DETERMINATION OF AMMONIACAL NITROGEN IN SOIL BY A KJELDAHL METHOD WITHOUT THE DISTILLATION PROCEDURE

MOHAMMAD ILYAS QURESHI, NAEEM SHAKIR AND M. K. BAHTTY

West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Lahore

MOHAMMAD ASHRAF

Pharmacy Department, Panjab University, Lahore

AND

R. A. SHAH

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

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The distillation step in the Kjeldahl determination of ammoniacal nitrogen in soil has been eliminated. Soil is digested in sulphuric acid with potassium and mercuric sulphates. The resulting ammonium sulphate is treated with an excess of hypochlorite in presence of sodium bicarbonate and potassium bromide. An excess of arsenite is then added and back-titrated with the hypochlorite using Bordeaux indicator. The method is comparable in accuracy to the A.O.A.C. method.

Nitrogen in soil plays an important role in the plant kingdom and has a dominant effect on the plant's growth. As a constituent of protoplasm, nitrogen is involved in the activity of every living cell. Plants obtain their nitrogen from the soil and hence the content of this element in soil is significantly important from the standpoint of plant nutrition.

The ammoniacal nitrogen in soil is determined by the Kjeldahl method.[1] Attempts have been made from time to time for its improvement. The time of digestion has been reduced by using various high boiling mixtures, oxidants and catalysts such as potassium permanganate,[2] sellenium oxychloride,[3] potassium hydrogen phosphate,[4] hydrogen peroxide,[5] barium oxide[6] and perchloric acid.[3,7] However, the present A.O.A.C. standard method recommends 2-4 hours digestion time and subsequent titration of the distilled ammonia. It follows, therefore, that the present method involves two distinct steps, viz., (1) the long digestion of soil and (2) the distillation of ammonia. The steps are obviously time-consuming and tedious, if rapid and convenient and multiple determinations are envisaged.

Improvements have, therefore, been made in the standard method in order to reduce the time of digestion and to eliminate the distillation step. It has been found that if proper digestion conditions are provided, the digestion period could be much shorter. These conditions have already been defined elsewhere.[8] The feasibility of the removal of the distillation procedure from the Kjeldahl method has been examined and found tenable for determination of nitrogen in agricultural and animal products[9] and in organic compounds on different scales of analysis.[10,11,12] In the present communication the method without distillation has been shown to be applicable to the determination of nitrogen in soil.

The modified method entails almost all the details of the A.O.A.C. method. However, nitrogen is directly determined by the oxidation of ammonia with sodium hypochlorite. The soil is, as usual, digested with sulphuric acid. Mercury-potassium sulphate mixture is used as a catalyst and the resultant ammonium sulphate, after the acid has been neutralized, is titrated with sodium hypochlorite, using Bordeaux as an indicator.[13] A single vessel as described in the experimental section is used for digestion and titration.

Experimental

Apparatus.—A B_{19}, 250 ml. short-necked round bottom flask, fitted with a B_{19} cone, was used as a digestion flask. After the digestion was complete, the cone was detached and the flask was used as a titration vessel.

An electrically heated disgestion stand was used for heating the digestion flasks. A water suction pump was used to eradicate the fumes from the manifold support tube of the digestion stand.

Reagents.—Sodium hypochlorite solution, 0.1N; arsenious oxide solution, 0.1N; Bordeaux indicator, 0.025% (aqueous); sodium hydroxide, 60% (w/v); sulphuric acid, d. 1.84; mercuric sulphate, A.R; potassium sulphate, A.R; sodium bicarbonate, A.R.; and potassium bromide, A.R.

Procedure.—One g. of homogenized and dried soil sample was accurately weighed out into the

flask. It was followed by 2.5 g. potassium sulphate and 0.3 g. mercuric sulphate as a digestion catalyst. The neck of the flask was washed down with 10 ml. sulphuric acid. The cone was attached to the flask, and digestion of the contents was carried out for forty minutes. After having cooled the flask, the cone was washed and detached. The digest in the flask was diluted with water, and sodium hydroxide solution was added drop by drop with an occasional shaking until a drop of sodium hydroxide gave a yellow precipitate of mercuric oxide. The solution was finally cooled and then totally neutralized by the gradual addition of sodium bicarbonate. A yellowish precipitate is evident after complete neutralization. Five g. potassium bromide were then added and the flask shaken until the contents were clear.

An excess of sodium hypochlorite solution was added till the solution turned pale yellow. After five minutes, a known excess of arsenious oxide solution was run in and the excess was back titrated with hypochlorite solution using Bordeaux indicator. The end point is from pinkish violet to colourless. A blank determination was carried out under similar conditions. Nitrogen was also determined by the A.O.A.C. method[1] for the sake of comparison.

Calculations: 1 ml 0.1 N NaOCl = 0.4670 mg. N_2.

Discussion

In all, nine different soil samples were analysed both by the A.O.A.C. and the modified methods. As is indicated by the results in Table 2, the difference in the nitrogen contents by the two methods can be considered insignificant and within the experimental error.

In the present method, the weight of the soil sample was kept to about 1 g. Larger samples offered no special advantage and were at the same time troublesome as the end point in the titration could not be marked clearly. The digest after cooling is usually not quite clear, and some residue settles down after dilution and neutralization. In one set of experiments the neutralized digest was filtered and the residue was washed thoroughly. The filtrate along with the washings were then titrated. Result thus obtained was also quantitative as shown in Table 1. However, the volume of the final solution was much increased in this case, and another 15-20 minutes were required for the filtration.

Studies were, therefore, carried out subsequently to titrate ammonia without any filtration.

TABLE 1.—DETERMINATION OF NITROGEN IN SOIL WITH FILTRATION.

Sample	AOAC method % N	Modified Kjeldahl method % N
I	0.075	0.074
	0.081	0.081
	0.075	0.074
	0.084	0.075
II	0.014	0.016
	0.015	0.018
	0.014	0.015
	0.009	0.014
III	0.061	0.063
	0.063	0.064
	0.061	0.061
	0.063	0.064
IV	0.072	0.073
	0.072	0.072
	0.071	0.074
	0.072	0.074
V	0.050	0.067
	0.058	0.058
	0.047	0.059
	0.059	0.058
VI	0.065	0.066
	0.067	0.065
	0.066	0.066
	0.068	0.067
VII	0.086	0.086
	0.085	0.085
	0.086	0.085
	0.087	0.086
VIII	0.071	0.072
	0.070	0.070
	0.071	0.071
	0.072	0.069
IX	0.070	0.067
	0.069	0.071
	0.067	0.065
	0.067	0.069

The figures recorded in Table 2 show that, even when there is no filtration, the results are quantitative. It was observed that Bordeaux indicator gave a sharp end point.

Therefore, as compared with the conventional method, with 2-4 hours digestion time and distillation procedure, the present method consumes only 40 minutes of digestion period. There is no distillation involved, and ammonia is determined directly. The method is rapid, convenient and accurate. The method will prove of considerable importance to analytical laboratories making multiple determination of nitrogen in soil.

TABLE 2.—DETERMINATION OF NITROGEN IN SOIL WITHOUT FILTRATION.

Sample	AOAC method % N	Modified Kjeldahl method % N
I	0.075	0.0749
	0.081	0.0750
	0.084	0.0780
II	0.014	0.015
	0.015	0.014
	0.014	0.016
III	0.061	0.0614
	0.061	0.0630
	0.063	0.0640
IV	0.072	0.073
	0.071	0.072
	0.072	0.072
V	0.050	0.058
	0.058	0.059
	0.047	0.058
VI	0.065	0.065
	0.067	0.067
	0.066	0.066
VII	0.086	0.085
	0.085	0.086
	0.087	0.085
VIII	0.071	0.071
	0.072	0.069
	0.072	0.072
IX	0.070	0.069
	0.069	0.068
	0.067	0.067

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References

1. Assoc. Offic. Agr. Chemists, *Official and Tentative Methods of Analysis*, 8th Ed., p. 12 (1955).
2. F.L. Ashton, J. Soc. Chem. Ind., (London), **56**, 101-4T (1937).
3. L. P. Pepkowitz, A.L. Prince, and E.F. Bear, Ind. Eng. Chem. Anal. Ed., **14**, 856-7 (1942).
4. A.L. Prince, J. Assoc. Offic. Agr. Chemists, **24**, 264-8 (1941).
5. Kleeman, Z. Angew. Chem., **34**, Aufsatzteil, 625-7 (1921).
6. A. Sreenivasan, Indian J. Agr. Sci., **4**, 546-53 (1934).
7. L.P. Pepkowitz, Ind. Eng. Chem. Anal. Ed., **14**, 915 (1942).
8. M. Ashraf, M.K. Bhatty and R.A. Shah, Pakistan J. Sci. Research, **13**, 171 (1961).
9. M. Ashraf, M.K. Bhatty and R.A. Shah, Pakistan J. Sci. Research., **12**, 3 (1960).
10. R. Belcher, T.S. West and M. William, J. Chem. Soc. (London), 4323 (1957).
11. R. Belcher and M.K. Bhatty, Mikrochim. Acta, 1183 (1956).
12. M., Ashraf, M.K. Bhatty and R.A. Shah, Pakistan J. Sci. Ind. Research, **3**, 1 (1960).
13. I.M. Kolthoff and R. Belcher, *Volumetric Analysis III*, (Interscience Publishers Ltd., London, 1957) p. 581-84.