PAKISTAN JOURNAL

OF

SCIENTIFIC AND INDUSTRIAL RESEARCH

Vol. 3, No. 1 January 1960

DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS WITHOUT DISTILLATION

Part I.—Determination of Ammoniacal Nitrogen in Organic Compounds

MUHAMMAD ASHRAF, *Department of Pharmacy, University of the Panjab, Lahore*

M.K. BHATTY, *West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore*

AND

R.A. SHAH, *Chemical Research Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

(Received November 25, 1959)

The distillation step in the macro-determination of ammoniacal nitrogen in organic compounds by Kjeldahl method is eliminated. After having digested the sample in sulphuric acid with potassium sulphate and mercuric sulphate, the acid is neutralised. The resulting ammonium sulphate is treated with an excess of hypochlorite inpresence of potassium bromide. An excess of arsenite is then added and back-titrated with hypochlorite using bordeaux indicator.

Attempts have been made from time to time to modify the Kjeldahl method to make it applicable to all types of nitrogenous material and to improve its accuracy as well as to reduce the time of nitrogen determination. By eliminating distillation procedure from the Kjeldahl method, the process becomes easier and determinations can be made in shorter time. Elimination of the distillation step by titrimetric methods is based either on the oxidative treatment of ammonia or on the reaction of ammonium sulphate with formaldehyde[1] to yield stoichiometric amount of sulphuric acid. Physical methods mostly rely upon reactions resulting in colour formation of ammonia with various reagents. Nesslerisation is one such reaction.

Haanapal[2] has used Rupp and Rossler's method[3] to eliminate the distillation in the Kjeldahl method by oxidizing ammonia to nitrogen in an alkaline solution by means of a standard hypobromite solution. The excess of the latter is determined by adding potassium iodide and acid, and titrating the liberated iodine with thiosulphate. The procedure, however, has the serious disadvantage that hypobromite solution is unstable at room temperature and must, therefore, be kept below 5°C. Pappaport and Pistine[4] estimated nitrogen in blood, and Harvey[5] determined it in unicellular algae on the submicro scale using a hypobromite titration.

Belcher and Bhatty[6] applied Kolthoff and Strenger's[7] method involving titrations of ammonium salts with calcium hypochlorite, for determining nitrogen in organic compounds on micro and semi-micro scales. The method is expeditious and is particularly suitable for multiple nitrogen determinations. Their method, however, cannot be used when the nitrogen in commercial commodities such as cereals, food-stuffs, drugs, etc., has to be determined. Also, facilities for a small-scale determination of nitrogen in most of the research and analytical laboratories are not always available. It was, therefore, considered desirable to modify the micro method of Belcher et al. (loc. cit.) to the macro for determining nitrogen without distillation.

The modified method has given satisfactory results for a number of organic compounds. The results obtained are given in Table 1.

The method was also used to determine nitrogen in the nitro compounds without using any reducing agent. The recovery of nitrogen from nitro compounds containing less than 10% of nitrogen was

TABLE 1.—DETERMINATION OF AMMONIACAL NITROGEN IN ORGANIC COMPOUNDS.

Compound	N Required	N found		
Ammonium sulphate	21.21	21.22	21.21	21.22
Hippuric acid	7.82	7.79	8.02	7.97
Acetanilide	10.36	10.22	10.43	10.36
Phthalimide	9.52	9.44	9.46	9.44
Phenacetin	7.82	7.87	7.91	8.02
8-Hydroxyquinoline	9.65	9.63	9.76	9.61
Benzamide	11.57	11.67	11.62	11. 4
Sym.-Diphenylthiourea	12.26	12.27	12.22	12.25
Uracil	24.98	24.93	24.89	25.01
Atropine	4.84	4.66	4.87	4.90
Brucine	6.50	6.47	6.43	6.46
Pilocarpine hydrochloride	11.45	11.27	11.23	11.24
Quinine sulphate ($2H_2O$)	7.16	7.22	7.25	7.18

almost quantitative. The recovery of nitrogen was not, however, quantitative when the amount of nitro-nitrogen was greater than 10%. The results for such determinations are recorded in Table 2.

TABLE 2.—DETERMINATION OF NITRO-NITROGEN IN ORGANIC COMPOUNDS WITHOUT PRE-REDUCTION.

	N required	N found		
o-Nitrobenzoic acid	8.38	8.12	8.11	8.12
5-Nitrosalicylic acid	7.65	7.59	7.52	7.58
p-Nitrobenzoic acid	8.38	8.18	8.20	8.11
2,4-Dinitrophenol	15.22	9. 0	9.08	9.05

A method, whereby greater percentages of reducible forms of nitrogen may also be determined without distillation, is being developed. Furthermore, since the macro-scale determination of nitrogen in organic compounds without distillation appears feasible, the method is being extended to cover nitrogen determination in commercial materials. Results of these findings will be communicated later.

Experimental

A. Reagents:

Sodium hypochlorite solution, 0.2 N
Arsenious oxide solution, 0.1 N
Bordeaux indicator (aqueous), 0.2%
Sodium hydroxide, 60 %
Sulphuric acid (d, 1.84), A.R.
Mercuric sulphate, A.R.
Potassium sulphate, A.R.
Sodium bicarbonate, A.R.
Potassium bromide, A.R.
Alundum (in pieces)

B. Procedure.—The compound (0.1 – 0.2 g.) was accurately weighed out into a 250 ml. Kjeldahl flask, and 5 g. of potassium sulphate and 0.6 g. of mercuric sulphate were added to bring about rapid digestion. The neck of the flask was washed down with 8 ml. of sulphuric acid. A few pieces of alundum were added to ensure smooth boiling. The digestion was carried out for 45 minutes if the nitrogen was present in the open chain and for 1½ hour if the nitrogen was present in a ring of the organic substance. After cooling, the digest was transferred to a 500-ml. conical flask with four washings. Sodium hydroxide solution was added drop by drop with occasional shaking until a yellow precipitate of mercuric oxide was formed. The solution was cooled and then totally neutralised by a gradual addition of sodium bicarbonate. Potassium bromide (4 g.) was then added and the flask shaken until the solution was clear.

An excess of sodium hypochlorite solution was added till the solution turned pale yellow. After 5 minutes, a known excess of arsenious oxide solution was run in and the excess was back-titrated with the hypochlorite solution using bordeaux indicator. The blank determination, using sucrose, was carried under similar conditions.

Calculation: 1 ml. 0.2 N NaOCl = 0.934 mg. N.

C. Discussion.—Normality of 1 N hypochlorite solution changed considerably at room temperature. It was found that 0.2 N solution of sodium hypochlorite in sodium hydroxide remained unchanged for about a week when kept in dark bottle at room temperature. For the sake of accuracy, however, hypochlorite was daily standardised before use.

A reversible indicator tartrazine was found suitable by Belcher[8] in the hypochlorite titration against sodium arsenite solution in low concentrations, but in the present investigations, where

concentrations of hypochlorite solution are higher, bordeaux was found more suitable indicator than tartrazine. On the present scale, when 0.2 N hypochlorite solution is used, the end point tends to be yellowish. As the colour of the titration solution with tartrazine is also yellow, the end point cannot be marked clearly. On the other hand, with bordeaux, the colour transition from pink to colourless is clearly discernible. When the compounds contain nitrogen in a chain such as in amines, amides, etc., the digestion proceeds with greater ease than when nitrogen is present as a part of a ring as in the case of uracil, 8-hydroxyquinoline, etc.

Nitro compounds which contain enough hydrogen in the molecule to form ammonia (containing less than 10% nitrogen) can be analysed by this method without pre-reduction.

As shown in Table 1, the method described yields good results in compounds having different nitrogen contents. The results compare favourably with those obtained by other workers in different ranges. The figures are within ± 0.2% of the expected results.

Acknowledgement

Our thanks are due to Dr. Karimullah, Director, West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore, for his helpful suggestions.

References

1. K. Marcali and W. Rieman, Ind. Eng. Chem., Anal. Ed., **18**, 709 (1946).
2. T.A.G. Haanapal, Pharm. Weekblad, **75**, 510 (1938).
3. E. Rupp and E. Rossler, Arch. Pharm., **243**, 104 (1905).
4. F. Pappaport, and R. Pistiner, Microchem., **18**, 43, (1935).
5. H.W. Harvery, Analyst, **76**, 657 (1951).
6. R. Belcher and M.K. Bhatty, Mikrochim. Acta, 1183 (1956).
7. I.M. Kolthoff, and V.A. Stenger, Ind. Eng. Chem., Anal. Ed., **7**, 79 (1935).
8. R. Belcher, Anal. Chim. Acta, **4**, 468 (1950).