Determination of Nitrate Nitrogen by the Strong Phosphoric Acid-Iodic Acid Decomposition Method

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In the previous papers[1,2] one of the authors reported new methods for the determination of nitrogen in organic compounds by the strong phosphoric acid (SPA)-iodic acid decomposition. Organic compounds such as amines and azo-compounds or ammonium salts are decomposed by heating with a mixture of SPA and potassium iodate to liberate the nitrogen contained in them. By sending the liberated nitrogen with carbon dioxide into an azotometer, filled with potassium hydroxide solution, the nitrogen can be determined gas-volumetrically. The nitrogen in nitro or oxime compounds can also be determined by the SPA-iodic acid decomposition method after their reduction with a mixture of metallic iron powder and diluted sulfuric acid to the corresponding amines.

The purpose of the present investigation is to extend these methods to the determination of nitrogen in nitrates. Since nitrates or nitro compounds can not be directly decomposed to free nitrogen by the SPA-iodic acid decomposition method, nitrates should be converted into amines or ammonium salts prior to the decomposition.

A recent paper of T. Nakamura and F. Yamazoe[3] describing various methods for the determination of nitrate nitrogen in fertilizers concluded that the iron reduction method followed by the Kjeldahl distillation

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[1] S. Ohashi, This Bulletin, 28, 177 (1955).

[2] S. Ohashi, This Bulletin, 28, 537 (1955).

[3] T. Nakamura and F. Yamazoe, *The Bulletin of the National Institute of Agricultural Sciences* (Japan), Series B, No. 2, 1 (1953).

was the best. In the first place it was tried in the present investigation to combine the iron reduction method with the SPA-iodic acid decomposition method. However, when a small amount of iron was used, the authors obtained low values for nitrogen, due to incomplete reduction of nitrate. In the case of a large amount of iron, high values for nitrogen resulted, probably because some iron remained in the reaction medium and hydrogen was liberated during the decomposition with a mixture of SPA and potassium iodate. So it was difficult to find out the optimum amount of iron to be used.

It was then tried to combine the modified Gunning method[4] with the SPA-iodic acid decomposition method. The modified Gunning method involves three main steps as follows: (1) Solution of the nitrate in salicylic-sulfuric acid, for converting the nitrate into nitrosalicylic acid. (2) Treatment of the nitro compound with sodium thiosulfate to reduce it to an amino or ammonium compound. (3) The Kjeldahl digestion and distillation of the resulting compound. In this investigation the Kjeldah digestion and distillation in the above mentioned steps were replaced by the SPA-iodic acid decomposition and statisfactory results were obtained.

Apparatus and Reagents

The apparatus used in the present experiment was almost the same as that described in the previous papers, but as shown in Fig. 1 a gas-safety bulb, filled with 42% aqueous solution of glycerine, was inserted between the reaction vessel and a Kipp's carbon dioxide generator in order to prevent a possible leak of the liberated nitrogen from the reaction vessel.

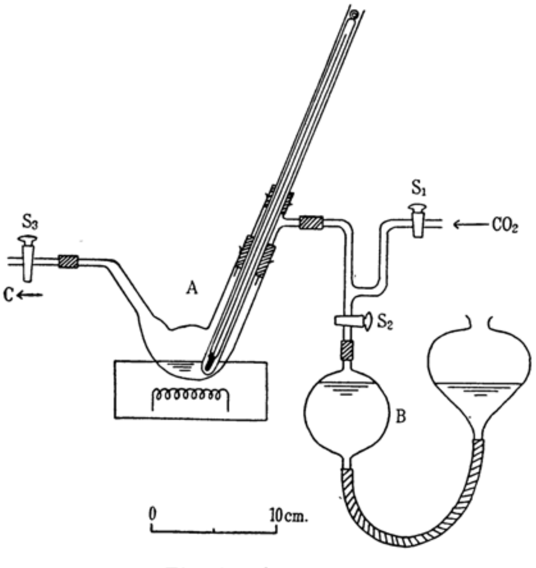

Fig. 1. Apparatus.

A: Reaction vessel B: Gas-safety bulb
C: Azotometer S_1–S_3: Stopcocks

The reagents were all of extra pure grade. The method for the preparation of strong phosphoric acid was described in the previous paper[1].

Results and Discussion

Since the decomposition process is carried out in a SPA medium, it seems to be convenient for the nitration process to be also done in the same medium. Therefore, at first, a mixture of salicylic acid and SPA was employed as a nitration reagent, but low results were given. Probably this may be due to the fact that salicylic acid is not easily dissolved in SPA. Using a common 89% orthophosphoric acid, also similar results were obtained. For this reason salicylic acid dissolved in concentrated sulfuric acid was used for the nitration. In the modified Gunning method the nitration is carried out by standing a reaction mixture for thirty minutes at room temperature. In the present study, however, according to the procedure suggested by W. E. Dickinson[5], the nitration was done by heating the reaction mixture for about fifteen seconds. For the reduction of the resulting nitrosalicylic acid, iron metal powder was tested as the reducing agent, but it was not favorable, as it required too much time and patience for the complete reaction. Thus, according to the general procedure, sodium thiosulfate was employed in its place. After examining several conditions for the determination of these facts, the following procedure was recommended.

Procedure.—Weigh a sample corresponding to about 6 to 12 mg. of NO_3 in a small weighing tube; place it in a reaction vessel and add 1.5 to 2.0 ml. of concentrated sulfuric acid containing 70 mg. of salicylic acid. Rotate the contents in the tip of a Bunsen burner for about fifteen seconds to dissolve all nitrate. To the still hot contents in the vessel add nearly 50 mg. of sodium thiosulfate and heat the contents with a small electric heater for four to five minutes until sufficient white fumes of sulfuric acid are produced. Add 5 ml. of strong phosphoric acid into the vessel. After completely cooling the contents, add 1.5 g. of potassium iodate to it. Now connect the reaction vessel with a carbon dioxide generator through the gas-safety bulb. After elevating the head of the liquid in the bulb slightly to the stopcock S_2, remove the air present in the vessel and connect it with an azotometer. Heat the mixture in the vessel with a small electric heater at 200 to 250°C and transfer the produced gas into the bulb. After the complete decomposition, transfer

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[4] H.C. Moore, *Ind. Eng. Chem.*, **12**, 669 (1920).

[5] W.E. Dickinson, *Anal. Chem.*, **26**, 777 (1954).

the liberated nitrogen into the azotometer by sweeping it with carbon dioxide. From the volume of the nitrogen collected in the azotometer deduct the blank value (about 0.04 ml. in the authors' experiment) and calculate the percentage of the nitrogen.

The data obtained for potasium nitrate by means of this method were shown in Table I. The calculated value of nitrogen in the Table was gravimetrically obtained by the nitron method. The accuracy for the results obtained is within ±2%. The time taken for an analysis is fifty to sixty minutes.

TABLE I

DETERMINATION OF NITROGEN IN POTASSIUM NITRATE

Sample Weight mg.	N, Calcd. %	N, Found %	Deviation %
10.4	13.47	13.2	−0.3
12.3	〃	13.6	+0.1
17.1	〃	13.5	0.0
18.2	〃	13.5	0.0
18.8	〃	13.3	−0.2
19.8	〃	13.3	−0.2

Since it was expected that this method can be effectively adopted to the analysis of nitrogenous fertilizers, some problems concerning this aspect were investigated. As shown in Table II, the presence of considerable amounts of chloride, ferrous and ferric iron, and calcium does not produce a serious error in the determination of nitrate nitrogen by this method. Of course a large amount of sulfate or phosphate has no injurious effect on this method. Nitrite can not be directly determined by this method. Therefore it seems that nitrite must be oxidized to nitrate prior to the nitration process.

TABLE II

EFFECT OF SEVERAL SUBSTANCES ON DETERMINATION OF NITROGEN IN POTASSIUM NITRATE

KNO_3-Sample Weight mg.	Other Salts mg.		N, Calcd. %	N, Found %	Deviation %
17.2	KCl	20	13.47	13.5	0.0
15.9	〃	30	〃	13.7	+0.2
15.7	〃	30	〃	13.4	−0.1
19.4	$FeSO_4$	20	〃	13.3	−0.2
18.6	$Fe_2(SO_4)_3$	20	〃	13.3	−0.2
19.1	〃	20	〃	13.2	−0.3
19.4	$CaCO_3$	20	〃	13.6	+0.1
18.5	〃	20	〃	13.2	−0.3

When both nitrate and ammonium salt are present the total nitrogen can be determined by this method and only the ammonium nitrogen can be directly determined by the SPA-iodic acid decomposition method after expelling nitric acid by heating with SPA. When nitrate, ammonium salt, and urea are present together the total nitrogen and the sum of nitrogen in ammonium salt and urea can similarly be determined. These results are summarized in Table III and IV.

TABLE III

DETERMINATION OF NITROGEN IN POTASSIUM NITRATE AND AMMONIUM SULFATE

Sample Weight mg.	Total N		
	Calcd. %	Found %	Deviation %
20.0	17.17	17.2	0.0
〃	〃	17.0	−0.2
〃	〃	16.8	−0.4
〃	〃	17.4	+0.2
〃	〃	17.1	−0.1

Sample Weight mg.	Ammonium N		
	Calcd. %	Found %	Deviation %
20.0	10.44	10.4	0.0
〃	〃	10.3	−0.1
〃	〃	10.4	0.0
〃	〃	10.4	0.0
〃	〃	10.4	0.0

TABLE IV

DETERMINATION OF NITROGEN IN POTASSIUM NITRATE, AMMONIUM SULFATE, AND UREA

Sample Weight mg.	Total N		
	Calcd. %	Found %	Deviation %
15.7	27.92	27.2	−0.2
15.0	27.00	26.7	−0.3
15.9	28.12	27.8	−0.3
15.1	27.06	26.7	−0.4

Sample Weight mg.	Ammonium N+Urea N		
	Calcd. %	Found %	Deviation %
15.1	22.69	22.2	−0.5
15.4	23.08	23.4	+0.3
14.6	21.77	21.9	+0.1

Summary

(1) The strong phosphoric acid-iodic acid decomposition method for the determination of nitrogen in organic compounds, which was already reported, has been extended to the analysis of nitrate nitrogen.

(2) In a reaction vessel salicylic acid was nitrated by heating with the sample and concentrated sulfuric acid and the product was reduced by heating with sodium thiosulfate. The resulting mixture was decomposed by heating with a mixture of strong phosphoric

acid and potassium iodate. The liberated nitrogen was measured gas-volumetrically.

(3) In the presence of nitrate, ammonium salt, and urea, the total nitrogen and the nitrogen except nitrate could be determined by the strong phosphoric acid-iodic acid decomposition method, respectively.

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