

## MODIFICATION OF METHODS FOR THE DETERMINATION OF NITROGEN IN SOILS

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Different methods for the determination of nitrogen in the soil were compared. The method using perchloric acid as an aid to digestion is rapid and efficient for nitrogen determination in soils. It takes only 35 minutes for digestion and is as effective as the standard method. The boric acid as an ammonia absorber is as accurate as sulphuric acid. It has special advantages over sulphuric acid, and is, therefore, recommended for adoption by workers carrying on nitrogen determination of soils.

### INTRODUCTION

Because of the importance of nitrogen in the nutrition of plants, the determination of nitrogen in soils is very important for a soil scientist. However, the methods in use are not entirely satisfactory and considerable difficulty is experienced in getting satisfactory results. The Kjeldahl method is the one which is almost universally employed for nitrogen determination in a variety of nitrogenous substances. This method is simple in principle but requires considerable skill and close attention to the minute details. It is time consuming and entails many difficulties. Although many modifications of this method have been proposed, some of the major difficulties have not yet been surmounted. The present paper suggests modification which is simple and reduces the time for the determination of nitrogen, without sacrificing the accuracy of the determination.

### REVIEW OF LITERATURE

Metallic mercury, mercuric oxide, copper sulphate and anhydrous sodium sulphate have been used individually or in various combinations to hasten the digestion process.

Osborn and Wilkie (1935) studied the effect of 39 different elements on the accuracy of nitrogen determination of gluten flour and found that mercury was the best catalyst followed by selenium, while copper ranked seventh in the list of catalysts.

Osborn and Krasnitz (1933) showed that as a catalyst, selenium or its oxychloride had a slight advantage over copper sulphate but was not better than

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mercuric sulphate. He further established that a combination of selenium with mercuric oxide or with copper sulphate had a great advantage over any of these catalysts when they were used alone.

The ferric sulphate method as proposed by Stubblefield and Dettl (1940) employs 10-12 gm dipotassium phosphate and 6 gm ferric sulphate along with mercury as metallic catalyst. The time of digestion by this modification was reduced from 2.5 hours to 30 minutes.

The use of perchloric acid in Kjeldahl digestion is considered to be hazardous, but Pepkowitz *et al.* (1940) carried out Kjeldahl digestion in the presence of perchloric acid and reported that by using perchloric acid after a 10-minute preliminary digestion with concentrated sulphuric acid and selenium oxychloride as catalyst, the digestion time could be reduced to 30 minutes.

The use of boric acid as ammonia absorber has been advocated by some investigators. Spears (1921) compared the boric acid absorption procedure with the ordinary Kjeldahl method employing sulphuric acid as ammonia absorber, and although he found almost complete agreement in the analysis of a number of feeding stuffs, he could not make much choice between the two methods.

Scale and Harrison (1920) in their experiments on the analysis of crops and soils used both sulphuric acid and boric acid for the absorption of ammonia and showed that both methods gave practically identical results.

## MATERIALS AND METHODS

Six soil samples from different localities were used for this investigation and the following methods were tried for nitrogen determination in these soils :

- (1) AOAC method. It was taken as standard for comparison.
- (2) Method employing sodium sulphate plus copper sulphate as catalyst, in the ratio of 1000 to 25 parts respectively.
- (3) Method employing sodium sulphate plus copper sulphate plus magnesium oxide as catalyst, in the ratios of 4 : 2 : 1 respectively.
- (4) Method employing mercury metal (0.65 gm) plus potassium sulphate (10 gm) as catalyst.
- (5) Method employing mercuric sulphate (1 gm) plus potassium sulphate (10 gm) as catalyst.

Ten gm soil in each case (Methods 2 to 5) was digested with 10 gm digestion mixture (as mentioned above), and 30 ml of concentrated sulphuric acid. The digestion was continued until the mixture was colourless or nearly so. Then it was cooled and contents of flask were diluted with water followed by the addition of 35 ml of 40 per cent sodium hydroxide (25 ml of 4 per cent sodium sulphide solution was also added to the diluted digest in case of mercury or mercuric sulphate as catalyst). The whole was then distilled for an hour or so.

## (6) Method using Perchloric acid as an aid to digestion.

Ten gm soil was digested with 30 ml sulphuric acid in the presence of 1 gm copper sulphate. The digestion was carried out vigorously for 10 minutes. The contents of flask were diluted and 10 drops of 35 per cent perchloric acid solution were added directly into the digest. Heating was resumed very carefully, so that the digest did not get over boiled and re-heated for 15 minutes. The contents of flask were cooled, diluted and distilled as usual.

To test the accuracy of above methods, a known quantity of nitrogen (at the rate of 15 mg/100 gm soil i.e., 0.015%) in the form of ammonium sulphate was added to each 10 gm sample and then immediately total nitrogen was determined to check the recovery of added nitrogen.

To see the effectiveness of different ammonia absorbers, used during distillation, the ammonia evolved in first three methods was absorbed both in 0.1N sulphuric acid and saturated boric acid solutions and the results were compared. In the case of remaining three methods, it was absorbed in boric acid solution only.

## RESULTS AND DISCUSSION

The results obtained by different methods and the percentage of added nitrogen recovered by different methods, are presented in Table. 1.

TABLE 1.—Comparison of nitrogen percentages obtained by different methods of nitr gen determination and the percentage recovery of added nitrogen

Ammonia Absorber	Average nitrogen percentage for all the soil samples with the following methods					
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>	M <sub>5</sub>	M <sub>6</sub>
(i) H <sub>2</sub> SO <sub>4</sub>						
Soils Alone	.0625*	.0636	.0597	—	—	—
Soils + .015 %N	.0775	.0785	.0747	—	—	—
(ii) H <sub>3</sub> BO <sub>3</sub>						
Soil Alone	.0634	.0643	.0603	.0635	.0641	.0616
Soil + .015 %N	.0784	.0791	.0748	.0784	.0791	.0771
%recovery of Added Nitrogen						
H <sub>2</sub> SO <sub>4</sub>	102	101	100	—	—	—
H <sub>3</sub> BO <sub>3</sub>	100	98	98	99	100	104

\*Each figure is the average of 14 observations for six different soils.

The method employing sodium sulphate plus copper sulphate plus magnesium oxide as catalyst gave lowest values of all the methods which are different from it significantly, while  $M_1$ ,  $M_3$  and  $M_4$  gave almost identical values for nitrogen as were obtained by the AOAC method. The results obtained by the method using perchloric acid as an aid to digestion were slightly lower than those obtained by the AOAC method but these were better than those obtained by  $M_2$  method.

As regards the time of digestion, AOAC and method 2 took 120 minutes while  $M_4$  and  $M_5$  took 90 minutes for complete digestion of soil samples.  $M_3$  and  $M_6$  required 100 and 35 minutes respectively for the same purpose. It is evident, therefore, that the time required for digestion by  $M_6$  is about one fourth of the time by AOAC method.

The recovery of added nitrogen was fairly satisfactory for all the methods. It ranged between 98 per cent to 104 per cent showing thereby that the methods employed were not otherwise defective.

On the basis of results obtained, method using perchloric acid may be sorted out as the most rapid and efficient for nitrogen determination in soils.

Table 1 shows that values for total nitrogen obtained by absorbing ammonia in boric acid and sulphuric acid solutions when compared visually or statistically were not significantly different from each other. However, boric acid has the following special merits over sulphuric acid.

- (i) Only one standard solution is required.
- (ii) There is no danger of spoiling a determination because of insufficient standard acid for ammonia absorption.
- (iii) If the content in receiving flask is sucked back to the distillation flask, distillation can be resumed and the sample is not spoiled.
- (iv) It simplifies calculations.

It is evident, therefore, that boric acid is an easier and efficient medium for ammonia absorption during distillation and hence its use should be encouraged.

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