DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

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The determination of nitrogen in nitro, nitroso and azo compounds is described. The compounds are digested with sucrose and sulphuric acid in a sealed tube. The digest is passed through two columns of anion-exchange resin, placed one above the other. The upper column contains the resin in the hydroxide form and the lower in the iodide form.

Introduction

A novel method[1] for the determination of ammoniacal nitrogen in organic compounds was described recently. The method employs sealed tube digestion of the compounds and the conversion, through ion-exchange resin, of ammonium sulphate to ammonium iodide which is then determined by the Leipert[2] amplification procedure.

A similar determination of nitrogen in the nitro, nitroso and azo compounds will enhance the applicability of the method provided the oxidized nitrogen is reduced with an agent which does not interfere subsequently. Metallic reductants such as stannous chloride, titanous chloride, zinc and hydrochloric acid, etc. cannot be used as they interfere with the subsequent column operations. However sucrose[3] or glucose[4] which leave no residue on digestion with sulphuric acid have already been effectively used for the determination of these forms of nitrogen. In the present studies sucrose (5-6 mg.) as reductant has, therefore, been used in addition to the reagents already reported.[5] The recovery of nitrogen in NO_2, NO and -N=N- compounds is correct within $\pm 0.3\%$.

Experimental

Reagents.—1. Ion-Exchange Resin:

Grind A.R. grade, strongly basic anion-exchange resin, Amberlite IRA-400(Cl) (Rohm & Hass Co. Ltd., Philadelphia, U.S.A.) to -40 mesh and +85 mesh. Treat it with 500 ml. of 2N H_2SO_4 and then wash it with water till free from the acid. Convert the resin to the hydroxide form by treating it with 1 litre of 2N NaOH. Wash it on a sintered glass funnel with deionized water till free from alkali. Convert 60 g. of this resin to the iodide form by treating it with 250 ml. of 2N potassium iodide. Wash it with deionized water till it is free from the excess of potassium iodide.

2. Sucrose A.R.
3. Concentrated sulphuric acid (E.Merck), G.R.
4. Bromine solution:

Dissolve 100 g. of potassium acetate in 1 litre of glacial acetic acid then add 4 ml. of M.A.R. bromine.

5. Formic acid 98-100 percent.
6. Sulphuric acid 2N.
7. Sodium thiosulphate solution 0.02N.
8. Starch indicator solution.
9. Deionised water: Deionise distilled water by passing it through a bed of Bio-deminerolite.

Apparatus

1. Digestion tubes: Thick walled pyrex glass tubes (10 × 100 mm.) size.
2. 1 ml. graduated pipette.
3. Heating Block.[5]

An electrically heated thermostatically controlled dural block with 8 holes to accommodate sealed digestion tubes.

4. Transfer pipette containing 2 ml. glass bulb in the stem.
5. Ion-exchange columns:

Fit together two air condensers 25 × 1.4 cm. each with B_{19} ground glass joints. Fill the upper column with the hydroxide resin and the lower column with the iodide to give a bed of 19 cm. in each column. Fit the upper column with 75 ml. pear-shaped funnel with B_{19} ground glass joint to serve as a wash water reservoir.

Experimental

(i) *Digestion.*—Weigh 1-1.5 mg. of an organic compound and (4-5 mg.) of sucrose into a clean digestion tube. Add 0.1 ml. of concentrated

sulphuric acid into the tube and seal it at about 1.5 cm. from the top. Heat it in the heating block at 400°—420°C. for half an hour. Remove the tubes from the heating block, allow them to cool and then centrifuge for 5 minutes. Open the tubes according to the method already described.[1]

(ii) *Column Operation.*—Wash the resin column with 600—700 ml. of the deionized water till the blank value for 100 ml. of the eluate is 0.5 ml. of 0.02N $Na_2S_2O_3$, determined according to the following procedure:

Fill the water reservoir and place it on top of the columns. Adjust the rate of flow so that 25 ml. water pass through the column in 20 minutes. After 20 minutes change the rate of flow so that another 75 ml. of water pass in

TABLE 1.—NITROGEN CONTENTS OF ORGANIC COMPOUNDS AS DETERMINED THROUGH ION EXCHANGE METHOD.

S. No.	Compound	Nitrogen content percent		
		Calculated	Found	Error
1.	m-Dinitrobenzene	16.67	16.85	+0.18
			16.81	+0.14
2.	O-Nitrobenzoic acid	8.19	8.08	—0.11
			8.06	—0.13
3.	p-Nitroanaline	20.29	20.01	—0.28
			20.41	+0.12
4.	1-Chloro 2-4 dinitrobenzene	13.82	13.96	+0.14
			14.02	+0.20
5.	p-Nitrobenzaldehyde	9.27	9.45	+0.18
			9.41	+0.14
6.	2,4-Dinitrophenol	15.22	14.94	—0.28
			15.37	+0.15
7.	p-Nitrobenzoic acid	8.38	8.24	—0.14
			8.27	—0.11
8.	3,5-Dinitrobenzoic acid	13.20	13.06	—0.14
			13.08	—0.12
9.	Chloro-2-Nitro-Phenylacetinilide	9.63	9.41	+0.22
			9.54	+0.09
10.	4-Ethoxy-2-Nitro-Phenyl-acetinilide	9.33	9.63	+0.30
			9.60	+0.27
11.	Azobenzene	15.38	15.32	—0.06
			15.46	+0.08
12.	α-Nitroso-β-naphthol	8.09	7.96	—0.13
			8.12	+0.03

the next 20 minutes. Maintain the same flow rates for the digest.

Dilute the digest of an organic compound with 3 ml. water and transfer the solution to the column by means of the transfer pipette. Wash out the two parts of the opened digestion tube with eleven more 2 ml. portions of water.

(iii) *Titration.*—Treat the 100 ml. eluate from the column with 5 ml. of bromine solution, allow it to stand for about a minute and then destroy the excess bromine with formic acid till the colour of bromine disappears. Stir the solution magnetically for 7 minutes to destroy bromine vapours from the container (a flask). Add 2 ml. of 10% solution of potassium iodide and 2 ml. of 4N sulphuric acid. Titrate the solution with 0.02N sodium thiosulphate using starch as an indicator.

Deduct the titre of a blank determination from the test titre and find out the nitrogen content on the basis of

1 ml. of 0.05N $Na_2S_2O_3 \equiv$ 0.0466 mg. of N.

Discussion

The method of column operation has been changed from the one previously described so as to reduce the blank value. The amount of water used for washing the column and its elution has been increased from 75 ml. to 100 ml. It is important that the same rate of flow is maintained for the elution of the column after passing the digest as used for the blank determination. Variable rates of flow of the wash water will give variable blank values.

The volume of concentrated sulphuric acid has remained 0.1 ml. with the result that the blank value is minimum. It was found that 5-6 mg. of sucrose was enough to reduce 1–1.5 mg. of nitrogenous compound completely without making it necessary to increase the amount of sulphuric acid. Six series of experiments can be carried out with the column lengths described.

Some results ($\pm$0.3 absolute % of nitrogen) for various types of organic nitrogen containing compounds are given in Table 1.

References

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