THE APPLICATION OF COLORIMETRY IN THE ULTRAVIOLET TO THE DETERMINATION OF THE STRENGTH OF ACIDS AND BASES

Sir:

The important problem of determining the base strengths of very weak bases (*e. g.*, most organic acids, esters, ketones, aldehydes, ethers, amines, and amides) has been solved by the methods of visual colorimetry for the limited group of bases whose ionization is accompanied by a change in color. Because of the great desirability of obtaining similar quantitative information for uncolored bases, we have investigated the validity of what may be called colorimetry in the ultraviolet as a method of measuring ionization and base strength. For this purpose the ultraviolet absorption spectra of a carboxylic acid (benzoic acid), of a phenolic acid (2,4-dinitrophenol), and of a singly charged acid (anilinium ion, which is the conjugate acid to the simple base aniline) have been measured under the following conditions: (1) in an acid solution in which the ionization of the acid is negligible; (2) in a basic solution in which the acid is completely ionized; (3) in a buffer solution of known acidity in which ionization is approximately half complete. In every case ionization was accompanied by a marked change in the absorption spectrum from which calculation of the extent of ionization was easily possible. The values of acid strength obtained are listed herewith, together with the values (derived from conductivity or hydrolysis measurements) given in the Landolt–Börnstein "Tabellen."

	pK (absorption spectra)	pK (L.–B.)
Benzoic acid	4.16 ± 0.11	4.18
Dinitrophenol	4.09 ± .04	4.10
Anilinium ion	4.62 ± .05	4.62

The deviations represent variations in the pK obtained from different regions of the spectrum.

Having thus demonstrated the validity of the method, we have further investigated the ionization of benzoic acid as a base

$$C_6H_5COOH + H^+ \rightleftarrows C_6H_5COOH_2^+$$

by determining its absorption spectrum in a series of increasingly acid sulfuric acid–water mixtures. A large change took place between concentrations of 70 and 95% sulfuric acid, and very little change in any other range of acidity. From these spectra and the visual colorimetric values of the acidity function H_0 for the sulfuric acid solutions, we obtain the following value for the base strength of benzoic acid

$$pK' \equiv\equiv -\log a_B a_{H^+}/a_{BH^+} = -7.25 \pm 0.25$$

The method will be applied to the determination of the base strengths of other colorless organic compounds.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
LOUIS P. HAMMETT
ANDREW DINGWALL
LEO FLEXSER

RECEIVED AUGUST 3, 1934

IRRADIATION OF YEAST ORYZANIN

Sir:

We have found that a one-hour irradiation of a solution containing 24.4 mg. per liter of yeast oryzanin kindly furnished by S. Ohdake and U. Suzuki, at a distance of 4.3 cm. from a Victor quartz lamp, destroyed its ability to alleviate the neurological symptoms of rats maintained on a vitamin B_1 deficient diet in doses as large as 12 γ. The original solution was active in doses of less than 3 γ. The two-peaked absorption of the compound, which resembles that of cytosine [THIS JOURNAL **56**, 1728 (1934)] is rapidly destroyed by the irradiation. On the other hand, irradiation with ultraviolet from which most of the radiations of wave lengths less than 2960 Å. have been filtered

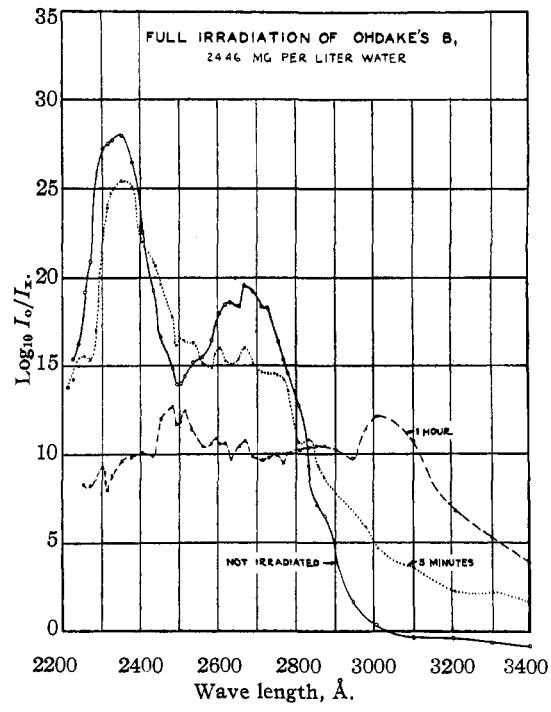

Fig. 1

out, for a period of thirty minutes produces a transient increase in the characteristic absorption, and even after four hours leaves the absorption bands still present, while the biological potency is