

# THE SPECTRAL TRANSMISSIVE PROPERTIES OF DYES:

## I. SEVEN PERMITTED<sup>1</sup> FOOD DYES, IN THE VISIBLE, ULTRA-VIOLET, AND NEAR INFRA-RED

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### ABSTRACT

This paper presents quantitative data on the spectral transmittancy of seven permitted food dyes in the ultra-violet, visible, and near infra-red, from wave length 240 to 1360 millimicrons. The dyes studied were Naphthol Yellow S, Orange I, Ponceau 3R, Amaranth, Erythrosine, Indigo Disulpho Acid, and Light Green S F Yellowish. All of these show the properties of indicators and were, with the exception of Erythrosine, all dissolved in distilled water containing a sufficient amount of an H-ion regulator to fix the acidity of the solvent within narrow limits. Erythrosine, however, was dissolved in pure distilled water.

The data are given in the form of graphs and tables and a tentative nomenclature for the subject presented. The graph forms show the transmittancy and  $-\log_{10}$  transmittancy as a function of wave length and frequency for different concentrations, thicknesses, and temperatures. Concentrations of 1, 10, 100, and 1000 centigrams per liter, thicknesses of 1, 2, 4, and 10 cm, and temperatures of 25 and 40° C, were used. The tables give the specific transmissive indices of the solutions for homogeneous light of various wave lengths throughout the visible spectrum, as obtained from mercury and helium lamps, and also the values of index and frequency (and wave length) of the maxima and minima of the absorption bands throughout the whole range of wave lengths investigated.

Four methods were used to obtain the data: (1) The visual method, using the König-Martens polarization spectrophotometer; (2) the photographic method, with the Hilger sector photometer and quartz spectrograph; (3) the photoelectric null method; and (4) the thermoelectric method. These methods are fully described and the apparatus illustrated by photographs and diagrams.

The data as actually observed are plotted on the graph forms, and the wave length ranges of the different methods overlap sufficiently to afford a thorough study of the accuracy of measurement attainable by these different methods.

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<sup>1</sup> Permitted in foods, confectionery, and beverages by the U. S. Government.

<sup>2</sup> The authors have had the advice and cooperation of Irwin G. Priest, who planned and initiated this investigation but was obliged to lay it aside on account of other duties.

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## I. INTRODUCTION

### 1. OUTLINE OF INVESTIGATION

The present interest and activity in the dyestuff industry makes highly desirable the publication of standard data relative to dyes. The optical transmissive and absorptive properties of dyes in solution are of primary and fundamental importance in practical analysis and identification, as well as in theoretical studies of chemical constitution. In addition to being of interest in the study of dyes themselves, such data are useful in the design of selective "ray filters" for various purposes. Selective absorption in the visible spectrum of course determines the color of the solution; but absorption of ultra-violet or infra-red radiant energy is of equal or greater objective interest.

There already exists a very voluminous literature on this subject extending over a long period of years, but the work has been largely qualitative or only crudely quantitative. Moreover, owing to the confusion existing in terms, symbols, and units, and the failure of authors to include essential incidental data in their papers, it is generally impossible to make any quantitative use or reliable interpretation of the published data.

As a part of its color-standardization program the Bureau of Standards plans to publish from time to time accurate quantitative data on the spectral transmissive properties of dyes as well as of other materials. The apparatus and methods to be used will be essentially as described in detail herein, and the data will be presented by means of tables and graphs similar to those given at the end of this paper.

In addition to the description of the methods and apparatus given in this paper, quantitative data are presented on the trans-

mittancy of seven of the permitted food dyes throughout the ultra-violet and visible and into the infra-red as far as 1 cm of water has any appreciable transmission (wave length range about 240 to 1360 millimicrons). These data are the results of a cooperative investigation by the Bureau of Chemistry, Department of Agriculture, and the Bureau of Standards, Department of Commerce. The Bureau of Chemistry supplied the dye solutions, ready-made, of given concentrations. All transmittancy measurements were made by the Bureau of Standards. In this paper the Bureau of Chemistry is responsible for the data in regard to the composition of the dyes and the concentrations of the solutions. The Bureau of Standards is responsible for the spectrophotometric and spectroradiometric data pertaining to these solutions.

Four entirely different methods of measurement have been employed in different spectral regions, as follows:

Method	Approximate wave length range Millimicrons (m $\mu$ )
Photographic.....	240-500
Photoelectric.....	380-600
Visual.....	436-710
Thermoelectric.....	600-1360

It will be noted that the ranges overlap, and this has given opportunity for checking and for eliminating systematic errors of method. The complete presentation of the original data in this paper affords a thorough study of the accuracy of measurement attainable with these various instruments and methods now in regular use in the colorimetry section of the Bureau of Standards.

It is not the purpose of the present publication to discuss the application of the fundamental data presented. Previous work by one of the authors<sup>3</sup> has indicated the analytical value of quantitative spectrophotometric data in the examination of dyes. It is obvious that methods of analysis based on quantitative data of the kind defined and given in this paper are of greater value than such methods as Formánek's,<sup>4</sup> for example, and with a suitable development of instruments and technique they would not be more difficult to apply.<sup>5</sup>

<sup>3</sup> Mathewson: (1) The use of the spectrophotometer for the examination of food coloring matter, *Assoc. Off. Agr. Chem.*, 2, No. 2, p. 164, 1916; (2) The combination of fractionation with spectrophotometry in proximate organic analysis, *J. Am. Chem. Soc.*, 42, No. 6, p. 1277, June, 1920; (3) The detection and estimation of yellow AB and yellow OB in mixtures, *J. Ind. and Eng. Chem.*, 12, No. 9, p. 883, September, 1920.

<sup>4</sup> Formánek's *Spektralanalytischer nachweis künstlicher organischer farbstoffe*, Berlin; 1900.

<sup>5</sup> To illustrate the possibility of rapid routine examination, it may be said that a direct-reading spectrophotometer for liquids has recently been designed and constructed at this Bureau and will probably be available commercially. See forthcoming B. S. Sci. Paper, "Measurement of the optical transmissive properties of liquids by means of the exponential law," by Irwin G. Priest.

## 2. NOMENCLATURE AND FORMS

Owing to the complexity of the subject, arbitrary conventions in nomenclature, symbols, and units have presented a troublesome problem in work of this kind. It has appeared advisable to formulate a complete system of nomenclature for the subject. This nomenclature was recommended to the Optical Society of America, 1919,<sup>6</sup> and used in part in B. S. Tech. Papers, No. 119, pp. 10-11, June, 1919. The definitions, symbols, and terms as presented here are consistent with the above-mentioned system.

The following terms relate to the rectilinear propagation of homogeneous radiant energy through a cell with plane, parallel sides, perpendicular to the direction of propagation, and containing a substance in homogeneous solution in a solvent:

The *transmission*,  $T$ , of this cell and its contents is defined as the ratio of the radiant power passing the last surface of the cell to that incident on the first surface.

The *transmittance*,  $T$ , of the contents of the cell is defined as the ratio of the radiant power incident on the second inner surface of the cell to that passing the first inner surface. (*Absorption*  $\equiv 1 - T$ .)

Further,

$[^{\text{sol}}T] \equiv$  Transmission of a given cell containing the solution.

$[^{\text{sov}}T] \equiv$  Transmission of the same (or a duplicate) cell containing pure solvent.

Then,

$$\frac{[^{\text{sol}}T]}{[^{\text{sov}}T]} \equiv \frac{[^{\text{sol}}T]}{[^{\text{sov}}T]} \equiv T \equiv \text{transmittancy},$$

$t \equiv \sqrt[bc]{T} \equiv \text{specific transmissivity},$

where  $b \equiv$  thickness of layer of solution,

$c \equiv$  concentration of dissolved substance.

$$k \equiv -\log_{10} t = -\frac{1}{bc} \log_{10} T \equiv \text{specific transmissive index},^7$$

$$bck \equiv -\log_{10} T.$$

In the work herein presented the transmission of a cell containing the solution is always compared with that of a duplicate cell containing the solvent. Hence, transmittancy is the quantity obtained from the actual observations on a solution of given thick-

<sup>6</sup> Op. Soc. of Am., Committee on Standards and Nomenclature, Subcommittee on Colorimetry, Report, 1919; preliminary draft by Irwin G. Priest. (Not printed; copy may be borrowed from Bureau of Standards library.)

<sup>7</sup> Various names have been used to designate this quantity, such as extinction coefficient, absorption index, etc.

ness and concentration.  $-\text{Log}_{10}$  transmittancy ( $-\log_{10} T$ ) is a quantity much used in this kind of work. It is identical with the product of thickness,  $b$ , concentration,  $c$ , and specific transmissive index,  $k$ , and will be referred to throughout the paper by the term  $bck$ . For unit concentration and thickness,  $-\log_{10}$  transmittancy becomes identical with specific transmissive index, which is the characteristic quantity determined for any solution at a definite wave length or frequency. The unit of thickness chosen in this work is the centimeter; the unit of concentration is 1 centigram of dye per liter of solution. These are convenient units for use with dyes, and the values of  $k$  for the maxima of the bands are thus expressed in convenient numbers.

The data are presented in the form of graphs and tables. The graph forms are of two kinds: (1) With  $-\log_{10}$  transmittancy from 0.00 to 2.00 as ordinates, and *wave length* in millimicrons from 390 to 770 as abscissas; (2) with ordinates the same as (1) and having as abscissas the *frequency* in vibrations per  $10^{-12}$  seconds from 300 to 1300. In both forms *transmittancy* may be read on the right-hand ordinate. In the second form *wave lengths* are indicated at the top of the figure. The reasons for the choice of such graphs are as follows:

1. Transmittancy is the quantity obtained directly from the observations, and thus the original data may be presented.

2.  $-\text{Log}_{10}$  transmittancy presents the absorption of the solution as it appears to the eye; it magnifies the absorption maxima, making them definite and easily read, as is not done on a transmittancy scale; and it makes the computation from one concentration or thickness to another extremely simple, the relation being linear.

3. The wave length form presents the visual data in a way easily comprehended, especially from the color or analytical standpoint.

4. Inasmuch as data in the ultra-violet and infra-red are of primary importance in a theoretical study of the relation between absorption and chemical constitution, frequency is used instead of wave length. Frequency is of more fundamental importance in this connection. It brings the infra-red, visible, and ultra-violet into a more suitable relative range than does the wave length scale. Instead of the reciprocal of the wave length usually used to represent frequency we have used the *true* frequency. This is more logical and is just as simple, for the transformation is  $\frac{3 \times 10^8}{\lambda}$

instead of  $\frac{10^6}{\lambda}$ , where  $\lambda$  represents the wave length in millimicrons.

It happens that this brings what may be considered the "limits"

of the visible spectrum within the same range as on the wavelength scale, namely, 400 and 750. The values 600 and 500 are likewise reversible, as well as 1000 and 300 and other easily remembered numbers.

The tables present the specific transmissive indices for homogeneous light of various wave lengths throughout the visible spectrum, and the values of index and frequency (and wave length) of the absorption bands throughout the whole range for theoretical as well as analytical purposes.

The graph forms (Figs. 11 to 64) and Tables 1 and 2 give an exact and complete summary and presentation of the data within the purposes of this investigation. Future papers will consist largely of data presented in this way.

## II. METHODS AND APPARATUS

More or less detailed descriptions of the apparatus used and the methods employed are given in the following pages. In addition to the various diagrams, actual photographs of the apparatus as set up and used in the visual, the photographic, and the photoelectric and thermoelectric methods are given (Figs. 1, 2, and 4). References to other papers will enable one to obtain more detailed information if desired.

### 1. THE VISUAL METHOD: KÖNIG-MARTENS SPECTROPHOTOMETER

The König-Martens spectrophotometer<sup>\*</sup> has been in use at the Bureau of Standards since 1912. Before beginning this work the instrument was taken apart and the optical surfaces thoroughly cleaned, so that, upon reassembling, the field was practically free from scattered light. The previous calibration of the scale in wave lengths was also checked. Measurements of the transmission of a sector disk having a known value of 0.500 were made at 10 different wave lengths in the range 420  $m\mu$  to 710  $m\mu$  without the use of light filters over the ocular. The instrument gave values all of which were within 2 per cent of this value.

In this instrument the two beams of light reaching the eye are polarized mutually perpendicular by means of a Wollaston prism and brought together to form the two halves of a photometric field. These are compared by means of a nicol prism in the rotating eyepiece of the instrument, and with both beams clear are brought to equality of brightness by the nicol at about 39° on the scale. The following description of the apparatus

<sup>\*</sup> Ann. der Phys. (3), 12, p. 985; 1903.

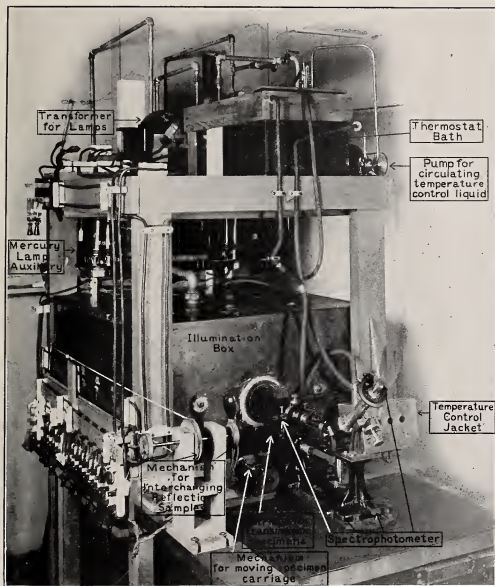


FIG. 1.—Apparatus for visual spectroradiometry. König-Martens spectrophotometer and accessory apparatus. (See section II-1)



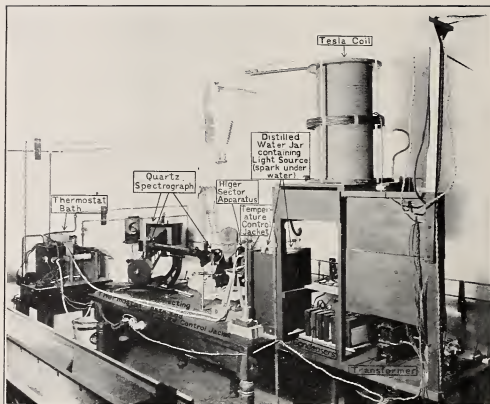


FIG. 2.—Apparatus for photographic spectroradiometry. (See section II-2, and diagram, Fig. 3)



employed for illumination of the spectrophotometer field is taken from B. S. Tech. Papers, No. 148:

1. The light sources are inclosed in a white lined diffusing box. There are receptacles in the box for ten 500-watt gas-filled tungsten lamps and space for three large mercury lamps.
2. The spectrophotometer is so placed as to "look into" this box through suitable diaphragmed apertures in one end of it, so that the illumination of the field is obtained from diffusely reflecting surfaces on the inside of the opposite end.
3. In measuring transmission the surfaces illuminating the field are both white (magnesium oxide or carbonate), and the sample intercepts the light from one of the surfaces in the space between the slits and the outside of the box.
4. In measuring reflection the sample is substituted for one of the white surfaces.
5. Both reflection and transmission measurements are made by the method of interchanging sample and standard before the two slits, and means are provided for doing this quickly and conveniently.
6. The illumination box is cooled by the circulation of water in an inclosing jacket.

Illumination of the spectrophotometer field for transmission measurements may also be secured from helium or other vacuum-tube lamps. For this purpose the magnesium-carbonate reflecting surfaces are readily removed and a small auxiliary white lined box containing the vacuum-tube lamps is inserted into the rear end of the main illumination box. A diffusely transmitting ground-glass window in the auxiliary box then serves to illuminate the spectrophotometer field, the sample occupying the same position as before.

In measuring transmittancies, as in this investigation, the cell containing the dye solution is placed in one beam and a similar cell containing the solvent placed in the other. These are interchanged as described above, and the nicol rotated in each case until an intensity match is obtained. For each position of the cells there are four settings of the nicol for which an intensity match can be obtained; that is, one in each quadrant of the circle. If the scale zero setting of the nicol is not coincident with the setting for extinction of one of the beams, the resulting error can be eliminated either by applying a correction to the observed angle or by making settings of the angle of match in each of the four quadrants and properly averaging the results.

For the instrument used in this investigation this zero correction was made as small as possible by adjustment of the Wollaston prism, so that any error due to this cause was negligible. The readings were therefore all taken in the first quadrant, from 4 to 10 settings of each angle of match being made. The transmittancy is then given as the product of the cotangent of the angle in one case by the tangent of the angle in the other. Slits of 0.10 mm were used for practically all work with the heterogeneous source. The amount of spectrum included by this

width of ocular slit was approximately  $1.5\text{ m}\mu$  at wave length  $500\text{ m}\mu$  and  $3.5\text{ m}\mu$  at  $640\text{ m}\mu$ .

In using the homogeneous light source the ocular and collimator slits were opened to  $0.5\text{ mm}$  and the field brightness thus obtained was ample enough in all cases to make good settings of the angle of match for values of  $bck$  as high as 1.6. With the Hg and He green and yellow lines very definite settings could be made at 2.0 and above. For low values of  $bck$  the field brightness for the Hg 546.1 line, with the wide slit, was too great for eye comfort, and a screen was used to reduce its intensity. Due to an inherent characteristic of this spectrophotometer, it was found impossible to obtain a good photometric field when the slits were narrowed in an endeavor to separate the two Hg lines 576.9 and 579.1. For this reason the measurements with the Hg source for these lines were made with the wide slits, which gives the combined effect for both lines.

## 2. THE PHOTOGRAPHIC METHOD: HILGER SECTOR PHOTOMETER, QUARTZ SPECTROGRAPH, AND AUXILIARY APPARATUS

The data in the ultra-violet and extending into the visible were obtained by the Hilger <sup>9</sup> sector-photometer method, with auxiliary source and quartz spectrograph (Figs. 2 and 3). The sector photometer <sup>10</sup> (Fig. 3) consists essentially of two quartz wedge lenses, on one side of which are the two rotating sector disks and on the other side the absorption cells. The quartz spectrograph is a Fuess instrument, 74 cm focal length of lenses, with a dispersion giving 13.9 cm between frequencies 600 and 1200 ( $500$  and  $250\text{ m}\mu$ ). A slit width of  $0.1\text{ mm}$  was used, corresponding to about 2.5 frequency units ( $1.5\text{ m}\mu$ ) at frequency 750 ( $400\text{ m}\mu$ ) and to about 2 units ( $0.5\text{ m}\mu$ ) at frequency 1200 ( $250\text{ m}\mu$ ). A quartz biprism is placed directly in front of the slit, with its refracting edge perpendicular to the slit.

The source of radiant energy is a high-voltage (Tesla coil) spark under water, which gives a continuous spectrum from the visible throughout the ultra-violet as far as the quartz system will transmit. The electrical connections for obtaining this spark are outlined in the figure and are patterned after those used by Howe.<sup>11</sup> The vertical spark used at the Bureau<sup>12</sup> has, however, proved much more satisfactory than the horizontal spark, for it keeps the two spectra in contact throughout their whole length. Brass, tungsten,

<sup>9</sup> Adam Hilger, Ltd., catalogue, Spectrophotometers, January, 1914.

<sup>10</sup> Made at the Bureau of Standards. Duplicate of the Hilger instrument.

<sup>11</sup> Phys. Rev. (2), 8, p. 674; 1916.

<sup>12</sup> E. P. T. Tyndall, B. S. Tech. Papers, No. 148, Appendix.

or molybdenum electrodes are used. A further improvement has been effected by making the length of the auxiliary spark-gap adjustable while in operation. This results in much better and easier control of the main spark.

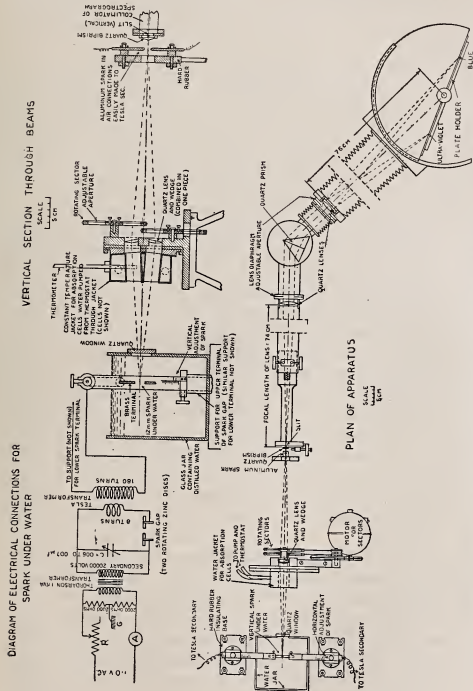


FIG. 3.—Diagram of Hilger sector photometer, quartz spectrograph, and accessory apparatus for ultra-violet spectroradiometry

The arrangement of the apparatus is shown in Fig. 3. Radiant energy emanating from the source may reach the slit by two alternative paths (see upper half of Fig. 3). An upper beam passes

through a quartz lens and wedge, is refracted downwards through a rotating sector disk of variable aperture, and is deviated by the lower half of the quartz biprism to pass axially along the collimator of the spectrograph. A lower beam traverses a similar path through the lower wedge lens and sector and is deviated by the upper half of the biprism to pass axially along the collimator like the first.

We thus have the spectrograph fed by two beams from the same source. These are dispersed by the quartz prism and a spectrum image of the slit formed on the photographic plate. This spectrum is divided into two halves by a fine line extending along its entire length, which is the spectrum image of the refracting edge of the biprism. One half of this spectrum results from the upper beam, the other half from the lower beam.

If the ratio of the upper to the lower sector opening is unity and if the spark is in correct alignment, the densities of the two halves will be equal throughout their entire length, thus indicating equal intensity of the two beams. The plate may be raised or lowered in the plane of the spectrum, thus permitting several photographs to be taken on one plate. Both sectors have a maximum opening of  $180^\circ$ , which may be adjusted to any desired value between  $180^\circ$  and zero. A scale on each sector wheel gives the opening in per cent of the maximum.

In measuring transmittancies a cell containing the solution is placed in one beam (generally the lower) and a duplicate cell containing the solvent in the other. (The cells are inserted in openings in the constant temperature jacket, Fig. 3, upper half.) A series of exposures is made, each for a different ratio of upper to lower sector opening, the total exposure time (time of operation of the spark) being adjusted to give a normal blackening on the plate in each case.

Let  $P$  and  $P'$  represent the radiant powers leaving the solution and solvent, respectively, along the lower and upper beams,  $S$  and  $S'$  the lower and upper sector openings,  $s$  and  $s'$  the corresponding effective exposure times through the rotating sectors.

The ratio  $P/P'$ , which is the transmittancy  $T$  of the solution, varies in general with the wave length of the radiant powers under consideration. For radiant powers of the particular wave length (or wave lengths) for which  $P/P' = S'/S = s'/s$  there will result equal products of radiant power and effective exposure time for each beam.

The assumption now made is that the equal quantities of energy thus delivered to the plate by each of the two beams produce equal blackenings on the plate at the wave length in question, or, in other words, that the transmittancy for any wave length at which equal blackenings are produced is given directly by the ratio of the sector openings.

The makers of the sector photometer do not assume such a simple relation, but, notwithstanding the fact that the exposures are made through sectors of different openings, assume a relation similar to that of Schwarzschild;<sup>13</sup> that is,  $\frac{P}{P'} = \left(\frac{s'}{s}\right)^n$ , the constant  $n$  having a value less than unity. Therefore, a calibration curve is supplied by which  $\log \frac{s'}{s}$ , and hence  $\log \frac{S'}{S}$ , may be reduced to  $\log \frac{P}{P'}$ .

Undoubtedly, however, for the sector photometer the value of  $n$  appears to be unity, within the experimental errors of photographic measurement, as was first clearly stated by Howe:<sup>14</sup> "The photographic plate, the use of which in photometric measurements is usually considered questionable, integrates intermittent exposures in such a way that the comparison of two intensities can be made directly in terms of sector openings provided that the time from the beginning to the end of the exposures is the same and that the two exposures produce equal blackenings of the plate." Why this is true may be seen from a consideration of the conclusions reached by various observers. If a plate is exposed to a constant radiant power for time  $s$  (continuous) and then exposed for the same effective time  $s$ , made intermittent by means of a rotating sector, the blackening produced in the second case is less than that produced in the first. This is sometimes called the Abney<sup>15</sup> relation. Weber<sup>16</sup> and Schwarzschild<sup>17</sup> find the difference in blackening to increase as the ratio of "exposure interval" to "darkness interval" gets less.

Assuming the Schwarzschild relation for continuous exposures as valid, then, if one considers two radiant powers  $P'$  and  $P$ , where  $P'$  is greater than  $P$  (say  $P = P'/a$ ), the blackening produced by  $P'$  in a time  $s/a$  (continuous) is greater than that produced by  $P'$  during the same effective time of intermittent exposure. Also, the blackening produced by  $P$  during the time  $s$  is less than that of  $P'$  during  $s/a$  (both continuous). It is therefore

<sup>13</sup> *Astrophys. J.*, 11, p. 89; 1900.

<sup>14</sup> See footnote 11.

<sup>15</sup> Abney, *J. of Phot. Soc.*; 1893-94.

<sup>16</sup> Weber, *Ann. der Phys.*, 45, p. 801; 1914.

<sup>17</sup> Schwarzschild, *Astrophys. J.*, 11, p. 91; 1900.

possible for the blackenings resulting from  $P'$  during  $s/a$ , intermittent, and  $P$  during  $s$ , continuous, to be the same. Weber<sup>18</sup> states this possibility in the beginning of his paper and proves it experimentally for various wave lengths and brands of plates, various times of exposures, and for a wide range of sector speeds. Howe<sup>18</sup> and Newcomer<sup>19</sup> also arrived at this same conclusion. This case would apply to the sector photometer with only one rotating sector.

In the case of the sector photometer as usually used and described in previous pages there are two intermittent exposures, in one of which, however, the ratio of "exposure interval" to "darkness interval" is kept at unity, while in the other this ratio is made smaller and smaller as lower transmissions are measured.

Here it is also true that  $\frac{P}{P'} = \frac{S'}{S}$ , where  $P$  and  $P'$  are the radiant powers passing through two sectors of angular openings  $S$  and  $S'$ , respectively, and producing equal blackening. This case was proved explicitly by Howe for a smoked-glass screen and is also substantiated by the various observations to be mentioned later. That this is true is probably due to the mutual working of the Schwarzschild relation and the fact, already mentioned, that the blackening decreases as the ratio of "exposure interval" to "darkness interval" decreases, even when the radiant power and effective time remain constant. There is no contradiction of the Schwarzschild relation or any assumption that  $n$  in that relation is unity, since the relation as usually stated,  $\frac{P}{P'} = \left(\frac{s'}{s}\right)^n$ , is valid only for continuous exposures or for exactly similar intermittent exposures.

Comparison with other methods of known reliability is the only final test for any method. It is therefore of interest to note the many investigations in which the relation found by Howe has been proved to be reliable by such comparison. Martin<sup>20</sup> found that "perfect agreement existed between the results when transmission was assumed proportional to the ratio of sector openings." His comparison was made with the Abney visual apparatus. Howe and others working with him<sup>21</sup> in later investigations verified the agreement between values found by his

<sup>18</sup> Phys. Rev. (2), 8, p. 678; 1916.

<sup>19</sup> Newcomer, Science; March 7, 1919.

<sup>20</sup> Trans. of the Optical Society, 18, p. 36; 1917.

<sup>21</sup> Howe and Gibson, Phys. Rev. (2), 10, p. 767; 1917. Other data, not yet published (by Howe and Tyndall).

method with the Hilger apparatus and those obtained visually on the Lummer-Brodhun spectrophotometer.

Still further evidence of the reliability of this photographic method has been obtained by investigations conducted at the Bureau of Standards,<sup>22</sup> comparison being made with the Lummer-Brodhun and König-Martens spectrophotometers and Martens photometer, all visual methods, and with the photoelectric null method described in this paper. Finally, the data presented in this paper seem to prove this conclusively. It may therefore be said that no discrepancies have ever been noted (between values of spectral transmission or similar quantities obtained by Howe's modification of the Hilger sector-photometer method and those obtained by the other methods above mentioned) which are larger than the experimental errors possible in the methods, and that where these discrepancies have occurred—for example, in this paper—they have not been consistently in any one direction.

The different operators of this apparatus at the Bureau have all concluded that the principal source of error in this method at present is a result of "vagaries" of the spark. The errors arising in this way may be of two natures: (1) That caused by a displacement of the electrodes, and therefore of the spark as a whole, from its proper position; and (2) that caused by nonuniformity in the spark itself.

After the apparatus has been once adjusted properly it is not very difficult to keep it so. This is tested on each plate by means of the comparison spectra which, if of equal density throughout, indicate that the first error has been eliminated. In the Bureau apparatus both sectors are variable, and by interchanging the solvent and solution and cutting down the other sector a value should be obtained which, if equal to that previously found, is proof that this error is not present. If different, the average should give the correct result. It is the second error which is thought to cause most of the occasional irregularities noticed in the photographic data.

In addition to the above factors certain others should be considered in a study of the data or a comparison of methods. One of these is the small dispersion in the blue. If an error of half a millimeter were made in the location of a point of equal density, this would appear relatively large in the blue on the wave length

<sup>22</sup> B. S. Tech. Papers, No. 119; June, 1919. B. S. Tech. Papers, No. 148; March, 1920.



scale and to a less extent on the frequency scale, whereas in the ultra-violet it might appear inappreciable. The error in locating the wave length or frequency of equal density has been made very small by the use of the special comparator made at the Bureau for this purpose and described in the appendix to B. S. Technologic Paper No. 148. The ease and accuracy of locating this point is much greater for low transmissions or where the transmission is varying rapidly. The agreement with other methods in the violet when  $T=0.01$  is usually remarkable.

The extreme range of the method in the ultra-violet is to a frequency of about 1360 (220  $m\mu$ ). In this investigation, however, the strong absorption of the solvent in the extreme ultra-violet limits the range of frequency to approximately 1250 (240  $m\mu$ ).

### 3. THE PHOTOELECTRIC NULL METHOD

The photoelectric method is the null method described in B. S. Scientific Paper No. 349. Fig. 5 is taken from that paper and with its key on the opposite page gives the principal details concerning the apparatus. The method of measuring transmissions may be briefly described as follows:

After the "dark currents" through the photoelectric cells  $P_1$  and  $P_2$  have been made approximately equal (by varying the ratio  $V_2/V_1$ ) the lamps  $L_1$  and  $L_2$  are lighted. By adjusting the currents through  $L_1$  and  $L_2$  the photoelectric currents through  $P_1$  and  $P_2$  may be made exactly equal, with the lamp  $L_2$  well back on the track. This equality of photoelectric currents is shown by the zero motion of the spot of light from the electrometer on the scale  $D$ . When this condition has been attained at any particular wave length, the distance of  $L_2$  from  $S_2$  is read on the scale.

Now let the specimen  $B$  whose transmission is to be measured be placed in the path of the radiant energy from  $L_2$  by moving the carrier  $C$ . This destroys the equality of the photoelectric currents; but, by moving  $L_2$  forward, a position may be found where the photoelectric current through  $P_2$  is again equal to that through  $P_1$ . The transmission of  $B$  is now very accurately given by the ratio of the squares of the distances of  $L_2$  from  $S_2$  when  $B$  is in and out of the beam. The rotating sector when used increases the effective distance of  $L_2$  from  $S_2$ .

This distance of  $L_2$  from  $S_2$  is the only variable in the process of measuring the transmission of  $B$  at any wave length, for the slit widths of  $S_1$ ,  $S_2$ , and  $S_3$ , the currents through  $L_1$  and  $L_2$ , the

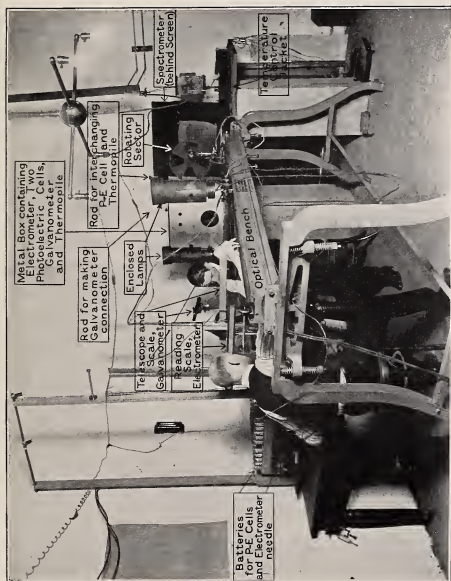


FIG. 4.—Apparatus for photoelectric and thermoelectric spectrometry. (See sections II-3, II-4, and diagram, Fig. 5)

irradiations of  $P_1$  and  $P_2$ , and the photoelectric currents through  $P_1$  and  $P_2$  are all unchanged whether the specimen is in or out. This method, therefore, eliminates all errors connected with the current-irradiation law or the "dark currents" of the photoelectric cells or with electrometer deflection methods, and no calibrations or corrections connected with them are necessary. For further details of the apparatus and method the original paper should be consulted.

In the present investigation the carrier  $C$  is lowered and supports the constant-temperature box, which, in turn, carries the similar cells filled with solvent and solution. These parts of the apparatus are described elsewhere. Then the ratio of the squares of the distances of  $L_2$  from  $S_2$ , when the cells containing the solution and solvent are in turn in the beam, gives the transmittancy of the dye in solution for that particular thickness and concentration. Before computing this transmittancy, however, correction must be made to the value of the distance of  $L_2$  from  $S_2$  as read on the scale. This observed distance is larger than the true optical distance, and in the present investigation, where water is the principal part of the solvent, one-quarter of the length of the solution, and of the solvent, is subtracted from the observed distances.<sup>23</sup> This correction is of considerable importance when the 4-cm cells are used and the transmittancy is low.

Inasmuch as this investigation affords such a fine comparison of methods, it is thought worth while to reproduce Fig. 6 from B. S. Scientific Paper No. 349. This shows the relative sensitivity of the method at the different wave lengths. In the present work the current through  $L_2$  was usually 19.0–19.5 amperes. Slits of 0.20 mm ( $S_2=S_3$ ) were always used, except when the transmittancy was very low or when measurements below 405  $m\mu$  were being made. The amount of the spectrum included by 0.20 mm slits is shown in the figure.

Although it seemed unnecessary in this investigation to measure transmittancies by this method at wave lengths greater than 555  $m\mu$ , this is not at all the upper limit, as is obvious from Fig. 6. Measurements may be made at 620  $m\mu$  with practically the same accuracy as at 390  $m\mu$ . This workable range, however, varies with the individual cells.

<sup>23</sup> Edser, *Light*, 1909, p. 55.

## KEY TO FIG. 5

[Apparatus drawn to scale shown in diagram except for batteries and a few other minor details.]

*FFFF*—Slate slab supported by two concrete pillars resting on basement floor.

*IIII*—Cast-iron base 3.5 cm thick resting upon slate slab.

*JJJJ*—Aluminum box 50 cm high, divided into three compartments by partitions *N* and fitting into brass channels on iron base. Has aluminum cover fitting into brass channels at top of box.

*E*—Dolezalek quadrant electrometer, resting on iron base, with aluminum disk *E'* suspended by platinized quartz fiber.

*P<sub>1</sub>P<sub>2</sub>*—Kunz potassium-hydride photoelectric cells supported by tripods resting on iron base.

*AAA*—Pieces of polished amber with brass rods through centers.

*GG'*—Ground-wire connections to water pipe. Cast-iron base, aluminum box, electrometer case, and one pair of quadrants permanently grounded.

*U*—U-tube filled with mercury into which dips a pointed amalgamated copper wire. Used for make-and-break ground connection for second pair of electrometer quadrants, controlled from *X*, *X'*, or *X''*.

*WW<sub>1</sub>W<sub>2</sub>*—Windows.

*H*—Hilger constant-deviation spectrometer, resting on slate slab, with glass prism and accurately adjustable bilateral slits *S<sub>2</sub>* and *S<sub>3</sub>*.

*T*—Track of iron Scimatco optical bench resting on ground floor.

*L<sub>2</sub>*—Mazda C moving-picture lamp rated at 600 watts (30 volts, 20 amperes), filament in one plane about 1 cm square, completely inclosed except for concealed ventilating openings and openings 3 cm in diameter in front and back of filament. *L<sub>2</sub>* is carried by a three-wheeled car moving along photometer track and carrying a marker directly beneath filament by which its distance from slit *S<sub>2</sub>* may be read on scale shown in diagram.

*Z*—Black felt screens, supported on *T*, enabling measurements to be made with other electric lights in the room.

*Y*—Leeds and Northrup rotating sector and motor *Y'*, supported on *T*, used to test inverse-square law for *L<sub>2</sub>* and to increase range of measurements.

*C*—Sliding carrier, supported on *T*, containing specimen *B*, whose transmission is to be measured. Carrier slides back and forth from *C* to *C'*.

*Q*—Container for selective ray filters.

*L<sub>1</sub>*—Mazda C automobile headlight lamp rated at 14 watts (7 volts, 2 amperes), inclosure similar to that for *L<sub>2</sub>*, supported by iron base. *L<sub>1</sub>* and *L<sub>2</sub>* are run in parallel with suitable adjustable resistances on a 60-volt storage battery.

*S<sub>1</sub>*—Accurately adjusted bilateral slit, supported on iron base, identical with *S<sub>2</sub>* and *S<sub>3</sub>*.

*Q'*—White opal glass screen.

*V*—Battery of Eveready cells, usually about +150 volts, by which electrometer disk may be charged through conducting suspension.

*V<sub>1</sub>V<sub>2</sub>*—Battery of Eveready cells, usually about 40 and 80 volts, respectively, of such value that the dark currents through *P<sub>1</sub>* and *P<sub>2</sub>* are approximately equal.

*R*—Adjustable high resistance.

*KK<sub>1</sub>K<sub>2</sub>*—Knife switches.

*L*—25-watt vacuum tungsten lamp. Light from filament is reflected and focused by small mirror on electrometer disk to give image on 50 cm ground-glass scale at *D*.

*X*—Approximate position of observer when scale is at *D*.

*X'D', X''D''*—Other positions of observer and ground-glass scale under conditions explained in paper. In these cases light from *L* is reflected to *D'* or *D''* by a mirror *M'* or *M''*.

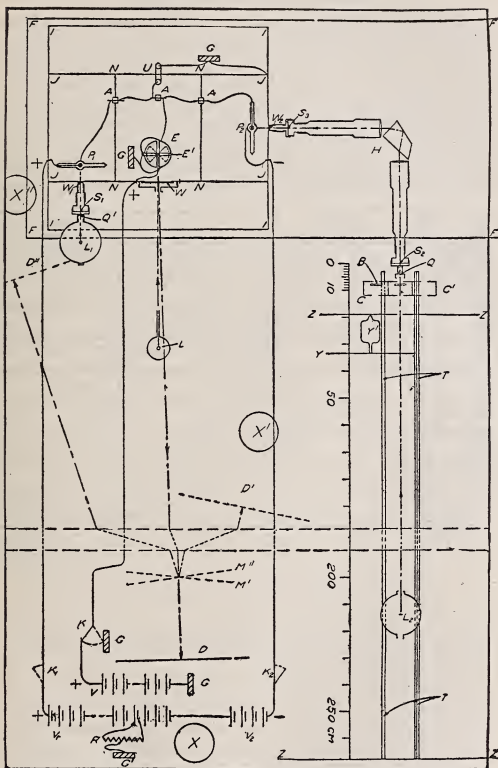


FIG. 5.—Diagram of photoelectric apparatus. (For explanation, see page 136.)

## 4. THE THERMOELECTRIC METHOD

In order to extend the measurements of transmittancy into the infra-red, some radiometric method was necessary. However, because of the strong absorption by the water itself, it seemed unnecessary to use a regular infra-red spectrometer with fluorite or rock-salt prism. Since 1 cm of water is practically opaque for all frequencies less than 210 (1430  $m\mu$ ), it was believed that the Hilger constant-deviation glass-prism spectrometer ( $H$  of Fig. 5) would suffice. This was not originally calibrated for frequencies less than about 385 (780  $m\mu$ ). Fortunately, however, the thread

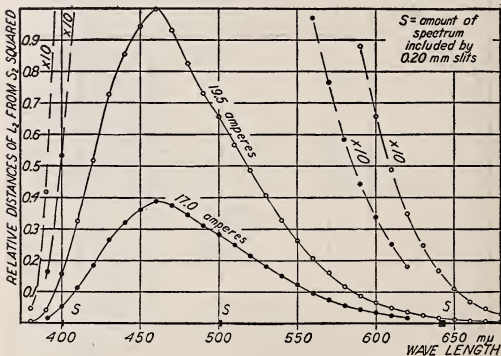


FIG. 6.—Curves showing spectral response of cell  $P_2$ , for currents of 19.5 and 17.0 amperes through  $L_2$ , under conditions of apparatus shown in Fig. 5

was cut considerably beyond this point, and it has been found possible to use the instrument throughout the range where water has any appreciable transmission.

Before the start of this investigation the calibration of the spectrometer was rechecked visually by means of the Hg lines (including the red line at 690.8  $m\mu$ ) and again checked photoelectrically and thermoelectrically at 436 and 546  $m\mu$  after the spectrometer was placed back in position. Then with a quartz-mercury lamp and thermopile the mercury lines at 1014 and 1129  $m\mu$ <sup>24</sup> were located on a circular scale attached to the end of

<sup>24</sup> Paschen, Ann. d. Phys., 27, p. 558; 1908.

the drum. The frequencies of these lines, together with those in the red, yellow, and green, were then plotted against circular-scale readings of drum, it being well known that the frequency dispersion curve is much nearer a straight line than the wave length dispersion curve.

The radiometric apparatus consisted of a thermopile and galvanometer, and the usual deflection method was used. The thermopile was of the linear type and was made by W. W. Coblenz. The galvanometer was a Leeds and Northrup high voltage-sensitivity type. The deflections were observed through the window *W* by a telescope and scale 165 cm from the galvanometer mirror.

It was desirable to disturb as little as possible the photoelectric method already in use. This was accomplished by placing the thermopile and photoelectric cell on a rod, so that, by raising or lowering the rod from the outside of the box, either could be brought in front of slit  $S_2$  (Fig. 5). The thermopile was connected through the wall to the galvanometer (placed beside the electrometer in the middle compartment of the box), there being a simple complete circuit between the thermopile and the galvanometer. The photoelectric circuit was unchanged.

The same source,  $L_2$ , was used as in the photoelectric method ( $L_1$  not lighted). It was moved to about 55 cm from the slit and a lens used to focus part of the filament on the slit. The rays thus did not pass parallel through the cells, but inasmuch as the path through the solution was identical with that through the solvent no error was introduced because of this. In future work, however, two lenses will be used, so placed that the rays between them will be parallel, and the solutions or other specimens will intercept these parallel rays.

The following readings of the galvanometer are taken in measuring transmittancy: (1) With the solution in the beam, (2) with the beam cut off (by the opaque box carrying the cells), (3) with the solvent in the beam, (4) repetition of (2), (5) repetition of (1). If corresponding readings do not check well or the deflections are very small, this series is continued or repeated. These readings are taken at equal intervals of 15 or 20 seconds. Errors which might enter, arising from the drift of the "zero" reading (beam cut off) or from slight variation of current through  $L_2$ , are, by the above method, practically eliminated.

In Fig. 7 are shown curves giving the size of the deflections of the galvanometer between frequencies 500 and 220 (600 and 1360  $m\mu$ ) under various conditions of the apparatus as herein used.



The slit widths for these curves,  $S_2 = S_3 = 0.25$  mm, in terms of frequency and wave length are shown in the figure. Curve 1 is that obtained when no substance is interposed between the lens, in front of the lamp, and the slit of the spectrometer. Curve 2 was obtained through a 1-cm cell (with glass end plates) of the acetate mixture (mainly water, described in section III-2), curve 3 through a 4-cm cell of the same solution. These three curves are meant to be illustrative only, to give one an idea of the probable accuracy of determinations made at the different frequencies under the different conditions. They illustrate why the 4-cm curves in the figures always end at 260 (1150  $m\mu$ ), that the

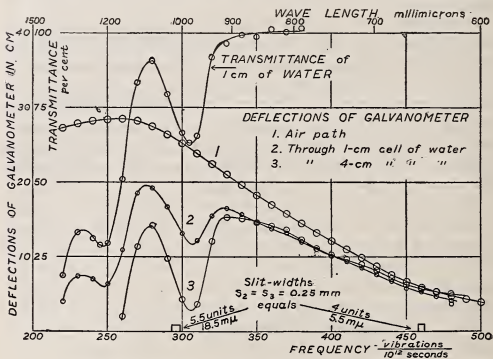


FIG. 7.—Characteristics of thermo-electric apparatus

probable accuracy of the 4-cm curves is much less at 300 (1000  $m\mu$ ) than at 280 or 320, and how it becomes increasingly difficult to get accurate results as the visible region is entered. But these curves were obtained at different times under probably somewhat varying circumstances, and the current through  $L_2$  (19.0–19.5 amperes) may have varied somewhat during any one of them. They therefore serve only as an approximate comparison with each other.

Special attention is called to the width of the slits, expressed in frequency or wave length, which is less than one-fifth of that sometimes used in this region with a regular infra-red spectrometer.

This enables bands to be measured which might otherwise be overlooked. It should also promote accuracy in all determinations.

In Fig. 7 is also shown the "transmittance" curves for 1 cm of water. The curve really represents the deflections through a 1-cm cell of water, with two glass end plates, divided by the deflections through two similar glass plates pressed closely together. The absorption of the glass is, therefore, entirely corrected for and reflection from the surfaces nearly so. Absolute values may not be quite true, not only because of this approximate correction but because the light did not pass through the cells in a parallel beam.

These water bands were located at frequencies 248 and 306,  $\lambda = 1210$  and  $980$  m $\mu$ . The only other values for these bands which have been found are those given by Ashkinass,<sup>25</sup> namely, at 1250 and 1000 m $\mu$ . Discrepancies in the location of the more intense water bands at longer wave lengths in the infra-red may also be noted.<sup>26</sup> It may be considered doubtful whether or not all these bands are in the exact harmonic series usually implied. In this connection a recent paper by Hettner<sup>27</sup> gives what seem to be very reliable data on the absorption bands of water vapor. These bands also form an approximate harmonic series, but at different frequencies from the water-liquid bands. There is also approximately a constant frequency difference between the corresponding liquid and vapor bands, although this, if exact, is of course irreconcilable with exact harmonic series in both liquid and vapor. Seemingly further work will have to be done on the absorption of water to clear up these relationships.

## 5. GENERAL COMPARISON OF METHODS

The agreements obtained between methods may be noted from the data as plotted (Figs. 11-64). When discrepancies occur, the curve as drawn shows which method is, in our opinion, the most reliable for that particular case. The following points are worthy of note in this connection:

In the first place, it will be noticed that there is very close agreement between the visual and photoelectric methods. (Agreements should be studied on the wave length graphs.) This is true not only between 500 and 550 m $\mu$ , where both methods are very reliable, but throughout nearly the whole range of either. The most

<sup>25</sup> Ann. d. Phys., 55, p. 401; 1895. While the present paper was in press, Collins, Phys. Rev. (2), 19, p. 396, 1922, has published values of 1200 and 976 for these bands.

<sup>26</sup> Paschen, Wied. Ann., 53, p. 336; 1894; Ashkinass, Ann. d. Phys., 55, p. 401; 1895; Coblentz, B. S. Bulletin, 7, p. 631; 1911; Baly, Astrophys. J., 42, p. 49; 1915.

<sup>27</sup> Ann. d. Phys. (4), 55, p. 476; 1918.

reliable region photoelectrically is 410 to 550  $m\mu$ , inclusive, that visually, 500 to 650  $m\mu$ . But the photoelectric method agrees with the visual usually to 600 and often to 650  $m\mu$ , though few data are given in this paper above 550  $m\mu$ . The use of homogeneous illumination, apart from elimination of slit-width errors, extends the reliability of visual determinations beyond the limits above given, especially in the blue. Visual readings with a heterogeneous source are seen to hold reliable usually to 460  $m\mu$ , and the helium line at 447.1 and the mercury line at 435.8 extend this to these wave lengths. Toward the red the helium line 667.8 is very reliable, but the 706.5 line less so. However, with a heterogeneous source little trouble is experienced getting readings visually as far as 680  $m\mu$ .

In comparing the photographic determinations with the visual or photoelectric, especially the latter, which seem to hold reliable usually to 390  $m\mu$ , it will be seen, in general, that the agreement is better the shorter the wave length, the lower the transmittancy, and the "steeper" the transmittancy curve. From the nature of the photographic method it is difficult to determine exactly the value of maximum or minimum transmittancy. But the agreements in the blue and violet indicate that in the ultra-violet, where the dispersion is greater, the method can be considered very reliable, especially for the determination of the frequency and magnitude of absorption bands, which is the main purpose of this part of the investigation. One great advantage of this method, possessed by no other, is that the record is permanent and may be studied at leisure. Undoubtedly, it is in every way better than the older photographic method. It is speedy as well as reliable, and, thanks in great part to the continuous source, does not overlook whole bands, to say nothing of weak bands appearing as "humps" on the curve.

Little need be said in addition in reference to the thermoelectric method, which has long been well known and proved, in general, reliable. The agreements with the visual method between 600 and 700  $m\mu$  indicate that no large errors are present. In fact, if it be remembered that with the usual infra-red apparatus (wherein, because of small dispersion in this region, 600–1340  $m\mu$ , the effective slit widths are very large) the water bands at 980 and 1210  $m\mu$  are sometimes entirely missed or only roughly indicated, it would seem that conditions could scarcely be better for an investigation in this part of the infra-red than are afforded by this particular apparatus.

## 6. TEMPERATURE CONTROL

Temperature control was effected in the same way for all four methods. The cells containing the solution and solvent were inserted in openings in a brass box (Figs. 1-4). This brought the brass sides of the cells in contact with the brass walls of the box, which were kept at constant temperature by water circulating inside. The glass or quartz end faces of the cells were in contact with the air of the room. The temperature of the circulating water in the box, read by a mercury thermometer, was taken as the temperature of the solution and solvent. While this method might be

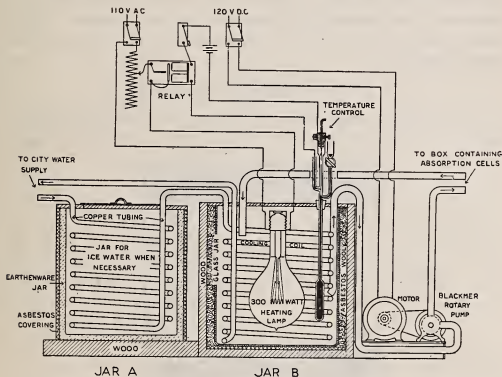


FIG. 8.—Thermostat and bath arrangement for temperature control of absorption cells

inaccurate at high temperatures, it is quite suitable in an investigation like the present where temperatures do not differ more than  $20^{\circ}$  from that of the room.

The circulation and constant temperature of the water in the box containing the cells were produced by the pump-and-thermostat arrangement, outlined in Fig. 8. The water in jar B is forced through the boxes containing the absorption cells and back to the jar again by the rotary pump. This water is kept at the proper temperature, as follows: Water from city mains, still further cooled, if necessary, in jar A, passes through the coils in jar B and returns to the mains. This cools the water in jar B. The 300-watt

Mazda-C lamp suspended in jar *B* heats the water when the current is on. This current through the lamp is controlled by the thermostat and relay as shown. When the water in jar *B* is too cool, the contact between the mercury and platinum rod in the thermostat is broken by the contraction of the mercury. This interrupts the current through the magnets of the relay, and the relay lever flies back and closes the circuit through the lamp. As the water in jar *B* now heats up, the expansion of the mercury in the thermostat brings it into contact with the platinum rod, the circuit is made, and the relay lever drawn toward the magnet, thus breaking the lamp circuit. This continued action keeps the temperature of the water in jar *B* constant within narrow limits. Any desired value is obtained by raising or lowering the platinum rod in the thermostat.

#### 7. TYPE OF ABSORPTION CELLS USED

The cells were made after the manner of those put out by Hilger for use with their sector photometer. This cell is com-

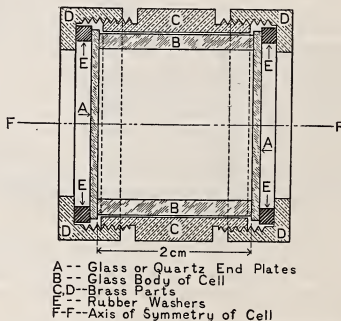


FIG. 9.—Type of cell used in measurement of spectral transmittancy of dyes in solution

pletely described in Fig. 9, where the 2-cm cell has been drawn to scale. This type of cell has many advantages, chief of which are the following: (1) Glass (or quartz) is the only material in contact with the solution; (2) no cement has been used in its construction, and it can therefore be used with any solvent; and (3) it has to be completely taken apart for each new solution and is therefore easily cleaned.

## III. DESCRIPTION OF DYE SAMPLES AND SOLVENTS

## 1. DYES

The dyes employed for this work were obtained from commercial samples of good quality. The Naphthol Yellow S, Orange I, Amaranth, and Erythrosine were purified in the laboratory by recrystallization and were believed to be free from impurities other than moisture and small quantities of subsidiary dyes. Commercial products were used directly in case of the Indigo Disulpho Acid, Ponceau 3R, and Light Green S F Yellowish, the analyses<sup>28</sup> of the samples employed showing that they contained total amounts of inorganic substances (other than moisture) ranging from 2 to 3 per cent. The dyes were examined in all cases for moisture, insoluble matter, sodium chloride, and sodium sulphate, and the total quantities of these determined, so that in making the solutions for the spectrophotometric examination such amounts of material could be weighed off as to give the desired concentration of pure coloring matter. An exception was made in the case of the Light Green S F Yellowish, the figure taken for pure coloring matter in this product being that obtained by titration with standard titanium trichloride solution,<sup>29</sup> the molecular weight of the substance being considered as 792.6. The Ponceau was not the pure chemical substance described by the Green-Schultz-Julius tables under No. 56, but the mixture of isomers obtained by coupling commercial cumidine of boiling point about 220–230° C with R-salt (disodium beta-Naphthol-Disulphonate).

The chief subsidiary coloring matters in the samples were determined and found not to exceed the percentages named below:

*Naphthol Yellow S*.—Less than 0.004 per cent Martius Yellow.

*Ponceau 3 R*.—Less than 2 per cent of azo derivatives of S-salt.

*Orange I*.—Less than 1 per cent of sulphobenzeneazo-beta-naphthol (Orange II), or sulphobenzeneazo-beta-naphthylamine.

*Amaranth*.—Less than 1 per cent of Fast Red E; less than 1 per cent of New Coccine.

*Erythrosine*.—Less than 1 per cent of Iodeosine G. (Iodine content: Observed, 57.62 per cent; theoretical, 57.70 per cent.)

*Light Green S F Yellowish*.—Less than 2 per cent of Guinea Green B, and similar lower sulphonated substances.

<sup>28</sup> The methods used for examining these products are described in U. S. Dept. of Agri., Bur. of Chem., Bulletin No. 147; U. S. Dept. of Agri., Bur. of Chem., Circular No. 113; J. Ind. and Eng. Chem., 5 (1913), p. 26; and U. S. Dept. of Agri., Bulletin No. 448.

<sup>29</sup> Knecht & Hibbert, New reduction methods in volumetric analysis, New York; 1910 and 1918.

## 2. SOLVENTS

It was desired to obtain the optical data under such conditions that it would be directly adaptable to analysis, especially to the estimation of dyes in admixture with each other. Pure water is the most convenient solvent for making the solutions of these substances and perhaps will be usually used in ordinary practical work. All of the dyes studied, however, have the properties of indicators, and as ordinary distilled water may show considerable variation in its hydrogen-ion concentration because of traces of carbon dioxide, ammonia, etc., it seemed desirable to add a sufficient amount of a salt-mixture regulator to fix the H-ion concentration within somewhat narrower limits. The solvent chosen for general use was a solution containing sodium acetate and acetic acid in the proportion of 0.01 mol of each per liter.<sup>30</sup> The acidity of this mixture is somewhat above that of pure water and is such as to bring out nearly the maximum absorptive effect of Light Green S F Yellowish, which is nearly colorless at low concentrations both in alkaline and strongly acid solutions.

The dilute acid acetate solution is more suitable than water for general use, as most common dyes are more stable chemically in slightly acid than in neutral solutions. The dyes investigated, with the exception of Light Green S F Yellowish and Erythrosine, show, however, nearly the same absorption in this mixture and in ordinary distilled water, the differences found in a very considerable number of experiments being less than the error of the individual readings. The solvent is not suitable for Erythrosine, and distilled water was employed with this dye, which, unlike the others, is most sensitive at acidities indicated by a hydrogen-ion exponent of less than seven. It is not, however, a very important dye commercially and is not often used in mixtures.

## IV. EXPERIMENTAL DATA

### 1. GRAPH FORMS AND TABLES

[See end of paper for tables and figures]

The original data—that is, the values of transmittancy (and  $-\log_{10}$  transmittancy) obtained experimentally—are shown in Figs. 11 to 64. As may be noted, the values obtained by the different methods are kept distinct. However, in order to avoid confusion, some points have occasionally been omitted on the

<sup>30</sup> The hydrogen potential of this regulator mixture is well established, especially by the thorough work of Walpole, *J. Chem. Soc.*, 105, pp. 2501, 2526; 1914.



frequency form, but all values are plotted on the wave length form, so as to afford a thorough comparison of methods. All thicknesses for a given concentration and temperature are given in one figure, but different concentrations and temperatures are put in different figures. Values of  $bck$  greater than 2.0 are indicated by the dotted lines. Usually the same set of values is given on both the wave length and frequency scales, but occasionally one or the other is omitted. Data for Orange I at  $c=100$  were obtained, but because of lack of reproducibility are not given. They were approximately what would be expected from Beer's law.

The only temperatures which were tried were 25 and 40° C. For various reasons the temperature occasionally deviated slightly from these figures, but inasmuch as the temperature change of transmittancy was found in all cases to be slight, no readings were discarded for this reason. Usually the temperature was within a few tenths of a degree of that stated. Occasionally, where no practical difference between the 25 and 40° curve was found, the 40° curve is omitted. This is noted in all cases.

In Table 1 has been summarized and recorded that part of the data which is of special interest from the analytical or theoretical standpoint. The frequencies of the maximum values of the specific transmissive index  $k$ —that is, of the absorption bands—are of primary importance from the latter standpoint. Any theory, however, to be complete must account also for the magnitude of the absorption bands; that is, the numerical values of  $k$ . In doing this, however, one should not accept the values of  $k$  unreservedly from the tables but should study them in connection with the curves, for many of the weaker bands are superposed on other bands or on the general absorption and, in fact, usually do not seem to be maxima at all. In such cases they may have large values of  $k$ , although being in reality weak absorption bands. In an attempt to partially eliminate this trouble the maximum values of  $k$  have been classed as definite and indefinite, the latter being those, usually, which appear merely as irregularities in the curve without having a true maximum value.

The values of  $k$  for homogeneous light were all obtained visually on the König-Martens spectrophotometer. They are computed from the original data and are not taken from the curves. However, a few values which did not agree closely with the curve were not used in these computations. In general, the following

wave lengths<sup>31</sup> have been found reliable: Hg, 435.8, 546.1, and 576.9 + 579.1 m $\mu$ ; He, 447.2, 471.3, 501.6, 587.6, and 667.8 m $\mu$ . Hg 404.7 + 407.8 and He 706.5 are not so reliable because of the difficulty of making observations where the eye is so insensitive. Hg 491.6 and He 492.2 have not proved satisfactory, and so are omitted entirely. Hydrogen wave lengths have not yet been tried.

The concentration and thickness were not, in all cases, such that the values of  $bck$  for the Hg and He lines were measured under the conditions of maximum photometric precision. As will be seen from an inspection of the plotted points, the measure-

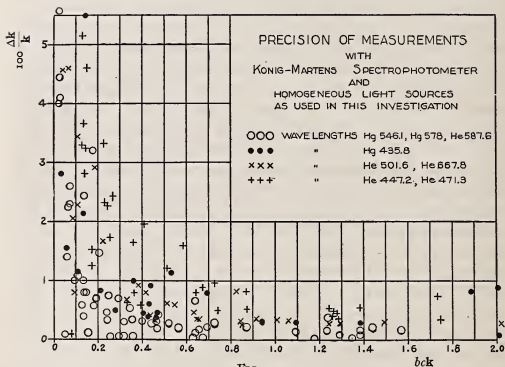


FIG. 10

ments of  $bck$  made with the König-Martens spectrophotometer and the homogeneous lights are in many cases made at low values (high values of transmittancy), for which the percentage error is likely to be high.

To obtain some indication as to the photometric precision obtained when the measurements of  $bck$  are made under the different conditions and for different wave lengths of homogeneous light, the probable error of  $k$ , designated by  $\Delta k$ , was computed from the residuals of the observed angles for each measured value

<sup>31</sup> In B. S. Tech. Papers, No. 148, will be found descriptions of selective ray filters by which some of these lines, and others, may be isolated for use with a simple photometer.

of  $bck$ , and the ratio  $\frac{\Delta k}{k}$  plotted as shown in Fig. 10. For the brighter lines, Hg 546.1, Hg 576.9+579.1, Hg 435.8, He 501.6, He 587.6, the percentage error is practically constant for values of  $bck$  between 0.3 and 2.0. For He 667.8, and particularly He 447.2 and 471.3, for which the field brightness is less, the percentage error is larger and increases more rapidly as the lower values of  $bck$  are approached. Several measurements made at values of  $bck$  between 2.0 and 3.0 indicate that the percentage error remains practically constant in that interval. In Tables 1 and 2 all values for which the measurements were made at  $bck < 0.4$  are marked with an asterisk (\*).

Thus, the values of  $k$  in Table 1, obtained with homogeneous light, are not necessarily the best possible set of values for use in chemical analysis. In Table 2 are given values chosen with special regards to the needs of the analytical chemist, the color being also given for convenience in analysis. All data available from this investigation, obtained by different methods with both heterogenous and homogeneous light sources and at different concentrations and thicknesses, have been considered. Only values of  $bck$  greater than 0.4 (except as indicated in the table) were used, and where two or more values were available their relative accuracy was estimated and weights assigned accordingly. Values for Hg 576.9 and 579.1 were all taken from the curves.

## 2. STATEMENT OF ACCURACY

It is of course difficult to make any general statement of the accuracy of work of this kind, and whatever statements are made apply to the dyes as analyzed. Errors in method have, we believe, been eliminated from the König-Martens spectrophotometer when homogeneous light is used.

It is probably true, therefore, that the possible errors in the values of  $k$  in Table 2 are principally experimental; that is, those arising from making and manipulating the solutions, and the usual errors of observation. The significant figures of this table have been chosen very carefully and are the best indication of our opinion of the reliability of the values of  $k$  as therein given. This is also true of the maximum and minimum values of  $k$  given in Table 1. The values of  $k$  for homogeneous light in these tables, however, have been computed directly from the data sheets, and thus give, in general, one more than the correct number of figures from the accuracy standpoint.

From a consideration of the data given in Tables 1 and 2 we believe the following statements to be true:

(1) In Table 2, excepting 8 very small values, the remaining 55 values of  $k$  are accurate within  $\pm 4$  per cent, and all but 4 of these 55 values are accurate within  $\pm 3$  per cent.

(2) In the same table, excepting 16 small values—i. e., 16 of those having one or more decimals before the first significant figure—all but 1 of the remaining 47 values of  $k$  are accurate within  $\pm 2$  per cent.

(3) In Table 1 the values of  $k$  for homogeneous light are not quite as accurate as those of Table 2.

(4) In Table 1 the definite maximum values of  $k$  (where two or more significant figures are given) are accurate within  $\pm 3$  per cent in the visible, but in the ultra-violet, because of certain characteristics of the method, the uncertainty may often be greater than this.

(5) In Table 1 the wave length and frequency of the definite maximum values of  $k$  for the visible are accurate within  $\pm 1$  unit of either, in the ultra-violet within  $\pm 2$  to 5 units of frequency and  $\pm 1$  unit of wave length.

## V. DISCUSSION OF RESULTS

As noted in the introduction, it is not the purpose of this paper to enter into any discussion as to the application to chemical analysis of the methods and data herein presented, nor is any theoretical discussion possible as regards the relation between chemical constitution and absorption. These seven dyes obviously were not chosen with this end in view. This is primarily an introductory paper to outline the scope of the investigation and the methods of obtaining and presenting the data. For this purpose the seven food dyes, differing widely in type of absorption and in chemical nature, were a very suitable collection, and the data obtained are applicable to practical chemical estimation of these substances.

The only similarity in the group seems to be the high transmittancy and lack of bands in the infra-red from frequencies 400 to 220 (750 to 1360  $m\mu$ ). Certain frequency relations have been observed between the absorption bands in the visible and ultra-violet which will doubtless be of theoretical or other value when data on a larger number of substances are available. For example, Light Green S F Yellowish has strong bands at frequencies 473, 706, 945, which values are almost exact multiples of 236. But there is no trace of a band at 236. Other observations, however,

which are of more immediate value in analysis, are presented in this section. These are (1) the effect of temperature, (2) deviation from Beer's law, and (3) comparisons between our data and those of other observers.

1. As regards the effect of temperature upon absorption in this investigation it should be clearly understood that the object of testing the dyes at different temperatures is not to obtain accurate measurements of the effect. If such were the case, a much larger range of temperature would, of course, be used. The purpose has been to see whether or not for analytical purposes it would be necessary to control the temperature of the dye closely or whether the room temperature of the ordinary laboratory is suitable. So far as the seven dyes of this paper are concerned, the latter is the case, except possibly with indigo in the ultra-violet. A study of the temperature changes shown in Table 1 by the unstarred homogeneous light values and the definite maximum values of  $k$  shows that the usual effect is a decrease in  $k$  with increase in temperature, the average value of this decrease being within experimental error. In some cases, however, this decrease is quite definite. It may be noted that the change of volume resulting from increasing temperature should cause a slight decrease in  $k$ .

The effect of temperature upon the transmission of glasses, crystals, organic and inorganic solutions, etc., has been widely studied and the effects are widely different. It is sufficient to say that little if any change in transmissive properties of substances similar to these dyes has been noted except for much larger ranges of temperature.

2. Beer's law, stated briefly, is to the effect that the specific transmissive index  $k$  is a constant regardless of thickness or concentration. As regards thicknesses, no deviation larger than experimental error has been detected in this investigation. This is well illustrated by the curves and, in fact, is often used to test the accuracy of the data. A study of these and Table 1 also shows no changes in  $k$  certainly larger than experimental error in the range of concentration from 1 to 10, with perhaps one or two exceptions. For the higher concentrations—100 and 1000—there is, for all the dyes, except Light Green S F Yellowish, an increase in the value of  $k$  over what would be expected if Beer's law held for the whole range of 1 to 1000.

3. Data on one or more of these 7 dyes have been found in papers or atlases by several authors. Mathewson <sup>22</sup> gives values

<sup>22</sup> See footnote 3.  
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of the specific transmissive index for all 7 dyes at fairly close intervals through the visual spectrum; Uhler and Wood<sup>33</sup> give wedge photographs of 6 out of the 7 dyes in the visible (continuous-spectrum source) and ultra-violet (spark-spectrum source) among a large number of dyes and other substances; Mees<sup>34</sup> gives wedge photographs in the visible of 3 of these dyes; Massol and Faucon<sup>35</sup> give data and curves in the visible and ultra-violet obtained by Hartley's qualitative method on these and other dyes authorized for use in France as coloring matter in confectionery; Hartley<sup>36</sup> gives qualitative data on Orange I in the visible and ultra-violet; Johnson and Spence<sup>37</sup> give data on Erythrosine (not in solution) in the infra-red beyond the range of the present investigation.

The data given by Hartley and by Massol and Faucon seem to be of little value in the ultra-violet. Hartley's method, used by these investigators, of observing the edges of the bands at different concentrations or thicknesses is in no way quantitative, in spite of the great amount of work which has been done by this method in connection with studies on the relation between absorption and chemical constitution. It affords fairly definite values as to the wave lengths of sharp bands in the visible where a continuous spectrum has been used, but broad or weak bands can be located only approximately, and in the ultra-violet, where a discontinuous or line spectrum has been almost universally used, whole bands are often overlooked, while it is almost impossible to locate even the strongest with accuracy.

This latter objection—the use of any but a continuous source in the ultra-violet—also applies to the data given by Uhler and Wood. These wedge photographs, not intended to be quantitative, are very good in a qualitative way wherever a continuous spectrum is employed. The atlases by Uhler and Wood and by Mees give this sort of data on a large number of dyes.

The paper by Mathewson is the only one which presents data comparable with the data presented herein, and this for the visible only. Values of  $k$  obtained by him are quite similar to those of this paper; but, inasmuch as the solvent used was slightly different from the acetate mixture employed in the present investigation, they are not given here.

<sup>33</sup> Atlas of absorption spectra, Carnegie Inst. of Washington, Pub. No. 71; 1907.

<sup>34</sup> An atlas of absorption spectra, Longmans, Green & Co.; 1909.

<sup>35</sup> Bull. de la Société Chimique de France (4), 13, p. 217, 513, 700, and 803; 1913.

<sup>36</sup> J. of the Chem. Soc., (London), 51, p. 152; 1887.

<sup>37</sup> Phys. Rev. (2), 5, p. 349; 1915.

## VI. SUMMARY

In this paper is presented the outline of an investigation of the spectral transmissive properties of dyes. The plans and purposes of this investigation are discussed, the methods and apparatus used to obtain the data described, and a tentative nomenclature presented. Four methods are used in the experimental work—the visual method, using the König-Martens spectrophotometer; the photographic method, with Hilger sector photometer; the photoelectric null method; and the thermoelectric method. The total range of measurement is from 240 to 1360 millimicrons.

As a beginning and to illustrate the methods of obtaining and presenting the data, the transmittancies of 7 permitted food dyes have been obtained in the visible, ultra-violet, and near infra-red at different concentrations, thicknesses, and temperatures. Discussion of the analytical and theoretical applications of the data is postponed until more data are available.

## VII. TABLES AND FIGURES.

TABLE 1.—Values of the Specific Transmissive Index  $a$  ( $k = -\frac{1}{bc} \log_{10} T$ ) at Various Wave Lengths, Frequencies, Concentrations,<sup>b</sup> and Temperatures

NAPHTHOL YELLOW S (Schultz and Julius, No. 4)

By Homogeneous Source

Frequency vibrations (seconds 10 <sup>12</sup> )	Wave length (millimicrons)	Specific transmissive index (k) at—					
		Temperature, 25° C for—				Temperature, 40° C for—	
		Concentrations of pure dye—					
		1 cg/l	10 cg/l	100 cg/l	1000 cg/l	1 cg/l	10 cg/l
He 449.3	667.8				*0.0000052		c*0.000005
He 510.5	587.6				*.0000143		c*.000014
Hg 518.0	579.1						
Hg 520.0	576.9				*.0000184		
Hg 549.4	546.1		*0.0001 <sub>5</sub>	*0.00011	.0001292		
He 598.1	501.6		*.0100	.01063			
He 636.5	471.3	0.146					
He 670.8	447.2	.404					
Hg 688.4	435.8	.468					

Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
700	429	0.49 <sub>2</sub>	.....	.....	.....	.....
763	393	.48	.....	.....	.....	.....
1165	257	.49	.....	.....	.....	.....
Maximum-indefinite						
950	313	.14	0.140	.....	.....	.....
1040	288	.28	.....	.....	.....	.....
Minimum-definite						
738	407	.45	.....	.....	.....	.....
900	333	.08 <sub>6</sub>	.087	.....	.....	.....

<sup>a</sup> All values for which the measurements were made at  $bck < 0.4$  are marked with an asterisk. They are less reliable than the other values.

<sup>b</sup> The solvent used was the acetate mixture described in III-2 except for Erythrosine, where distilled water was used.

<sup>c</sup> These values are for concentrations equal to 1000 instead of 10.



TABLE 1—Continued  
ORANGE I (Schultz and Julius, No. 85)  
By Homogeneous Source

Frequency vibrations (seconds 10 <sup>13</sup> )	Wave length (millimicrons)	Specific transmissive index (k) at—					
		Temperature, 25° C for—				Temperature, 40° C for—	
		Concentrations of pure dye—					
		1 cg/l	10 cg/l	100 cg/l	1000 cg/l	1 cg/l	10 cg/l
He 449.3	667.8	.....	*0.0016	0.00162	.....	.....	
He 510.5	587.6	.....	*.0130	.....	*0.010	.....	
Hg 518.0	579.1	.....	.....	.....	.....	.....	
Hg 520.0	576.9	} *0.0196	*.0196	.....	*.011	.....	
Hg 549.4	546.1	} *.099	.1097	.....	*.091	.....	
He 598.1	501.6	.649	.....	.....	.630	.....	
He 636.5	471.3	.873	.....	.....	.854	.....	
He 670.8	447.2	.640	.....	.....	.627	.....	
Hg 688.4	435.8	.471	.....	.....	.473	.....	

## Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
632	475	0.88 <sub>2</sub>	.....	.....	.....	0.85
1120	268	.37 <sub>2</sub>	.....	.....	.....	.36 <sub>2</sub>
Maximum-indefinite						
900	333	.19	.....	.....	.....	.20
1030	291	.32	.....	.....	.....	.33
Minimum-definite						
810	370	*.05 <sub>2</sub>	.065	.....	.....	*.06 <sub>2</sub>
1195	251	.25	.....	.....	.....	.24

## PONCEAU 3R (Schultz and Julius, No. 56)

## By Homogeneous Source

He 449.3	667.8	.....	*0.0001	.....	.....	*0.0005	.....
He 510.5	587.6	.....	*0.008	*.0139	.....	*.007	.....
Hg 518.0	579.1	.....	.....	.....	.....	.....	.....
Hg 520.0	576.9	.....	*.018	*.0292	.....	*.017	.....
Hg 549.4	546.1	.....	.294	.....	.....	.290	.....
He 598.1	501.6	.....	.508	.....	.....	.494	.....
He 636.5	471.3	.....	.321	.....	.....	.309	.....
He 670.8	447.2	.....	.170	.1738	.....	.....	.....
Hg 688.4	435.8	.....	.134	.1382	.....	.130	.....

## Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
595	504	0.51	.....	.....	.....	0.50
910	329	.18 <sub>2</sub>	0.168	.....	.....	.19
Maximum-indefinite						
560?	535?	.....	.....	.....	.....	.....
765	392	.13	.128	.....	.....	.13
1020	294	.16	.144	.....	.....	.16
Minimum-definite						
830	361	.11	.106	.....	.....	.11
985	305	.14	.113	.....	.....	.13

TABLE 1—Continued

AMARANTH (Schultz and Julius No. 107)

By Homogeneous Source

Frequency vibrations (seconds 10 <sup>12</sup> )	Wave length (millimicrons)	Specific transmissive index (k) at—					
		Temperature, 25° C for—				Temperature, 40° C for—	
		Concentrations of pure dye—					
		1 cg/l	10 cg/l	100 cg/l	1000 cg/l	1 cg/l	10 cg/l
He 449.3	667.8	.....	*0.0008	*0.00072	0.000822	.....	.....
He 510.5	587.6	*0.060	.0654	.....	.....	*0.060	0.0632
Hg 518.0	579.1	.119	.1231	.....	.....	.117	.....
Hg 520.0	576.9	.346	.3398	.....	.....	.337	.....
Hg 549.4	546.1	.385	.....	.....	.....	.....	.....
He 598.1	501.6	.219	.....	.....	.....	.....	.....
He 636.5	471.3	.126	.1258	.....	.....	.....	.....
He 670.8	447.2	.108 <sub>5</sub>	.1091	.....	.....	.109	.....
Hg 688.4	435.8	.....	.....	.....	.....	.....	.....

Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
576	521	0.42 <sub>5</sub>	.....	.....	.....	0.41 <sub>5</sub>
905	332	.16	0.168	.....	.....	.....
Maximum-indefinite						
1050	286	.22	.....	.....	.....	.....
Minimum-definite						
805	373	.....	.078	.....	.....	.....
980	306	.....	.141	.....	.....	.....

ERYTHROSINE (Schultz and Julius No. 517)

By Homogeneous Source

He 449.3	667.8	.....	.....	*0.000009	.....	.....
He 510.5	587.6	*0.001	.....	*0.00192	.....	.....
Hg 518.0	579.1	.....	*0.0018	.00643	.....	*0.004
Hg 520.0	576.9	.267 <sub>5</sub>	.2636	.....	.....	.284
Hg 549.4	546.1	.427	.....	.....	.....	.419
He 598.1	501.6	*.136	.1261	.....	.....	*.116
He 636.5	471.3	*.043	*.0399	.....	.....	*.088
He 670.8	447.2	*.032	*.0277	.....	.....	*.029
Hg 688.4	435.8	.....	.....	.....	.....	.....

Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
570	526	1.13	.....	.....	.....	1.13
855	351	*.05 <sub>5</sub>	0.056	.....	.....	*.06
970	309	.16 <sub>5</sub>	.165	.....	.....	.16
1150	261	.43	.....	.....	.....	.41
Maximum-indefinite						
610	492	.35	.....	.....	.....	.35
725	414	*.03	.023	.....	.....	0.023
Minimum-definite						
780	385	*.02	.015	0.0152	.....	*.02
890	337	*.04 <sub>5</sub>	.049	.....	.....	*.05
1040	288	.14	.128	.....	.....	.13

TABLE 1—Continued  
INDIGO DISULPHO ACID (Schultz and Julius No. 692)

By Homogeneous Source

Frequency vibrations (seconds 10 <sup>12</sup> )	Wave length (millimicrons)	Specific transmissive index (k) at—					
		Temperature, 25° C for—				Temperature, 40° C for—	
		Concentrations of pure dye—					
		1 cg/l	10 cg/l	100 cg/l	1000 cg/l	1 cg/l	10 cg/l
He 449.3	667.8	0.055	0.0622				
He 510.5	587.6	.360					
Hg 518.0	579.1	.309				0.306	
Hg 520.0	576.9						
Hg 549.4	546.1	.157				.157	
He 598.1	501.6	.046	.0457				
He 636.5	471.3	*.036	.0361				
He 670.8	447.2	*.037	.0367				
Hg 688.4	435.8	*.036	.0350			*.037	

Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
492	610	0.44				0.43 <sub>5</sub>
660	455	*.03 <sub>5</sub>	0.036			
1045	287	.76				.71 <sub>5</sub>
1190	252	.52				.46
Maximum-indefinite						
870	345	.23				.22
985	305	.58				.52
Minimum-definite						
632	475	*.036	.035 <sub>5</sub>			
745	403	*.02 <sub>5</sub>	.029			
1130	265	.35				.29 <sub>5</sub>

LIGHT GREEN S F YELLOWISH (Schultz and Julius No. 435)

By Homogeneous Source

He 449.3	667.8	0.321				*0.339
He 510.5	587.6	.441				*.456
Hg 518.0	579.1					
Hg 520.0	576.9	.340				*.366
Hg 549.4	546.1	.102				*.123
He 598.1	501.6	*.017	*0.0166	0.01499		*.019
He 636.5	471.3	*.020	*.0248			*.015
He 670.8	447.2	.125	.1386			*.129
Hg 688.4	435.8	.202	.2066			*.223

Maximum and Minimum Values—by Heterogeneous Source

Maximum-definite						
473	634	1.13				1.17
706	425	.23	0.223			.22 <sub>5</sub>
945	318	.31 <sub>5</sub>				.31 <sub>5</sub>
Maximum-indefinite						
Minimum-definite						
615	488	*.013	.012	0.0117		*.01
845	355	*.03 <sub>5</sub>	.040			*.03 <sub>5</sub>
1090	275		.128			.13

TABLE 2.—Specific Transmissive Indices of the Permitted Food Colors

Values chosen especially for use in chemical analysis. They were obtained by a careful consideration of all the data available from this investigation at these wave lengths. (See sec. IV—1). Only measured values of *bck* greater than 0.4 were used, except as indicated below by an asterisk (\*).

Name of dye <sup>a</sup>		Specific transmissive index (k) at wave lengths (mμ)								
		Hg 435.8	He 447.2	He 471.3	He 501.6	Hg 546.1	Hg 576.9	Hg 579.1	He 587.6	He 667.8
Naphthol Yellow S	k	0.47 <sub>5</sub>	0.40 <sub>5</sub>	0.150	0.0106	0.00013	*0.00002	*0.00002	*0.00001	*0.00001
	colog	.323	.393	.824	1.975	3.886	4.7	4.7	5.	5.
Orange I	k	.47	.64	.88	.65	.110	.021	.019	.013	*.001 <sub>5</sub>
	colog	.328	.194	.055	.187	.958	1.678	1.721	1.886	2.82
Ponceau 3 R	k	.137	.171	.32	.51	.29 <sub>5</sub>	*.032	*.027	*.014	.0001 <sub>5</sub>
	colog	.863	.767	.495	.292	.530	1.495	1.568	1.854	3.824
Amaranth	k	.109	.126	.22	.38 <sub>5</sub>	.34 <sub>5</sub>	.130	.115	.065	.0008 <sub>5</sub>
	colog	.962	.900	.657	.414	.462	.886	.939	1.187	3.07
Erythrosine	k	.027 <sub>5</sub>	.040	.126	.42 <sub>5</sub>	.264	.0075	.0058	*.0019	*.00001
	colog	1.561	1.398	.900	.372	.578	2.125	2.237	2.721	5.
Indigo Disulpho Acid	k	.035	.036 <sub>5</sub>	.036	.046	.157	.31	.32	.36	.062
	colog	1.456	1.438	1.444	1.337	.804	.509	.495	.444	1.208
Light Green S F Yellowish	k	.204	.132	.024	.016	.100	.33	.35	.44	.32
	colog	.690	.879	1.620	1.796	1.000	.481	.456	.356	.495

<sup>a</sup> Acetate mixture was used as a solvent for all but Erythrosine, for which water was used.

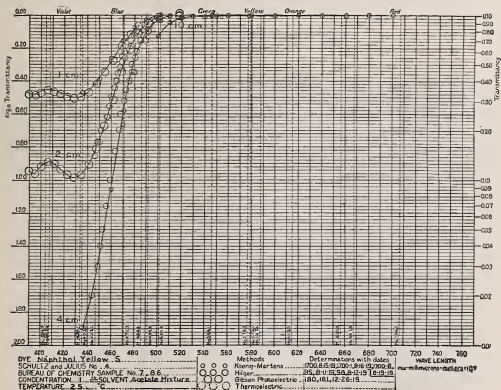


FIG. 11.—Transmittancy curves for Naphthol Yellow S



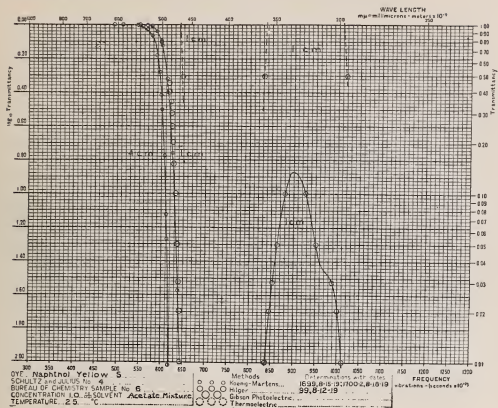


FIG. 14.—Naphthol Yellow S

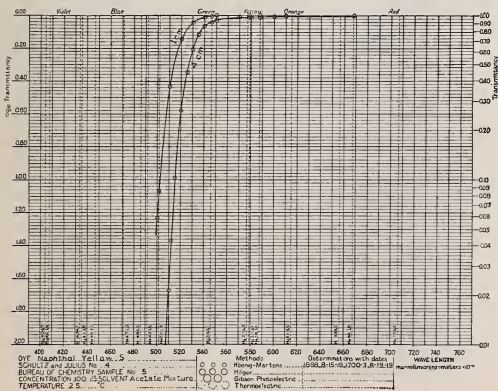


FIG. 15.—Naphthol Yellow S



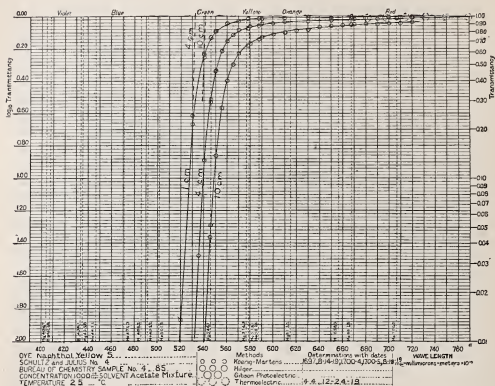


FIG. 16.—Naphthol Yellow S

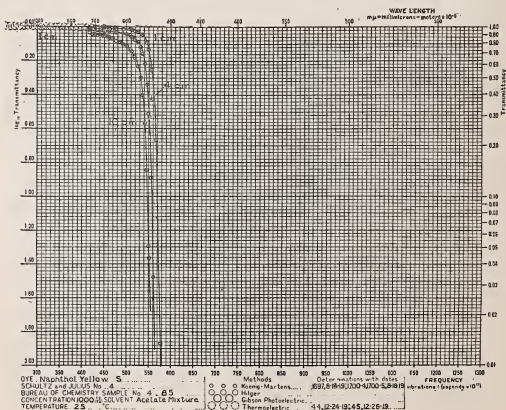


FIG. 17.—Naphthol Yellow S



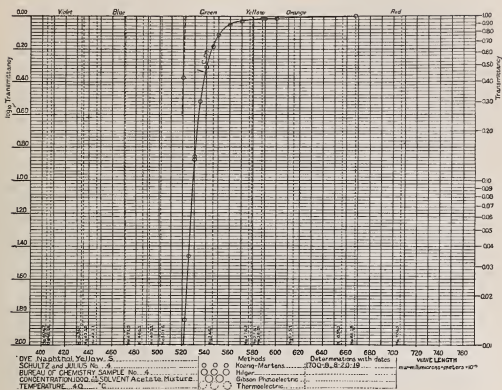


FIG. 18.—*Naphthol Yellow S*

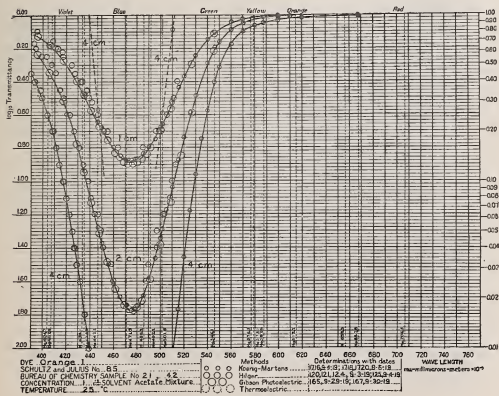


FIG. 19.—Orange I

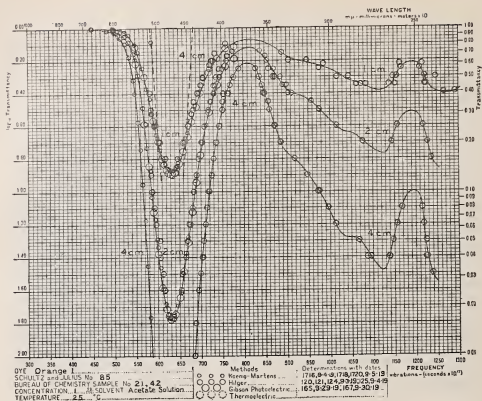


FIG. 20.—Orange I

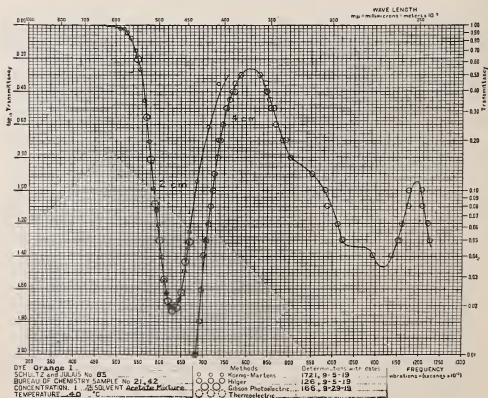


FIG. 21.—Orange I

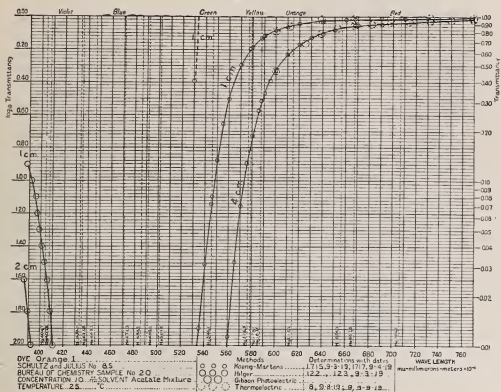


FIG. 22.—Orange I

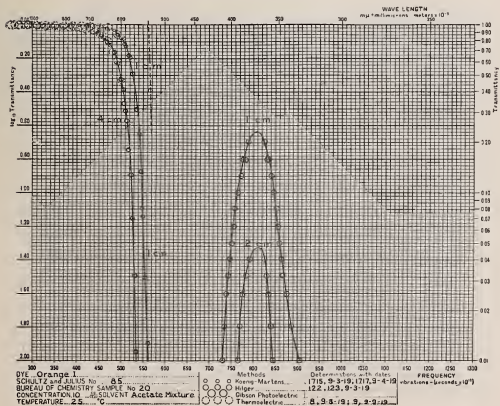


FIG. 23.—Orange I

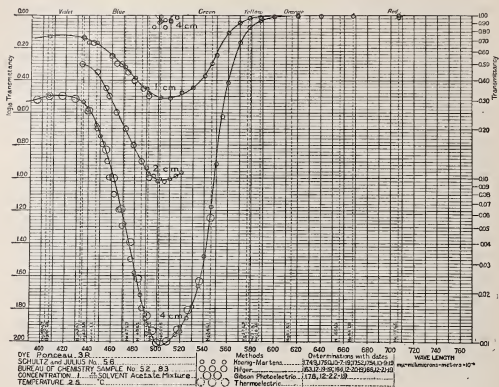


FIG. 24.—Ponceau 3R

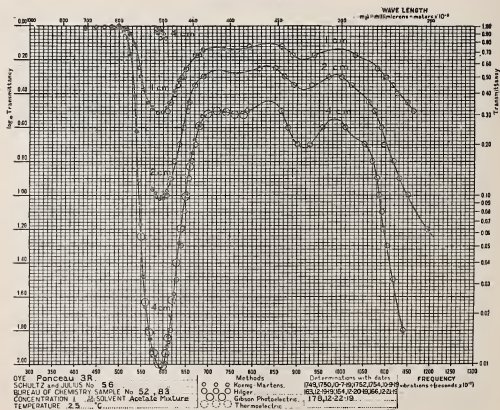


FIG. 25.—Ponceau 3R



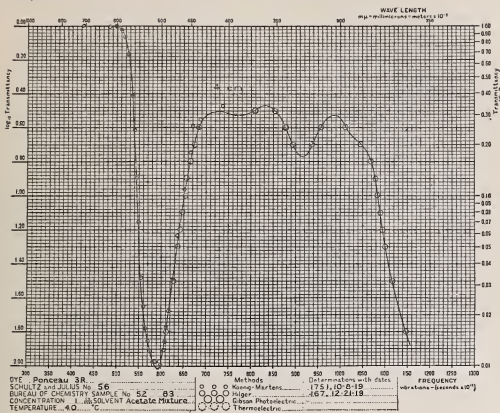


FIG. 26.—Ponceau 3R

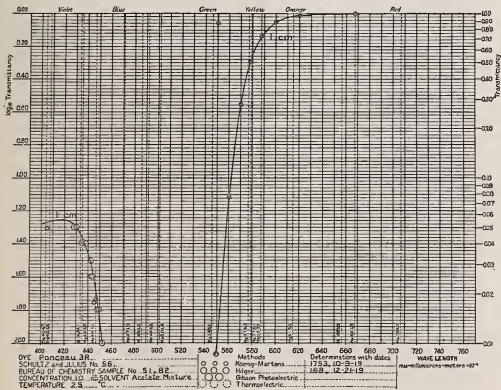


FIG. 27.—Ponceau 3R

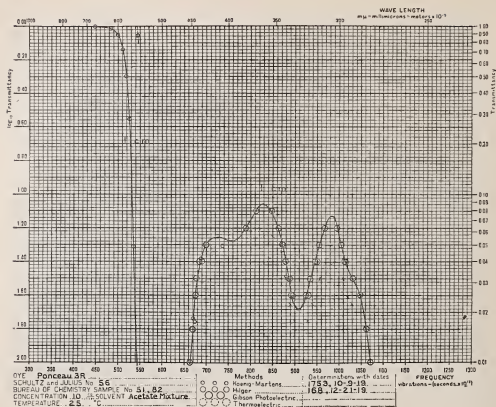


FIG. 28.—Ponceau 3R

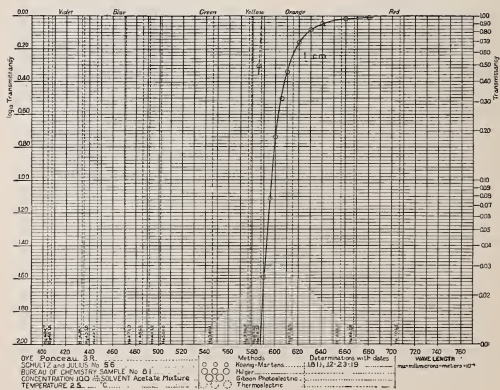


FIG. 29.—Ponceau 3R

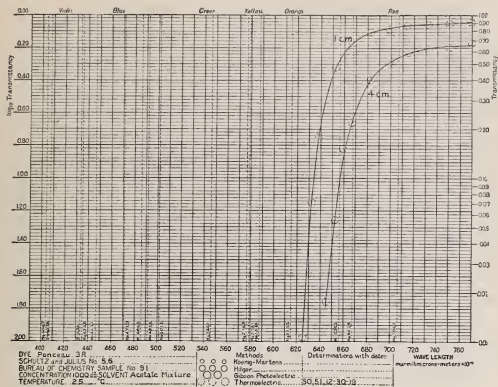


FIG. 30.—Ponceau 3R

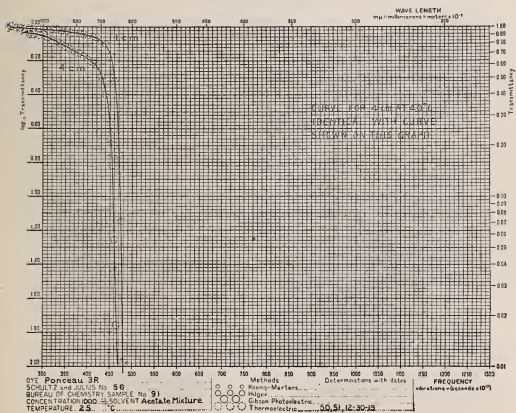


FIG. 31.—Ponceau 3R





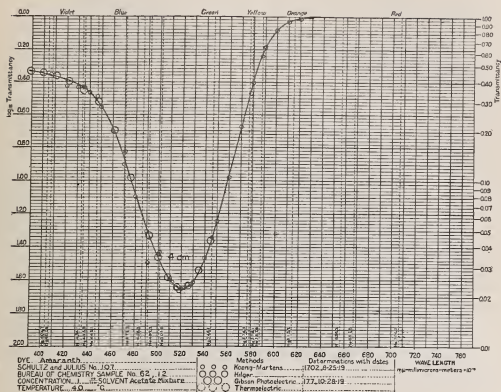


FIG. 34.—Amaranth

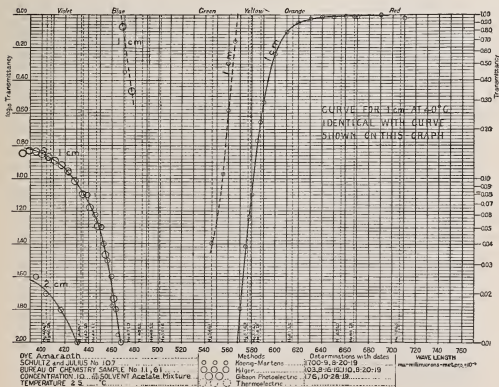


FIG. 35.—Amaranth

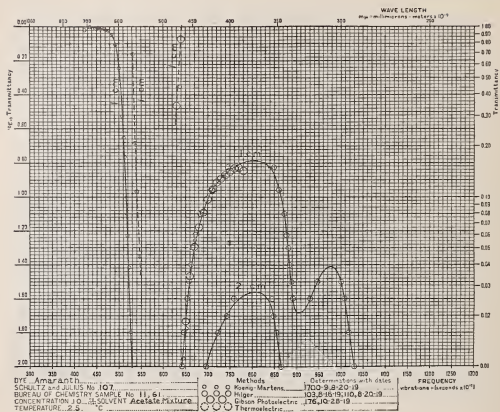


FIG. 36.—Amaranth

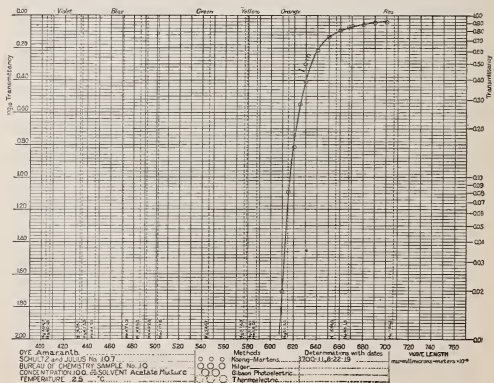


FIG. 37.—Amaranth

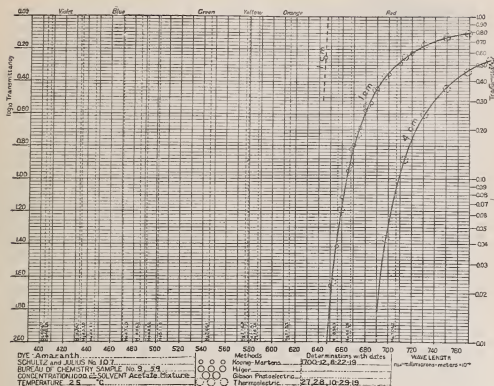


FIG. 38.—Amaranth

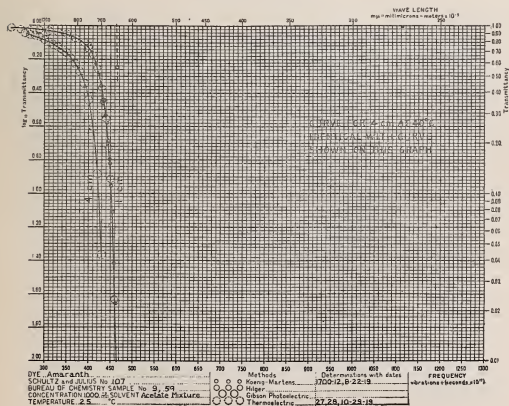


FIG. 39.—Amaranth

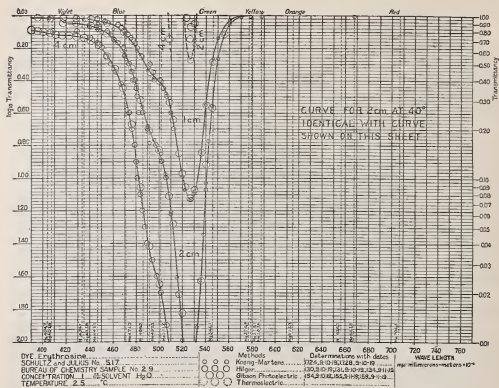


FIG. 40.—Erythrosine

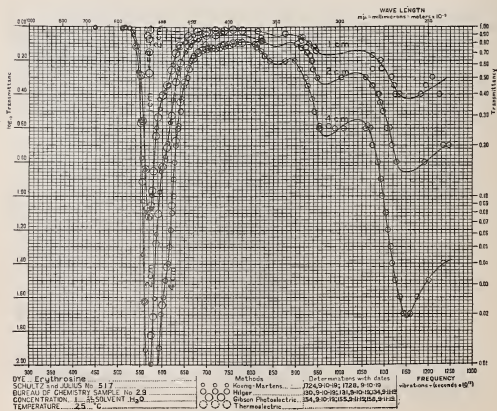


FIG. 41.—Erythrosine



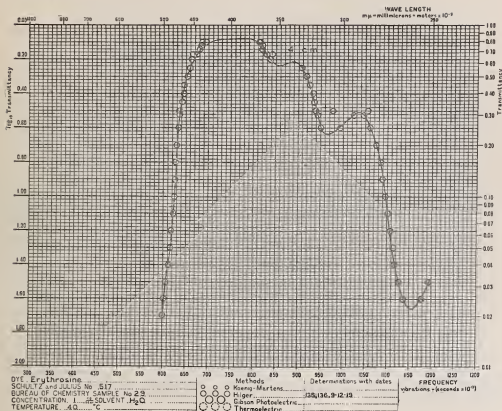


FIG. 42.—Erythrosine

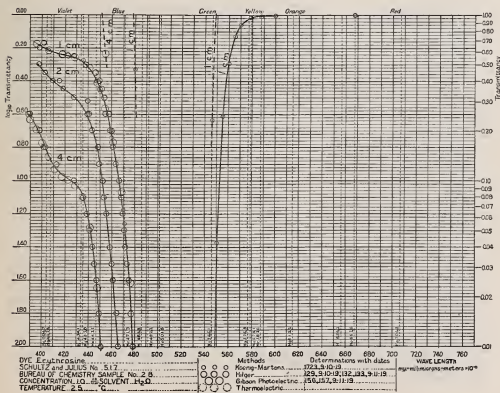


FIG. 43.—Erythrosine

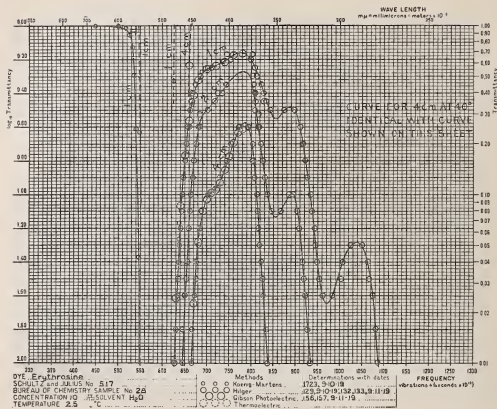


FIG. 44.—Erythrosine

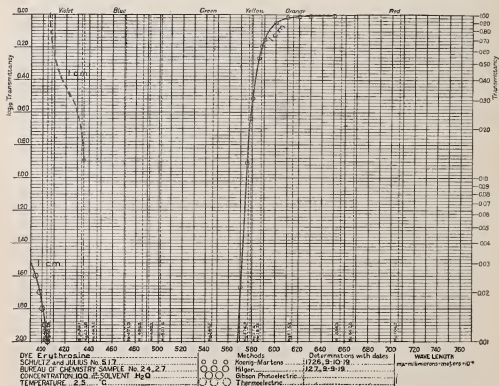


FIG. 45.—Erythrosine



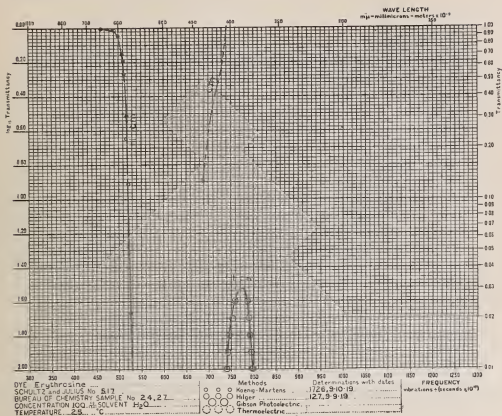


FIG. 46.—Erythrosine

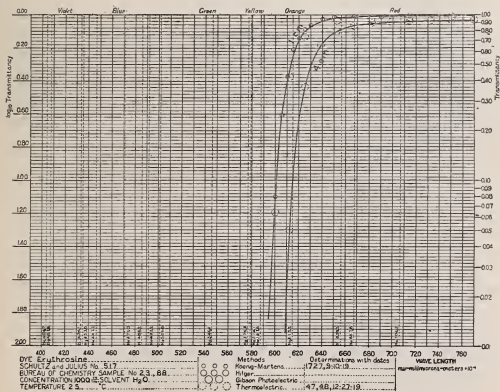


FIG. 47.—Erythrosine

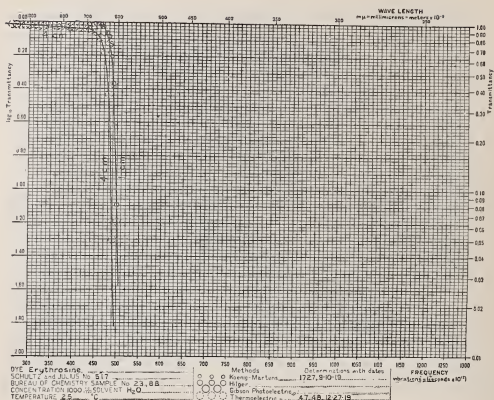


FIG. 48.—Erythrosine

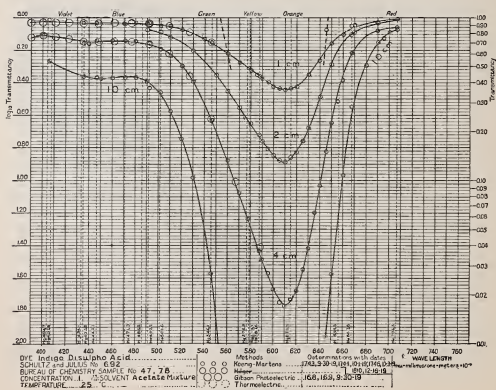


FIG. 49.—Indigo Disulpho Acid

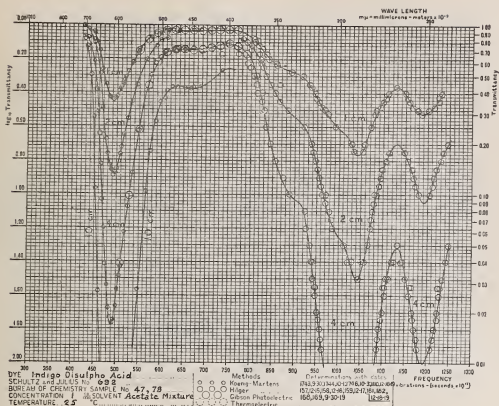


FIG. 50.—Indigo Disulpho Acid

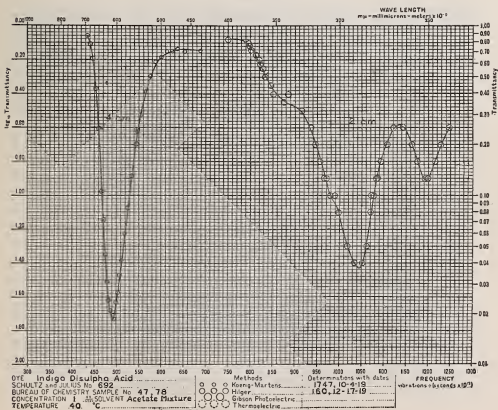


FIG. 51.—Indigo Disulpho Acid

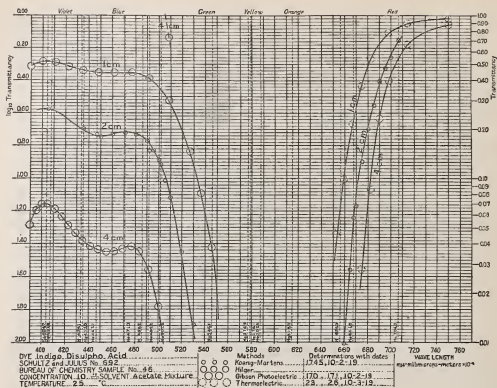


FIG. 52.—Indigo Disulpho Acid

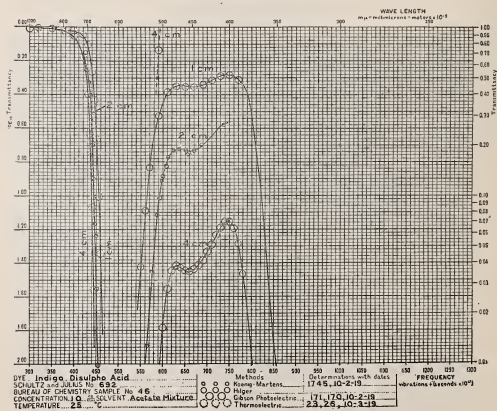


FIG. 53.—Indigo Disulpho Acid



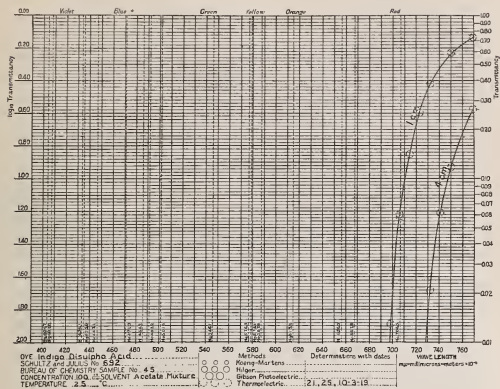


FIG. 54.—Indigo Disulpho Acid

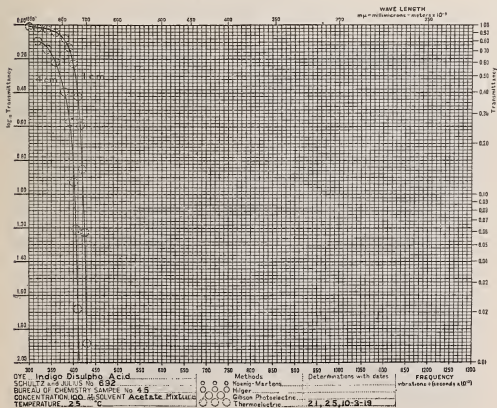


FIG. 55.—Indigo Disulpho Acid



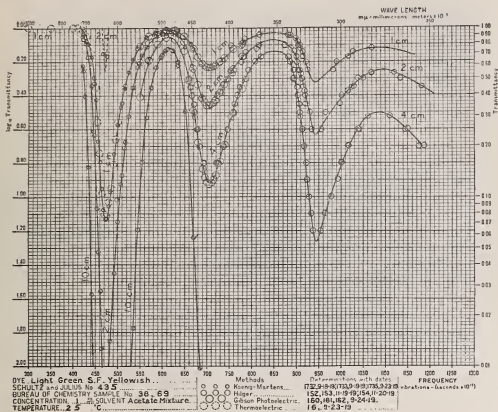
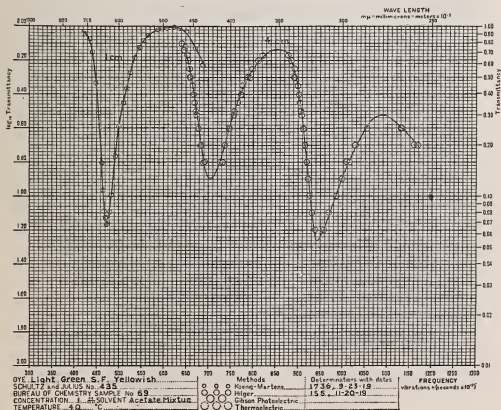


FIG. 58.—*Light Green S F Yellowish*





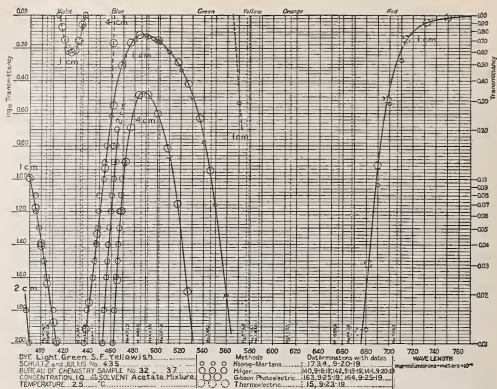


FIG. 60.—Light Green S F Yellowish

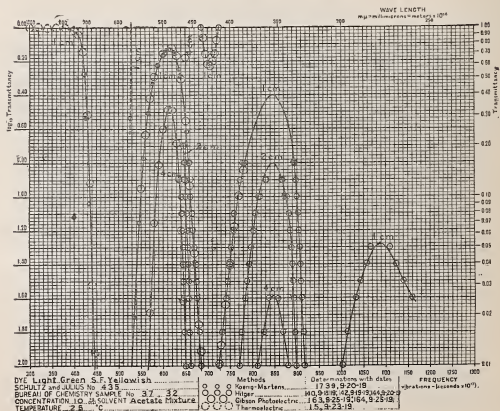


FIG. 61.—Light Green S F Yellowish

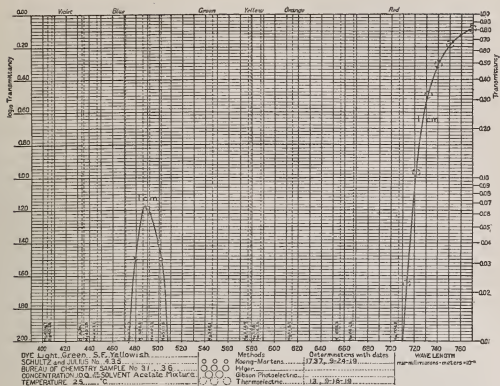
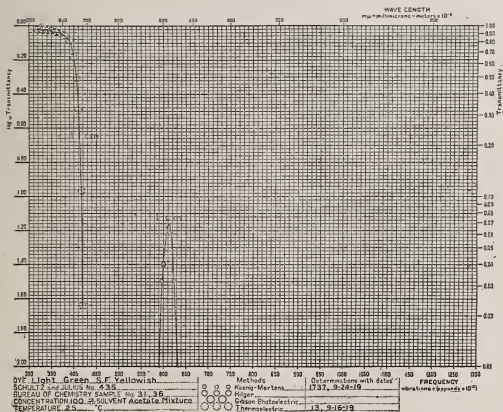


FIG. 62.—*Light Green S F Yellowish*



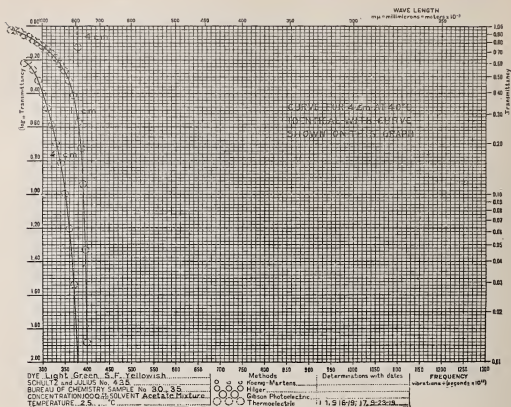


FIG. 64.—*Light Green S F Yellowish*

WASHINGTON, July 19, 1921.