate, permanganate or dichromate solution. Add 5 g of potassium bromide and immediately fit in the *N* tube containing 35 m*l* of sodium hydroxide solution. In the case of potassium dichromate, add 15 m*l* of sodium hydroxide solution into the *N* tube. Keep the tubes neck open and heat the flask at 70°C. Continue heating for 15 min. Cool the flask and add the remaining 20 m*l* of the sodium hydroxide solution into the tube and stopper it.

Transfer the alkali portion-wise from the *N* tube to the cold contents of the flask by tilting the system slightly. Shake the flask and allow it to stand for 10—15 min. Add 8 g of potassium iodide followed by 25 m*l* of 10 N hydrochloric or sulphuric acid through the *N* tube. Allow to stand for another 5 min, remove the *N* tube and titrate the liberated iodine with sodium thiosulphate solution, using starch solution as an indicator. Carry out a blank determination under similar conditions.

Calculation. 1 m*l* 0.1 N $KBrO_3$ or $KMnO_4$ or $K_2Cr_2O_7$=0.4667 mg. N_2

Discussion and Conclusion

Potassium bromate is a primary standard and advantages realised by its use in nitrogen determination on the micro and semi micro scales have already been listed.[3] Potassium permanganate and dichromate have been used for nitrogen determination for the first time. Their solutions when prepared and stored according to the established practice, can work as well as that of bromate.

The results (Table 1) show that the reagents are applicable to the determination of all those types of organic nitrogen which either as such or after reduction can be digested into ammonium sulphate. It has also been shown (Table 2) that these reagents in general and potassium bromate in particular can be employed with advantage for a variety of nitrogenous commercial materials.

TABLE 1. RECOVERY OF NITROGEN

Compound	Required %	Found by Bromate %	Found by Permanganate %	Found by Dichromate %
Ammonium sulphate	21.21	21.37, 21.31	21.11, 21.32	21.36, 21.26
DL-Alanine	15.72	15.65, 15.59	15.75, 15.79	15.74, 15.54
Acetanilide	10.36	10.53, 10.35	10.49, 10.54	10.36, 10.42
Diphenylamine	8.28	8.21, 8.04	8.37, 8.21	8.31, 8.19
Phenacetin	7.82	7.95, 7.73	7.75, 7.83	8.01, 7.71
Hippuric acid	7.82	7.97, 7.99	7.84, 7.99	7.71, 7.56
Quinine sulphate	7.16	7.23, 7.16	7.23, 7.10	7.12, 7.33
Atropine	4.84	4.84, 4.93	4.91, 5.00	4.71, 4.90
Phenyl thiourea	18.41	18.35, 18.30	18.21, 18.51	18.32, 18.51
α-Nitroso *β*-naphthol	8.09	8.16, 8.10	8.00, 8.15	—
p-Nitroaniline	20.29	20.22, 20.09	20.25, 20.29	—
o-Nitrobenzoic acid	8.38	8.49, 8.38	8.32, 8.47	—
Azobenzene	15.38	15.27, 15.29	15.51, 15.37	—

TABLE 2. RECOVERY OF NITROGEN

Commercial materials	Found by Hypochlorite %	Found by Bromate %
Wheat	1.84, 1.83	1.84, 1.90
Rice	1.18, 1.17	1.19, 1.20
Gram (black)	3.49, 3.51	3.61, 3.56
Peas (green)	1.01, 0.98	1.07, 1.05
Milk (Lahore milk plant)	0.49, 0.49	0.50, 0.51
Blood (crude)	11.90, 12.09	11.96, 11.99
Tea leaves (Brook Bond)	4.35, 4.17	4.42, 4.39
Meat (goat)	3.29, 3.14	3.37, 3.34

Some difficulties are encountered when nitrogen is determined in the agricultural and animal products by the hypochlorite-arsenite method.[6] For example the neutralized digest in the case of tea leaves becomes reddish brown on the addition of sodium hypochlorite solution with the result that it becomes difficult to mark the end point. Similarly, for larger than 1 g of meat and 0.2 g of blood samples, a yellow precipitate appears after the addition of the hypochlorite. This colour changes to greyish black on the addition of sodium arsenite solution, thus making it difficult to mark the end point.

In the present method, involving the use of potassium bromate, however, the above mentioned difficulties do not arise. The method gives good results even if comparatively large amount of tea leaves, meat and blood samples are used for analysis. It further shows that the present method can also be applied to materials containing metals like iron. It has also been observed that the results are higher when digestion is incomplete. This is due to the fact that some bromine or even acidic potassium permanganate is consumed in the oxidation of the undigested organic matter. Therefore, the present method can not be applied to the determination of ammonia nitrogen in the undigested sample.

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