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PHOTOELECTRIC "COLORIMETERS"

The recent advent of the "barrier-layer" type of photoelectric cell has furnished the incentive for the design and manufacture of a considerable number of photoelectric instruments advertised as colorimeters, color matchers, color comparators, or color analysers, as well as others advertised under trade names which include "color" as an integral part. In addition, there are several similar instruments which are advertised to measure transmission, reflectance, opacity, turbidity, or other similar quantities and which in some cases extend their range of application by the use of selective spectral filters. Likewise there are similar instruments in which the electron-emission type of cell is used, requiring an external voltage supply, but which are otherwise similar in purpose and scope to those noted above.

The bureau is often requested to advise regarding the suitability and reliability of such instruments. Although but two or three of these instruments have been examined or used at the bureau, it is obvious from the descriptive material available that various features are common to many of them and it is readily possible to point out certain of the advantages and limitations of these photoelectric instruments without having had personal experience with them.

It should be noted at the outset that the present discussion does not include the subject of spectrophotometers, except as some of the instruments noted may be considered as abridged spectrophotometers. It is generally recognized that accurate spectrophotometric data when accompanied by adequate colorimetric computations, comprise the most fundamental of all colorimetric specifications. With most spectrophotometers, however, the obtaining of such data and specifications requires considerable time. It is because of their relative speed and simplicity of operation, combined with the fact that fundamental data and specifications are often not needed, that the photoelectric "colorimeters" have such an appeal (1).

(1) For general information regarding colorimetry and spectrophotometry, the reader should consult the following publications:

1. Optical Society of America Committee on Colorimetry, L. T. Troland, Chairman, Report for 1920-21, J. Opt. Soc. Am. and Rev. Sci. Inst., 6, 527 (1922).
2. Judd, Deane B., The 1931 I.C.I. Standard Observer and Coordinate System for Colorimetry, J. Opt. Soc. Am. 23, 359 (1933).

3. Optical Society of America Committee on Colorimetry, L. A. Jones, Chairman, Eastman Kodak Company Rochester, N. Y. Report in preparation.

4. Hardy, Arthur C., Handbook of Colorimetry, The Technology Press, Cambridge, Mass., 1936.

5. Optical Society of America Committee on Spectrophotometry, K. S. Gibson, Chairman, Report for 1922-23, J. Opt. Soc. Am., 10, 169 (1925).

6. Gibson, K. S., The Use of the Photoelectric Cell in Spectrophotometry, Photoelectric Cells and Their Applications (The Physical and Optical Societies, London, England; also obtainable from Adam Hilger, Ltd., London), p. 157, 1930.

7. Ives, H. E., and Kingsbury, E. F., The Applicability of Photoelectric Cells to Colorimetry, J. Opt. Soc. Am. 21, 541 (1931).

8. Gibson, K. S., Visual Spectrophotometry, J. Opt. Soc. Am., 24, 234 (1934).

The primary purpose of these photoelectric "colorimeters", reflectometers, opacimeters, etc., is in most cases to obtain, by photoelectric methods, data which will agree with similar data obtained visually or which will correlate with the results of visual grading. This is obviously true of most of these instruments which are claimed to give a measurement of color. It is likewise true of those instruments designed to measure illumination, reflectance, opacity, and turbidity, for there would be little interest in the readings so obtained if they were not thought to agree, at least approximately, with corresponding visual determinations. Why then is it desired to "eliminate the human eye", if it is, after all, visual values which are sought? The reason is, of course, that photoelectric instruments can be made to operate with greater speed and precision and are less tedious to use over an extended period of time than similar visual instruments. These advantages are considerable and if reliable results are at the same time obtainable the instrument becomes a very useful tool for testing and control work. It is, therefore, of importance to note the various factors which must be considered if a photoelectric instrument is to give results in agreement with visual data, or is to be judged suitable and reliable on the basis of some other criterion. It is convenient to discuss these factors under four headings which will be considered in turn, viz., (1) the use of the photoelectric cell to determine values of luminous quantities, (2) its use with spectral filters in abridged spectrophotometry, (3) its use in the various types of "colorimeters", and (4) miscellaneous factors affecting the reliability of such instruments.

1. The Use of the Photoelectric Cell to Determine Values of Luminous Quantities.

Such quantities are illumination, luminous reflectance, opacity, turbidity, etc., which are associated with the brilliance of the light or the lightness of the color, but not with the chromaticity in either case. Visually, they depend upon the operation of the so-called spectral visibility (luminous efficiency) curve of the human eye, but not upon the chromatic sense of the observer. This visibility curve expresses the relation between light and energy throughout the visible spectrum, the visibility of energy being a maximum in the yellow-green and becoming zero in the ultraviolet and infra-red parts of the spectrum. When radiant energy enters the eye it is automatically weighted according to the visibility curve. The observer is, however, unable to assign any but the crudest absolute value to this visibility-weighted energy, which is called light or luminous energy. Nevertheless, by the usual photometric procedure, which by necessity employs a null method, he is able to determine relative light quantities -- with considerable precision if they are of the same chromaticity and with less precision if they are of different chromaticities, the lack of precision increasing with the difference in chromaticities.

It is well known that the visibility curves of any two observers may differ notably in relative value through the spectrum (2). When, therefore, the relative intensities of two

(2) See, for example, the composite plot of the visibility curves of 125 individuals, published by Coblentz and Emerson, BS Sci. Paper No. 303, Fig. 13, 1917.

lights of differing relative spectral energy distribution are measured, even by the relatively precise method of flicker photometry, different values will be obtained by different observers and the magnitudes of the differences so obtained will depend both on the differences in spectral energy distribution of the lights compared and on the differences in spectral visibility among the observers. These differences among observers are of such importance in photometry that a standard set of visibility data representative of a normal average observer was recommended by the International Commission on Illumination in 1924 (3) and has been in use since then. Only by the use of

(3) The values adopted by the I.C.I. were those recommended by Gibson and Tyndall (BS Sci. Paper No. 475, Table 3, last column, 1923) as a result of measurements by themselves and previous investigators on a total of about 200 individual observers.

some such defining set of data can we give an immediate unambiguous answer to the problem of the relative luminous intensities of two lights of differing chromaticity or of the luminous reflectance of a chromatic surface.

Now the point to this is that the spectral response curves of the various types of photoelectric cells differ widely among themselves and in most cases from that of the standard visibility curve. In general, therefore, the values obtained with photoelectric cells will not agree with the values derived on the basis of the standard visibility data, and the degree of departure from such standard visual values will depend on the same two factors that make visual values obtained by any single observer differ, in general, from the standard visual values, viz (1) departure of the various spectral response curves of the detectors from the standard visibility curve, and (2) relative spectral selectivity in the lights compared. The importance of either factor depends upon the other as is shown in the following discussion, where the importance of the two factors is considered in turn.

(1) If the spectral response curve of a given cell duplicated the standard visibility curve exactly, being thereby zero in the ultraviolet and infra-red parts of the spectrum, it would always give correct luminous values regardless of selectivity in the luminous quantities compared. No such cell is available. It is, therefore, a question of the degree of approximation of the cell's response curve to the visibility curve. These response curves can be obtained from the manufacturers of the cells, along with other detailed information regarding their operating characteristics (4). If the spectral response of the

(4) It should be remembered, however, that a curve so supplied is merely representative of the type of cell and that the spectral response may differ considerably from one cell to another of the same make. Unless the particular cell has been subjected to individual test the values supplied by the manufacturer or dealer will not, except by accident, apply exactly to the cell purchased.

cell differs widely from the standard visibility curve, the cell should not be used to measure the luminous values of lights or objects differing considerably in spectral selectivity. In some cases, however, the response curve crudely approximates the visibility curve, or a filter is used which converts the response to an approximation of the visibility curve. Even with such an approximation that the resultant response differs from the standard visibility by no more than is to be expected for any chance observer, large errors may result if one attempts to measure the luminous transmissions or reflectances of highly selective materials. The same reasons that made it necessary to

establish a standard visibility curve for highly accurate, unambiguous measurements of lights of different chromaticities, make the use of photoelectric cells, even with a visibility filter, unsuitable for such measurements, unless very careful tests with a particular cell and filter show it to be suitable for the purpose.

(2) On the other hand, there are many types of measurement for which photoelectric cells are eminently suitable and where their speed and precision render them greatly superior to the eye. In this class are many kinds of geometrical distribution measurements, such as the measurement of the distribution of intensity about a lamp or lighting fixture, or of the distribution of reflectance at various angles from a surface, where the spectral quality of the light is unchanged throughout. Even here, however, it is doubtless best to use a cell whose response does not deviate too widely from the visibility curve, in order that unsuspected deviations in spectral quality, even though small, may introduce no important error. Likewise photoelectric cells are useful for measurements of illumination in different parts of a room under a given, constant lighting condition, although in this case one must guard against variations in spectral quality due to variations in colors of the walls, the curtains, etc. Of course, in many such cases, errors of as much as a factor of 2 may not seriously matter, in which case no such care need be exercised. The measurement of the reflectance of samples of nearly constant spectral reflectance, such as white enamels, or of the relative reflectance of two samples of nearly identical selectivity of spectral reflectance, is another problem where the photoelectric cell may prove of great usefulness, even though its spectral response differs somewhat from the standard visibility curve. The limit of such usefulness depends on the accuracy desired, the relative amount of spectral selectivity in the compared samples, and the deviations of the spectral response of the cell from the standard visibility curve. A cell which was calibrated to give reliable measurements of illumination from incandescent lights of differing chromaticities might be seriously in error in its reading for daylight illumination. A cell giving reliable results in the measurement of the reflectance of white enamels might be seriously in error in similar measurements of colored enamels; likewise with papers, paints, etc.

2. The Use of the Photoelectric Cell with Spectral Filters in Abridged Spectrophotometry.

The usefulness of the photoelectric cell or instrument containing such cell is often greatly extended by the use of filters which limit the spectral range of radiant energy incident upon the cell. The use of such filters, one after the other, affords a crude spectrophotometric analysis, similar to that obtained when a corresponding visual instrument is used with similar filters for the same purpose. Filters often used for this purpose are red, green, and blue, and because three

stimuli in additive combination are, in general, necessary and sufficient to produce and specify a color and because the stimuli often chosen produce red, green, and blue colors taken separately, it has apparently been assumed that the use of any three such filters would entitle a photoelectric instrument to be called a colorimeter. This, however, is not at all true, and the necessary conditions to be fulfilled before an instrument may legitimately be called a colorimeter (5) are discussed in the

(5) This point is noted by J. Guild, The Instrumental side of Colorimetry, J. Sci. Inst. 9, 78 (1934).

following section. In the present section will be considered the use of photoelectric instruments with selected filters as abridged spectrophotometers.

In a true spectrophotometer one is enabled by means of a prism and slits to isolate a narrow wave length band at any place in the spectrum for which the instrument and detector are suitable, and with a series of such isolated bands, each of nearly homogeneous energy, to measure relative spectral distributions of incident, transmitted, or reflected energy. Such an analysis yields a spectral transmission or reflectance curve, or a relative spectral energy curve, which if accurately obtained throughout the whole visible spectrum affords a fundamental and the only fundamental basis for general colorimetry. Contrary to the case discussed in section 1, in which the ability of the photoelectric cell to determine standard luminous quantities was considered, the shape of the spectral response curve of the detector (cell or eye) is of no consequence in spectrophotometry, provided the response is adequate for the purpose and that suitable precautions are taken to avoid slit-width and stray-light errors.

Because of the difficulty of making slit-width corrections, it is very desirable in spectrophotometry to use slits so narrow that any error introduced by the widths used is unimportant. This error, however, depends on the type of transmission or reflectance curve being measured as well as on the slit-width used, being dependent on the second derivative of the spectral luminosity curve (6). If relatively non-selective samples are being

(6) For further discussion of this question, see Gibson, ref. (1) - 8, above.

measured the slits may be greatly widened without introducing important errors. The use of very wide slits on a spectrophotometer isolates a spectral region comparable in extent to that isolated by various available spectral filters. It is, therefore, possible with certain types of samples to obtain adequate spectrophotometric analysis by means of a photometer and set of suitable filters, and visual and photoelectric instruments for this type of measurement have been available for years.

It is important to note just what is involved in filter photometry of this type. If the measured quantity were determined without any filter, the value obtained might depend very importantly on the spectral response of the cell, as discussed above in Section 1, and also on the spectral energy distribution of the illuminant. When the filters are used -- placed in turn at some position between the illuminant and the cell -- the value obtained in each case not only may depend on these two factors, though to a less extent, but in addition will depend very importantly on the spectral transmission of the filter and to some extent on the spectral selectivity of the quantity being measured, as noted further below. The instrument may, therefore, be used in two ways:

(1) The operator may have little knowledge of the various spectral characteristics involved. In this case, the instrument may be of temporary value in control work. Nothing fundamental will be obtained but as long as all the various spectral characteristics remain unchanged the values obtained will be comparable from day to day and one would, thereby, be enabled to control the quality of his output. Unfortunately, however, there is no guarantee of constancy either in cell, illuminant, or filter. Any one of the three may change with time, or may be damaged and have to be replaced. Little is known about the constancy of the spectral response of the various types of photoelectric cells with time, but as already noted, there may be considerable variations from one cell to another. The ordinary tungsten-filament lamps become yellower with use, due to deposit of tungsten on the inside of the bulb, and different lamps may have widely differing normal operating characteristics, though different lamps of the same type usually differ but slightly. Glass filters are mostly very stable in the visible spectrum with ordinary usage, and dyed gelatine filters somewhat less so. In case of loss or damage, however, it is difficult to get an exact duplicate; this is particularly true of a glass filter from a different melt than the original. The net result of all this is that there is always some doubt whether results today are comparable with those obtained a few weeks or a few months back; this is especially true where replacements of the above listed items have been necessary. A partial remedy for this situation is possible if one has available a reliable control sample with which to test the instrument.

(2) However, if the various spectral characteristics of the instrument are known, the measurements made will be of permanent value. For many materials they will afford a sufficient spectrophotometric analysis, the values being plotted as a function of wave length, as for regular spectrophotometric data. The wave length, λ' , at which to plot the value is the one for which:

$$R_{\lambda'} = \frac{\int_0^{\infty} sETRd\lambda}{\int_0^{\infty} sETd\lambda}$$

where

s is the spectral response of the cell for an equal-energy spectrum,

E is the spectral energy of the illuminant,

T is the spectral transmission of the filter,

R is the spectral distribution of the measured quantity,

and

λ is the wave length.

Since, in general, R is unknown, this relation is not useful. As a first approximation to λ' , it is customary to use the spectral centroid, λ_c (or $\lambda_{c'}$), of the effective cell response, as given by the following relations:

$$\lambda_c = \frac{\int_0^{\infty} sET\lambda d\lambda}{\int_0^{\infty} sETd\lambda}$$

or

$$\lambda_{c'} = \frac{\int_0^{\infty} sETR\lambda d\lambda}{\int_0^{\infty} sETRd\lambda}$$

Values of $\lambda_{c'}$ need be used only for highly selective materials and for such cases the values of R must be estimated by deriving first the values of λ_c . For nearly achromatic materials such as white or near-white enamels, papers, etc., the variation in R is so small as to be negligible and values of λ_c may be used without question. In general, it is much more important to know the values of T accurately than the values of s and E, and the narrower is the region transmitted by the filter, i.e., the more restricted is the range of T, the less accurately will the values of s and E need to be known. The integrations are usually made by summations at every 10mp; but if the filter is very restrictive, 5mp intervals are necessary.

It is apparent that an accurate knowledge of these various spectral characteristics, particularly the values of T, makes the determinations of permanent value and enables one to know whether he has duplicated any damaged part. Even if, for example, one could not duplicate the values of T exactly for any particular filter, he can derive new values of λ_c which may be plotted at the appropriate wave lengths, and correlation with previous measurements will thus not be lost.

3. The Use of the Photoelectric Cell in "Colorimeters".

Two types of so-called colorimeters may be noted:

(1) Those used for quantitative chemical analysis. These are really instruments of the type just discussed under parts 1 and 2 above, and, in fact, are not always called colorimeters. Where it is used the designation, colorimeter, has doubtless been applied from similarity to or association with colorimeters of the Duboscq type, which, however, do not measure color or color stimuli, nor yield a color specification, but merely use a color match or nearest color match as a criterion for the quantitative determination of the concentration of a solution in terms of a calibrated standard. It is recommended that the word colorimeter be not used for such instruments. They might better be called, simply, comparators; or, where filters are used and a photometric measurement made, they might be called filter photometers. Scientific descriptions of instruments of this type, with discussion of sources of error and their elimination, have been published (7). They are apparently very sensitive and

(7) See, for example: (1) The photometer and its use in the clinical laboratory, A. H. Sanford, Charles Sheard, and A. E. Osterberg, *Am. J. Clinical Pathology*, 3, 405 (1933); and (2) A photoelectric colorimeter, J. H. Yoe and T. B. Crumpler, *Ind. Eng. Chem (anal. ed.)* 7, 281 (1935); (3) A variable layer photoelectric comparison photometer, A. Goudsmit, Jr., and W. H. Summerson, *J. Biol. Chem.* 3, 421 (1935).

while not affording the complete analysis given by the spectrophotometer are very useful in chemical and biochemical analysis when used intelligently and with adequate knowledge of the various factors involved.

(2) Those advertised for general colorimetric use. The following statements have appeared in current or recent advertising literature:

".....is an electro-optical instrument for making any and all colorimetric and turbidimetric measurements".

"All the factors required to specify the visual sensation of color are directly obtained from calibrated scales. The most up-to-date practices of the highest authorities in the field of colorimetrics have been adhered to and their recommendations followed. Results are obtained in units which are in universal use by standard laboratories and bureaus".

"Present practice in measuring the color of liquids is purely comparative, there being no means for absolute measurements".

".....is a scientifically designed instrument which accurately matches or compares colors, registering variations indiscernible to the human eye. It provides a color check heretofore impossible".

"To make color comparison, simply place the instrument over the surface of the proper color, press the switch, note the reading; then do the same on the color to be matched. Comparison of the readings indicates the existing discrepancy to the millionth degree".

"From these and other problems arose the demand for a universal color-matching, color checking device that could be used by the most inexperienced. The need for just such an instrument has been met, with the invention of....".

"Note thatcan 'see' ultraviolet and infra-red rays, both invisible to the human eye".

"This has been developed to provide for all requirements of science and industry,....".

"An unerring device for matching colors".

".....the disclosure of exact color truth is a certainty".

"Its reaction is governed by immutable laws, and its findings are as dependable as the multiplication table".

"..... not subject to color blindness".

Such statements are either false or seriously misleading, and are apparently due to lack of adequate knowledge of the science of colorimetry. It should be obvious that any claim to universality of colorimetric measurements is a great exaggeration. There is little if anything new, in principle, in the design and purpose of these instruments. They add nothing to the "absolute measurement" of color. All photoelectric cells of whatever type are totally color-blind. If the cell or instrument can "see" ultraviolet and infra-red rays, it is a serious defect for colorimetric purposes. Unless the filters are of very special type, the instrument will certainly not be of "an unerring type for matching colors". If operated by the "most inexperienced", the findings may well be as dependable as the multiplication table in the hands of a beginner in the kindergarten, even though both the instrument and the operator are governed by "immutable laws".

The question may then properly be asked, to what extent and under what conditions can these instruments give reliable colorimetric data? The answer is two-fold:

(1) From any one reading or determination, with or without a filter, no value can be obtained which may properly be called colorimetric, unless previous calibration of the instrument combined with knowledge of the material being tested makes it possible for such a reading to be safely interpreted in colorimetric terms;

(2) If readings are made through three filters properly chosen with respect to the accompanying photocell and illuminant, these readings may serve to give trichromatic coefficients such that two samples which gave identical readings would be of the same color when compared visually and such that any differences in readings could be correlated with differences in the colors of the samples. However, the usual red, green, and blue filters will not adequately serve for this purpose, nor will any three which are mutually exclusive with respect to the spectral region transmitted.

Here again, as was the case with the visibility data discussed above, it is found that data representing the chromatic vision of normal observers differ considerably and it is, therefore, necessary in this case also to select data representative of an average normal observer and duplicate this by means of filters as accurately as possible. Such an observer was established in 1931 at the meeting of the International Commission on Illumination and is known as the 1931 I.C.I. standard observer (8)

(8) The standard data are based on measurements by Guild and Wright on 17 normal observers (see Guild, The Colorimetric Properties of the Spectrum, Phil. Trans. Roy. Soc. A230, 149 (1931)).

Data defining a standard trilinear coordinate system, incorporating the standard visibility data, were also adopted as well as standard illuminants A, B, and C, representative of incandescent light (gas-filled, tungsten-filament lamps), noon sunlight, and average daylight, respectively (9).

(9) For further information see Judd, Ref.(1)-2, above.

An understanding of the principles underlying 3-filter photoelectric colorimetry can perhaps best be obtained by treating the subject under the following headings: (1) Derivation and use of the ideal filters for obtaining values exactly on the 1931 I.C.I. basis, (2) approximation to these ideal filters obtainable in actual filters, and (3) the nature of the errors involved in 3-filter photoelectric colorimetry.

(1) Derivation and Use of the Ideal Filters for Obtaining Values Exactly on the 1931 I.C.I. Basis.

Let X, Y, and Z be the distribution coefficients defining the 1931 I.C.I. standard observer according to the 1931 I.C.I. coordinate system, these being a function of wave length and referring to an equal-energy spectrum. The ideal filters for use with a photoelectric cell, by means of which colorimetric data may be accurately obtained for this 1931 I.C.I. standard observer and coordinate system, are given by the following equations:

$$T_x = \frac{k_x X E'}{s E}$$

$$T_y = \frac{k_y Y E'}{s E}$$

$$T_z = \frac{k_z Z E'}{s E}$$

where X, Y, and Z are the spectral distribution coefficients just noted, E is the spectral energy of the illuminant used with the filters and cell in the measurements, E' is the spectral energy of average daylight or other illuminant by which the samples are ordinarily viewed, s is the spectral response of the photocell to an equal-energy stimulus, k_x, k_y, k_z are constants, and T_x, T_y, T_z are the desired spectral transmissions of the three respective filters. If with such filters the instrument scale readings be designated as a_t with the test sample in position and a_o with the standard of reflectance (or transmission) in position, the ratios of such readings through the three filters in turn are designated as

$$\bar{x}' = \left(\frac{a_t}{a_o}\right) \text{ x filter}$$

$$\bar{y}' = \left(\frac{a_t}{a_o}\right) \text{ y filter}$$

$$\bar{z}' = \left(\frac{a_t}{a_o}\right) \text{ z filter}$$

The quantities, \bar{x}' , \bar{y}' , and \bar{z}' may in themselves serve as a colorimetric specification of the sample relative to the reference standard. In order, however, to express the specification in terms of the 1931 I.C.I. standard observer and coordinate system, the I.C.I. colorimetric values of the reference standard must be known. If R_o represents the spectral distribution of reflectance (or transmission) of the reference standard, the tristimulus values (see reference (1)-3, above) of this standard for illuminant E' are defined as

$$\bar{x}_o = \int_0^\infty X E' R_o d\lambda$$

$$\bar{y}_o = \int_0^\infty Y E' R_o d\lambda$$

$$\bar{z}_o = \int_0^\infty Z E' R_o d\lambda$$

and will be expressed on a scale such that $\int_0^{\infty} YE'd\lambda = 1.000$.

On this scale, by virtue of the fact that in the 1931 I.C.I. system the Y distribution function was taken equal to the standard visibility function, the value of \bar{y}_0 is equal to the luminous reflectance (or transmission) of the reference standard for illuminant E'.

A second method of expressing the colorimetric values of the reference standard is by way of the trilinear coordinates (also called trichromatic coefficients), combined with the value of \bar{y}_0 . The trilinear coordinates of the reference standard are defined as

$$x_0 = \frac{\bar{x}_0}{\bar{x}_0 + \bar{y}_0 + \bar{z}_0}$$

$$y_0 = \frac{\bar{y}_0}{\bar{x}_0 + \bar{y}_0 + \bar{z}_0}$$

$$z_0 = \frac{\bar{z}_0}{\bar{x}_0 + \bar{y}_0 + \bar{z}_0}$$

The chromaticity of a color is indicated by the trilinear coordinates, and since the sum of these quantities is always unity, any two of them may serve to specify chromaticity. The color of the reference standard for illuminant E' may, therefore, also be adequately specified in terms of x_0 , y_0 , and \bar{y}_0 .

It is desired to express the tristimulus values, \bar{x} , \bar{y} , and \bar{z} , or the trilinear coordinates, x , y , z , of the test sample in terms of the measured quantities, \bar{x}' , \bar{y}' , \bar{z}' , and either \bar{x}_0 , \bar{y}_0 , \bar{z}_0 or x_0 , y_0 , z_0 pertaining to the reference standard. This is done by means of the following relations:

$$\bar{x} = \bar{x}' \bar{x}_0$$

$$\bar{y} = \bar{y}' \bar{y}_0$$

$$\bar{z} = \bar{z}' \bar{z}_0$$

$$x = \frac{\bar{x}' \bar{x}_0}{\bar{x}' \bar{x}_0 + \bar{y}' \bar{y}_0 + \bar{z}' \bar{z}_0}$$

$$y = \frac{\bar{y}' \bar{y}_0}{\bar{x}' \bar{x}_0 + \bar{y}' \bar{y}_0 + \bar{z}' \bar{z}_0}$$

$$z = \frac{\bar{z}' \bar{z}_0}{\bar{x}' \bar{x}_0 + \bar{y}' \bar{y}_0 + \bar{z}' \bar{z}_0}$$

The color of the test sample for illuminant E' may, thereupon, be expressed in terms of the 1931 I.C.I. standard observer and coordinate system by giving values of \bar{x} , \bar{y} , and \bar{z} or x , y , and \bar{y} . It may be noted that if the reference standard is non-selective with respect to wave length, i.e., R_0 is constant throughout the visible spectrum, the values of x_0 , y_0 , and z_0 become equal to the respective similar quantities for the illuminant E'.

(2) Approximation to the Ideal Filters Obtainable in Actual Filters.

In attempting to duplicate the ideal values of T_x , T_y , and T_z defined above, it will be found that the problem is greatly simplified if the X distribution function is treated as if the parts above and below 505mp were separate functions⁽¹⁰⁾. Further-

(10) See Guild, reference (5), above.

more, below 505mp the X function has relative values very similar to those of the Z function. For practical purposes, therefore, it is necessary to duplicate T_x only at wave lengths greater than 505mp, the transmission of the filter being zero below this wave length. Such a filter may be designated as an (x) filter, with spectral transmission values $T(x)$. In this case, the value of \bar{x} ' may be taken as equal to

$$0.83\left(\frac{at}{a_0}\right)(x) \text{ filter} + 0.17\left(\frac{at}{a_0}\right)z \text{ filter},$$

the values, 0.83 and 0.17, being proportional to the areas of the X curve above and below 505mp. Values of \bar{y}' , and \bar{z}' are obtained and computations of \bar{x} , \bar{y} , \bar{z} , and x , y , z made as described in the previous section.

Values of T_x , $T(x)$, T_y , and T_z have been computed for values of a representative of Weston photronic, Westinghouse photox, and General Electric Hewlett cells, and with values of I.C.I. illuminant C taken for E' and I.C.I. illuminant A for E. These values are available upon request to the colorimetry section of the National Bureau of Standards. They are, of course, valid only to the extent that the values of s assumed in the several cases apply to any particular cell. They show clearly, however, that yellow, green (11) and blue filters, rather than red, green,

(11) The green filter is unnecessary with a photox cell. The sensitivity of this cell is so low in the blue, however, that it is not recommended for 3-filter colorimetry. On the other hand, its spectral response curve approximates the visibility curve better than do the response curves of the other cells noted; for this reason it is somewhat more suitable than they for the measurement of luminous values (see section 1, above) when no correcting filter is used with the cell.

and blue filters, are necessary to duplicate $T(x)$, T_y and T_z , respectively. As a further guide to the proper kind of filters, it may be noted that a first, though very crude, approximation to the desired values of $T(x)$, T_y and T_z is afforded, in the case of photonic and Hewlett cells, by filters composed of the following glasses: (1) dark railroad signal yellow plus pale sextant green for $T(x)$, (2) pale sextant green for T_y and (3) very dark signal blue plus noviol A for T_z . These combinations effectively exclude the ultraviolet and infra-red regions.

In case it is not desired to obtain data on the I.C.I. basis but merely to obtain adequate colorimetric data for accurate matching or control purposes, the filters just suggested, or any others which will give curves more closely approximating the ideal $T(x)$, T_y , and T_z curves, should be satisfactory for most purposes. In such use of the filters one need not compute the \bar{x}' value, as was done above by weighting the values of a_t/a_0 obtained through the (x) and the z filters, but can use values of $(\bar{x})'$, \bar{y}' , and \bar{z}' , directly. In this case, further, if magnesium oxide is used as the reference standard, one may consider that

$$(\bar{x})_0 = \bar{y}_0 = \bar{z}_0 = 1.00$$

and

$$(x)_0 = y_0 = z_0 = 1/3$$

and that the effective illuminant E' (which will probably approximate daylight) will have the same values. The values of the trilinear coordinates (x), y, and z will, therefore, be simply

$$x = \frac{(\bar{x})'}{(\bar{x})' + \bar{y}' + \bar{z}'}$$

$$y = \frac{\bar{y}'}{(\bar{x})' + \bar{y}' + \bar{z}'}$$

$$z = \frac{\bar{z}'}{(\bar{x})' + \bar{y}' + \bar{z}'}$$

(3) The Nature of the Errors Involved in 3-filter Photoelectric Colorimetry.

When colorimetry is attempted with a photoelectric cell and a set of three filters such as described above, the nature of the errors which may be present will depend, of course, on whether or not one is attempting to obtain data on the 1931 I.C.I. basis. If one desires to get values of x, y, and \bar{y} on this standard basis, of as high accuracy as are obtainable with good spectrophotometric data and computations, he will probably be disappointed except in the measurement of small differences where values for the standard are independently known. The method may prove of considerable accuracy for white or near-white materials, although

actual test will be necessary in any case to determine the exact magnitude of the errors involved.

If one is not attempting to obtain data on the I.C.I. basis, the only criterion for accuracy is the consistency obtained with the results of visual grading or examination. Reproducibility will prove nothing if the filters are of the wrong type. It should be emphasized that the reliability of such a method over a period of time is dependent on the constancy and reproducibility of the various parts contributing to the colorimetric values obtained.

The method outlined above for using a photoelectric 3-filter instrument for colorimetric purposes, whereby values of \bar{x} , \bar{y} , and \bar{z} or x , y , and \bar{y} , or similar quantities, are obtained suitable for specification of the color, is probably the best general procedure for such work. In many cases these values are sufficient in themselves. In others, it is found that still greater usefulness is obtainable for certain purposes by using combinations of these quantities as the important variables, such as x/y or $(\bar{x}-\bar{z})/\bar{y}$, which may be found satisfactory for representing differences in yellowness, or red-green differences, etc. This depends on the particular problem. Other schemes are possible such as successive subtraction of the least of the quantities, \bar{x} , \bar{y} , \bar{z} , then the least of the residuals, etc., but it is doubtful that such systems are as useful as the more direct methods of specification.

4. Miscellaneous Factors Affecting Reliability of Data Obtainable with the Instruments Described Above.

In the previous sections consideration has been given almost entirely to the spectral characteristics of the various parts of the instrument contributing to the determination of the various colorimetric data. In addition, however, there are several other factors that must be considered in any careful study of the reliability of the various instruments. These may be considered under four headings:

(1) Mechanical Stability. The instrument should be of sufficiently rigid construction that ordinary accidental pressure on any part will not affect the readings. The sample holder should be of such design and construction that the samples can always be placed precisely in a definite reproducible position.

(2) Thermal Stability. The operating characteristics of the cells may be affected by change of temperature, likewise the spectral transmissions of the selective filters. Certain filters, such as those made of selenium glass are very responsive to temperature change and should not be used. The construction of the instrument should be such that the heat from the illuminant upon both the cells and the filters, either by radiation or convection, is reduced to a minimum.

(3) Electrical Characteristics. Three factors are to be considered: (1) Stability of the response. Certain cells are admittedly somewhat unstable; different readings may be obtained depending on whether the cell has just previously been exposed to strong or to weak irradiation. (2) The electric circuit used. The important question is, if the incident radiant energy is increased or decreased by any definite amount, its spectral distribution being unchanged, will the instrument reading be increased or decreased in precisely the same proportion? Under certain conditions the failure of the proportionality may be serious. The makers of the cells give considerable information on these points and their descriptive circulars should be consulted. Circuits and cells which have proved satisfactory are described in a number of references, some of which are listed below (12). (3) The permanence of the response characteristics

(12) Wood, L. A., A Differential Circuit for Blocking-Layer Photo-Cells, R. S.I., 5, 295 (1934); Wood, L. A., Zero-Potential Circuit for Blocking-Layer Photo-Cells, R.S.I., 7, 157 (1936); Zinzadze, Ch., Photoelectric Photometers for Use in Colorimetry, Ind. Eng. Chemistry (anal. ed.) 7, 280 (1935); See also, Instruments for Use with Photoelectric Cells, Electrical Measurements, Vol. 1, No. 4 (July, 1935), published by Sensitive Research Instrument Corporation, 4545 Bronx Blvd., New York City.

of the cells. It is known that some cells deteriorate so that their response to a given illumination may be appreciably lower at the end of a year than it was at the beginning. If a meter is calibrated to register a definite value for a given illumination, it is particularly important to know that the cell being used is stable in its response. In instruments where the cell response for unknown samples is compared periodically with its response for known standard samples, or where ratios only are determined, this deterioration factor is automatically compensated.

(4) Optical Characteristics. The optical design of an instrument will, of course, depend on the purpose for which it is designed. This purpose may be the measurement of absorption, reflectance, opacity, turbidity, or color. In some instances adequate diagrams showing the optical and mechanical details are apparently not available. In many cases also scientific publications describing the instrument have not been issued. It is, therefore, impossible to judge properly regarding the design of these instruments. It is furthermore impossible with present space, in view of the great variety in design and purpose of the various instruments, to do more than indicate a few points of importance in any consideration of such instruments.

In any measurement of absorption, it is important that the light pass through the solution or other sample approximately at right angles to the end surfaces of the material. Otherwise the values obtained apply to greater than the measured thicknesses. It is furthermore important in accurate work to insure that the multiple reflections between the samples and the optical parts of the instrument do not introduce error in the results. For example, if one attempts to measure the transmission of a non-diffusing, non-absorbing glass plate by inserting it in the beam directly in front of a dry-disc type of cell, about 8% of the light reflected from the cell is reflected back to the cell from the plate and makes the value of transmission obtained too high. The error may in many cases be computed but it is best to eliminate it entirely if possible. If the transmission of diffusing materials is being measured, the angular conditions of illumination and observation are also of importance, as in the case of reflectance measurements.

Several factors are of importance in measuring the apparent reflectance of materials relative to a reference standard, which is the sort of measurement for which many of these instruments are designed. These will be enumerated in turn.

(1) The angular conditions of illumination and observation. These should be explicitly and accurately stated, if results obtained by one design of instrument are to be compared with similar results by another design. Not only are the angles of incidence and reflection of importance but also the angular apertures of the beams. However, the importance of these factors in affecting the readings depends notably on the diffusing properties of the material being studied. They are of great importance in the case of a material such as aluminum paint, whose apparent reflectance may vary from less than 0.25 to more than 1.00 depending upon these conditions of measurement. They are of relatively little importance in the case of matt surfaces such as certain paints, papers, etc. The most suitable conditions to use depend on the material to be measured and the purpose of the measurements. Conditions which have been commonly used are (1) diffuse illumination and normal viewing, which, if the illumination is completely diffused gives values of apparent reflectance equal to the reflectance for unidirectional normal illumination, and (2) 45° unidirectional illumination and normal viewing, conditions recommended by the International Commission on Illumination, and the equivalent condition of normal illumination and 45° viewing.

(2) The reference standard of reflectance. Formerly magnesium carbonate has been widely used. However, the reflectance of this material is apparently much more variable than is that of magnesium oxide which is gradually superseding the former for this purpose. Information regarding the preparation and colorimetric properties of a magnesium-oxide reflectance standard is published in NBS letter circular, LC-395.

(3) Equality of illumination on sample and standard. Any failure in this respect will, of course, produce error. Lack of equality may be caused by (a) poor optical or mechanical construction, and (b) difference in illumination of sample and standard caused by their own differences in reflectance, this possibility occurring in instruments using illuminating spheres, hemispheres or other inclosures, where both sample and standard are not simultaneously illuminated (13), and in the use of cover glasses over sample and standard (14).

(13) A. C. Hardy and A. W. Pineo, The Errors due to the Finite Size of Holes and Samples in Integrating Spheres, J.O.S.A. 2, 502 (1931).

(14) D. B. Judd and K. S. Gibson, Note on the Effect of a Cover Glass in Reflectance Measurements, J. Research NBS 16, 261 (1936); PF 372.

