

Variation of Absorptance-Curve Shape With Changes in Pigment Concentration*

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A complete quantitative analysis is presented of changes in the shape of the spectral absorptance curve of any Beer's-law pigment solution (or other Bouguer's-law material) as concentration of the pigment, or thickness of the solution layer, is varied. The relative absorptance curve, normalized to unit maximum, is taken as defining the shape of the absolute absorptance curve, and the index of shape change is taken to be the difference between the normalized curves. All concentration changes from infinite decrease to infinite increase are covered, with some extreme cases requiring limit methods. Formulas and graphs are given for determining, as a function of concentration change and peak absolute absorptance of the original curve, where along the curve the shape change is greatest, and how large the maximum change is. Implications for color vision theory are discussed and it is shown that the assumption of low peak absorptances ($< 10\%$) for the visual photopigments accounts for the constancy of the color-matching functions for moderate luminances, but not, in itself, for the breakdown of matches at high luminances; while the assumption of high peak absorptances ($\approx 80\%$), although it contradicts recent microspectrophotometric measurements, seems to account for both phenomena.

Key Words: Absorption; adaptation; Beer's law; chromatic adaptation; color vision; concentration; cones; curve shape; high luminance; metameric matches; pigment; photopigment; vision.

1. Introduction

The theory that chromatic adaptation is explainable by changes in the concentrations of the visual photopigments has lost some adherents in recent years to the notion that adaptation is a neural or synaptic phenomenon [1, 2, 3].¹ One of the objections which has been raised [3] to the pigment-concentration theory is that a change in the concentration of a pigment in solution necessarily changes the shape of the absorptance curve of the pigment solution, because of the nonlinear (exponential) character of Beer's Law. A sufficient change in shape of the absorptance curves of the visual photopigments would be behaviorally detectable, since the color-matching functions would be altered. On the other hand, the empirical evidence indicates that the color-matching functions are independent of chromatic adaptation [4] over an unlimited range of chromaticities and a wide, but not unlimited [5, 6] range of luminances, the implication being that the shapes of the absorptance curves of the photopigments do *not* vary significantly with nonextreme changes in the adaptive state.

It appears to be generally understood [7] that the changes in shape of the absorptance curves are not significant if the initial (dark-adapted) concentrations of the photopigments are sufficiently low. The purpose of this paper is to specify quantitatively the nature and extent of the shape changes induced in the absorptance curve of a layer of pigment by changes in the concentration of the pigment (or the thickness of the layer). Although the final treatment will be completely

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¹ Figures in brackets indicate the literature references at the end of this paper.

general and will apply to any real pigment, there are two basic decisions to be made in advance that are determined by the primary purpose of the study, which is investigation of visual photopigments.

The first decision is what is to be meant by the "shape" of a curve. The definition to be developed is based on the convention that multiplying the ordinates of a curve by a constant does not change its "shape." As applied to visual photopigment absorbance curves or the color-matching functions of a colorimetric system, this convention is the appropriate one, because the facts of metamerism (that is, which spectral radiance distributions match in color) would be left unchanged if the spectral absorbance curve of any of the visual photopigments were to be changed by multiplication by a constant factor; and, correspondingly, the predictions of metamers of a colorimetric system are invariant under any scale-factor change in any of the color-matching functions.

These same considerations determine the other basic decision as well: what specific measure of amount of light absorption by a pigment should be used. It is *absorbance* that counts directly in color vision, not any other measure, such as optical density, commonly used in other contexts.

2. Beer's Law

Given a layer of pigment in solution, Beer's Law [7a] permits us to calculate the spectral absorbance, α_λ ,² of the layer. If c is the concentration of the pigment in the solvent, x is the thickness of the solution layer, and β_λ is the spectral absorption coefficient of the pigment, then the expression for α_λ is:

$$\alpha_\lambda = 1 - \exp(-\beta_\lambda cx), \quad (1)$$

provided we neglect surface reflections, scattering, and the absorbance of the solvent; in other words, if we assume that all light not transmitted by the layer is absorbed by the pigment. In the case of the visual photopigments, the solvent is presumably a clear gel and these simplifying assumptions probably do not introduce too much of a distortion in the analysis.

Now suppose that the action of a bleaching light reduces the concentration of the pigment (or, equivalently, the thickness of the pigmented layer)³ to $1/n$ times its original value. Then the new absorbance, $\alpha_\lambda^{(n)}$, is given by:

$$\alpha_\lambda^{(n)} = 1 - \exp(-\beta_\lambda cx/n). \quad (2)$$

In the case of the visual photopigments, it is possible that significantly absorbing breakdown products are produced by bleaching, but this investigation will be confined to consideration only of the absorbance of the original pigment.

If we isolate the exponential term in eq (1) and raise both sides to the power $1/n$, the result is:

$$(1 - \alpha_\lambda)^{1/n} = [\exp(-\beta_\lambda cx)]^{1/n} \equiv \exp(-\beta_\lambda cx/n); \quad (3)$$

and, from (2) and (3), we see that

$$\exp(-\beta_\lambda cx/n) = 1 - \alpha_\lambda^{(n)} = (1 - \alpha_\lambda)^{1/n}. \quad (4)$$

² In current international practice, a subscript λ denotes a spectral concentration; a dimensionless function of wavelength like absorbance is properly denoted $\alpha(\lambda)$. However, in order to avoid complicating the many equations in this paper with another level of parentheses, the subscript notation will be used throughout. No ambiguity can arise, since no quantity referred to in the paper is a spectral concentration.

³ This parenthetical alternative should be understood implicitly wherever "concentration" is referred to in the remainder of this paper. Although this paper is phrased in terms of a pigment solution, it should also be understood that all results apply to any pigment suspension, whether a true solution or not, as long as the suspension follows Beer's law; and also to any transmitting substance whatever that follows Bouguer's law.

Thus we conclude from (4) that

$$\alpha_{\lambda}^{(n)} = 1 - (1 - \alpha_{\lambda})^{1/n}. \quad (5)$$

The transformation (5) from α_{λ} to $\alpha_{\lambda}^{(n)}$ is order-preserving. That is, if for wavelengths μ and ν ,

$$\alpha_{\mu} > \alpha_{\nu}, \quad (6)$$

it is also true that

$$\alpha_{\mu}^{(n)} > \alpha_{\nu}^{(n)} \quad (\text{all } n).^4 \quad (7)$$

The proof of this property is equivalent to proving that $\alpha_{\lambda}^{(n)}$ is a monotonically increasing function of α_{λ} , for any n , and this is in turn equivalent to showing that the derivative of $\alpha_{\lambda}^{(n)}$ with respect to α_{λ} is always positive.

Differentiating (5), we find that

$$\frac{\partial \alpha_{\lambda}^{(n)}}{\partial \alpha_{\lambda}} = \frac{(1 - \alpha_{\lambda})^{\frac{1}{n} - 1}}{n}. \quad (8)$$

We see that the derivative (8) is indeed always positive, for any (positive) n and any $\alpha_{\lambda} < 1$. (The fact that the derivative reaches zero at $\alpha_{\lambda} = 1$, for $n < 1$, is irrelevant to the order-preserving property, since no α_{λ} can be greater than unity.)

The fact that the transformation preserves order implies in particular that at any wavelength at which α_{λ} has a maximum or a minimum, $\alpha_{\lambda}^{(n)}$ has a corresponding maximum or minimum. Thus we know that whatever distortions in the absorbance curve may be produced by a change of pigment concentration, there is no shifting of the wavelengths at which the peaks and valleys occur.

3. Normalized Absorbance Curves

The object of this analysis is to deal quantitatively with the "shapes" of functions.⁵ In discussions of vision, and in other contexts where functions are known only to within a scale factor (or where the absolute size of the ordinates is irrelevant to the purpose at hand), it is commonly said that the shape of a function—let us say of wavelength—is unchanged if we multiply the function by a fixed constant at every wavelength. This convention can be used as the basis for formulating a definition of "shape." If we want to find out whether two given functions have the same shape, it is clear that what we want to do is to divide each function by some constant so that both sets of values are reduced to the same scale. The original curves have the same shape if the adjusted curves are identical.

A familiar way of reducing curves to the same scale is to divide each curve by its own maximum value. Another way of describing this procedure is to say that we are "normalizing" each curve so that it will have a maximum of unity.

⁴ Naturally, negative values of n are excluded as meaningless. Normally, it should be understood that $n > 0$, but the limiting case $n = 0$ (an infinite increase in pigment concentration) will be considered where appropriate. It will prove helpful to keep in mind that n is the factor by which the original concentration is divided—not multiplied—so that reductions of concentration ("bleaching") are implied by the range $1 < n \leq \infty$ and increases of concentration by the range $0 \leq n < 1$. This choice of meaning for n was dictated by the relatively greater interest in bleaching than in concentration increase in the field of visual pigments.

⁵ Technically speaking, it is the curves representing the functions that have shapes, but it is convenient to speak interchangeably of the shape of the curve or the function.

If we let M be the (or a) wavelength at which α_λ has its maximum value, α_M , then we have shown previously that the maximum value of $\alpha_\lambda^{(n)}$ is, for all n , the value of $\alpha_\lambda^{(n)}$ at that same wavelength M . In short, taking note of (5), we may write:

$$\max \alpha_\lambda^{(n)} = \alpha_M^{(n)} = 1 - (1 - \alpha_M)^{1/n}. \quad (9)$$

Now let us define a normalized function, $\hat{\alpha}_\lambda$, as the function α_λ divided by its maximum value:

$$\hat{\alpha}_\lambda = \alpha_\lambda / \alpha_M, \quad \alpha_M \neq 0. \quad (10)$$

Similarly, we define a normalized function, $\hat{\alpha}_\lambda^{(n)}$, by:

$$\hat{\alpha}_\lambda^{(n)} = \alpha_\lambda^{(n)} / \max \alpha_\lambda^{(n)} = \frac{1 - (1 - \alpha_\lambda)^{1/n}}{1 - (1 - \alpha_M)^{1/n}}, \quad \alpha_M \neq 0. \quad (11)$$

The case $\alpha_M = 0$ represents a pigment that does not absorb at all ($\alpha_\lambda \equiv 0$). There is little to be gained by defining the normalized functions in this degenerate situation (one can argue for choosing either a constant value of unity or of zero), and it will be assumed tacitly from here on that $\alpha_M > 0$. For the sake of completeness, however, we will consider later the limiting behavior of certain functions as α_M approaches zero.

The normalized functions $\hat{\alpha}_\lambda$ and $\hat{\alpha}_\lambda^{(n)}$ are equal to unity (and consequently to each other) at all wavelengths at which α_λ takes on its maximum value. Moreover, the functions are also equal (to zero) at all wavelengths at which $\alpha_\lambda = 0$. The question we are interested in pursuing is how different are $\hat{\alpha}_\lambda$ and $\hat{\alpha}_\lambda^{(n)}$ at other wavelengths?

Before developing an answer to this question, let us first investigate a few important properties of the normalized absorbance curve $\hat{\alpha}_\lambda^{(n)}$ defined by (11).

In Appendix A it is proved that

$$\hat{\alpha}_\lambda^{(p)} < \hat{\alpha}_\lambda^{(q)} \quad \text{for } p > q \quad (12)$$

[except for wavelengths for which the absorbance, α_λ , is 0 or the maximal value, α_M , in which cases an equality sign replaces the less-than sign in (12)]. In other words, as n increases (concentration decreases), the values of $\hat{\alpha}_\lambda^{(n)}$ become smaller and smaller: the sequence of curves $\hat{\alpha}_\lambda^{(n)}$ is monotonically decreasing. Since all the curves of the sequence $\hat{\alpha}_\lambda^{(n)}$ have a common maximum of unity at the same wavelength(s), a simple statement of the situation is that the normalized absorbance curve (or the shape of the absorbance curve) "narrows" as pigment concentration decreases; or, more precisely, the half-peak width of the primary absorption band covers a smaller wavelength range.

No matter how much the concentration is reduced, the normalized absorbance curve continues to narrow, but the decreases in the values of $\hat{\alpha}_\lambda^{(n)}$ become smaller and smaller as n grows larger. In fact, the sequence of curves $\hat{\alpha}_\lambda^{(n)}$ approaches a limiting curve, $\hat{\alpha}_\lambda^{(\infty)}$, as n becomes indefinitely larger (concentration approaches zero). If we try to evaluate this limit by letting n approach infinity in the expression (11) for $\hat{\alpha}_\lambda^{(n)}$, we are initially frustrated by the fact that both the numerator and denominator approach zero, the result being indeterminate. The limit can be evaluated, however, by an application of L'Hospital's rule, which says that in such an instance, the limit is unaffected by differentiation of both numerator and denominator. Thus:

$$\hat{\alpha}_\lambda^{(\infty)} = \lim_{n \rightarrow \infty} \hat{\alpha}_\lambda^{(n)} = \lim_{n \rightarrow \infty} \frac{1 - (1 - \alpha_\lambda)^{1/n}}{1 - (1 - \alpha_M)^{1/n}} = \lim_{n \rightarrow \infty} \frac{(1 - \alpha_\lambda)^{1/n} \ln(1 - \alpha_\lambda)}{(1 - \alpha_M)^{1/n} \ln(1 - \alpha_M)} \quad (13)$$

or

$$\hat{\alpha}_\lambda^{(\infty)} = \frac{\ln(1 - \alpha_\lambda)}{\ln(1 - \alpha_M)}; \quad \alpha_M, \alpha_\lambda \neq 1. \quad (14)$$

If any amount of pigment is present, the normalized absorbance curve is broader and greater than the limiting curve defined in (14). For sufficiently low concentrations, however, the curves become insignificantly different from the $\hat{\alpha}_\lambda^{(\infty)}$ curve. It should be stressed that this conclusion applies to any absorbance curve whatever.

When any $\alpha_\lambda = 1$, it follows that also $\alpha_M = 1$, since no absorbance can be greater than unity. In that case, it is clear from (11) that

$$\hat{\alpha}_\lambda^{(n)} = 1, \quad \text{for } \alpha_\lambda = 1 \text{ (all } n); \quad (15)$$

so that also the limit

$$\hat{\alpha}_\lambda^{(\infty)} = 1, \quad \text{for } \alpha_\lambda = 1. \quad (16)$$

Finally, when $\alpha_M = 1$:

$$\hat{\alpha}_\lambda^{(n)} = 1 - (1 - \alpha_\lambda)^{1/n}, \quad \text{for } \alpha_M = 1; \quad (17)$$

and

$$\hat{\alpha}_\lambda^{(\infty)} = 0, \quad \text{for } \alpha_M = 1, \alpha_\lambda \neq 1. \quad (18)$$

Equations (16) and (18) together indicate that if there is any wavelength at which absorbance is complete—if $\alpha_M = 1$ —then the limiting normalized absorbance curve, $\hat{\alpha}_\lambda^{(\infty)}$, takes on a discontinuous line or rectangular form which is unity where the original absorbance curve, α_λ , is unity, and is zero everywhere else. This is the ultimate in narrowing, and is not seen unless there is a wavelength at which absorbance is total.

It is also of interest to consider what happens when the concentration of the pigment becomes much greater than the initial value. Physically, the increase in concentration is limited by the solubility of the pigment in the solvent, but for theoretical purposes, we can consider the consequences of letting n approach 0. (If we consider the physical dimension being varied to be the thickness of the solution layer, rather than the concentration of the pigment in the solvent, the case of infinitesimal n becomes operationally meaningful.) We see from (11) that

$$\hat{\alpha}_\lambda^{(0)} = \lim_{n \rightarrow 0} \hat{\alpha}_\lambda^{(n)} = \lim_{n \rightarrow 0} \frac{1 - (1 - \alpha_\lambda)^{1/n}}{1 - (1 - \alpha_M)^{1/n}} = \frac{1}{1} = 1, \quad \text{for } \alpha_\lambda \neq 0. \quad (19)$$

When $\alpha_\lambda = 0$, we have:

$$\hat{\alpha}_\lambda^{(0)} = \lim_{n \rightarrow 0} \hat{\alpha}_\lambda^{(n)} = \lim_{n \rightarrow 0} \frac{0}{1 - (1 - \alpha_M)^{1/n}} = \frac{0}{1} = 0, \quad \text{for } \alpha_\lambda = 0. \quad (20)$$

Thus, as the pigment concentration is greatly increased, the normalized absorbance curve (in other words, the shape of the absorbance curve) approaches a rectangular, discontinuous function which is zero wherever $\alpha_\lambda = 0$, and is unity wherever $\alpha_\lambda > 0$. This is the ultimate in broadening, and is associated with infinitely dense layers of any pigment whatever.

Most of the relationships discussed above are illustrated in figure 1a, which represents the variation of the normalized spectral absorbance of macular pigment with concentration or thickness. Similar families of curves have been published previously for other visually significant pigments, such as visual purple, by Dartnall [8]; and the hypothetical cone pigments based on the Judd [9] primaries, by Terstiege [10].

The curve taken as the original α_λ [that is, $\alpha_\lambda^{(1)}$] for the construction of figure 1a is the equivalent of the macular pigment density curve given by Wyszecki and Stiles [11], with an arbitrary

extrapolation by the present author down to 340 nm, based on Wald's [12] indication that the absorptance of the macular pigment is essentially zero by 350 nm. Figure 1a confirms that as concentration increases, the absorptance curve broadens, progressively obscuring the fine structure, and approaches a rectangular form covering the entire wavelength range over which the pigment absorbs at all.

On the other hand, the most conspicuous aspect in figure 1a of the changes occurring with decreasing concentration is the quite limited extent of these changes. The curve for infinite decrease of concentration is indeed the narrowest and lowest of all, but it is not much narrower or lower than the original curve. The curve representing a mere halving of the concentration is already about half way from the curve for the original concentration toward the curve for an infinite decrease in concentration. Concentration decrease will be seen to cause some sharpening of the fine structure. Because the peak absorptance of the original absolute curve is only 0.684 (density = 0.5), the limiting curve for infinite concentration decrease does not even approach the line spectrum required by eqs (16) and (18) when the absorptance is 1.0 at one or more isolated wavelengths (or the rectangular curve resulting when the original absorptance is 1.0 over a continuous range of wavelengths).

Figure 1b illustrates the approach to a line spectrum for a fictitious pigment having as its *absolute* spectral absorptance curve the *normalized* curve for one layer of the macular pigment on which figure 1a is based. In other words, the new absorptance curve is simply the absolute curve for one layer of macular pigment divided by the constant 0.684 (actually, $1-10^{-0.5}$) so as to have a peak absorptance of 1 instead of 0.684.

Such an absorptance curve would be difficult to find in any real pigment. For one thing, an absorptance actually equal to 1 (infinite density) at any given concentration requires an absorptance of 1 at *all* concentrations, but all real pigment layers become quite transparent at all wavelengths if the concentration or thickness is made sufficiently small. Secondly, even if the peak absorptance is only near 1 (say 0.99999) instead of equal to 1, the absorptance would not drop off from the peak

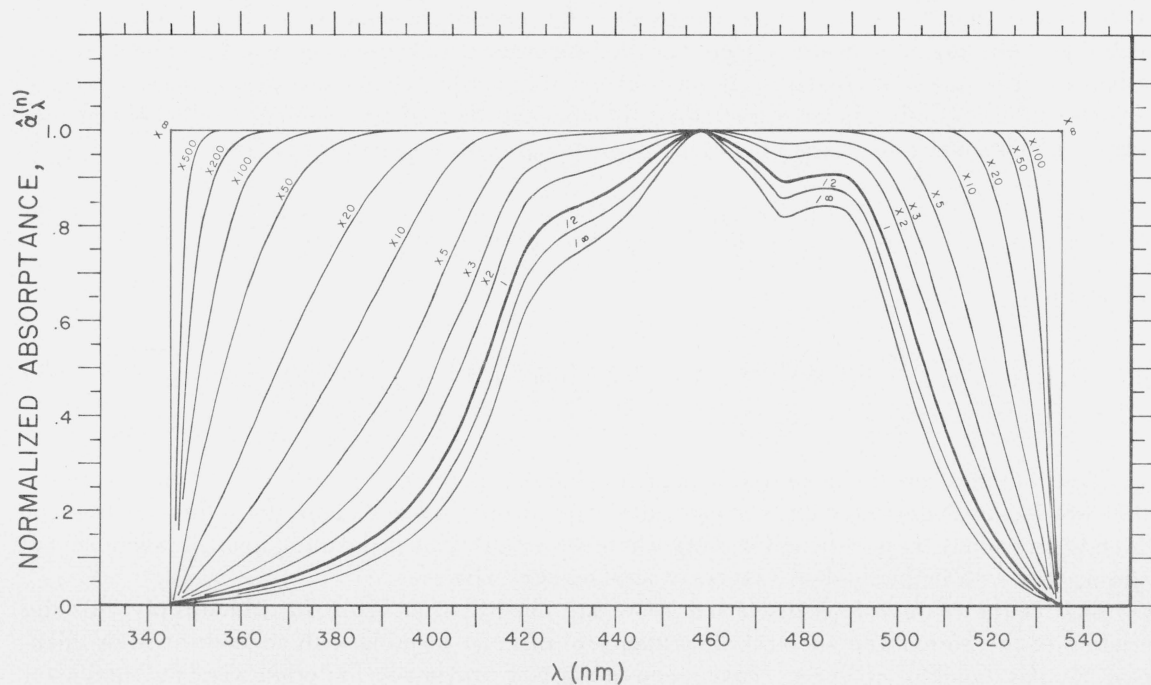


FIGURE 1a. Variation in the shape of the spectral absorptance curve of macular pigment (normalized to unit maximum) as the pigment concentration changes.

The curve labeled "1" is the original curve (peak absolute absorptance = 0.684), " $\times 2$ " denotes a doubling of concentration (or thickness), and " $/2$ " denotes a halving of concentration. The right sides of the $\times 200$ and $\times 500$ curves are omitted for clarity.

as rapidly as in our fictitious example. A real pigment layer with such a high absorbance anywhere within the interior of its absorption spectrum would have to either be very thick (compared to a layer that transmits substantially at all wavelengths) or contain an extremely high concentration of pigment. Therefore its absorbance curve would be of the flat, near-rectangular form characteristic of high concentration multiples. The curve for such a layer does not come close to reaching the "spike" form, no matter how much the concentration is reduced. In fact, the "×10" curve in figure 1a, corresponding to a layer of macular pigment 10 times thicker or more concentrated than the standard layer, does represent a peak absolute absorbance of 0.99999. Obviously the bleaching of such a layer would follow the course represented by the curves below it in figure 1a, and the limiting curve for infinite bleaching is the very same curve as the "/∞" curve in that graph. While the "/∞" curve is considerably more spiky than the "×10" curve, it is very far indeed from being a line spectrum.

Except for the limiting top ($n=0$) and bottom ($n=\infty$) curves in figures 1a and 1b, the other curves were generated by use of eq (11) in a computer program. In order to obtain a rough picture of how much the shape of any absorbance curve changes for any specified change in concentration of the pigment, it is sufficient to make use of figure 2, which is based on eq (5) and gives the relationship between the absolute absorbances $\alpha_\lambda^{(n)}$ and α_λ for various values of n . When the absolute absorbance curve has been sketched out through the use of figure 2, it is easy enough to divide by the maximum value to obtain the normalized curve.

The parameter numbers on the curves in figure 2 do not represent n , the concentration reduction factor, but instead represent P , the percentage bleach. The relationship between these quantities is given by the equations

$$P = 100 \left(1 - \frac{1}{n} \right); \quad (21)$$

$$n = \frac{100}{100 - P}. \quad (22)$$

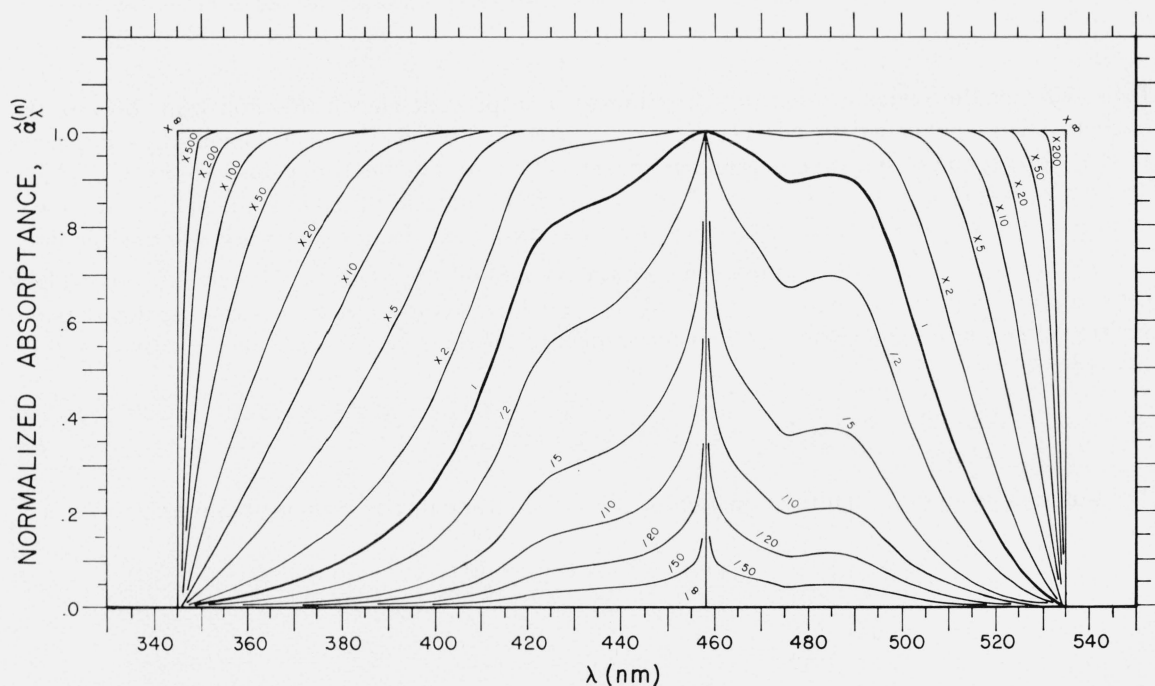


FIGURE 1b. Same type of plot as figure 1a, but here the "1" curve (identical to that in fig. 1a) corresponds to a fictitious macular-like pigment with a peak absolute absorbance of 1.

The right sides of the × 100 and × 500 curves are omitted for clarity.

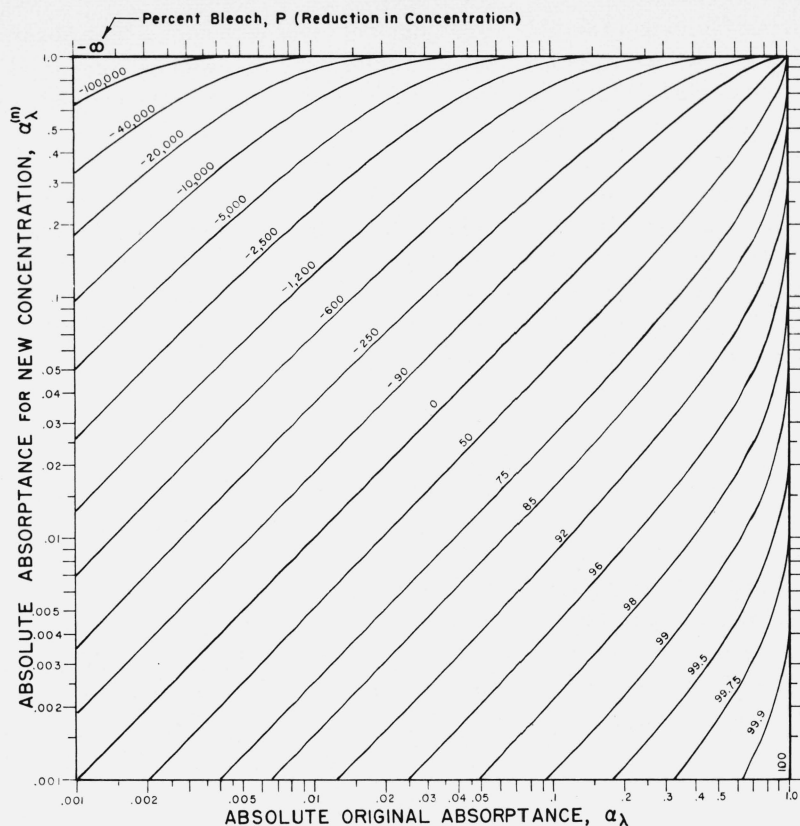


FIGURE 2. Variation of (absolute) absorbance with pigment concentration (or thickness). This graph applies to any pigment solution layer that follows Beer's law, or to any material that follows Bouguer's law.

Negative values of the parameter refer to percentage concentration increases. All the curves converge on and reach the point (1,1); despite appearances, none of the curves for $P \neq -\infty$ reaches $\alpha_\lambda^m = 1$ until $\alpha_\lambda = 1$. Also all the curves converge on and reach the point (0,0), although this is not evident because the graph is a log-log plot.

Thus, halving the concentration ($n=2$) produces a 50 percent bleach ($P=50$), while leaving the concentration unchanged ($n=1$) results in a 0 percent bleach ($P=0$). Concentration increases ($n < 1$) correspond to negative percentage bleaches ($P < 0$). The limiting values are $n=0$, $P=-\infty$; and $n=\infty$, $P=100$. In some contexts, P is a more natural measure than n , while in other frames of reference the reverse is true. The reason for preferring P in the present work will emerge later.

In figure 2, an at least approximate symmetry around the diagonal ($P=0$) is evident. It is easy to prove that the curve for $n=k$ is actually symmetric to the curve for $n=1/k$. For any function $y=f(x)$, the curve symmetric to $f(x)$ with respect to the 45° line $y=x$ has the equation $x=f(y)$. If we define

$$y = f_k(x) \equiv 1 - (1-x)^{1/k} \quad (23)$$

[the function of eq (5)], then the equation of the symmetric curve is representable as

$$x = f_k(y) \equiv 1 - (1-y)^{1/k}. \quad (24)$$

Solving eq (24) for y yields:

$$y = 1 - (1-x)^k, \quad (25)$$

and this is precisely $f_{(1/k)}(x)$, as was to be proved.

Since the curves for n and n' in figure 2 are symmetrical when

$$n = \frac{1}{n'}, \quad (26)$$

we know from (22) that the curves for P and P' are symmetrical when

$$\frac{100}{100-P} = \frac{100-P'}{100} \quad (27)$$

or

$$P' = \frac{-100P}{100-P}. \quad (28)$$

The curves in figure 2 were selected to have simple values of P , and the pairs of approximately symmetric curves are related according to (28) closely but, in most cases, not precisely. The symmetry is therefore not exact, although a perfectly symmetrical set of curves could be produced if desired.

4. Changes in Shape

We are now ready to deal with our basic problem: the extent of the difference between the shapes of α_λ and $\alpha_\lambda^{(n)}$. Definition of a quantitative index of shape difference is the first requirement, and since we identify the shapes of absolute absorptance curves with the corresponding normalized absorptance curves, it is tempting to define the index simply as:

$$\delta_\lambda^{(n)} = \hat{\alpha}_\lambda^{(n)} - \hat{\alpha}_\lambda. \quad (29)$$

This measure is not an overall index of shape difference between two curves, but rather a definition of shape difference at each wavelength.

In (29) the index is defined specifically for the case of interest here: namely, two different concentrations of a single pigment; but the difference between the normalized curves is meant to be a measure of shape difference applying generally to any two absorptance curves. Brief consideration reveals that this index behaves with intuitive reasonableness at the extremes. If two normalized curves are equal at a given wavelength, then the curves have the same shape there; that is, there is a 0 percent shape discrepancy. The most extreme possible shape difference at any particular wavelength exists when one absorptance curve has its maximum at that point and the other is zero. In terms of the normalized curves, this is a difference between 1 and 0, or a shape change of 1 (100%). It should be emphasized that if we are comparing two absorptance curves at a wavelength where one curve is 2 percent of its peak value and the other is 1 percent of its peak value, the shape difference according to the index we have defined is 1 percent and not 50 percent; it is the difference and not the ratio that counts. Clearly, the amount of shape difference in this case is intuitively more comparable in significance to the shape difference where one curve is 80 percent of its peak and the other 79 percent of its peak, than it is to the shape difference where one curve is 80 percent of its peak and the other 40 percent. The point of view here is of course directed toward the relevance of absorptance-curve shape changes to detectable changes in color-matching behavior, and the difference in the relative rates of light absorption by a receptor system with two different absorptance functions depends on the arithmetic difference in the normalized absorptance curves at each wavelength.

By substituting into (29) the expressions for $\hat{\alpha}_\lambda$ and $\hat{\alpha}_\lambda^{(n)}$ given by (10) and (11), we obtain the formula:

$$\delta_\lambda^{(n)} = \frac{1 - (1 - \alpha_\lambda)^{1/n}}{1 - (1 - \alpha_M)^{1/n}} - \frac{\alpha_\lambda}{\alpha_M}. \quad (30)$$

Various measures of overall shape difference between the curves α_λ and $\alpha_\lambda^{(n)}$ can be defined in terms of the index for shape difference at individual wavelengths specified in (29) or (30). If K and L are the lower and upper limits, respectively, of the wavelength range of interest, we might for different purposes be interested in any one of a number of measures such as the following:

$$\frac{1}{L-K} \int_K^L [\delta_\lambda^{(n)}]^2 d\lambda; \quad \frac{1}{L-K} \int_K^L |\delta_\lambda^{(n)}| d\lambda; \quad \max_\lambda |\delta_\lambda^{(n)}|. \quad (31)$$

Since our interest here is primarily in determining upper limits of change, let us choose the simple measure listed last in (31). Let

$$S^{(n)} = \max_\lambda |\delta_\lambda^{(n)}| = \max_\lambda |\hat{\alpha}_\lambda^{(n)} - \alpha_\lambda| \quad (\lambda = K \text{ to } L). \quad (32)$$

In the remainder of the paper, any indication of a maximum over λ refers to the wavelength range $\lambda = K$ to L .

5. Location of the Maximum Discrepancy

Since $\delta_\lambda^{(n)} \geq 0$ for $n \leq 1$ and $\delta_\lambda^{(n)} \leq 0$ for $n \geq 1$, we can write the first equality in (32) as:

$$S^{(n)} = \max_\lambda [\pm \delta_\lambda^{(n)}], \quad (33)$$

the plus sign applying when $n \leq 1$ and the minus sign when $n \geq 1$. Since, in general, for any function f ,

$$\max_\lambda [-f(\lambda)] = -\min_\lambda f(\lambda), \quad (34)$$

an equivalent of (33) is:

$$S^{(n)} = \max_\lambda \delta_\lambda^{(n)}, \quad n \leq 1; \quad (35a)$$

$$S^{(n)} = -\min_\lambda \delta_\lambda^{(n)}, \quad n \geq 1. \quad (35b)$$

For any n , then, the maximum absolute discrepancy, $S^{(n)}$, between the normalized curves, occurs at a critical point of the function $\delta_\lambda^{(n)}$, and hence in all cases we can find the value of α_λ yielding the greatest discrepancy by setting the derivative of $\delta_\lambda^{(n)}$ with respect to α_λ equal to zero.

We have from (18) that

$$\frac{\partial \delta_\lambda^{(n)}}{\partial \alpha_\lambda} = \frac{(1 - \alpha_\lambda)^{\frac{1}{n} - 1}}{n [1 - (1 - \alpha_M)^{1/n}]} - \frac{1}{\alpha_M}. \quad (36)$$

Setting the derivative equal to zero to obtain the critical point and solving for α_λ , we conclude that

$$\alpha_\lambda = 1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \quad (37)$$

for maximum discrepancy between $\hat{\alpha}_\lambda^{(n)}$ and $\hat{\alpha}_\lambda$.

To convert the absolute absorbance in (37) to a normalized absorbance, we need only divide through by α_M , the result being:

$$A^{(n)}(\alpha_M) = \hat{\alpha}_\lambda \text{ for } \max_{\lambda} |\delta_\lambda^{(n)}| = \frac{1}{\alpha_M} \left\langle 1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle. \quad (38)$$

Equation (38) tells us that at the wavelength(s) where the original absolute absorbance curve, α_λ , has dropped to that fraction, $A^{(n)}(\alpha_M)$, of its maximum value, α_M , specified by the right side of (38), the greatest discrepancy in shape between α_λ and $\alpha_\lambda^{(n)}$ exists; that is, the magnitude of the difference between the curves $\hat{\alpha}_\lambda$ and $\hat{\alpha}_\lambda^{(n)}$ is greatest. This result applies to any absorbance curve whatever, the normalized form of which contains the critical $\hat{\alpha}_\lambda$ value, $A^{(n)}(\alpha_M)$, defined by (38). For the treatment of exceptions— $\hat{\alpha}_\lambda$ curves that fail to contain the value $A^{(n)}(\alpha_M)$ over the wavelength range of interest—see appendix B. The actual wavelength where the maximum $|\delta_\lambda^{(n)}|$ occurs depends, of course, on the shape of the particular absorbance curve being considered.

The expression (38) is not defined for four special cases: $\alpha_M = 0$, $n = 0$, $n = 1$, and $n = \infty$. These cases, and their various combinations, have all been worked out by defining the value of (38) as the value of the limit of (38) as the special values are approached. In evaluating the limits for the three special n values, it emerges that $\alpha_M = 1$ is also a special case in combination with these n values only. To avoid circumlocution, further reference to the “special” or “limiting” values will include this fifth case of $\alpha_M = 1$.

The evaluation of the various limits is discussed in appendix C. Table 1 gives a complete summary of the formulas for all cases. A graphical representation of all the results is given in figure 3, which plots $A^{(n)}(\alpha_M)$, the $\hat{\alpha}_\lambda$ for maximum $|\delta_\lambda^{(n)}|$, as a function of the peak absolute absorbance, α_M , of the original curve, with percent bleach, P , as the parameter.

A number of significant features can be observed in the family of curves of figure 3. To begin with, a bleach of -100 percent—that is, a doubling of concentration—plays a unique role (although the case $n = \frac{1}{2}$ is not “special” in the sense of requiring the use of limit methods). The graph shows that if the concentration of any pigment is doubled, the maximum shape change occurs where the original absorbance curve has exactly half its maximum value, regardless of what that maximum absolute absorbance may be. For no other concentration change is the location of the point of maximum shape change independent of the peak absolute absorbance of the original curve.

TABLE 1. Formulas for calculating $A^{(n)}(\alpha_M)$, the normalized absorbance ($\hat{\alpha}_\lambda$) for which the greatest amount of shape change, $|\delta_\lambda^{(n)}|$, occurs when the pigment concentration is reduced by a factor of n

The maximum absolute absorbance for the original pigment concentration is α_M .

	Increases of concentration			lim $n \rightarrow 1$	Decreases of concentration	
	lim $n \rightarrow 0$	$0 < n < 1$ ^a	$n = \frac{1}{2}$ ^b		$1 < n < \infty$ ^a	lim $n \rightarrow \infty$
lim $\alpha_M \rightarrow 0$	0.5	0.5	0.5	0.5	0.5	0.5
$0 < \alpha_M < 1$	0	$\frac{1}{\alpha_M} \left\langle 1 - \left\{ \frac{n[1 - (1 - \alpha_M)^{1/n}]}{\alpha_M} \right\}^{\frac{n}{1-n}} \right\rangle$	0.5	$\frac{1}{\alpha_M} \left[1 - \frac{1/e}{(1 - \alpha_M)^{1/\alpha_M}} \right]$ $1/e \approx 0.367879441$	$\frac{1}{\alpha_M} \left\langle 1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle$	$\frac{1}{\alpha_M} - \frac{1}{\ln(1 - \alpha_M)}$
lim $\alpha_M \rightarrow 1$	0	$1 - \frac{n}{n^{1-n}}$ ^c	0.5	$1 - \frac{1}{e}$ ≈ 0.632120559	$1 - \frac{1}{n^{n-1}}$ ^c	1

^a These are the ordinary ranges of values of n , and the same formulas apply in both cases. In each case, the formulas have been expressed in a form that makes the exponents positive, but either of the equivalent forms is valid over both ranges.

^b The case $n = \frac{1}{2}$ is tabulated here because of its uniqueness, but it is not a limiting case.

^c No limits are involved in these cases; simply set $\alpha_M = 1$ in the regular formula ($0 < \alpha_M < 1$).

For concentration increases of less than 100 percent and for all concentration decreases—even infinite decrease—we see that $A^{(n)}(\alpha_M)$ is not much greater than 0.5, as long as the peak absolute absorbance, α_M , is not too great. When α_M is very close to 1 and the bleach is very severe, the critical $\hat{\alpha}_\lambda$ value approaches 1; that is, the greatest discrepancy occurs where the curve is close to its peak height. This result corresponds to either of two previously discussed situations: the absorbance curve of a pigment that absorbs *completely* at some wavelength approaches a spikelike form as bleaching is carried toward completion (see fig. 1b); or, if the limiting curve is not close to a spike, for an original curve with a peak absolute absorbance just less than 1, the original curve must be flat around the peak—that is, very close to its peak height over a considerable wavelength range (compare the “ $\times 10$ ” and “ $/\infty$ ” curves in fig. 1a).

For concentration increases of more than 100 percent, the critical $\hat{\alpha}_\lambda$ value, $A^{(n)}(\alpha_M)$, is seen from figure 3 to be always less than 0.5. For very great increases of concentration, $A^{(n)}(\alpha_M)$ approaches 0 for any except very low α_M values; that is, the greatest discrepancy occurs near the end of the absorption range. This result corresponds to the previously discussed fact that the absorbance curve of any pigment approaches a rectangular form as the concentration is increased enormously. Figure 1a provides a clear picture of why the greatest discrepancy occurs near where the curve drops to zero when the concentration increase is carried very far.

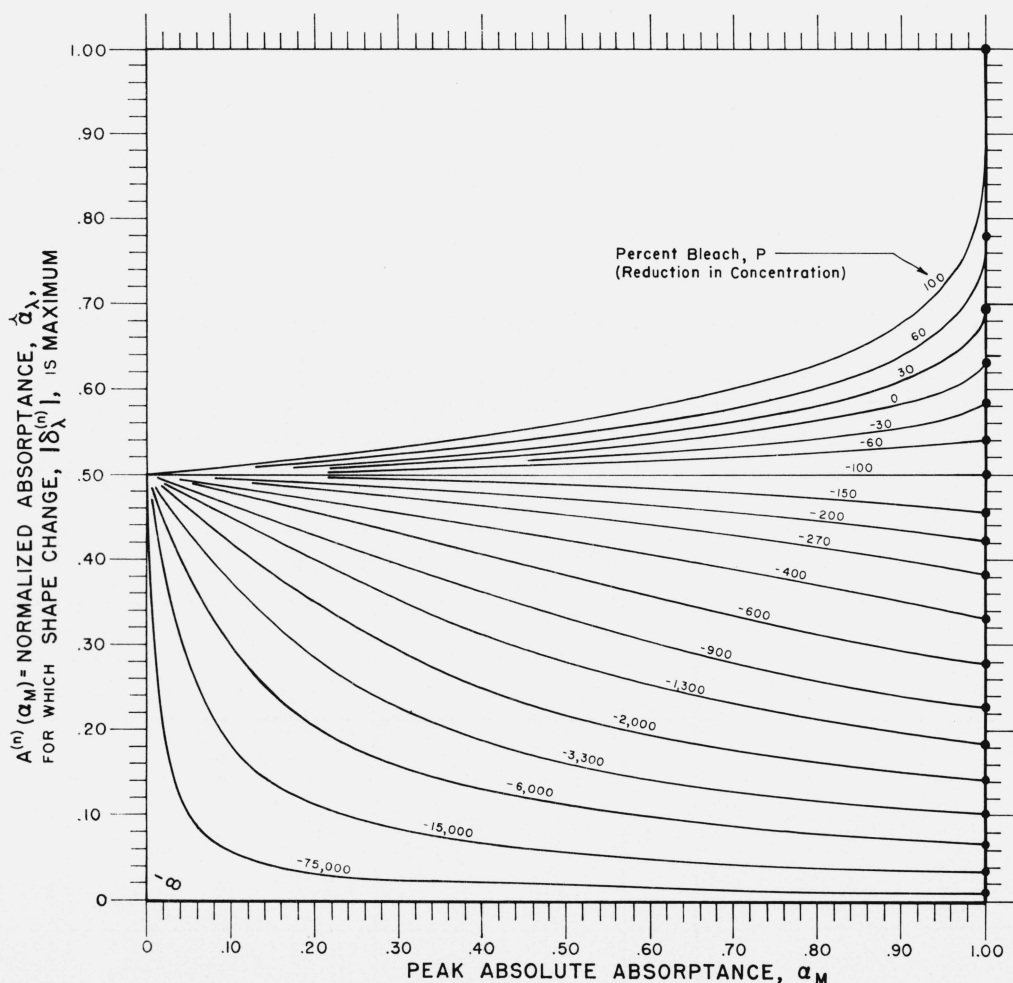


FIGURE 3. Location of the point at which the shape of the spectral absorbance curve of a pigment solution layer changes most as concentration (or thickness) varies. These results apply to any pigment solution obeying Beer's law, or to any material obeying Bouguer's law.

"Shape" change is defined as the difference between the normalized absorbance curves. The critical point is specified (ordinate) in terms of the normalized absorbance, $\hat{\alpha}_\lambda$ of the original pigment layer. The critical $\hat{\alpha}_\lambda$ is shown as a function of (abscissa) the peak absolute absorbance, α_M , of the original pigment layer. The circles along the right edge of the graph indicate the termination points of the curves.

One aspect of figure 3 is particularly non-intuitive: the curve for no bleaching at all ($P=0$; $n=1$) indicates that the location of the maximum discrepancy varies with the peak absolute absorbance, α_M , of the original pigment. Obviously, when there is no bleaching there is no discrepancy, so the maximum discrepancy, zero, occurs *everywhere* along the curve. In particular, it does occur at the $\hat{\alpha}_\lambda$ values indicated in the $P=0$ curve, so that the curve is not incorrect, only incompletely informative. (The true complete function for $P=0$ covers the entire area of the graph.) The reason for choosing the particular curve presented in figure 3 to represent $P=0$ is to preserve continuity: the curves for very slight bleaching and very slight concentration increase approach the $P=0$ curve as the amount of concentration change becomes smaller and smaller. The procedure of defining the function in (38) to be equal to the limit at those values of n and α_M for which the expression is not defined is the source of this continuity.

6. The Size of the Maximum Discrepancy

Since we now know where the maximum discrepancy, $S^{(n)}$, occurs, we need only substitute the expression for the critical α_λ given in (37) into eq (30) to obtain the amount of this largest shape difference. The result, which unfortunately does not seem to be expressible in an appreciably simpler form, is:

$$S^{(n)} = \max_{\lambda} |\delta_{\lambda}^{(n)}| = \left| \left\langle \frac{1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}} \right\rangle - \left(\frac{1}{\alpha_M} \right) \left\langle 1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle \right| \quad (39)$$

The expression in (39), like that in (38), is not defined for the special cases $\alpha_M=0$, $n=0$, $n=1$, $n=\infty$, and, in combination with the latter three cases, $\alpha_M=1$. Here, too, the function approaches a limit in each special case, and can conveniently be defined as equal to the limiting value in each of these cases. The evaluation of these limits is discussed in appendix C. Table 2 provides a complete summary of the formulas for all cases, but the functions tabulated are not the

TABLE 2. Formulas for calculating $D^{(n)}(\alpha_M)$, the shape change $[\delta_{\lambda}^{(n)}]$ of maximum size,^a produced when the pigment concentration is reduced by a factor of n

The maximum absolute absorbance for the original pigment concentration is α_M .

	Increases of concentration			Decreases of concentration		
	$\lim_{n \rightarrow 0}$	$0 < n < 1$ ^b	$n = \frac{1}{2}$ ^c	$\lim_{n \rightarrow 1}$	$1 < n < \infty$ ^b	$\lim_{n \rightarrow \infty}$
$\lim_{\alpha_M \rightarrow 0}$	0	0	0	0	0	0
$0 < \alpha_M < 1$	1	$\left\langle \frac{1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{1-n}}}{1 - (1 - \alpha_M)^{1/n}} \right\rangle$ $-\left(\frac{1}{\alpha_M} \right) \left\langle 1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{1-n}} \right\rangle$	$\frac{\alpha_M}{4(2 - \alpha_M)}$	0	$\left\langle \frac{1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}} \right\rangle$ $-\left(\frac{1}{\alpha_M} \right) \left\langle 1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle$	$\frac{1 - \ln \alpha_M + \ln [-\ln (1 - \alpha_M)]}{-\ln (1 - \alpha_M)} - \frac{1}{\alpha_M}$
$\lim_{\alpha_M \rightarrow 1}$	1	$(1 - n)n^{\frac{n}{1-n}}$ ^d	0.25	0	$-\frac{(n-1)}{n^{n-1}}$ ^d	-1

^a Note that this table does not list $S^{(n)} = \max_{\lambda} |\delta_{\lambda}^{(n)}|$, but gives $D^{(n)}(\alpha_M)$, the corresponding $\delta_{\lambda}^{(n)}$ with the correct algebraic sign. The sign is negative for concentration decreases and positive for increases. (To obtain the absolute value, change the sign of all the formulas for concentration decreases.)

^b These are the ordinary ranges of values of n , and because the algebraic sign has been retained, the same formulas apply in both cases. In each case, the formulas have been expressed in a form that makes the exponents positive, but either of the equivalent forms is valid over both ranges.

^c The case $n = \frac{1}{2}$ is tabulated here because of its uniqueness, but it is not a limiting case.

^d No limits are involved in these cases; simply set $\alpha_M = 1$ in the regular formula ($0 < \alpha_M < 1$).

absolute values specified in (39); instead the algebraic sign is retained, so that the formulas for decreases of concentration produce immediately recognizable negative numbers. On those occasions that the absolute value is desired, it is only necessary to change the sign in all of the formulas for concentration decreases; the quantities generated by the concentration-increase formulas are already positive.

It will be convenient to have a separate symbol, $D^{(n)}(\alpha_M)$, to denote the signed $\delta_\lambda^{(n)}$ value of maximum absolute size, as listed in table 2. Thus,

$$S^{(n)} = |D^{(n)}(\alpha_M)|. \quad (40)$$

A warning is necessary concerning the numerical evaluation of the function in (39), or its limiting forms given in table 2. The two quantities between which the difference is taken in (39) are in many cases equal for the first several significant figures, so that the value of $S^{(n)}$ is determined by differences existing out as far (in the very worst instances) as the ninth or tenth significant figure. An attempt to evaluate $S^{(n)}$ by the use of tables of logarithms (to assess the exponential expressions) is almost certainly doomed to failure, unless a table with extraordinarily many places of both the argument and the function is available. If a particular n is chosen, and an attempt to evaluate $S^{(n)}$ for a number of values of α_M is made, the values obtained by the use of tables may form a reasonable, smooth curve, but the curve may deviate quite badly from the true curve, especially at the ends.

The only practical method of generating values directly from (39) is through the use of a digital computer. It was found that for extreme values of α_M (near 0 or 1), and extreme values of n (near 0, ∞ , or the "special" value 1) even the 8-place arithmetic of an ordinary digital computer may generate significantly erroneous values of $S^{(n)}$, so that recourse to double-precision (16-place) computer arithmetic was required in some cases. To insure accuracy, therefore, the curves of figures 4 and 5, which graphically summarize the relationships embodied in eq. (39), were all obtained by means of such 16-significant-figure calculation. Analogous considerations, it must be pointed out, are applicable to the functions in (38), table 1, and figure 3.

Figure 4 is a plot of $S^{(n)}$, the maximum amount of shape change at any wavelength, against α_M , the peak absolute absorbance of the original α_λ curve, for bleaching ($n > 1$); figure 5 is the corresponding plot for concentration increases ($n < 1$). The numerical parameter identifying the curves on each graph is not n , but the percentage bleach, P , defined by (21). Because a wide range of P values is of interest for different purposes, as well as a wide range of α_M values, it seemed most useful to plot figures 4 and 5 on log-log coordinates, so that several orders of magnitude of each variable can be represented.

Nothing shown in figure 4 seems intuitively unreasonable. The maximum shape change increases with the degree of bleaching, and approaches a limiting value for total bleaching ($P = 100\%$; $n = \infty$). For any particular degree of bleaching, the maximum shape change is an increasing function of α_M , the initial peak absolute absorbance. Because the origin is at infinity in a log-log plot it is not clear in figure 4, but is nevertheless a fact, that all the curves pass through the point ($\alpha_M = 0$, $S^{(n)} = 0$). Thus, as is obvious, pigment that does not absorb at all undergoes no shape change whatever, no matter how much "bleaching" occurs. (This is again a matter of behavior in the limit, if we consider lower and lower densities of any pigment at all.) Finally, the greatest possible shape change $-S^{(n)} = 1$ —occurs only for the single case of infinite bleaching of a pigment that absorbs completely at some wavelength ($\alpha_M = 1$), this case being again a matter of behavior in the limit. [The perfect absorber ($\alpha_\lambda \equiv 1$), as well as the other exceptional cases discussed in appendix B, of course are not covered by table 2 or figs. 4 or 5.]

For concentration increases, shown in figure 5, a few additional considerations arise. As expected, the maximum shape change increases with the extent of the concentration increase, and approaches a limiting value for infinite increase in concentration ($P = -\infty$; $n = 0$). The limiting value for $P = -\infty$ is the greatest possible value, $S^{(n)} = 1$, and is constant for any $\alpha_M > 0$. For

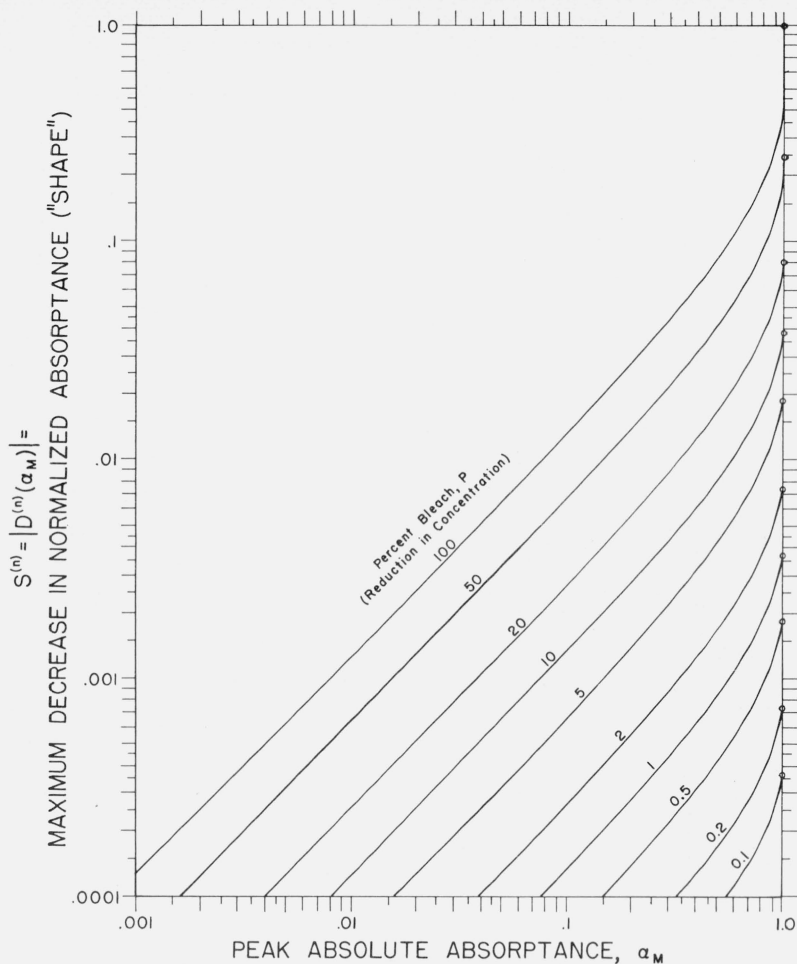


FIGURE 4. The amount of the greatest change, as concentration (or thickness) is reduced, in the shape of the spectral absorbance curve of any pigment solution layer obeying Beer's law, or of any material obeying Bouguer's law.

The maximum shape change is given (ordinate) in terms of the difference between the normalized absorbance curves for the original and reduced concentrations. The abscissa variable is the peak absolute absorbance, α_M , of the original pigment layer. The circles along the right edge of the graph indicate the points at which the curves terminate. All the curves reach the point (0,0), which is not shown because both scales are logarithmic.

anything less than infinite concentration increase, $S^{(n)}$ is an increasing function of α_M . All the curves in figure 5, as in figure 4, pass through the origin. The limiting curve for $P = -\infty$ is thus of a rectangular form, in linear coordinates, with the discontinuity at $\alpha_M = 0$, just as the " ∞ " curves in figures 1a and 1b are analogously discontinuous.

It can be observed in table 2 that the curve for $n = 1/2$ ($P = -100\%$) in figure 5 is of unique form. In linear coordinates, this one curve is a portion of a rectangular hyperbola, but because the origin is not the center of this hyperbola, the use of log-log coordinates in figure 5 does not rectify the curve. If instead of plotting $S^{(n)}$ against α_M , as in figure 5, we had plotted $S^{(n)} + 1/4$ against $2 - \alpha_M$, in log-log coordinates, the curve for $n = 1/2$ would have been a straight line (and the only straight line).

*The final aspect of figures 4 and 5 to which attention will be drawn here is the marked similarity between figure 4 and the diagonally lower half of figure 5 (the curves for $P \geq -100$). It will be found that the curve for P in figure 4 is virtually the same curve as that for $-P$ in figure 5, not merely in shape but in actual value. For small absolute values of P , the corresponding curves in the two figures appear to be quite identical, and even for large percentage changes in concentration (P), the lower parts of the curves ($\alpha_M \ll 1$) are indistinguishable. However, observation of the upper limits of the curves, for $\alpha_M = 1$, reveals some discrepancy for the highest few curves,

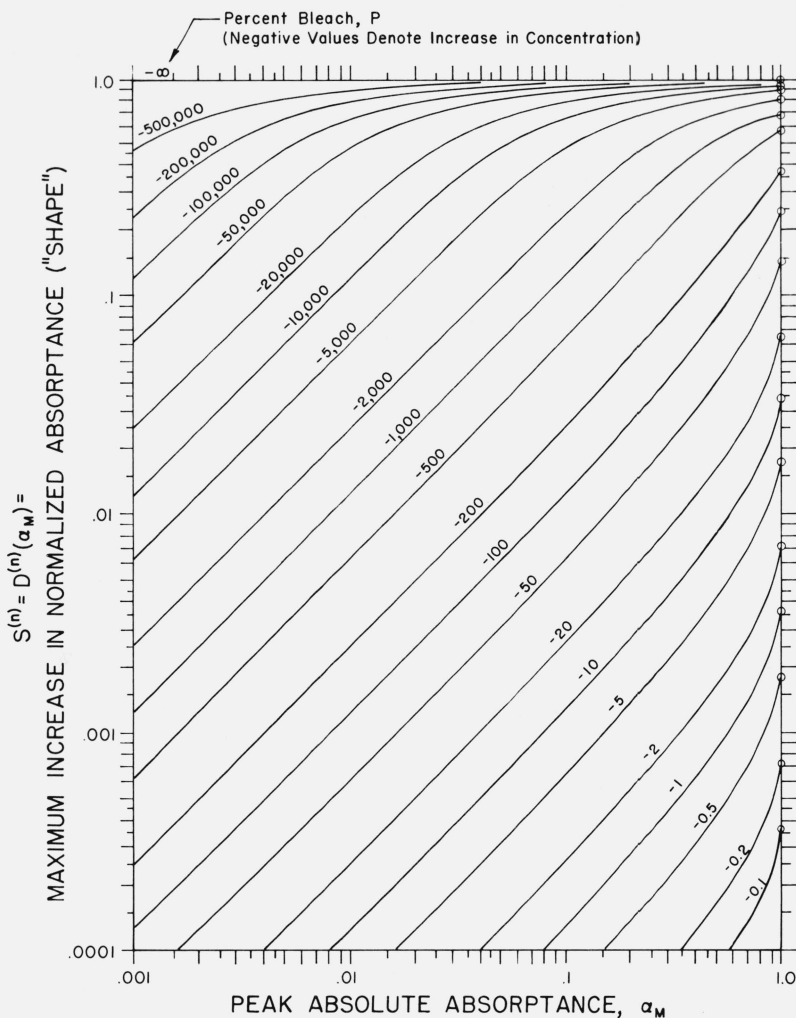


FIGURE 5. Same type of plot as figure 4, but for increases in concentration.

The terminations of the five curves for $-500,000 \leq P \leq -20,000$ are omitted for clarity; all of these terminal $S^{(n)}$ values are slightly less than 1, and only for $P = -\infty$ does $S^{(n)} = 1$.

and, in fact, the correspondence between P and $-P$ is really only approximate, the approximation being better for values of P or α_M near 0.

It was this close correspondence between the maximum shape changes for a given percentage bleach and for the same percentage increase in concentration (negative bleach) that dictated the choice of P as the most informative parameter for these curve families. It is interesting to observe in figure 3 that an approximate correspondence between P and $-P$ exists for the *locations* of the maximum shape changes as well. In figure 3, however, the correspondence does not involve an identity or a mirror symmetry of curve shape, but rather equal distances above and below the upward bending curve for $P = 0$.

7. Implications for Vision

The information summarized in figure 4 constitutes a set of restrictions to which any theory of color vision based on the idea of photopigments in solution must conform. The constancy of metameric matches under nonextreme levels of adaptation implies that within the applicable luminance range, the shape changes produced in the pigment absorbance curves by bleaching are so small as to be not behaviorally detectable. It is difficult to say how large a maximum shape change [$S^{(n)}$] in these absorbance curves would have been noticed in the various experiments

that have been conducted, but a maximum shape change of 1 percent seems likely to be safely below the threshold of detectability. In other words, the new color-matching functions determined by such a change in the pigments would not differ from the initial functions by amounts greater than the experimental uncertainties customary in color-matching data.

Figure 4 reveals that even if bleaching were virtually total ($P=100\%$), the maximum shape change from the absorptance curves of the unbleached pigments can be kept below 1 percent provided the peak absorptances of the dark-adapted pigments are no greater than $7\frac{1}{2}$ percent. As it happens, this is just about the order of magnitude of the peak absorptances found by the recent microspectrophotometric measurements of the absorptances of single cones [13, 14, 15]. Thus a *sufficient* explanation for metamer constancy is an upper limit of, say, 10 percent on the maximum absorptances of the photopigments, regardless of how much bleaching of the pigments occurs during adaptation.

On the other hand, the low-absorptance explanation is by no means *necessary*. If chromatic adaptation actually involves only limited degrees of pigment bleaching, over the constant-metamer range of luminance, then much higher initial peak absorptances are allowable. Rushton's work [16] with fundus reflectometry indicates that a considerable degree of light adaptation can occur in the cones with little bleaching of pigment. If no more than a 5 percent bleach occurs, for example, figure 4 indicates that shape changes can be limited to a maximum of 1 percent even when the peak absorptances are as high as 84 percent. It should be pointed out in this connection that there is a minority of workers in color who still support (or at least, until recently supported) the notion of high-absorptance pigments. Brindley [6] hypothesized an absorptance peak of nearly 70 percent and Walraven [17] estimates the peak absorptances at 80 percent. These researchers, and others [18], are evidently somewhat dubious about the low absorptance peaks claimed in the microspectrophotometric work. They presumably suspect some sort of artifact or misinterpretation leading to spuriously low estimates of the absolute absorptance levels of the curves, but no specific statement of their suspicions seems to have appeared in print. In any event, it is clear that high absorptance peaks are not inconsistent with metamer constancy if not much bleaching occurs during light adaptation within the applicable range of luminance.

An important fact of color vision, that has been stressed particularly by Walraven [19] in recent years, is the breakdown of metameric matches that does occur with very high retinal illuminances (above 10^4 trolands) [5, 6, 20]. It is not yet known what the cause of this breakdown is, but if it is shape changes in the pigment absorptance curves brought about by relatively extreme degrees of bleaching, figure 4 provides some quantitative restrictions. Walraven's [21] analysis of Brindley's [6] data on changes in the Rayleigh match with very high levels of adaptation led him to the conclusion that the spectral character of the changes in color-matching behavior are indeed what would be expected on the basis of bleaching of the photopigments: namely, a narrowing of the absorptance curves (particularly the red curve).

Just as we had to choose 1 percent more or less arbitrarily as an amount of maximum shape change that would almost surely be behaviorally nondetectable, we are also faced with choosing a figure to represent a degree of maximum shape change that would in all likelihood produce evident behavioral consequences; 10 percent seems a reasonable round number that is probably not much, if at all, above the minimum detectable level. The question now is: what is the *lowest* peak absorptance that will allow for shape changes at least as great as 10 percent?

Figure 4 tells us that if the pigments are nearly completely bleached ($P \approx 100\%$) when the metamer breakdowns occur, the peak absorptances of the photopigments must be at least 55 percent to allow for maximum shape changes of 10 percent or more. Rushton [22] regularly refers to "complete bleaching" after adaptation to very bright lights, so this estimate must be taken seriously. If, on the other hand, 5 percent bleaching were the most extreme attainable for even dazzling luminances (a seemingly unrealistic assumption), then we would have to abandon the hypothesis that the high-luminance breakdown of metameric matches is due simply to pigment bleaching, since the most extreme shape change possible for 5 percent bleaching is only 1.9 percent, no matter how high the initial peak absorptance (α_M) is. In fact, it is impossible to reach

a 10-percent shape change unless the bleach is greater than about 30 percent, and then only in the extreme case of $\alpha_M=1$. Figure 4 indicates that if there are levels of adapting luminance high enough to produce a maximum photopigment shape change of 10 percent—that is, a clearcut disturbance of metameric matches—but which entail no more than a 50-percent bleaching of the pigments, then the pigments must have $\alpha_M \geq 0.82$.

The conclusion that must be drawn is that if the breakdown of metameric matches at high luminances is due to bleaching changes alone, and if a maximum shape change of at least 10 percent is necessary to make the breakdown experimentally evident, then the visual photopigments *must* have peak dark-adapted absorptances greater than 55 percent, and might possibly have peaks over 80 percent. If, therefore, any researcher's overall view of all the relevant evidence leads him to reject the hypothesis of high-absorptance pigments, it appears to be necessary also to reject the notion that the high-luminance breakdown of metameric matches can be attributed solely to changes in shape of the photopigment absorptance curves due to bleaching. An alternative explanation then becomes necessary and the most obvious candidate is the accumulation of significant quantities of one or more spectrally selective breakdown products.

One might imagine these products diffusing relatively uniformly over the retina and playing a role similar to that of the macular pigment; that is, acting as a filter in front of all the receptors. Brindley [6] interprets his data on high-luminance metamer breakdown as refuting this "screening pigment" model. Another possibility is that the breakdown products do not leave the receptors at all, but accumulate and regenerate in the individual cones in which they are formed. In that case, each of the three cone types can be thought of as covered by a filter the density of which is a direct function of the rate of absorption of the incident light by that class of cone. A still more complicated variant of this hypothesis allows for differences in the kinds of breakdown products formed from each of the cone pigments, so that the filters over the three types of cones vary not only in density but also in the gross spectral form of their absorptances.

Finally, there is even the possibility that it is not the products of the photopigment degenerations that accumulate, but that the extremely intense illumination of the eye causes spectrally selective changes in one of the normally photostable, nonvisual ocular pigments such as the macular or lens pigment. Brindley's [6] rejection of any "screening pigment" hypothesis of course applies to this explanation as well as to the hypothesis of photoproduct diffusion. Goldstein and Williams [6a], on the basis of extensive direct computations of the effect, also consider a significant role in human vision by screening pigments unlikely, provided the peak absorptances of the dark-adapted photopigments are sufficiently low. If in fact the breakdown of metameric matches at high luminances cannot be ascribed to any screening-pigment accumulation, the believers in low-absorptance photopigments face the challenge of providing a less obvious but more plausible hypothesis.

Those workers who believe in high-absorptance photopigments need not concern themselves with any of these alternative explanations for high-luminance breakdown of metamers; their belief is consistent with the simple bleaching model. One problem they do face is to show quantitative experimental evidence that the degree of pigment bleaching produced in the upper reaches of the constant-metamer range of luminance is low enough to produce shape changes of a size consistent with the nondetectability of the changes in the color-matching functions.

If we take 10^4 trolands as approximately the upper end of the constant-metamer range [4], and consult Rushton's measurements [16] of percentage cone pigment bleached as a function of the adapting retinal illuminance, we find that during steady-state adaptation to 10^4 trolands, only about 20 percent of the pigment is bleached away. We see in figure 4 that 20 percent bleaching of a pigment having a peak absolute absorptance of 80 percent yields a maximum shape change of only about 4 percent, a change quite possibly below the threshold of behavioral detectability.

Thus, if Rushton's data and his interpretation of them are substantially accurate, the assumption of photopigment absorptance curves with maxima of 80 percent accounts for both the constancy of metameric matches at moderate luminance levels and the breakdown of these matches at higher luminance levels. The most serious challenge to the high-absorptance theory, then,

would seem to be finding a flaw in the claimed absolute absorptance scales of the single-cone microspectrophotometric measurements that find low absorptance peaks for the pigments. Although parsimony makes the high-absorptance model logically attractive, it must be recognized that there is a definite possibility that in this case nature did not choose the simplest way. However, the very latest word available to the author as this article goes to press is encouraging for the high-absorptance theorists: MacNichol [23] has stated that the current estimate in his laboratory is that the peak absorptance of the cone pigments is of the order of at least 1.8 percent *per single micron of receptor length*. This measure would make the total absorptance of a cone with a pigmented length of 40 μm equal to nearly 52 percent at the peak [calculated from eq (5) with $n = 1/40$], in marked contrast to the 3 to 6 percent peaks mentioned in the work from MacNichol's laboratory published in 1964 [13]. It remains to be seen whether similar re-evaluations emerge from the other two laboratories that have published [14, 15] this type of measurement.

8. Appendix A. Proof of Inequality (12)

Given $p > q$, we wish to show that

$$\hat{\alpha}_\lambda^{(p)} < \hat{\alpha}_\lambda^{(q)}, \quad (41)$$

in the range

$$0 < \alpha_\lambda < \alpha_M (\leq 1). \quad (42)$$

By formula (11), we can write (41) as:

$$\frac{1 - (1 - \alpha_\lambda)^{1/p}}{1 - (1 - \alpha_M)^{1/p}} < \frac{1 - (1 - \alpha_\lambda)^{1/q}}{1 - (1 - \alpha_M)^{1/q}}. \quad (43)$$

In order to simplify the analysis, let us introduce new variables v and b defined by:

$$e^{-v} = 1 - \alpha_\lambda; \quad e^{-b} = 1 - \alpha_M. \quad (44)$$

By virtue of (42), we can see that

$$0 \leq e^{-b} < e^{-v} < 1 \quad (45)$$

or

$$0 < v < b \leq \infty. \quad (46)$$

Substituting (44) into (43), we have:

$$\frac{1 - e^{-v/p}}{1 - e^{-b/p}} < \frac{1 - e^{-v/q}}{1 - e^{-b/q}}. \quad (47)$$

Because $p > q \geq 0$, it follows that

$$1/p < 1/q; \quad (48)$$

and it is therefore sufficient, for the purpose of establishing (47), to prove that the function

$$f(x) \equiv \frac{1 - e^{-vx}}{1 - e^{-bx}} \quad (0 < v < b) \quad (49)$$

is monotonically increasing for positive x .

To establish monotonic increase, we will demonstrate the positivity of $f'(x)$. Since $f(x)$ is obviously positive for positive x , we can choose equivalently to show the positivity of $f'(x) \cdot [x/f(x)]$, a maneuver that simplifies the algebra in the present case. From (49) we derive that

$$\frac{xf'(x)}{f(x)} \equiv \frac{vx}{e^{vx} - 1} - \frac{bx}{e^{bx} - 1} \quad (0 < v < b). \quad (50)$$

To show that the expression in (50) is positive, it is sufficient to demonstrate that the function

$$g(z) \equiv \frac{z}{e^z - 1} \quad (51)$$

is monotonically decreasing for $z > 0$, since the right side of (50) is $g(vx) - g(bx)$, with $0 < vx < bx$.

We proceed by showing that $g'(z)$ is negative for positive z . Since

$$g'(z) \equiv \frac{e^z(1-z) - 1}{(e^z - 1)^2}, \quad (52)$$

we need to prove that

$$e^z(1-z) - 1 < 0 \quad (z > 0); \quad (53)$$

or, defining

$$h(z) \equiv e^z(1-z), \quad (54)$$

we must establish that

$$h(z) < 1 \quad (z > 0). \quad (55)$$

Since

$$h'(z) \equiv -ze^z < 0 \quad (z > 0), \quad (56)$$

we know that $h(z)$ decreases monotonically from its value at $z=0$. Thus the proof of (55) is concluded by simply noting that $h(0)=1$.

9. Appendix B. Treatment of Special Cases: Discontinuous Absorbance Curves and Curves Maintaining High Absorbance to the Ends of the Spectral Range Considered

There are several situations in which the $\hat{\alpha}_\lambda$ curve fails to take on at *any* wavelength the value specified by the expression (38). Only two basic cases need be distinguished: (a) all $\hat{\alpha}_\lambda$ values in the interval $K \leq \lambda \leq L$ are greater than the critical value specified by (38) because the absorbance simply has not dropped off far enough at the ends of the specified wavelength interval; or (b) the $\hat{\alpha}_\lambda$ curve contains absorbance values both greater than and less than the critical value,

but not equal to it because the curve has discontinuities in the form of either absorption lines (zero bandwidth) or vertical edges representing jumps from one continuum level to another.

In case (a), the maximum $|\delta_{\lambda}^{(n)}|$ will occur at the wavelength(s) at which $\hat{\alpha}_{\lambda}$ is minimum—and hence closest to the critical value. This result follows because $|\delta_{\lambda}^{(n)}|$ has but a single maximum (over the $\hat{\alpha}_{\lambda}$ range 0 to 1) and decreases monotonically to zero as $\hat{\alpha}_{\lambda}$ progresses from the critical value toward either 0 or 1. It is irrelevant whether the $\hat{\alpha}_{\lambda}$ curve possesses discontinuities or not.

A unique example of this case deserves separate mention: the perfectly nonselective absorber. If, over the wavelength range K to L , $\alpha_{\lambda} \equiv c$, where $0 < c \leq 1$, then the flat curve has its maximum (and only) value everywhere, so that $\hat{\alpha}_{\lambda} \equiv 1$, $\hat{\alpha}_{\lambda}^{(n)} \equiv 1$ (all n), and $\delta_{\lambda}^{(n)} \equiv 0$ (all n). In short, as is obvious, the shape of the absorbance curve of a nonselective pigment does not change with concentration.

Case (b) is physically nonexistent, since all “lines,” whether absorption, transmission, or emission, have finite width according to quantum theory; and no abrupt transition from one level of absorbance to another can be literally discontinuous. However, because real measurements cannot be made with infinite resolving power, one can be faced with effectively discontinuous curves. Mathematically, this situation can be treated by restricting attention to only two $\hat{\alpha}_{\lambda}$ values: the least upper bound⁶ (l.u.b.) of the values less than the critical value and the greatest lower bound (g.l.b.) of the values greater than the critical value. Since in general the falloff of $|\delta_{\lambda}^{(n)}|$ from its maximum value is not symmetrical with respect to variation of $\hat{\alpha}_{\lambda}$ above and below the critical value, one cannot simply see which of the aforementioned two significant $\hat{\alpha}_{\lambda}$ values is closer to the critical value. It is necessary actually to evaluate $|\delta_{\lambda}^{(n)}|$ for both $\hat{\alpha}_{\lambda}$ values by use of eq (30). If the function values are sufficiently different, it may be possible to make the decision by using figure 2 appropriately.

Although in case (a) the location of the point on the curve for which $|\delta_{\lambda}^{(n)}|$ is maximum is simple, the evaluation of $\delta_{\lambda}^{(n)}$ at that point must also be accomplished by the use of eq (30), or, if a rough estimate is satisfactory, by the use of figure 2.

10. Appendix C. Evaluation of Limits

As was pointed out earlier, the fundamental expressions (38) (plotted in fig. 3) and (39) (plotted in figs 4 and 5) are indeterminate for several special values of the variables n and α_M . We have already made use of L'Hospital's rule [see eq (13)] to evaluate a limit that took the form 0/0. With appropriate rearrangements of terms, the same device is sufficient to evaluate the limits of (38) and (39) as all the special values are approached, with the exception of the limits as α_M approaches 0. In the latter case, it was found necessary to use the technique of replacing part of the function by its power series expansion; this procedure will be illustrated later.

As an example of the method of application of L'Hospital's rule, let us develop the limit of the expression for $A^{(n)}(\alpha_M)$ in (38) as n approaches infinity (complete bleaching). Let

$$B^{(\infty)} = \lim_{n \rightarrow \infty} \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}}. \quad (57)$$

The exponent, $n/(n-1)$, approaches 1 as n approaches infinity. The part of the overall limit in (57) that requires manipulation is the limit of the denominator. Let

$$C^{(\infty)} = \lim_{n \rightarrow \infty} n[1 - (1 - \alpha_M)^{1/n}]. \quad (58)$$

The expression (58) approaches the indeterminate form $\infty \cdot 0$. Whenever L'Hospital's rule is to be used, the core of the problem is to rearrange the expression into a fraction to which the

⁶The use of the l.u.b. and the g.l.b. allows for open intervals of $\hat{\alpha}_{\lambda}$ values, which can arise if there is either a locally nonconstant absorbance continuum with a peak on which an absorbance line is superimposed or a jump discontinuity between locally nonconstant continua. Those not familiar with or interested in this fine point can read “largest” for “least upper bound” and “smallest” for “greatest lower bound.”

rule can be successfully applied. The requirements are that the fraction approach a limit of the form $0/0$ or ∞/∞ and be of such a form that differentiation simplifies, rather than complicates, the limit evaluation. In the case of the limit in (58), a suitable expression is:

$$C^{(\infty)} = \lim_{n \rightarrow \infty} \frac{1 - (1 - \alpha_M)^{1/n}}{1/n}, \quad (59)$$

which is of the form $0/0$.

L'Hospital's rule yields:

$$C^{(\infty)} = \lim_{n \rightarrow \infty} \frac{-(1 - \alpha_M)^{1/n} \ln(1 - \alpha_M) \cdot (-1/n^2)}{-1/n^2} = \lim_{n \rightarrow \infty} -(1 - \alpha_M)^{1/n} \ln(1 - \alpha_M). \quad (60)$$

As long as $\alpha_M \neq 1$ (it being kept in mind, of course, that $0 \leq \alpha_M \leq 1$):

$$\lim_{n \rightarrow \infty} (1 - \alpha_M)^{1/n} = (1 - \alpha_M)^0 = 1; \quad (61)$$

so

$$C^{(\infty)} = -\ln(1 - \alpha_M), \quad \alpha_M \neq 1. \quad (62)$$

By applying (62) to the original limit (57), we conclude:

$$B^{(\infty)} = \frac{\alpha_M}{-\ln(1 - \alpha_M)}, \quad \alpha_M \neq 1. \quad (63)$$

Thus, finally, the limit of (38) as $n \rightarrow \infty$ is seen to be:

$$\begin{aligned} A^{(\infty)}(\alpha_M) &= \hat{\alpha}_\lambda \text{ for } \max_\lambda |\delta_\lambda^{(\infty)}| = \frac{1}{\alpha_M} \left[1 - \frac{\alpha_M}{-\ln(1 - \alpha_M)} \right] \\ &= \frac{1}{\alpha_M} - \frac{1}{-\ln(1 - \alpha_M)}, \quad \alpha_M \neq 0, 1. \end{aligned} \quad (64)$$

The uppermost curve in figure 3 is a plot of the function given in (64).

Since the second term of (39), which corresponds to the critical $\hat{\alpha}_\lambda$, is given by (38), we know that once (38) has been evaluated for any of the special arguments, the problem of evaluating (39) reduces to evaluating the first term, which corresponds to the critical $\hat{\alpha}_\lambda^{(n)}$. In the case under consideration, $n \rightarrow \infty$, we have already found the general expression for $\hat{\alpha}_\lambda^{(\infty)}$ in eq (14). We could, therefore, obtain the critical α_λ by multiplying (64) by α_M and then simply substitute into (14) to obtain the critical $\hat{\alpha}_\lambda^{(\infty)}$ as a function of α_M . However, to prove that the single expression (39) really does give rise to all the special cases, let us evaluate the first term of (39) directly as a limit. Let

$$G^{(\infty)} = \lim_{n \rightarrow \infty} \frac{1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}} \quad (65)$$

$$= \lim_{n \rightarrow \infty} \frac{1 - \left\{ \frac{\alpha_M}{C^{(\infty)}} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}}, \quad (66)$$

where $C^{(\infty)}$, defined by (58), is given explicitly by (62). Thus

$$G^{(\infty)} = \lim_{n \rightarrow \infty} \frac{1 - \left\{ \frac{\alpha_M}{-\ln(1 - \alpha_M)} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}}. \quad (67)$$

As $n \rightarrow \infty$, the exponents in both the numerator and denominator of (67) approach 0, so that, as long as $\alpha_M \neq 0$ or 1, the exponential terms both approach 1. The expression in (67) therefore approaches the form

$$\frac{1-1}{1-1} = \frac{0}{0} \quad (68)$$

and is consequently eligible for direct application of L'Hospital's rule. The result of the differentiation of the numerator and denominator of (67) is:

$$G^{(\infty)} = \lim_{n \rightarrow \infty} \frac{- \left\{ \frac{\alpha_M}{-\ln(1 - \alpha_M)} \right\}^{\frac{1}{n-1}} \ln \left\{ \frac{\alpha_M}{-\ln(1 - \alpha_M)} \right\} \cdot \left[\frac{-1}{(n-1)^2} \right]}{- (1 - \alpha_M)^{1/n} \ln(1 - \alpha_M) \cdot \left(\frac{-1}{n^2} \right)} \quad (69)$$

$$= \frac{\ln \left\{ \frac{\alpha_M}{-\ln(1 - \alpha_M)} \right\}}{\ln(1 - \alpha_M)} = \frac{\ln \alpha_M - \ln[-\ln(1 - \alpha_M)]}{\ln(1 - \alpha_M)},$$

$$\alpha_M \neq 0, 1. \quad (70)$$

The complete evaluation of (39) as $n \rightarrow \infty$ can now be obtained by combining (70) and (64), the result being:

$$S^{(\infty)} = |D^{(\infty)}(\alpha_M)| = \max_{\lambda} |\delta_{\lambda}^{(\infty)}| = \left| \frac{\ln \alpha_M - \ln[-\ln(1 - \alpha_M)]}{\ln(1 - \alpha_M)} - \left[\frac{1}{\alpha_M} - \frac{1}{-\ln(1 - \alpha_M)} \right] \right|$$

$$= \left| \frac{1 - \ln \alpha_M + \ln[-\ln(1 - \alpha_M)]}{-\ln(1 - \alpha_M)} - \frac{1}{\alpha_M} \right|, \quad \alpha_M \neq 0, 1. \quad (71)$$

The function (71) is plotted as the uppermost curve in figure 4, and $D^{(\infty)}(\alpha_M)$ (the function with the absolute value signs omitted) is listed in table 2.

As has been mentioned, all of the limiting-case formulas were derived by methods similar to the L'Hospital's-rule manipulations employed above, except for the case $\alpha_M \rightarrow 0$, for which a different method was found necessary. It is possible that some sequence of imaginative rearrangements of terms could allow this case, too, to be treated solely by L'Hospital's rule, but in the absence of such a derivation, the proof to be given here is based on a series expansion, namely:

$$(1-x)^{1/n} = 1 - \frac{x}{n} - \left(\frac{n-1}{2n^2} \right) x^2 + R_3(x) \quad (x^2 < 1), \quad (72)$$

where the remainder series $R_3(x)$ is of order x^3 (that is, the leading term contains x^3 as a factor and all succeeding terms contain higher powers of x).

We apply the series (72) by letting $x = \alpha_M$, and replacing $(1 - \alpha_M)^{1/n}$ in (38) by the resulting expression. With suitable regrouping of terms, the new form of (38) is then:

$$A^{(n)}(\alpha_M) = \frac{1}{\alpha_M} \left\langle 1 - \left[\frac{1}{1 + \left(\frac{n-1}{2n}\right)\alpha_M - R_2(\alpha_M)} \right]^{\frac{n}{n-1}} \right\rangle, \quad (73)$$

where $R_2(\alpha_M)$ is a series of order α_M^2 .

Straightforward rearrangement allows (73) to be written in the form:

$$A^{(n)}(\alpha_M) = \frac{\left[1 + \left(\frac{n-1}{2n}\right)\alpha_M - R_2(\alpha_M) \right]^{\frac{n}{n-1}} - 1}{\alpha_M} \cdot \frac{1}{\left[1 + \left(\frac{n-1}{2n}\right)\alpha_M - R_2(\alpha_M) \right]^{\frac{n}{n-1}}}. \quad (74)$$

We now make use of the fact that as α_M approaches 0, each term of $R_i(\alpha_M)$ (for any $i \geq 1$) approaches 0, so that the sum of the entire R_i series also approaches 0. Thus, letting α_M approach 0, we see that the second factor in (74) approaches $1/1 = 1$ (as long as $n \neq 0$ or 1), so that the overall limit is equal to the limit of the first factor. The first factor approaches $(1-1)/0 = 0/0$, so that L'Hospital's rule can be applied. Differentiating numerator and denominator, we obtain:

$$A^{(n)}(0) = \lim_{\alpha_M \rightarrow 0} A^{(n)}(\alpha_M) = \lim_{\alpha_M \rightarrow 0} \frac{\left(\frac{n}{n-1}\right) \left[1 + \left(\frac{n-1}{2n}\right)\alpha_M - R_2(\alpha_M) \right]^{\frac{n}{n-1}-1} \left[\left(\frac{n-1}{2n}\right) - R_1(\alpha_M) \right]}{1}, \quad (75)$$

where $R_1(\alpha_M)$ is a series of order α_M .

Finally, letting α_M approach 0 in the numerator of (75), we find that the final limit is:

$$A^{(n)}(0) = \left(\frac{n}{n-1}\right) [1] \left[\frac{n-1}{2n}\right] = \frac{1}{2} \quad (n \neq 0, 1). \quad (76)$$

The invalidity of (76) for the two values $n=0$ and 1 is a reflection of the fact that the original expression (38) is not defined for those values. Since (76) does hold for all other values of n , however, we can evaluate the limit of (76) as n approaches 0 and 1, and also as n increases without limit ($n \rightarrow \infty$), and define the function values as equal to these limits. Thus

$$A^{(0)}(0) = \lim_{n \rightarrow 0} A^{(n)}(0) = \lim_{n \rightarrow 0} \frac{1}{2} = \frac{1}{2} \quad (77)$$

$$A^{(1)}(0) = \lim_{n \rightarrow 1} A^{(n)}(0) = \lim_{n \rightarrow 1} \frac{1}{2} = \frac{1}{2} \quad (78)$$

$$A^{(\infty)}(0) = \lim_{n \rightarrow \infty} A^{(n)}(0) = \lim_{n \rightarrow \infty} \frac{1}{2} = \frac{1}{2}. \quad (79)$$

In other words, the value of $A^{(n)}(\alpha_M)$ as $\alpha_M \rightarrow 0$ may be taken as $1/2$ for *any* value of n .

In order to find $D^{(n)}(0)$, the limit as α_M approaches 0 of the function in (39) with the absolute value signs omitted, we have to evaluate the limit of the first term only, since the second term is the same as (38), which we have just shown approaches $1/2$. Let

$$L_0 = \lim_{\alpha_M \rightarrow 0} \frac{1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}}. \quad (80)$$

Again we use the device of series expansion, converting (80) to the form

$$G_0 = \lim_{\alpha_M \rightarrow 0} \frac{1 - \left\{ \frac{\alpha_M}{n \left[1 - \left[1 - \frac{\alpha_M}{n} + \left(\frac{n-1}{2n^2} \right) \alpha_M^2 + R_3(\alpha_M) \right] \right]} \right\}^{\frac{1}{n-1}}}{1 - \left[1 - \frac{\alpha_M}{n} + \left(\frac{n-1}{2n^2} \right) \alpha_M^2 + R_3(\alpha_M) \right]} \quad (81)$$

After terms are combined in (81), it is clear that the expression approaches the limit $(1-1)/0 = 0/0$ ($n \neq 0, 1$), so that L'Hospital's rule can be applied. The result of differentiating the numerator and denominator and then allowing α_M to approach 0 is:

$$G_0 = \frac{\frac{1}{2n}}{\frac{1}{n}} \equiv \frac{1}{2} \quad (n \neq 0, 1). \quad (82)$$

Thus as α_M approaches 0, both the first and second terms of $D^{(n)}(\alpha_M)$ in (39) approach $1/2$, and hence the difference approaches 0, for any n other than 0 or 1. In short,

$$D^{(n)}(0) \equiv 0 \quad (n \neq 0, 1). \quad (83)$$

Continuity considerations analogous to those leading to eqs (77) to (79) allow us to make the definitions

$$D^{(0)}(0) = \lim_{n \rightarrow 0} D^{(n)}(0) = \lim_{n \rightarrow 0} 0 = 0 \quad (84)$$

$$D^{(1)}(0) = \lim_{n \rightarrow 1} D^{(n)}(0) = \lim_{n \rightarrow 1} 0 = 0 \quad (85)$$

$$D^{(\infty)}(0) = \lim_{n \rightarrow \infty} D^{(n)}(0) = \lim_{n \rightarrow \infty} 0 = 0. \quad (86)$$

In other words, the value of $D^{(n)}(\alpha_M)$ as $\alpha_M \rightarrow 0$ may be taken as 0 for *any* value of n .

No further resort to series expansion will be necessary. Let us turn now to the case $n = 1$ and evaluate (38) as n approaches 1. Let

$$A^{(1)}(\alpha_M) = \lim_{n \rightarrow 1} \frac{1}{\alpha_M} \left\langle 1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle \quad (87)$$

$$= \frac{1}{\alpha_M} \langle 1 - B^{(1)} \rangle \quad (\alpha_M \neq 0), \quad (88)$$

where

$$B^{(1)} = \lim_{n \rightarrow 1} \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}}. \quad (89)$$

In order to convert a limit of the form of (89) into a simple ratio form, it is only necessary to take the logarithms of both sides:

$$\ln B^{(1)} = \lim_{n \rightarrow 1} \left(\frac{n}{n-1} \right) \ln \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\} \quad (90)$$

$$= \lim_{n \rightarrow 1} \frac{n \{ \ln \alpha_M - \ln n - \ln [1 - (1 - \alpha_M)^{1/n}] \}}{n-1} \quad (\alpha_M \neq 0). \quad (91)$$

The expression in (91) approaches 0/0 as $n \rightarrow 1$, so L'Hospital's rule is applicable. The result is, for $\alpha_M \neq 0$ or 1:

$$\ln B^{(1)} = \lim_{n \rightarrow 1} \frac{n \left\{ -\frac{1}{n} + \frac{(1 - \alpha_M)^{1/n} \ln(1 - \alpha_M) \left(-\frac{1}{n^2} \right)}{1 - (1 - \alpha_M)^{1/n}} \right\} + \{ \ln \alpha_M - \ln n - \ln [1 - (1 - \alpha_M)^{1/n}] \} \cdot 1}{1}. \quad (92)$$

As n approaches 1, the second term in (92) vanishes, while the first term approaches

$$-1 - \frac{(1 - \alpha_M) \ln(1 - \alpha_M)}{\alpha_M}. \quad (93)$$

Rearrangement of terms then allows us to write:

$$\ln B^{(1)} = \ln \left[e^{-1} \cdot (1 - \alpha_M)^{-\left(\frac{1 - \alpha_M}{\alpha_M} \right)} \right]. \quad (94)$$

Thus, taking antilogs and substituting for $B^{(1)}$ in (88), we have:

$$A^{(1)}(\alpha_M) = \frac{1}{\alpha_M} \left[1 - \frac{1/e}{(1 - \alpha_M)^{\frac{1 - \alpha_M}{\alpha_M}}} \right] \quad (\alpha_M \neq 0, 1). \quad (95)$$

Evaluating (95) as α_M approaches 0 or 1 would complete the calculation of a double limit; that is, the limit as $\alpha_M \rightarrow 0$ (or $\alpha_M \rightarrow 1$) of the limit as $n \rightarrow 1$ of (38). Both double limits happen to be much easier to evaluate when the limits are taken in reverse order; that is, when the calculation is of the limit as $n \rightarrow 1$ of the limit as $\alpha_M \rightarrow 0$ (or $\alpha_M \rightarrow 1$) of (38). Such interchange of the order of limits does not change the final value for continuous functions, and, as a check, the limits were derived both ways to be sure (although the more difficult methods will not be shown here). The limit as $\alpha_M \rightarrow 0$ was already found, quite easily, in (78). The case $\alpha_M = 1$, for values of n other than 0, 1, or ∞ , is not a limiting case, and simple substitution in (38) yields the expression:

$$A^{(n)}(1) = 1 - \frac{1}{n^{\frac{n}{n-1}}}. \quad (96)$$

Similarly, setting $\alpha_M = 1$ in (39) gives:

$$D^{(n)}(1) = -\frac{n-1}{n^{\frac{n}{n-1}}}. \quad (97)$$

Finding the limit of (96) as $n \rightarrow 1$ is equivalent to finding the limit as $\alpha_M \rightarrow 1$ of (95).

By taking the logarithms of both sides and then applying L'Hospital's rule, it is easy to derive that

$$\lim_{n \rightarrow 1} n^{\frac{n}{n-1}} = e. \quad (98)$$

With (98) established, it follows directly from (96) and (97) that

$$A^{(1)}(1) = 1 - \frac{1}{e} \quad (99)$$

and

$$D^{(1)}(1) = 0. \quad (100)$$

We now complete the case $n \rightarrow 1$ by finding $D^{(1)}(\alpha_M)$ corresponding to $A^{(1)}(\alpha_M)$ in (95). We need only find the limit as $n \rightarrow 1$ of the first term in (39), the limit of the second term being equal to $A^{(1)}(\alpha_M)$. Let

$$G^{(1)} = \lim_{n \rightarrow 1} \frac{1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}} \quad (101)$$

$$= \frac{1 - \lim_{n \rightarrow 1} \langle B^{(1)} \rangle^{1/n}}{\alpha_M} \quad (\alpha_M \neq 0), \quad (102)'$$

where $B^{(1)}$ is defined by (89) and evaluated in (94). We conclude from (102) that

$$G^{(1)} = \frac{1}{\alpha_M} \langle 1 - B^{(1)} \rangle \quad (\alpha_M \neq 0); \quad (103)$$

and (88) establishes that

$$G^{(1)} = A^{(1)}(\alpha_M). \quad (104)$$

Thus, since

$$D^{(1)}(\alpha_M) = G^{(1)} - A^{(1)}(\alpha_M) \quad (105)$$

[a special case of eq (39)], (104) implies that

$$D^{(1)}(\alpha_M) \equiv 0 \quad (\alpha_M \neq 0). \quad (106)$$

We have now shown that for *any* value of α_M , there is no shape change at all for $n=1$. This conclusion is obviously correct, since with no change of concentration there is no change of shape. Although we have proved above by limit methods that eq (39) correctly implies this fact, a much more straightforward proof of (106) is obtained by simply setting $n=1$ in (30). [The restriction $\alpha_M \neq 0$ in (30) is tacit, as explained following (11)]. The resulting conclusion,

$$\delta_\lambda^{(1)} \equiv 0 \quad (\alpha_M \neq 0), \quad (107)$$

means that for $n=1$ there is no shape change anywhere along the curve, so that, in particular, the shape at the point where $\hat{\alpha}_\lambda = A^{(1)}(\alpha_M)$ (that is, the maximum change) is also zero.

Returning to formulas (96) and (97), we can now easily fill in the limits for the case $n \rightarrow \infty$ for $\alpha_M \rightarrow 1$. The same values could also have been obtained by the reverse ordering of the limits; that is, by letting $n \rightarrow \infty$ in (64) and (71); these latter derivations are omitted here. By (96), we have:

$$A^{(\infty)}(1) = \lim_{n \rightarrow \infty} A^{(n)}(1) = \lim_{n \rightarrow \infty} \left[1 - \frac{1}{n^{\frac{n}{n-1}}} \right] = 1 - \frac{1}{\lim_{n \rightarrow \infty} n^{\frac{n}{n-1}}}. \quad (108)$$

Let

$$H^{(\infty)} = \lim_{n \rightarrow \infty} n^{\frac{n}{n-1}}. \quad (109)$$

Then, taking logarithms and applying L'Hospital's rule, we find that

$$H^{(\infty)} = \infty, \quad (110)$$

and, substituting (110) into (108), we conclude:

$$A^{(\infty)}(1) = 1 - \frac{1}{\infty} = 1 - 0 = 1. \quad (111)$$

By (97), we have:

$$D^{(\infty)}(1) = \lim_{n \rightarrow \infty} D^{(n)}(1) = \lim_{n \rightarrow \infty} \frac{-1}{n^{\frac{1}{n-1}}} + \lim_{n \rightarrow \infty} \frac{1}{n^{\frac{n}{n-1}}}. \quad (112)$$

The second limit in (112) is the reciprocal of $H^{(\infty)}$, defined in (109) and evaluated in (110) as equal to ∞ . Hence the second limit is $1/\infty = 0$.

The first limit in (112) is the negative reciprocal of

$$J^{(\infty)} = \lim_{n \rightarrow \infty} n^{\frac{1}{n-1}}. \quad (113)$$

Taking logarithms and applying L'Hospital's rule, we conclude that

$$J^{(\infty)} = 1. \quad (114)$$

Thus the first limit in (112) is the negative reciprocal of 1, which is -1 . Therefore

$$D^{(\infty)}(1) = -1 + 0 = -1. \quad (115)$$

The last limits remaining to be worked out here are those for $n \rightarrow 0$. Let

$$A^{(0)}(\alpha_M) = \lim_{n \rightarrow 0} \frac{1}{\alpha_M} \left\langle 1 - \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \right\rangle \quad (116)$$

$$= \frac{1}{\alpha_M} \langle 1 - B^{(0)} \rangle \quad (\alpha_M \neq 0), \quad (117)$$

where

$$B^{(0)} = \lim_{n \rightarrow 0} \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{n}{n-1}} \quad (118)$$

or

$$\ln B^{(0)} = \lim_{n \rightarrow 0} \left\langle \left(\frac{n}{n-1} \right) \ln \left\{ \frac{\alpha_M}{n[1 - (1 - \alpha_M)^{1/n}]} \right\} \right\rangle \quad (119)$$

$$= \lim_{n \rightarrow 0} \frac{n \cdot \ln \alpha_M}{n-1} - \lim_{n \rightarrow 0} \frac{n \ln n}{n-1} - \lim_{n \rightarrow 0} \frac{n \ln [1 - (1 - \alpha_M)^{1/n}]}{n-1} \quad (\alpha_M \neq 0). \quad (120)$$

The first term in (120) is simply equal to 0 as it stands. To evaluate the second limit, we divide numerator and denominator by n and apply L'Hospital's rule, the result being a limit of 0.

To evaluate the last limit in (120) we observe that if

$$0 < \alpha_M < 1, \quad (121)$$

then also

$$0 < 1 - \alpha_M < 1. \quad (122)$$

If a quantity properly between 0 and 1 is raised to a power that grows larger without limit, the result approaches 0. Hence

$$\lim_{n \rightarrow 0} (1 - \alpha_M)^{1/n} = 0 \quad (\alpha_M \neq 0, 1), \quad (123)$$

so that

$$\lim_{n \rightarrow 0} \ln [1 - (1 - \alpha_M)^{1/n}] = \ln [1 - 0] = \ln 1 = 0 \quad (\alpha_M \neq 0, 1). \quad (124)$$

Thus all three limits in (120) are 0, and

$$\ln B^{(0)} = 0 - 0 - 0 = 0 \quad (\alpha_M \neq 0, 1), \quad (125)$$

or

$$B^{(0)} = 1 \quad (\alpha_M \neq 0, 1). \quad (126)$$

We conclude from (117) that

$$A^{(0)}(\alpha_M) = \frac{1}{\alpha_M} \langle 1 - 1 \rangle = 0 \quad (\alpha_M \neq 0, 1). \quad (127)$$

To evaluate $D^{(0)}(\alpha_M)$ we need the limit as $n \rightarrow 0$ of the first term of (39). Let

$$G^{(0)} = \lim_{n \rightarrow 0} \frac{1 - \left\{ \frac{\alpha_M}{n [1 - (1 - \alpha_M)^{1/n}]} \right\}^{\frac{1}{n-1}}}{1 - (1 - \alpha_M)^{1/n}} \quad (128)$$

$$= \lim_{n \rightarrow 0} \frac{1 - \left\{ \frac{n [1 - (1 - \alpha_M)^{1/n}]}{\alpha_M} \right\}^{\frac{1}{1-n}}}{1 - (1 - \alpha_M)^{1/n}}. \quad (129)$$

Taking note of (123), we see immediately that

$$G^{(0)} = \frac{1 - \left\{ \frac{0 [1 - 0]}{\alpha_M} \right\}^{\frac{1}{1-0}}}{1 - 0} = \frac{1 - 0^1}{1} = \frac{1}{1} = 1 \quad (\alpha_M \neq 0, 1). \quad (130)$$

Thus, from (127) and (130) we see that

$$D^{(0)}(\alpha_M) \equiv G^{(0)} - A^{(0)}(\alpha_M) \equiv 1 - 0 \equiv 1 \quad (\alpha_M \neq 0, 1). \quad (131)$$

Obviously, by (127),

$$A^{(0)}(1) = \lim_{\alpha_M \rightarrow 1} A^{(0)}(\alpha_M) = \lim_{\alpha_M \rightarrow 1} 0 = 0; \quad (132)$$

and, by (131),

$$D^{(0)}(1) = \lim_{\alpha_M \rightarrow 1} D^{(0)}(\alpha_M) = \lim_{\alpha_M \rightarrow 1} 1 = 1. \quad (133)$$

Reassuring confirmations of these limits are easily obtained by reversing the order of the variables. We see from (96) that

$$A^{(0)}(1) = \lim_{n \rightarrow 0} A^{(n)}(1) = 1 - \frac{1}{\lim_{n \rightarrow 0} n^{\frac{n}{n-1}}}. \quad (134)$$

Evaluation of the limit in (134) by the now-familiar procedure of taking logarithms and then applying L'Hospital's rule yields a limit of 1, and so we conclude that

$$A^{(0)}(1) = 1 - \frac{1}{1} = 1 - 1 = 0, \quad (135)$$

in confirmation of (132).

Similarly, (97) tells us that

$$D^{(0)}(1) = \lim_{n \rightarrow 0} D^{(n)}(1) = \lim_{n \rightarrow 0} \left[-\frac{n-1}{n^{\frac{n}{n-1}}} \right] \quad (136)$$

$$= -\frac{1}{\lim_{n \rightarrow 0} n^{\frac{1}{n-1}}} + \frac{1}{\lim_{n \rightarrow 0} n^{\frac{n}{n-1}}}. \quad (137)$$

The second limit in (137) is the same as that in (134) and is equal to 1. The first limit (denominator) requires no manipulation, and is directly equal to $0^{-1} = \infty$. Thus (137) becomes

$$D^{(0)}(1) = \frac{-1}{\infty} + \frac{1}{1} = 1, \quad (138)$$

in confirmation of (133).

Each of the six limits $A^{(\infty)}(0)$, $A^{(\infty)}(1)$, $A^{(1)}(0)$, $A^{(1)}(1)$, $A^{(0)}(1)$, and $A^{(0)}(0)$, and each of the six corresponding D limits, can be derived from two different more general formulas. These are the cases for which one can proceed by taking the n limit first and the α_M limit second, or the reverse. Only for the limits $A^{(0)}(1)$ and $D^{(0)}(1)$ that have just been discussed have we actually shown the consistency of the two possible evaluations of such limits, but consistency exists in all the other cases, too, *except for* $A^{(0)}(0)$ and $D^{(0)}(0)$.

If we define $A^{(0)}(0)$ as

$$\lim_{n \rightarrow 0} A^{(n)}(0),$$

as we in fact did in (77), we arrive at a limit value of 0.5, the value characterizing $\alpha_M = 0$ for all other n values. If, however, we define $A^{(0)}(0)$ as

$$\lim_{\alpha_M \rightarrow 0} A^{(0)}(\alpha_M),$$

it is clear from (127) that we would arrive at a limit of 0, the value characterizing $n = 0$ for all other α_M values. Thus, whether we choose to define $A^{(0)}(0)$ as 0.5 or 0, we will be violating continuity in one respect or another. The decision as to which definition to adopt must therefore be made on some basis other than the simple preservation of continuity.

Inspection of figure 3 reveals the basis for adopting the definition $A^{(0)}(0) = 0.5$. The alternative definition, $A^{(0)}(0) = 0$, would preserve the full continuity of the single curve for $n = 0$ ($P = -\infty$), but would destroy the continuity of the entire family of curves. It is obvious that as one moves downward in figure 3 ($n \rightarrow 0$), the vertical and horizontal legs of the curves become progressively straighter and the bend between these legs becomes progressively sharper. The limiting curve ought to have a vertical leg, just as all the others do, and the visual impression is compelling that the limiting curve is the right angle formed by the vertical and horizontal axes of the graph. It appears intuitively that it would constitute a more serious violation of the overall scheme to have the limiting curve of the family be of a grossly different character than all the other curves, than it would to have that one limiting curve possess a truly vertical leg—that is, a discontinuity. It is, in fact, precisely this vertical leg that makes the $n = 0$ curve fit in with the rest of the curve family.

As for $D^{(0)}(0)$, it could reasonably be defined either as 0, as it was in (84), or as 1, as it would be if it were calculated as

$$\lim_{\alpha_M \rightarrow 0} D^{(0)}(\alpha_M)$$

[see eq (131)]. Because figure 5 is a log-log plot, it does not provide a compelling geometrical impression of what the top limiting curve ($P = -\infty$) ought to be; an arithmetical plot would have shown that the limiting curve appears to be not the upper edge of the graph [the line $S^{(n)} = 1$], but the right angle formed by the upper and left edges [the horizontal line $S^{(n)} = 1$ and the vertical line $\alpha_M = 0$]. However, a consideration of the *meaning* of the case $\alpha_M = 0$, $n = 0$ leads to the inevitable conclusion that $D^{(0)}(0) = 0$ is the reasonable choice. If $\alpha_M = 0$, we are dealing with a pigment with a perfectly flat absorptance curve ($\alpha_\lambda \equiv 0$), and the shape of a flat curve stays the same—namely, flat—no matter how much the concentration of the pigment is changed. Thus the shape difference everywhere along the curve, and consequently the maximum difference $D^{(0)}(0)$ as well, is zero.

The argument for $D^{(0)}(0) = 1$ is wholly unconvincing; in fact it turns into an additional argument for $D^{(0)}(0) = 0$. When $n = 0$, we are dealing with an infinitely increased concentration (or thickness) of pigment. We know that wherever a pigment has any absorptance at all, it absorbs completely when infinitely concentrated, so the maximum shape change is infinitesimally different from 1⁷ for a pigment that contains a continuous range of absorptances including 0 and extending any finite amount above 0. However, at any wavelength where the original absorptance is actually 0, it remains 0 no matter how much the concentration is increased. Therefore, if an absorptance curve is 0 everywhere, the reasoning that leads to a maximum shape change of 1 for more ordinary curves breaks down, and the shape change is 0 everywhere.

⁷ More precisely, the least upper bound (l.u.b.) of the shape changes is 1.

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