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Spectrographic Analysis of the Nessler-Ammonia Reaction.

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Various attempts have recently been made to develop a direct method for estimating ammonia by correlating the ammonia content of a solution with the intensity of the orange-red color produced in it by the action of Nessler's reagent.[1] Such a method would be expected to yield the most satisfactory results when monochromatic light at or near the wave-length of maximum absorption is employed, but so far as we are aware the absorption spectrum of the Nessler-ammonia color has not hitherto been investigated. We have, therefore, measured this property both for Nessler's solution itself (pre-

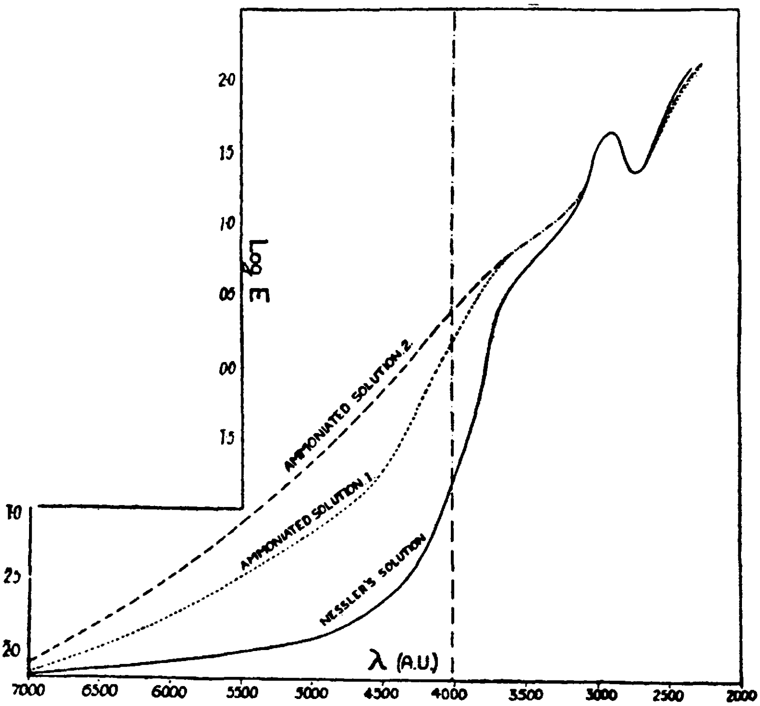

FIG. 1.
Solution 1 contained 0.08 mg. NH_3 in 100 cc.; solution 2, 0.2 mg. in 100 cc. E = 100 d/cl, where d = optical density of the solution; c = number of cc. of Nessler's solution per litre; l = thickness of liquid.

[1] *Cf.* Urbach, *Biochem. Z.*, 1932, **252**, 292, 406.

pared according to the directions of Folin), and for 2 colored solutions containing different proportions of ammonia, the solution in each case being stabilized by the addition of gum ghatti.

The results are shown in Fig. 1. The curve for Nessler's solution is similar to that recorded for yellow-colored K_2HgI_4,[2] and consists of a strong band at 2900 A.U., 1000 times more intense than the absorption in the visible spectrum, with a "step-out" at 3500 A.U. The addition of ammonia produces no change in the position or intensity of the head of this absorption band, and does not seriously affect the absorption at long wave-lengths, but that in the blue and near ultra-violet regions appears to be enhanced. The orange-red color of the ammoniated solutions cannot, therefore, be attributed to any change in the maximum of absorption, and we suggest that it is more probably the result of light-scattering than of light-absorption.

The following evidence can be cited in support of this view: 1. The colored solutions are colloidal and flocculate rapidly unless a stabilizer is added. 2. The substitution of ammonia for potassium in the unionized double-salt would not be expected to produce such a change in the "shape" of the absorption band without affecting its position and intensity. 3. Serious deviations from Beer's law were observed in this region of the spectrum. 4. The yellow color of colloidal sulphur solutions results from scattering, and not from absorption.[3] 5. An examination of the colored solutions under the ultra-microscope indicated the presence of large particles with strong scattering. 6. The intensity of the light scattered by a particle is proportional to the square of its volume while the absorption depends only on the first power, so that as particle size increases, the scattering becomes relatively more important than the absorption. A comparison can thus be drawn between the intensification of the Nessler color during flocculation of unstabilized solutions and that of As_2S_3 during precipitation, as studied by Boutaric and Vuillaume.[4]

It is therefore concluded that until more is known of the optical properties of ammoniated Nessler's solutions, great caution must be exercised in attempts to estimate the ammonia by methods involving the use of interpolation curves which are based on measurements of the intensity of the light transmitted through them.

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[2] Goldstein, Thesis, Cambridge University, 1926.

[3] Keen and Porter, *Proc. Roy. Soc.*, A, 1914, **89**, 370.

[4] Boutaric and Vuillaume, *J. Chim. Physique*, 1925, **21**, 247.