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DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS WITHOUT
DISTILLATION

Part II.—Determination of Nitrogen in Nitro, Nitroso and Azo Compounds

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A Kjeldahl method for the determination of nitrogen in nitro, nitroso, and azo compounds without resorting to the usual distillation step is described. These compounds are reduced with glucose to amino compounds which yield ammonium sulphate on digestion with sulphuric acid. The ammonium sulphate is determined titrimetrically, after hypobromite oxidation. The accuracy of the method is $\pm 0.2\%$.

The Kjeldahl method cannot be directly employed for determining nitrogen in the compounds containing N-N, NO and NO₂ groups. Clark¹ strongly recommended the Friedrich² method for the analysis of such compounds. According to this method, the reduction of organic compounds is brought about with hydroiodic acid previous to kjeldahlisation. Nitrogen in hydrazines, dinitrohydrozones, osazones, oximes, nitro, nitroso and azo compounds is determined with great accuracy by this method. It cannot, however, be applied to diazoketones (R-CO-CHN₂) which split off the whole of their elementary nitrogen with hydroiodic acid.

The use of salicylic acid³ and sodium thiosulphate for the reduction of organic substances has also been found effective because the former compound in the presence of sulphuric acid gets converted to nitrosalicylic acid which can be reduced to amino compound by sodium thiosulphate. After digestion, the compound delivers nitrogen quantitatively as ammonia. This method has been further improved by using thiosalicylic acid which converts oxidized nitrogen to ammoniacal⁴ form. Bradstreet⁵ used 1-naphthol-pyrogallol and obtained better results than when he used salicylic or thiosalicylic acid. The addition of phenol and

zinc dust,⁶ phenol, resorcinol or phloroglucinol alone,⁷ zinc⁸ alone, potassium persulphate and zinc dust,⁹ stannous chloride¹⁰ and sulphur¹¹ was also suggested for the analysis of nitro, azo and similar compounds by digestion with sulphuric acid.

Dickinson¹² reduced nitro nitrogen and nitrogen-nitrogen single bond nitrogen almost quantitatively to amino compounds by zinc dust. The reduction was carried out in non-oxidizing acid solutions using formic, acetic, phosphoric and hydrochloric acids prior to Kjeldahl digestion. Iron and aluminium were also used as reductants. This method, like various other methods mentioned above, involves an additional difficult procedure before proceeding for digestion and much time is required for making the determination. Belcher and Bhatt¹³ determined nitrogen on the micro scale in nitro, nitroso and azo organic compounds by first reducing the compounds with chromous chloride and then distilling off ammonia from the digest.

Basis of the New Method

These methods, however, involved the presence of residues from reductants which would interfere in one way or the other if distillation in the

Kjeldahl method was to be eliminated. The application of glucose or sucrose as a reducing agent has also been reported^{14, 15} and it has been shown that oxidized nitrogen is quantitatively converted to ammonia. Glucose¹⁴ 1g. (or 0.5 g. sucrose¹⁵) was added to 0.1 g. of the sample and digestion and distillation were carried out by the usual Kjeldahl method. Such a reduction process appeared direct, easy and rapid. It would also save time from additional reduction prior to digestion. Besides, since the distillation step in the Kjeldahl method can be eliminated by a titrimetric method, the presence of interfering compounds is not called for as glucose or sucrose is got rid of during digestion of the substance with sulphuric acid. In the present investigations, glucose has been used as a reductant for nitro, nitroso and azo compounds, and the nitrogen has been determined without distillation by the modified Kjeldahl method.

The reducible form of nitrogen in a number of compounds has been determined by this method and results have been compared in Table 1. These results have been obtained by adding 2 g. of glucose to 0.1 to 0.2 g. of sample. The procedure used in Part I¹⁶ has been slightly modified and employed in this case also. As additional carbon from glucose depletes the acid materially, the volume of sulphuric acid has been increased from 8 to 15 ml. Total time required to complete the reduction and digestion in this case is two hours. Recoveries of nitrogen from *m*-dinitrobenzene are

TABLE I.—THE DETERMINATION OF NITRO, NITROSO AND AZO NITROGEN IN ORGANIC COMPOUNDS WITHOUT DISTILLATION.

No.	Compound	Required				Found			
1.	2,4-Dinitrophenol	15.22	15.23	15.12	15.00				
2.	3,5-Dinitrobenzoic acid	13.20	13.40	13.37	13.24				
3.	<i>o</i> -Nitrophenol	10.07	10.06	9.99	10.08				
4.	5-Nitrosalicylic acid	7.65	7.59	7.58	7.52				
5.	α -Nitroso- β -naphthol	8.09	8.11	7.95	8.00				
6.	<i>p</i> -Nitroaniline	20.29	20.39	20.40	20.31				
7.	<i>o</i> -Nitrobenzoic acid	8.38	8.42	8.22	8.25				
8.	<i>p</i> -Nitrobenzaldehyde	9.27	9.24	9.29	9.25				
9.	Azobenzene	15.38	15.42	15.41	15.44				
10.	<i>p</i> -Nitrobenzoic acid	8.38	8.22	8.18	8.31				
11.	<i>m</i> -Dinitrobenzene*	16.67	16.58	16.51	16.49				

*Quantities of the reductant and sulphuric acid, and the time of reduction as well as of digestion were increased.

low when this procedure is rigidly followed. However, when 3 g. of glucose and 30 ml. of sulphuric acid are used and heating is carried out below 50° C. for 1 hour and then at 360° C. for 3 hours, the recovery of nitrogen is quantitative.

Discussion

It is evident from the results shown in Table 1 that an accurate determination of the reducible forms of nitrogen, such as nitro, nitroso and azo in organic compounds, is possible. The addition of glucose helps the reduction in the majority of cases, although for compounds like *p*-nitrophenylhydrazine and dinitrophenylhydrazine, satisfactory results have not been obtained.

With the development of this method it is now possible to determine almost all types of nitrogen with a single uniform procedure in which distillation has been eliminated.

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References

1. E.P. Clark, *Semimicro Quantitative Organic Analysis*, New York Academic Press, Inc., (1943).
2. A. Friedrick, *Z. physiol. Chem., Hoppe-Seyler's*, **216**, 68 (1933).
3. Assoc. Offic. Agr. Chemists, *Official and Tentative Methods of Analysis*, 6th ed., Method A.O.A.C., Feb. 27, (1945).
4. Mc. Philip and W.F. Roth, *Ann. Chem.* **24**, 369 (1952).
5. R.B. Bradstreet, *Ann. Chem.*, **26**, 235 (1954).
6. M. Jodlbauer, *Chem. Zentr.*, (3), **17**, 433, (1886).
7. B.M. Margosches and E. Scheinost, *Chem., Ber.*, **58**, 1850 (1925).
8. W. Dafert, *Z. Ann. Chem.*, **27**, 222, (1888).
9. J. Milbauer, *ibid.*, **42**, 725 (1903).
10. M. Kruger, *Chem. Ber.*, **27**, 1633, (1894).
C. Flamand and B. Prager, *Chem. Ber.*, **38**, 559 (1905).
11. A. Eckert, *Monatsh*, **34**, 1964 (1913).
12. W.E. Dickinson, *Ann. Chem.*, **30**, 992 (1958).
13. R. Belcher and M.K. Bhatta, *Analyst.*, **81**, 124 (1956).
14. A. Elek and H. Sobotka, *J. Am. Chem. Soc.*, **48**, 501 (1926).
15. R.B. Bradstreet, *Ann. Chem.*, **32**, 114 (1960)
16. M. Ashraf, M.K. Bhatta and R.A. Shah, *Pakistan J. Sci. Ind. Research*, **3**, 1 (1960).