LETTERS TO THE EDITORS

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Elementary Isotopic Analysis: Determination of Nitrogen

WE have recently described an isotopic method for the determination of oxygen¹ and carbon² in organic compounds by using heavy oxygen (O^{18}) and carbon (C^{13}) respectively in conjunction with a mass spectrometer. Using the same method, higher precision is possible in the determination of nitrogen and hydrogen, since N^{15} and H^2 (deuterium) are available in higher concentrations (30–35 per cent for N^{15}) than the oxygen isotope (1.2 per cent) and the carbon isotope (10–20 per cent).

In order to extend this method to nitrogen, we have made the following four determinations. Representatives of two types of compounds, heterocyclic and nitro, were chosen in view of the well-known difficulties of analysing them by the standard Kjeldahl method. The compounds used were pyridine ($n_{D_{20}}^{20} = 1.5090$) and nitroethane ($n_{D_{20}}^{20} = 1.3912$).

A known weight of substance (a) was burned simultaneously with a known weight (b) of pure isotopic $N^{15}H_3$ in a quartz tube, in the presence of an excess of copper oxide, copper and platinum wire, for 45–60 minutes. (Copper and platinum were inserted, of course, to reduce and equilibrate any oxides of nitrogen.) Both the pyridine and the nitroethane were burned at $750^\circ C$. The percentage of nitrogen (x) was calculated from our usual formula: $x = 100 b(m - n)/an$, where m and n are, respectively, the initial and the final percentage excess of N^{15} in the ammonia and nitrogen.

Any air leakage into the sample, either during the run or during analysis, can be corrected for by calculating the air nitrogen contribution from the argon (mass = 40) peak. In a good determination the air nitrogen should be less than 3 per cent of the total nitrogen.

The results obtained are as follows:

	Pyridine, C_5H_5N		Nitroethane, $C_2H_5NO_2$	
Analysis	1	2	3	4
a , mgm. substance	25.56	30.02	25.04	16.97
b , mgm. N^{15}_3 , added as NH_3 (using normal at. wt. of $N = 14.008$)	1.79 ₆	4.27	4.43	3.43
m , % excess of N^{15} above normal (= 0.76%)	34.84	34.84	32.10	32.10
N^{15} content of equilibrium mixture (%)	10.52	16.30	16.50	17.55
	10.59	16.18	16.38	17.54
			16.34	17.47
				17.43
				17.56
Average	10.55 ± 0.04	16.24 ± 0.13	16.41 ± 0.06	17.51 ± 0.05
n , average % excess of N^{15} in equilibrium mixture	9.79	15.48	15.65	16.76
% N in substance, experimental	17.96 ± 0.09	17.79 ± 0.26	18.60 ± 0.14	18.52 ± 0.13
% N , theoretical	17.74	17.74	18.66	18.66

The mean probable deviation from the theoretical value is 0.4 per cent of the nitrogen content; it is

within the accuracy and precision of the Consolidated Engineering Corporation's mass spectrograph that we used.

A detailed description of our experiments will be published later.

Difficulties are encountered in the determination of hydrogen by this method because of wide differences in the rates of diffusion of protium and deuterium. Additional precise calibrations or changes in the construction of the present mass spectrographs would be necessary before our method can be successfully applied.

We are indebted to Dr. D. Rittenberg of Columbia University for the sample of $N^{15}H_3$ used.

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April 9.

¹ Grosse, A. V., Hindin, S. G., and Kirshenbaum, A. D., *J. Amer. Chem. Soc.*, **68**, 2119 (1946).

² Grosse, A. V., Kirshenbaum, A. D., and Hindin, S. G., *Science*, **105**, 101 (1947).

A Semi-Quinonoid Oxidation Product of 4 : 4-Diethoxydinaphthyl

THE communication from Messrs. Hughes, Hush and Mellor¹ reporting a green oxidation product of tetramethyl-benzidine and the projected extension of work to related compounds renders desirable some account of our own work on the green colour instantly developed when 4 : 4'-diethoxydinaphthyl is dissolved in a large excess of concentrated sulphuric acid. The increase of intensity of absorption (measured at 660 $m\mu$) is linear with that of concentration of the dinaphthyl until this reaches c. 310 mgm./litre. The solubility of oxygen in sulphuric acid being 33 mgm./litre², calculation shows the green colour to arise from the action of c. 8 gm. oxygen per gm. mol. diethoxydinaphthyl. A similar result follows if selenium dioxide or nitrous acid be used to intensify the colour. We therefore attribute the structure I to the green product.

We expect to find that the blue, green and red colours developed by oxidation of diphenol³, 3 : 3'-dimethyl-4 : 4'-dinaphthol⁴, and dianthranol⁵ respectively are of the same semi-quinonoid character and will develop in excess of sulphuric acid without further addition of an oxidizing agent.

So far we have been less concerned with isolation of the semiquinonoid product (I) than with the general significance of the facts that: (1) the green colour is destroyed on addition of 1-ethoxynaphthalene, which is itself then converted to 4 : 4'-diethoxydinaphthyl; (2) 1-ethoxynaphthalene itself causes