

new pipette for the next transfer. In a routine experiment a single operator prepared 823 individual dilutions in a total elapsed time of 114 minutes, an average of 7.2 per minute.

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A NEW COLORIMETRIC REAGENT FOR TITANIUM

IN a report on their investigation of disodium-1,2-dihydroxybenzene-3,5-disulfonate [$C_6H_2(OH)_2(SO_3Na)_2 \cdot H_2O$] as a reagent for the colorimetric determination of iron, Yoe and Jones¹ observed that it gives an intense yellow solution with Ti^{+4} . Their preliminary observation indicated the sensitivity to be about 1 part of titanium in 200 million parts of solution when comparisons are made in 50 ml, tall-form Nessler cylinders. This observation has been substantiated.

The color intensity of the titanium complex is independent of acidity over the range pH 4.3–10, the color does not change in intensity or tint over periods of several months, and it obeys Beer's law over the useful range of concentration.

The number of interfering ions is small. Aluminum, calcium and tungsten reduce the intensity of the color; this can be largely overcome by adding an

excess of reagent. Iron, vanadium and uranium develop colors with the reagent, but only the first is commonly encountered. The purest available reagents used for opening up samples contain sufficient iron to give an off-tint color to the titanium complex. The iron interference may be eliminated by buffering the solution at pH 4.7 with acetic acid and sodium acetate in a 1:1 molar ratio and adding 50 mg of sodium hydrosulfite per 100 ml of solution. Under these conditions the iron is reduced to the ferrous state and gives no color with the reagent, and hydrosulfite solutions show no turbidity for 20 minutes.

If titanium and iron are both to be determined, this may be done with the same solution. Add the reagent (about 0.1 g), adjust to pH 4.7, measure the absorbency (-log of transmittency) at 560 mμ (the maximum for the iron complex at pH 4.7), then reduce with sodium hydrosulfite and measure the absorbency at 410 mμ. The amount of iron and titanium may be determined from previously prepared graphs.

A more extensive report on the use of this reagent for the colorimetric determination of titanium will be published elsewhere in the near future.

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DISCUSSION

THE PHYSICAL CHEMISTRY OF COLOR VISION

THE manifold and long-continued research work of Selig Hecht and his collaborators on the nature of vision and visual response to light has culminated or converged, in one aspect, that of color vision, in a rather radical transformation of the trichromatic theory initiated by Thomas Young, developed by Clerk-Maxwell and Helmholtz, disputed by Hering and exploited practically in various processes of color photography. This transformation is proposed by Dr. Hecht most concisely, for present reference, in his paper on "The Development of Thomas Young's Theory of Color Vision" and very important confirmatory and extensory investigations are given in a more recent paper by J. Mandelbaum and E. U. Mintz.¹

The basic nature of the transformation is evident on comparing the accepted trichromatic "excitation" (or sensitivity) curves of Koenig, Abney, Wright and others² and those introduced by Hecht. These, instead of differing widely throughout the spectrum, are close together, and have maxima in the yellow-green

part of the spectrum near the region of maximal photopic visibility; the shape of the curves varies but little one from another, and from the photopic-visibility curve.

As pointed out by Mandelbaum and Mintz, "The virtue of Hecht's formulation is that for the first time much of the data relevant to color vision is included."

Hecht has stated the difficulties of the physico-technical theory³ for the physiological (and chemico-physical) picture as follows: referring to the accepted values of the excitation curves adopted by the American Optical Society and the visibility curve (of Gibson and Tyndall) he says: "These are all unimpeachable facts. But they make it extremely difficult to formulate a physiological picture of what they mean, especially in the matter of treating the excitation curves or the *Grundempfindungen* as the real physiological primaries which must accomplish what Thomas Young's notion expects them to." In face of the difficulties, Hecht has proposed, as he himself, I think too modestly, has said, a set of "Variations on a Theme by Thomas Young." It is, incidentally, a part of the intention of this note to suggest that there has been so radical a transformation of the theme as to

³ Thus to designate the current theory.

¹ *Ind. Eng. Chem., Anal. Ed.*, 16: 111, 1944.

² *Am. Jour. Ophthalm.*, 24: 1241, 1941.

³ *Jour. Ophthalm. Soc. America*, 20: 231, 1931.

create a new symphony. This because, if the relation of Hecht's suggestions to those that follow be in any way grounded, the dominant triune or Pythagorean threefold character of the original theme is in course of replacement by a numerical discontinuum of order \approx and generally < 5 , but probably not essentially and always 3. The meaning of this will be clear, when it is allowed that for protanopes the number of color-processes could be $= 1$ or > 1 , but not $= 2$,⁴ for deuteratopes 2 or 3, and for normal polytopes, 3 or greater.⁵ This is one consequence of the concept of closely overlapping curves—conforming to Hecht's conclusions, but admitting statistical variates. Mandelbaum and Mintz suggest:

From a phylogenetic and from a photochemical point of view, the concept of closely overlapping curves is more probable than is that of the widely separated curves of classical formulation. Their differences in sensitivity may well be due to slight differences in their absorption spectra, for in the case of both visual purple and visual violet the spectral sensitivity is determined by the absorption spectrum. Such slight differences in spectral absorption could easily be accounted for by small molecular rearrangements, or the simple addition of a methyl or ethyl group.

What we wish to point out, as a mere suggestion for possible further prosecution by physiologists and biochemists, is that well-ordered and physico-chemically controlled modifications of the absorption spectrum exist in dyes of many types, which would permit the closely overlapping curves of the Hecht theory to arise for the same dye as well as by essential, though small, chemical modifications of a dye molecule. Such alterations can be determined by molecular aggregations of a reversible character, controlled by the parameters of the thermodynamic environment. We propose to group such variations under the general term, allelochromy,⁶ and may mention two principal directions in which conditions for fulfillment of the closely overlapping trinity—or multiteity—of sensitivity curves might be sought. These are (1) spectral absorption variation by dimerization⁷ and (2) by heteropolymerization of dyes in lyotropic mesophase formation.⁸ These are quite distinct processes, though liable to appear with the same dye molecules, and for

the good reason that both depend upon the possibility of sterically unimpeded side-by-side parallel coherence, in the first case in pairs of two ions, in the second, in a species of one dimensional or filamentous quasi-crystallization of large numbers of like dye molecules acting as a unit.

Spectral variations in the first case can be produced by variation of concentration and medium. A pronouncedly amphipathic substance,⁹ such as the nucleoprotein of nerve-fiber, should be ideal in respect of such control. *Per contra*, the other state of ordering also deserves consideration. While the striking spectral absorption of the mesophase of 1,1'-diethyl-2,2'-cyanine chloride, discovered by E. E. Jelley¹⁰ and, independently, by G. Scheibe,¹¹ has concentrated attention on this narrow band type from symmetrical molecules, it deserves to be noted that with asymmetrical dye molecules of the cyanine dye family, co-operative spectra giving absorption curves of much broader form may be obtained, and, again, by small variations of the proportions of reversibly heteropolymerized ions, allow controlled variation of the absorption.¹² In this case, with *two* not too dissimilar but isomorphous dye ions, A and B, *three* packets of A, AB and B could give curves of near overlap. The writer has commented elsewhere¹² on the analogies of the combinations such dye ions can make with proteins, with the spatial arrangements made probable for thymo-nucleic acid molecules.¹³ The conditions by which, in these multi-molecular assemblages, excitation-conductance becomes possible, also would seem to deserve attention in connection with the theory of vision.

It is an interesting thought that while the widely separated curves of the classical trichromatic theory have well served the mimetic development of color photography, operation on the basis of such closely overlapping curves as those proposed by Hecht would probably have been technically impossible, or, in any case, impractical.

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PROPOSED UNIT FOR HIGH VACUUM

F. H. TOWNSEND¹ suggests a new unit for the measurement of vacuum which has the virtue of expressing increasing vacuum—decreasing pressure—in terms of

⁴ Fractional values referring to statistical variations of the distributions of operative processes (1, 2, 3, 4 or 5) in rod and cone populations.

⁵ Just as in multicolor printing, it could be a matter of economy *vs.* efficacy whether two, three or more components were employed. But, for vision, it is rather the (statistical) frequency of certain dye molecules in the populations of rods and cones.

⁶ Cf. allelochromy and signifying alternative or contrasting coloration.

⁷ S. E. Sheppard and A. L. Geddes, *Am. Chem. Soc.*, 66: 1995, 1944, Part IV.

⁸ S. E. Sheppard, *Reviews of Modern Physics*, 14: 303-340, 1942.

⁹ S. E. Sheppard and A. L. Geddes, Amphipathic Character of Proteins and Certain Lyophilic Colloids as Indicated by Absorption Spectra of Dyes, *Jour. Chem. Phys.*, 13, 63, 1945.

¹⁰ E. E. Jelley, *Nature*, 138: 1009, 1936.

¹¹ G. Scheibe *et al.*, *Naturwiss.*, 25: 75, 1937.

¹² S. E. Sheppard, *SCIENCE*, 93: 42, 1941.

¹³ K. Linderstrom-Lang, *Trans. Farad. Soc.*, 31: 324, 1935.

¹ *Nature*, 155: 545, 1945.