Spectrophotometry

(200 to 1,000 millimicrons)

United States Department of Commerce
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Circular 484

UNITED STATES DEPARTMENT OF COMMERCE • Charles Sawyer, *Secretary*
NATIONAL BUREAU OF STANDARDS • E. U. Condon, *Director*

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By Kasson S. Gibson

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Preface

The spectrophotometer has long been recognized as a valuable analytical and standardizing instrument. For over 100 years photographic methods in the ultraviolet region of the spectrum, and visual methods in the visible region have afforded valuable means of research in the properties of matter, and the study of chemical structure. At first the spectrophotometer was seldom found outside of the college laboratory. Later it became a basic instrument also in the standardizing laboratory. With the development of the photoelectric cell, and the resulting design and construction of photoelectric instruments—direct reading, rapid to use, some of them automatically operated—the spectrophotometer found widespread use in the commercial laboratory, and thousands of them are now in daily use in research or control work.

Spectrophotometry is not only a research and an analytical tool in physics, chemistry, engineering, and technology. One of its most important uses relates also to the subject of color. It is the fundamental basis of colorimetric analysis, standardization, and specification. This has become axiomatic in psychophysical colorimetry. It is the only fundamental means of analyzing a color for research or other purposes. It is the only means of standardizing a color that is independent of material color "standards" (always of questionable permanence) and independent of abnormalities of color vision (existing among even so-called normal observers), and in this sense it is the fundamental basis for color specification.

The National Bureau of Standards has applied the spectrophotometer to its color research, development, and testing, and to various other work, for nearly 40 years. It pioneered in the development of the photoelectric spectrophotometer and in its application to the colorimetry of diffusing materials. With the advent of commercial photoelectric spectrophotometers, the Bureau began preparing and issuing spectrophotometric standards of various kinds, and hundreds of these standards are now in use, affording checks on the reliability of the various instrumental scales.

This Circular is issued to make available to users of spectrophotometers the experience, techniques, and data that have resulted from the Bureau's work in this field. Various instruments and methods are described, with emphasis on the basic principles, and various possible errors and the means used to eliminate them are considered in some detail. The various types of spectrophotometric standards are also described.

E. U. Condon, *Director.*

Contents

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This paper describes various spectrophotometric instruments and methods for use in the ultraviolet, visible, and near infrared spectral regions. These include photographic, visual, and photoelectric methods, but not the radiometric methods so widely used throughout the infrared. Errors and their elimination are discussed, and various types of spectrophotometric standards are described.

I. Introduction

1. Definition

Spectrophotometry is a term that by practically universal usage is taken to refer to the relative measurement of radiant energy or radiant flux as a function of wavelength. By strict derivation the term might be restricted to such measurements made visually, but in actual practice the word has long been applied also to photographic and photoelectric methods of measurement, in both the ultraviolet and the visible regions of the spectrum. More recently the term has been extended in application to cover also all such relative measurements in the infrared—throughout the region where the term "spectroradiometric" had heretofore been widely used, because the detectors necessarily used were of the type conveniently covered by the word "radiometer." The present extended usage is good, however, as it frees the word "spectroradiometric" for the absolute measurement of spectral distributions, as contrasted with the relative measurements for which the word "spectrophotometry" is so generally applied.

The significance of the word *relative* in this connection is that in spectrophotometry the measurements are always made relative to some standard. What this standard may be in any case depends on the type of measurement. For example, in spectral reflection measurements it may be a standard magnesium oxide surface; in transmission measurements it may be either the blank beam or a similar material or cell free of the absorbing constituent; in measuring the spectral distributions of light sources it may be a source of known spectral distribution. But in all cases what is measured is merely the ratio of two quantities, wavelength by wavelength, throughout the spectral range of interest.

2. Applications

The numerous applications of spectrophotometry may be grouped into three main categories:

1. Spectrophotometry may be used as a general research tool in investigations of the properties of materials. These investigations may be concerned with the relation between absorption and constitution or structure, the eye-protective qualities of glasses and other materials, the connection between absorption and fluorescence, the study and selection of optical filters, the bleaching or rancidity of vegetable oils, the fading of dyed materials, and many other types of work.

2. Spectrophotometry is of great usefulness in the rapid chemical analysis of solutions, and other materials. Such measurements in the ultraviolet and visible spectral regions have long been valuable for this purpose, and in recent years similar measurements in the infrared have been found of immense importance, particularly in the petroleum industries. In the visible spectrum this type of analysis is often referred to as color analysis or chemical colorimetry, but such work should not be confused with the type of colorimetry referred to below in the third application.

It should be pointed out in this connection that the present paper is concerned primarily with instruments and instrumental techniques, particularly as bearing on the reliability of the data obtained, and not with the treatment of spectrophotometric data for any of the three categories listed. The applications and use of such data have been thoroughly covered in numerous publications in physical, chemical, and optical literature.

3. Spectrophotometry is the fundamental basis of colorimetric analysis, standardization, and specification. This has become axiomatic in psychophysical colorimetry. It is the only fundamental

means of analyzing a color for research or for other purposes. It is the only means of standardizing a color that is independent of material color "standards" (always of questionable permanence), and independent of abnormalities of color vision (existing even among so-called normal observers), and in this sense it is the basis for fundamental color specification. But while serving as the *basis* for color specification, a spectrophotometric curve (or table of data) is quite inadequate as a color specication in itself, particularly if colorimetric tolerances are desired as part of the specification. For adequate color specifications with tolerances the spectrophotometric data must be converted to some form of tristimulus specification by means of methods and data defining a standard observer, a standard coordinate system, and a standard illuminant.

Only in the last application above is the spectral range of interest limited to the visible spectrum. In the first two applications any division of the spectrum into ultraviolet, visible, and infrared is essentially arbitrary and pointless. For example, the Beckman quartz photoelectric spectrophotometer covers the range from about 200 to about 1,200 mμ, and its usefulness is in no wise limited as we enter or leave either end of the visible spectrum.

However, in the neighborhood of 1,000 or 1,200 mμ (1 or 1.2 μ) there is a natural division, particularly as to instruments and methods. Neither the sensitized photographic plate nor the common types of photoelectric cells show much useful response above this wavelength. Radiometric methods on the other hand, with the thermopile, bolometer, or other similar detector, which are universally used throughout most of the infrared, are but little used below 1 μ, particularly since the development of the cesium oxide and other phototubes of high sensitivity. Accordingly the techniques used above and below 1 μ are in general widely different, even though the type of measurement is often essentially the same. To a less extent this wavelength marks also a division in the types of materials investigated—for example, petroleum products above 1 μ, dyes and camouflage materials below 1 μ—but with many other materials such as glasses no such division is apparent. This circular therefore covers the range from 200 mμ to 1,000 mμ, approximately.

3. Historical

As already implied, the spectrophotometric methods to be considered here include the visual, the photographic, and the photoelectric. However, consistent with the purposes of the circular this is not primarily an historical résumé of the subject. Rather, an effort has been made to make the treatment such as to have the greatest utility to present-day users of spectrophotometers. Naturally this results in considering spectrophotometers commercially available and widely used to a much greater extent than various spectrophotometers that have been individually designed and used in various laboratories, but are not readily available to others.

It is accordingly desirable to list various published articles on spectrophotometry or related subjects that treat the matter historically, are of résumé nature, or give extensive bibliographies, so that those who wish may pursue the subject to any desired extent. Listed chronologically, with comments, these are as follows, the complete reference being given in section VIII.

Spectrophotometry, Report of Optical Society of America Progress Committee for 1922–23. A fairly complete treatment of the science as it existed at that time [1].[1]

The use of the photoelectric cell in spectrophotometry, K. S. Gibson. A résumé of the subject up to 1930 [2].

The practice of absorption spectrophotometry with Hilger instruments, F. Twyman and C. B. Allsopp (1934). Special emphasis on photographic methods, but describes other instruments [3].

Current advances in photographic photometry, G. R. Harrison (1934). Includes absorption spectrophotometry; contains references to work in extreme ultraviolet [4].

Visual spectrophotometry, K. S. Gibson. Describes visual instruments in common use in 1934 [5].

Measurement of Radiant Energy, W. E. Forsythe, Editor (1937). Contains the following chapters of interest in spectrophotometery: I, Fundamental concepts and radiation laws (Forsythe); II, Sources of radiant energy (Worthing); III, Analysis of radiation (Adams); IV, Spectrometric instruments and their adjustments (Kurtz); V, The spectrometer as an optical instrument (Barnes); VII, Measurement of spectral radiation by means of the photoelectric tube (Koller); VIII, Measurement of radiant energy with photographic materials (Jones); XI, (Visual) Spectrophotometry (Gibson); XIII, Photometry (Forsythe and Ives) [6].

The role of spectrophotometry in colorimetry, M. G. Mellon (1937). Of primary interest to the chemist [7].

Photoelectric methods in analytical chemistry, R. H. Müller (1939). Much of the information given would be useful in photoelectric spectrophotometry [8].

Spectrophotometric methods in modern analytical chemistry, S. E. Q. Ashley (1939). Of primary interest to the chemist [9].

Survey of spectrophotometers, Kasson S. Gibson (1940). Discusses the measurement of spectral directional reflectance [10].

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

Chemical spectroscopy, Wallace R. Brode (1943). Includes absorption spectrophotometry by visual, photographic, and photoelectric methods [11].

Spectrophotometry in medicine, Ludwig Heilmeyer, translated by A. Jordan and T. L. Tippell (1943). Absorption spectrophotometry [12].

Photoelectric photometers: Their properties, use and maintenance, J. S. Preston (1943). Much of the information given would be useful in photoelectric spectrophotometry [13].

Photometry and spectrophotometry, David L. Drabkin. A chapter in Medical Physics (1944). Absorption spectrophotometry, including filter photometry [14].

Bibliography of photoelectric spectrophotometric methods of analysis for inorganic ions, J. W. Stillman (1945). Of primary interest to the chemist [15].

Absorption spectrophotometry, G. F. Lothian (1949). This is a revision and extension of Twyman and Allsopp's treatise, reference [3] above. [16].

Spectrophotometry and colorimetry, Wallace R. Brode. A chapter in Physical Methods in Chemical Analysis [17].

Practical Spectroscopy, G. R. Harrison, R. C. Lord, and J. R. Loofbourow (1948). Includes chapters on photographic photometry and absorption spectrophotometry [18].

Analytical Absorption Spectroscopy, M. G. Mellon, editor [127].

II. Nomenclature—Quantities Measured.

In order to discuss the applications of spectrophotometry in the measurement of the spectral energy distribution of sources of light and radiant energy, and in the measurement of the spectral transmission and reflection characteristics of materials, it is necessary to define clearly various terms used in such work, and to assign symbols to these terms for convenient use.

Various groups and individuals have done this in the past, and various systems of terminology are thus available. Many of these are excellent in themselves, and they have served their purposes well. For example, may be noted (1) in radiation, the definitions and symbols proposed and used in the book entitled, Measurement of Radiant Energy, chapter 1 [6] (2) the photometric terminology prepared and issued by the Illuminating Engineering Society and the American Standards Association [19], and (3) various reports prepared by special committees of the Optical Society of America, dealing with colorimetry and spectrophotometry [1, 20, 21].

Naturally, however, such divergent groups and purposes have resulted in systems that are often inconsistent with one another. Furthermore, because of the extent and detail of some of these systems, recourse has often been made to Greek, bold-face, script, or other symbols that are inconvenient to use. Encouraging in this connection is the fact that the Illuminating Engineering Society Nomenclature Committee, and the Optical Society of America Colorimetry Committee have recently come into agreement on many terms and definitions relating to radiometry and photometry. In spectrophotometry, however, there is still no extensive agreement on terminology. In 1947, accordingly, a restricted set of terms for use in transmission and absorption measurements appeared in Letter Circular LC857 of the National Bureau of Standards [22]. These terms were agreed upon by various members of the optics and chemistry groups of the Bureau and appear to be a satisfactory compromise of the various terms and symbols used in the past.

These transmission and absorption terms of LC857 are given in this Circular, together with a few other terms useful in the spectrophotometry of light sources and reflecting materials.

1. Spectral Energy Distribution

In any fundamental consideration of the radiation characteristics of light sources, or of sources emitting radiant energy at any wavelengths in the ultraviolet, visible, or infrared regions of the spectrum, one must consider the space and time variants involved in the radiation processes. This has been done to a greater or less extent in the nomenclatures and terminologies to which reference has just been made. In such we find, for example, definitions and terms for radiant energy, the time rate of flow of radiant energy, the solid-angular flux density in a given direction, the areal density of radiant flux from a source or on a surface, the space density of radiant energy, and so on, together with the luminous analogues for the same terms.

For our purposes *radiant energy* is defined as energy traveling through space in the form of electromagnetic waves of various wavelengths. It is the entity that is emitted from radiators; that is reflected, refracted, absorbed, or transmitted by various objects or materials; and that is incident upon the various detectors such as the thermopile, the photographic plate, the eye, and the phototube.

Radiant flux (power) is the time rate of flow of radiant energy.

In some cases the integrated amount of radiant energy is what is primarily measured by the detector; this is true of the photographic plate as customarily used and of the phototube if connected to certain electrometers or "photon-counters". In other cases the radiant flux is the quantity which the detector primarily indicates. This is true of the eye, and of the phototube and thermopile with galvanometers or other devices as ordinarily used. It is often convenient, therefore, to consider the radiant flux as the entity to be measured or discussed.

In spectrophotometry, where at any frequency or wavelength only the ratio of two quantities is measured, it is usually possible and convenient to ignore the spatial and temporal variants of radiant energy and speak simply of the radiant energy itself, denoted graphically by an arrow and symbolically by the letter I. If I_o refers to the standard at any wavelength and I to the unknown at the same wavelength, the quantity I is derived immediately from the measured ratio, I/I_o, and expressed in whatever units are used or known for I_o. In deriving the transmission terms given below, it will be noted that I and I_o are no longer needed after the initial definitions of transmittance.

It is occasionally desirable, however, even in spectrophotometry, to refer to certain spatial variants of radiant flux and these are accordingly defined here. The terminology agreed to by the Optical Society of America and the Illuminating Engineering Society committees is followed.

Radiant intensity of a source of radiant energy is defined as the radiant flux per unit solid angle in a given direction.

Radiance is the radiant intensity per unit projected area of the source.

Irradiance is the radiant flux per unit area incident upon a surface.

Before considering the transmission and reflection terms, a few other comments may be made.

Radiant energy and light. Light is the aspect of radiant energy of which a human observer is aware through the visual sensations arising from stimulation of the retina of the eye. Quantitatively light is radiant energy evaluated in terms of the standard luminosity function (see section IV–1 below). Usually radiant energy must have wavelengths between approximately 380 and 770 mμ if it is to have a luminous aspect. But it is not proper to state that radiant energy of wavelengths 380 to 770 mμ is synonymous with light. Consistent with this definition of light, the expressions "ultraviolet light" and "infrared light" are incorrect, and the word "light" is seldom used in this Circular even when visual spectrophotometry is under consideration.

In this connection may be noted the luminous analogues for the radiation terms just defined, starting with light or luminous energy, the standard luminosity function being the correlating factor in every case. Thus may be defined *luminous flux*, *luminous intensity* (candlepower), *luminance* (photometric brightness) and *illuminance* (illumination) [21, 19]. It may be further noted that new photometric units were introduced in this and other countries as of January 1, 1948 [23].

It is unfortunate that a short single word for radiant energy, analogous to light, has not come into common use. Lacking such a word we shall often use simply the word "energy", where the context makes clear that radiant energy is meant. The use of "radiation" or "radiations" for radiant energy, as for example in the expression "radiations of various wavelengths," is inconsistent with the modern usage that words ending in -tion (or -sion) are to be reserved for the designation of processes or for general and adjectival use.

Wavelength and frequency. The symbol for the wavelength of radiant energy is λ. The units in which wavelengths are expressed are restricted to those conventionally used for each spectral range; i. e., millimicrons (mμ) or angstroms (A) for the ultraviolet and visible and microns (μ) for the infrared. The symbol for frequency is ν. In place of true frequency a term designated as *wave number* is widely used, defined as $1/\lambda_{\mathrm{vac}}$ (the unit of λ in this usage being usually the centimeter).

The relation between wavelength and frequency is $\nu = c/\lambda$, where c is the velocity of propagation of radiant energy. It may perhaps be emphasized that both c and λ change whenever radiant energy of frequency ν passes from a medium of one refractive index to a medium of different index. The frequency itself does not change, however, and is thus more fundamental than wavelength for theoretical studies.

2. Spectral Transmission and Absorption

In this section all of the terms derived relate to the rectilinear transmission of radiant energy and no consideration is given to radiant energy that may be deviated or scattered from its original direction. By far the greater amount of spectral transmission and absorption measurements are of this type, made upon materials such as liquids, solutions, glasses, or other nonscattering materials. If the material is turbid or translucent, the radiant energy scattered from its original direction must be considered. If this scattered energy is slight in amount and unavoidable, it may need consideration along with other sources of error. If the material is more highly diffusing the measured transmittance will be importantly dependent upon the geometrical conditions of irradiation and reception; the situation is then analogous to that considered in some detail in section II–3 for reflection measurements.

1. *Terms relating to the rectilinear transmission of homogeneous radiant energy (that is, radiant energy of a "single" frequency) through a homoge-*

neous, isotropic, nonmetallic medium having plane, smooth, parallel surfaces.

In figure 1 let I_1 be the radiant energy incident upon the first surface of the sample, I_o that entering the sample, I that incident upon the second surface, I_2 that leaving the sample.

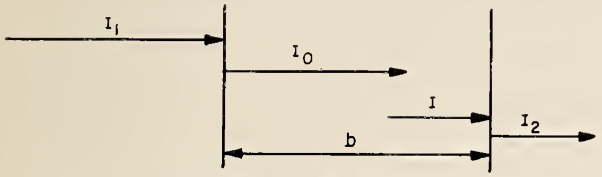

FIGURE 1. *Transmittance, T, is defined as the ratio, I_2/I_1; internal transmittance, T_i, as the ratio, I/I_o.*

$T=I_2/I_1=$*transmittance* of the sample. (100 $T=$percentage transmittance)

$T_i=I/I_o=$*internal transmittance* of the sample.

$A_i=-\log_{10}T_i=\log_{10}1/T_i=\log_{10}I_o/I=$*absorbance* of the sample.

Let b represent the length of absorbing path in the sample.

$a_i=A_i/b=$*absorbance index* of the material.

Other quantities derived from the above are occasionally used. These are $T_i^{1/b}$, which has been called *transmissivity*, $1-T_i^{1/b}$, which has been called *absorptivity*, and $1-T_i$, which has been called *absorptance.*

In the above, the thickness, b, or the unit of thickness, should always be given. The temperature of the sample during the measurements should also be stated when this is a matter of importance.

2. *Terms relating to the rectilinear transmission of homogeneous radiant energy through a homogeneous, isotropic, nonmetallic medium such as a liquid, mixture, solution, vapor or gas confined between the windows of a cell.*

Let T_{soln} be the (over-all) transmittance of a given cell containing a solution or homogeneous mixture of solids, liquids, vapors, or gases, of which the compound of interest is the solute or one constituent. Let T_{solv} be the (over-all) transmittance of the same or a duplicate cell containing pure solvent, or containing the same mixture in the same relative proportions minus the constituent of interest.

$T_s=T_{\text{soln}}/T_{\text{solv}}=$*transmittancy* of the sample. (100 T_s=percentage transmittancy.) (T_s does not precisely equal $(T_i)_{\text{soln}}/(T_i)_{\text{solv}}$. However, with end plates of refractive index not greater than 1.5, the error is negligible for most purposes.)

$A_s=-\log_{10}T_s=\log_{10}1/T_s=$*absorbancy* of the sample.

Let b represent the length of absorbing path between the boundary layers of the solution, and c the concentration of the solute or constituent of interest.

$a_s=A_s/bc=$*absorbancy index* of the material.

a_M is the *molar absorbancy index*, c being expressed in moles per liter, and b in centimeters, and the temperature being given.

In the above, the thickness and concentration, or the units, should always be given. The temperature of the sample during the measurements should also be given when this is a matter of importance.

In connection with these definitions it is desirable to point out certain alternative symbols and terms that have been widely used in chemical literature or elsewhere. Thus d, l, and x have often been used for thickness, rather than b. The symbol, T is often used for transmittancy, rather than T_s, particularly by chemists who in general have little interest in the concepts of transmittance and internal transmittance as defined above. Analogously, A and a would be used in place of A_s and a_s. However, the term, specific extinction, with symbol k, is widely used by chemists instead of the term, absorbancy index, a_s. Similarly the term, molar extinction, with symbol ϵ, is preferred in place of the term, molar absorbancy index, a_M. The molar extinction is usually recorded or plotted as $\epsilon\times10^{-2}$ or as $\log_{10}\epsilon$.

3. Spectral Reflection

Differing from the case of spectral transmission measurements, where the great majority of substances measured are not importantly scattering, and accordingly where only rectilinear transmission was considered, most materials whose spectral reflecting properties are of interest are more or less highly diffusing. Such materials include papers, textiles, structural glass, paints, ceramics, etc., for which the analysis and specification of color is so important. However, the derivation of reflection terms herein is limited to those that are useful for spectrophotometry. Those who wish to consider the subject in greater detail should consult other papers on the subject [24, 25].

Three quantities are of primary importance in reflection spectrophotometry, designated as (total) reflectance, specular reflectance and directional reflectance. Again we are dealing with homogeneous radiant energy in these definitions.

Reflectance is defined as the ratio of the radiant energy reflected from an object to that incident upon the object. Since no restriction is placed upon the directions of the reflected energy this type of reflectance is often designated as the (total) reflectance. The (total) reflectance will vary with the direction or directions of the incident energy but cannot exceed unity.

Specular reflectance is the ratio of reflected to incident energy taken only in the direction of mirror reflection. It is the type of reflection given by perfectly polished glasses, metals, or other mirror-like surfaces, without scatter. The specular reflectance of an object will vary with the angle of incidence but, again, cannot exceed unity.

Directional reflectance (formerly called apparent reflectance [24]) may be defined loosely as the reflectance that an object appears to have in any direction or group of directions. It is the type of reflectance measured by most reflection spectrophotometers and it is therefore of considerable importance that its meaning be fully understood, and the factors affecting its measurement be fully taken into account.

The concept is most easily defined in terms of a perfectly diffusing surface. With such a surface the ratio of the radiance to the irradiance (section II–1) is constant for all angles of reflection. Furthermore the magnitude of this ratio for a perfectly diffusing surface is independent of the angle or angles of irradiation provided only that the irradiance is constant. (If the radiant energy is in the visible spectrum, the perfectly diffusing surface will appear equally bright when viewed from any direction.)

The *directional reflectance* of a surface may accordingly be defined as the ratio of the radiance that the surface has under any specified set of irradiating and receiving conditions to the radiance that a perfectly reflecting, perfectly diffusing surface would have under the same conditions. Differing from the (total) reflectance or the specular reflectance, neither of which can exceed unity, the directional reflectance can have any value between zero and infinity.

Since no actual surfaces are perfectly diffusing the values of directional reflectance for any sample will depend on the geometrical conditions of both the irradiating and the receiving beams. The importance of the precise specification of these geometrical conditions depends on the purpose of the measurements and on the degree of departure of the surface from the completely diffusing condition. Which of the numerous possible conditions to use also depends on the purpose of the measurements and, in spectrophotometry, is determined partially by the degree of conservation of radiant flux which various conditions will afford with diffusing materials.

Symbols for reflection terms have varied from group to group and author to author. For purposes of this circular, (total) reflectance is designated by R. If it is desired to indicate the angle of incidence of the irradiating energy, a subscript may be added, as R_0 or R_{45}. If the irradiation is perfectly diffused the symbol is R_D; if nearly diffused, the symbol is R_d.

Specular reflectance is often equivalent to (total) reflectance and the above symbols may be used. If it is desired to designate specifically that the reflectance is specular, the symbol R_S may be used, combined if necessary with the angle of irradiation, as R_{S45}.

Directional reflectance is designated by the symbol R with subscripts attached to indicate the directions of the respective irradiating and receiving beams as $R_{0,45}$, $R_{D,60}$, $R_{45,-45}$, $R_{d,0}$, etc. In this connection it must be emphasized, however, that only the subscript D is specific. The angle subscripts refer to the directions of the axes of the respective beams. The angular spreads of these beams are also in many cases of considerable importance and should be given in any complete specification of irradiating or receiving conditions.

Reflectance, total or directional, has been defined above as a property of the object. In some cases, for example with papers and textiles, the reflectances and directional reflectances will vary with the thickness or number of layers of the material used in the measurement and may be affected by the reflectance of the backing used. If the reflecting properties characteristic of the material are desired, it is customary to measure the reflectance in such a thickness that any increase in thickness will not change the measured value and the reflectance of the backing will accordingly have no effect on the value. Reflectance measured under this condition is termed *reflectivity* or *directional reflectivity* and is designated by the symbol r. Subscripts have the same meaning as when used with the symbol R.

An important relation in this connection is that known as the Helmholtz [26] reciprocal relation. As stated by McNicholas [24], "the loss in flux density which an infinitely narrow bundle of rays of definite wavelengths and state of polarization undergoes on its path through any medium by reflection, refraction, absorption, and scattering is exactly equal to the loss in flux density suffered by a bundle of the same wavelength and polarization pursuing an exactly opposite path". By this relation it is shown that, for example,

$$R_{45,0}=R_{0,45}$$

and

$$R_{D\,60}=R_{60}$$

In other words, the numerical value of directional reflectance obtained with irradiation at 45° and reception at 0° is the same as that obtained with irradiation at 0° and reception at 45° (and similarly for any other pair of angles); and the value of directional reflectance obtained with perfectly diffused irradiation and reception at 60° is the same as the value of (total) reflectance obtained with irradiation at 60° (and similarly for any other angle).

No commercial spectrophotometer has been designed to measure directly the spectral distribution of radiant energy scattered from diffusing materials, except as the measurement of spectral directional reflectance may be so considered. Those wishing to investigate the relation between scattering, reflectance, and opacity should consult a paper by Judd [25] and papers to which reference is made therein.

III. Spectrometry

Every spectrophotometer includes at least 5 principal constituents: (1) a source of radiant energy adequately covering the spectrum range of interest for the measurements; (2) a spectral dispersing system by means of which radiant energy of any desired frequency or wavelength (in reality, usually a more or less narrow range of frequencies or wavelengths) may be isolated and used in the desired measurements; (3) a photometric system, by means of which the desired ratio of energies may be determined at the various wavelengths; (4) a suitable detector of radiant energy which may or may not be a direct part of the photometric system; and (5) a sample holder, for transmission and reflection measurements.

Many of the details connected with these divisions of spectrophotometry are considered in connection with the various instruments discussed below. Many others, however, can best be treated in sections by themselves largely independent of the instruments (because they are pertinent to all instruments). The present sections accordingly deal with item (2), the spectral dispersing systems of spectrophotometers (section III–1) and with means for the wavelength calibration or check of such instruments (section III–2). The other items are considered in the sections on Photometry (sections IV–1 and IV–2).

1. Elements of Spectrometer

Three methods are commonly used to effect spectral dispersion and isolation in the region from 200 to 1,000 mμ. The dispersion may be obtained by means of refraction through a prism, or it may be obtained through the diffraction and interference associated with the fine-line diffraction grating; or there may be no dispersing system in the ordinary sense, the spectral isolation being effected by means of optical filters. The present section deals only with the prism and grating spectrometers. The use of spectral filters is considered in section V–4.

(a) Prism Spectrometers

Glass or quartz prisms of 60° refracting angle, or equivalent prisms, have been widely, almost universally, used in prism spectrophotometers for the ultraviolet and/or visible. Two types are shown in figure 2, taken from the O. S. A. Spectrophotometry Committee report [1].

One of the simplest forms is type A. Although simple, this illustrates all of the essential elements of a spectrometer. These consist of the dispersing prism, P, with the 60° refracting angle at r, a collimator, C, carrying a lens and an entrance slit, S_C, and a telescope or second collimator, T, with lens and exit slit, S_T. The slits, S_C and S_T, and the refracting edge of the prism at r are parallel to each other and extend (usually vertically) at right angles to the plane of deviation and dispersion.

By means of the collimator slit and lens, radiant energy from a suitable source, L, is formed into a beam, the various elements of which are approximately parallel. (These elements are closely parallel in the horizontal plane because of the narrowness of the slit, but in the vertical plane the direction of the elements may deviate from the horizontal by varying amounts determined by the length of the slit and the focal length of the lens.) This "parallel beam" undergoes dispersion by passage through the prism, the angle of refraction

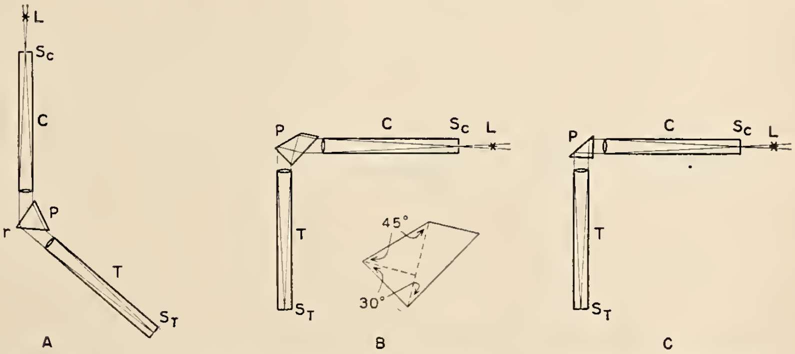

FIGURE 2. *Three types of spectrometers that have been used in spectrophotometers.*

A is the simple 60° prism type; B, the constant-deviation 60° prism type; C, the transmission-grating type. In C the replica grating is placed on one of the right-angle faces of P.

varying with the wavelength, and a spectrum image of S_C is formed in the plane of S_T.

By moving the telescope in the horizontal plane about a vertical axis located in the plane bisecting the angle r, the desired wavelengths may be selected at will for use in the observations. If the source, L, is one emitting radiant energy at certain wavelengths only (not a continuous spectrum), the images of S_C will appear as spectral "lines" characteristic of the particular source used. The width and length of these lines will vary with the width and length of S_C. If a source such as an incandescent-filament lamp is used (having a continuous spectrum), no lines are visible and the purity of the radiant energy isolated depends importantly on the widths of the slits, S_C and S_T.

Another type of spectrometer design is shown in *B* of figure 2. In this design the collimator and telescope are fixed at right angles to each other. Dispersion is effected by means of a constant-deviation prism. As shown in the enlarged diagram of *P*, this prism is equivalent to a 60° prism, consisting in effect of two 30° prisms separated by a right-angle totally reflecting prism. This type of spectrometer has two advantages over that shown in A. (1) Both telescope and collimator are fixed in position, and change of wavelength is effected by rotating the prism, *P*. (2) The rays accepted for measurement are closely at minimum deviation regardless of wavelength. Item (1) is of considerable advantage in connection with the construction of auxiliary equipment for use with the spectrometer; item (2) is less important in spectrophotometry. A disadvantage of this type of prism is the greater energy loss by absorption within the dispersing prism caused by the increased length of path.

Modifications of these simple types of spectrometer are illustrated below in connection with certain of the spectrophotometers, such as the use of two spectromenters in series, and the use of a 30° dispersing prism with reflecting face. Still other designs of spectrometer, used principally in infrared work, are illustrated in references [6] and [21].

(b) Grating Spectrometers

The theory and use of diffraction gratings may be found in text books on optics. Concave reflecting gratings and plane transmission gratings have both been used in spectrophotometry, particularly in the form of replicas. A simple form of spectrometer of this type is shown in *C* of figure 2. The grating is cemented onto one of the faces of the right-angle glass prism, *P*. The prism also serves to redirect the beam as shown, giving a convenient form of constant-deviation spectrometer. Wavelength is varied by turning *P*.

(c) Transmission and Dispersion of Prism and Grating Instruments

In most applications the spectral transmittance of a spectrophotometer is of little importance so long as it transmits sufficiently to give adequate sensitivity. However, all prism material will absorb strongly at either end of its normal usable range and it is a matter of some interest to know what the transmittance of certain typical prism or grating instruments may be.

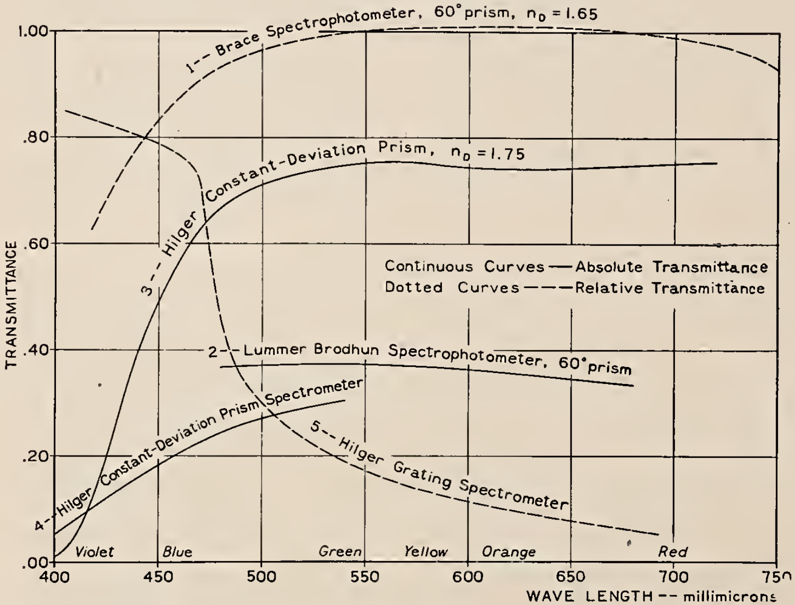

FIGURE 3. *Spectral transmittance curves of various glass prisms or prism instruments, and of a grating spectrometer.*

In figure 3, taken from the O. S. A. Spectrophotometry Committee report [1], are shown various transmittance curves of certain dispersing prisms and prism instruments, curves 1 to 4. Most of the absorption in the visible spectrum in a prism spectrophotometer is caused by the prism itself. The selectivity depends of course on the type of glass and the length of path in the prism. It is obvious from this illustration that any constant-deviation glass instrument cannot be used much below 400 mμ.

An additional factor limiting the transmission of glass instruments in the ultraviolet is the Canada balsam used in the achromatic lenses of the collimators. A thin film of this absorbs strongly below 360 mμ.

In figure 3, curve 5, is shown the relative transmittance curve of a replica-grating spectrometer, and in figure 4, curves 1 and 2, the absolute transmittance curves of a grating monochromator in the first and second order as determined by French, Rabideau, and Holt [27]. In actual use, of course, for any one setting of the grating, the two orders do not overlap as shown.

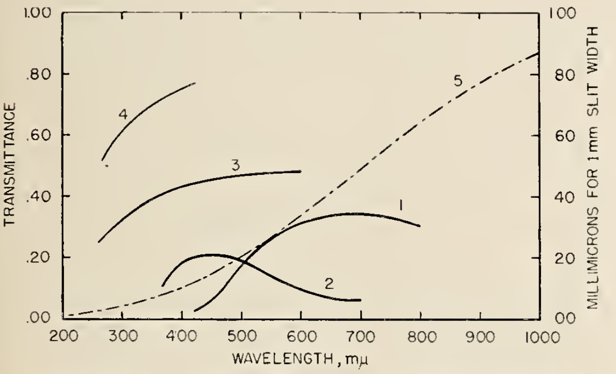

FIGURE 4. *Spectral transmittance curves of certain spectrometers.*

Curves 1 and 2, a grating spectrometer in the first and second orders, respectively; curve 3, a 2-prism crystalline-quartz monochromator; curve 4, a single-prism fused-quartz monochromator. Curve 5 is the dispersion curve of a quartz spectrophotometer.

Spectral transmittance curves for quartz-prism monochromators have been determined in the ultraviolet—for a crystalline-quartz 2-prism instrument by Forsythe and Barnes [28], and for a fused-quartz single-prism instrument by Kay and Barrett [29]. These are shown in figure 4, curves 3 and 4, together with the dispersion curve for a quartz-prism spectrophotometer, curve 5. The dispersion data are taken from one of the Beckman bulletins [30].

In figure 5, taken from the O. S. A. Spectrophotometry Committee report [1], are shown (1) a dispersion curve, dashed line, of a typical glass-prism spectrophotometer, (2) at top and bottom, the amounts of pure spectrum transmitted by this particular instrument for an ocular slit set at 0.20 mm width, in terms of frequency and wavelength, and (3) wavelength and frequency calibration curves (which are considered further below). In figure 5 the dispersion is plotted as angular scale divisions per millimicron, in figure 4, as millimicrons per millimeter of slit width. For comparison it may be noted that at 525 mμ the glass-prism instrument transmits about 4 mμ of pure spectrum and the quartz-prism instrument about 5 mμ of pure spectrum, for an exit slit set at 0.20 mm.

Figures 4 and 5 illustrate how the extent of pure spectrum transmitted by an exit slit of constant mechanical width varies through the spectrum with a prism instrument. At the longer wavelengths the wavelength range thus transmitted is several times that transmitted at the shorter wavelengths. In general, therefore, the longer the wavelength, the smaller must be the mechanical width of slits to obtain the same purity of spectrum band for use in the measurements. Accordingly, if one wishes to maintain a constant spectral purity at the various wavelengths he must continually change the slit widths mechanically or use some form of cam arrangement that will do this automatically.

In a grating instrument, because of the normal dispersion, the amount of spectrum transmitted by slits of constant mechanical width is unchanging through the spectrum.

In the above, reference has been made to the amount of "pure spectrum" transmitted by the exit slit of a spectrophotometer, and this is the customary way of expressing the slit widths of such instruments. By a pure spectrum is meant one that is formed with the entrance slit set at an infinitesimal width. In order to secure sufficient spectral energy for practical use, however, the entrance slit must be set at finite width, and it has become customary to set the entrance and exit slits at the same width. With an incandescent or other continuous-spectrum source, however, this results in an extension of the wavelength range transmitted by the exit slit beyond that for a pure spectrum.

This is illustrated schematically in figure 6. In this figure, b represents the exit slit width, a the entrance slit width, both expressed in wavelength units. In *A*, slit a is very narrow and b is set at any nominal width. In *B* and *C*, slit b has been left unchanged and slit a widened to equal $0.5b$ and b, respectively, as shown. Relative amounts of energy transmitted by slit b are shown vertically as a function of wavelength, it being assumed that the spectral distribution of the energy arriving at slit b is constant in amount over the range $b+a$.

The important thing to note is the additional wavelength range that is transmitted by b as a is widened. This is shown by the triangle-shaped areas in *B* and *C* that are shown on either side

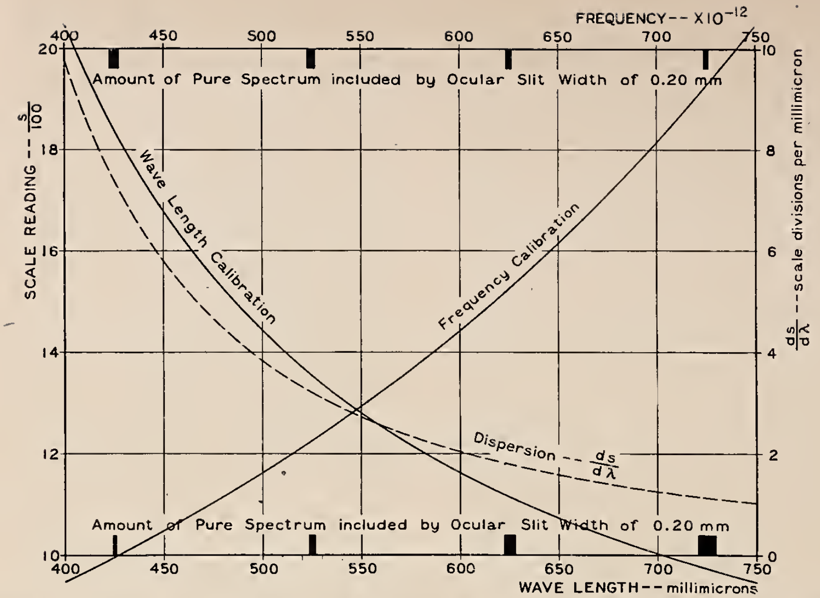

FIGURE 5. *Wavelength, frequency, and dispersion characteristics of a typical glass-prism spectrophotometer not having a direct-reading wavelength scale.*

beyond the extent of *b*. When the two slits are equal, case *C*, the total range of wavelengths transmitted by *b* is 2*b*, although the fraction of energy transmitted by *b* at these additional wavelengths is only one-fourth of the total, and is weighted in accordance with the triangular outline. (For a prismatic spectrum the triangle of figure 6, *C*, is not perfectly symmetrical because of the variable dispersion, but the differences are negligible with any reasonable slit width.) Slit widths are considered further in section VI-6.

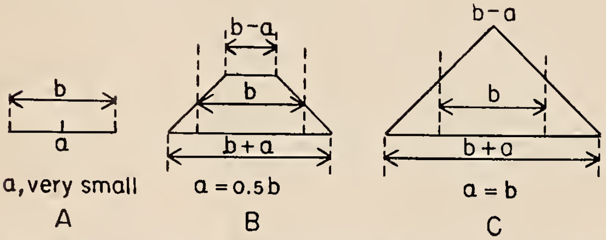

FIGURE 6. *Relative transmittance of energy by a spectrophotometer at any nominal wavelength as the entrance slit width, a, is varied relative to the exit slit width, b.*

Spectrophotometer slits are usually set at equal widths, illustrated in C, and the extent of spectrum transmitted is notably greater than that expressed in terms of either slit alone, as in A. It is customary to designate slit widths in terms of b alone, and designate them as nominal slit widths, and this is done in the present paper; but it is well to remember that the effective slit width is always somewhat greater than b, the nominal slit width.

2. Wavelength Calibration

The older spectrophotometers were usually designed with an arbitrary angular or linear scale for the wavelength setting. Such a scale had to be calibrated in terms of wavelengths or frequencies, somewhat as illustrated in figure 5 by the respective continuous curves. The wavelength calibration curve can be more or less represented by various dispersion formulas, such as

$$\frac{1}{s-s_o}=A+B\lambda$$

or

$$\frac{1}{s-1}=A+B\lambda^2,$$

wherein s is the scale reading, λ is the wavelength, and A, B, and s_o are constants to be determined. In general, however, these formulas will not give an adequate calibration except over a very short wavelength range. Their principal advantage is, perhaps, to facilitate calibration by enabling Δs, instead of s, to be plotted as a function of wavelength.

Most of the present-day spectrophotometers have a direct-reading wavelength scale; that is, the scale, instead of being divided in uniform linear or circular measure, is divided and engraved directly in millimicrons. This greatly facilitates setting the instrument at any desired wavelength. The accuracy of many of these direct-reading wavelength scales is remarkably good, when put in the best average adjustment, considering the difficulties of quantity production of such scales. When so adjusted, it is not uncommon to find them in error by not more than 1 mμ throughout the ultraviolet and visible spectrum. However, if one wishes the uncertainties in his wavelength settings to be of the order of 0.1 mμ, a careful check of these direct-reading scales is necessary.

The best procedure to use for checking the wavelength scale of a spectrophotometer depends on whether it is a nonrecording or a recording spectrophotometer.

(a) For Nonrecording Spectrophotometers

The best procedure for checking the wavelength scale of a nonrecording spectrophotometer is by direct use of a source of radiant energy having spectral lines of suitable intensity and adequately spaced throughout the spectral range of interest. Various sources are available and can be recommended for such purpose. How many sources, or how many wavelengths, to use in such a calibration depends, of course, on the accuracy desired by the individual investigator.

In this connection it should be noted that the number of significant figures of importance in spectrophotometry (including "absorption spectroscopy") is of a different order of magnitude than that used in emission spectroscopy or in standard wavelength tables. In the visible spectrum with the usual type of spectrophotometer it seems impossible to maintain the wavelength calibration with uncertainties less than about 0.1 mμ. While the uncertainty may be less in the ultraviolet with a prism instrument, there seems no purpose served in giving standard wavelengths to better than 0.01 mμ for spectrophotometric calibration.

Two of the most suitable sources for wavelength calibration of spectrophotometers are the quartz or glass mercury arc and the ordinary helium vacuum tube in glass. If the range from 220 to 1,014 mμ is of interest the quartz-Hg arc is by far the best single source. A glass-Hg arc gives the same wavelengths as the quartz arc above 310 mμ.

The helium lines are especially well placed for wavelength calibration in the visible spectrum, and the strong lines at 388 and 1,083 mμ are also often very useful. Many other sources, flame or arc, are available for visual wavelength calibration [1, 31] but most of these are too unstable for accurate calibration with a photoelectric detector.

These same sources and many others are also useful for the wavelength calibration of spectrographs used in photographic spectrophotometry. Between 200 and 400 mμ the series of doublets obtained from the aluminum spark in air is very useful because they are so readily recognized.

The wavelengths characteristic of the above sources, with a few others that have proved useful, are noted in table 1. All values are consistent with those published in the MIT wavelength tables [31]. Not all of the lines for any of the sources are given but only those that are considered especially suitable for the purpose. Furthermore, not even all of those listed for any one source may be suitable for any one particular instrument. The mercury arc in quartz is a good example. All of the lines listed (and still others) could be used for wavelength calibration of a photographic spectrophotometer over the range of sensitivity of the plate used. And all of the lines from 404.7 to 690.7 mμ can be used for visual calibration of a spectrophotometer. But not all of the lines are suitable for calibration of a photoelectric instrument, and those that prove adequate will depend on the sensitivity and slit widths characteristic of any particular instrument. One must be very careful that other lines are not included, in addition to the one on which the settings are supposedly being made, of sufficient intensity to affect the wavelength setting.

Special attention should perhaps be called to the use of a cesium arc at 852.1 and 894.3 mμ [32]. From table 1 it is apparent that suitable lines between 706.5 and 1,014.0 mμ are otherwise mostly unavailable, particularly from steady sources necessary or desirable in the calibration of photoelectric spectrophotometers. The neon discharge tube gives many lines between 750 and 1,000 mμ [31] but these have not been found satisfactory in the calibration of photoelectric spectrophotometers. In the orange and red the neon lines are useful for visual calibration and many of these can be used to calibrate photoelectric spectrophotometers [33] if the sensitivity is such that very narrow slits can be used. The relative intensities given [34] will help in case of overlapping.

The best technique to use in wavelength calibration of nonrecording spectrophotometers, given a suitable source, will vary from instrument to instrument and method to method. A few general principles can be given here, however.

In photographic spectrophotometry it usually is sufficient to photograph a known spectrum at the top and bottom of the plate, unless the source used for the absorption spectra itself carries such known reference lines. A few of these reference lines will then serve to correlate that particular plate with whatever complete calibration curve has previously been established by more extensive measurements with the various sources.

On visual and photoelectric nonrecording spectrophotometers, for highest precision, it usually is necessary to have a basic reference line to which all of the other wavelengths are compared by direct check. At the Bureau the Hg yellow lines have proved most suitable on the König-Martens visual spectrophotometer [35]. At the slit widths used the overlapping of the two lines gives a central brighter "line" taken as 578.0 mμ with a luminous background against which the slit jaws are readily seen. A luminous background, or slight illumination of the ocular slit, always facilitates calibration when an eyepiece is used. Visual calibration without an eyepiece is usually less precise unless very narrow slits are used.

Incidentally, the curvature of spectrum lines produced by a prism with straight entrance slit is readily observed in visual calibration with an eye-

Table 1. *Sources and wavelengths suitable for the calibration of spectrophotometers*

Wavelengths for				
Mercury arc in quartz (same wavelengths in glass above 300 mμ)	Footnote	Aluminum spark in air	Helium discharge tube in glass	
mμ		mμ	mμ	
205.29		216.88	318.77	
222.47		217.40	361.36	
223.41			363.42	
225.88		220.46	370.50	
230.21		221.00	381.96	
232.32		226.35	388.86	
235.25		226.91	396.47	
237.83			402.62	
239.94	1	236.71	412.08	
239.97		237.21	414.38	
		237.31		
244.69		237.34	438.79	
246.41		237.84	443.75	
248.20	2		447.15	
248.27		256.80	471.31	
248.38		257.51	492.19	
		257.54		
253.48	3		501.57	
253.65		263.16	504.77	
257.63			587.56	
260.32		265.25	667.81	
265.20	4	266.04	706.52	
265.37		281.62	728.13	
265.51			1083.0	
269.95		308.22		
275.28		309.27		
275.97			Neon discharge tube	
		358.69		
280.35	5			
280.45		394.40	Wavelength	Relative intensity
284.78		396.15		
289.36				
292.54				
		Hydrogen, sodium, cesium arcs	585.25	5.2
296.73			588.19	3.9
302.15	6		594.48	7.7
302.35			597.55	1.7
302.56		H 434.05	603.00	2.3
302.75		H 486.13		
		Na 589.00	607.43	7.8
312.57		Na 589.59	609.62	13.0
313.15	7	H 656.28	614.31	24.6
313.18		Cs 852.11	616.36	5.9
334.15		Cs 894.35	621.73	3.9
349.28				
			626.65	11.4
365.01	8		630.48	4.3
365.48			633.44	19.9
366.29			638.30	22.8
366.33			640.22	100.0
390.64				
			650.65	38.6
398.40			653.29	7.9
400.63			659.90	11.8
404.66			667.83	23.4
407.78			671.70	14.0
435.83				
			692.95	23.0
491.60			702.41	2.–
546.07			703.24	44.9
576.96	9		705.91	----------
579.07			717.39	4.9
623.44				
			724.52	17.3
671.62			743.89	4.5
690.72			748.89	----------
1014.0			753.58	----------
1128.7			754.40	----------

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[1] A value of 239.95 is recommended for the unresolved pair.

[2] A value of 248.3 is recommended when the 3 lines are unresolved.

[3] The intensity of 253.48 is negligible compared to that of 253.65. The latter value should be used when the lines are unresolved.

[4] The 265.20 line is somewhat stronger than the others, and a value of 265.3 is recommended when the three lines are unresolved.

[5] These two lines are of approximately the same intensity and a value of 280.40 is recommended for the unresolved pair.

[6] The two shorter lines are considerably stronger than the other two. It is probable that a value of 302.25 should be used for the unresolved lines.

[7] A value of 313.16 is recommended for the unresolved pair.

[8] With the arc used on the Beckman spectrophotometer the ratio of intensities for 365.01: 365.48: 366.33 is 100:48:36, approximately. The intensity of the 366.29 line appears negligible relative to that of 366.33.

[9] These two lines are of approximately the same intensity and a value of 578.0 is recommended for the unresolved pair.

piece. This curvature is caused by the fact that the ray from the center of the slit is passed at less deviation than the rays from other parts of the slit. Some instruments are made with one or the other of the slits curved to remedy this defect. If both slits are straight there is an effective broadening of the slit width and, visually, a greater uncertainty of wavelength calibration unless the lengths are kept rather small.

Two techniques have been used at the Bureau in the calibration of nonrecording photoelectric spectrophotometers. On the Gibson spectrophotometer [36] the slits are always 0.1 mm or greater and the most reliable calibration is obtained by plotting galvanometer deflections at closely adjacent wavelengths. This is illustrated in figure 7. The most probable value for the wavelength reading is given by the intersection of the two straight lines as shown, the correction being given by the difference between this value and the true wavelength.

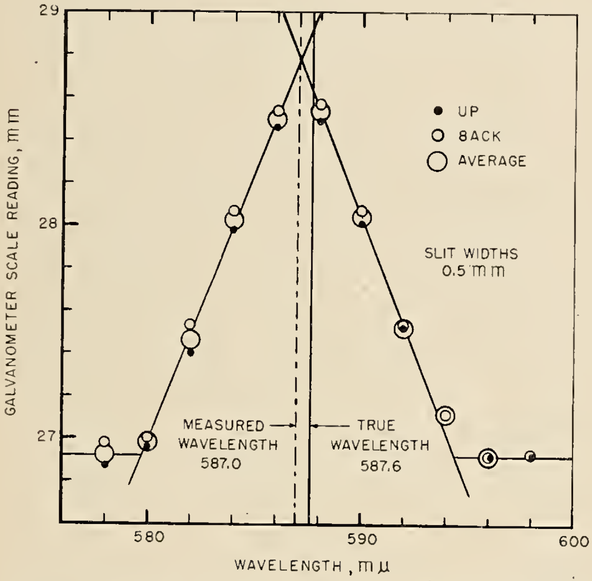


FIGURE 7. *Illustrating one method of checking the wavelength calibration of a direct-reading nonrecording photoelectric spectrophotometer.*

Zero deflection of the galvanometer happened to be at 26.92 mm in this illustration.

On the Beckman spectrophotometer the same method has been used [37], but at the Bureau it has seemed preferable, and is much more rapid, to calibrate with a narrow slit and note the farthest throw to the left (of the rapidly responding needle) as the wavelength dial is slowly turned. The most suitable reference line on two of the Bureau's instruments has proved to be the Hg green line [33].

(b) For Recording Spectrophotometers

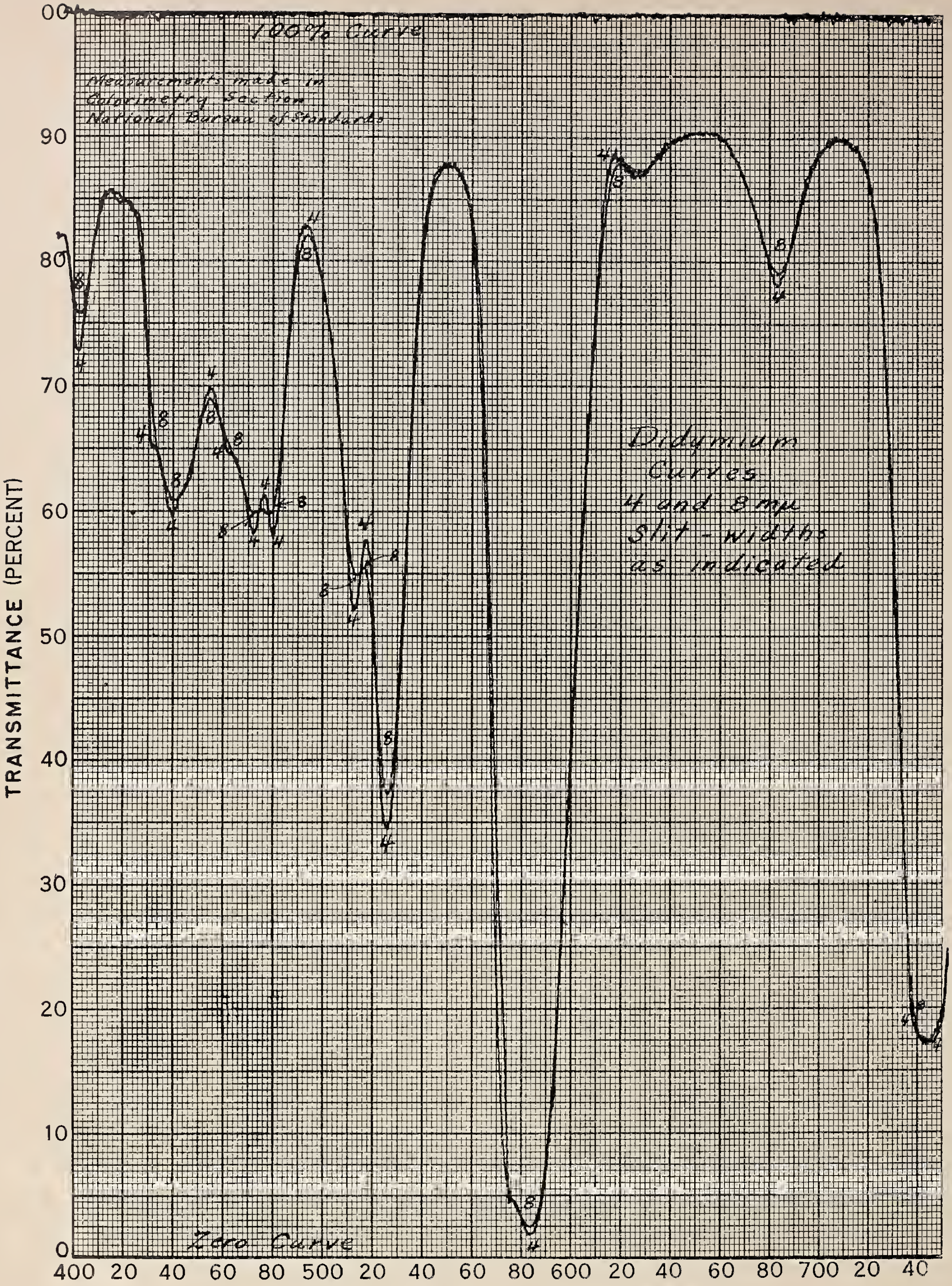
The initial wavelength calibration of a recording spectrophotometer, such as the manufacturer must carry out in connection with cutting his cams or preparing his reading scale, is not here considered, but only the check of such a calibration by the user of the instrument.

Such a user can, of course, follow the procedure prescribed above for checking the wavelength calibration of nonrecording spectrophotometers. However, there are two important reasons for following a different procedure for recording spectrophotometers. For such instruments it is desirable to have a calibration that is made with the instrument operating. It is further desirable in many kinds of work to have this calibration appear on the graph sheet so that worries connected with positioning of the sheet, expansion or contraction of the paper with humidity or temperature, or instrumental variations can be eliminated.

Wavelength calibrations of this kind can be made if a material is available having a number of strong and narrow absorption or transmission bands suitably spaced over the spectral range of interest. Two materials have been used or suggested for this purpose: (1) Didymium glasses have been used for many years at the National Bureau of Standards [38] and many have been calibrated and issued to others for similar use, (2) quartz-Polaroid combinations have been proposed [39] and may prove useful for such work.

The use of a didymium glass in this manner would not in general be accurate unless it is calibrated at closely the same slit widths at which it is to be used. Most of the absorption bands that are usable for the purpose are multiple bands and the wavelengths of maximum absorption often depend on the slit widths. This is illustrated in figure 8 where the curves recorded on a General Electric spectrophotometer [40, 41, 42] at the National Bureau of Standards [38] are shown for slits equivalent in width to 4 and 8 mμ of spectrum approximately.

The NBS didymium glass standards were carefully calibrated by point-by-point measurements on the König-Martens visual and Gibson photoelectric spectrophotometers with slit widths approximating the 4, 8, 10 and 20 millimicron slits used on the NBS General Electric spectrophotometers. Some of these values have been published [43]. Although these initial calibrations were tedious and time-consuming, the time and worry eliminated by the use of such standards are enormous. Once calibrated it has been very simple to derive corresponding values for glasses submitted for calibration by recording their transmittance curves on a sheet along with the curves for the NBS calibrated standards.



(Legend on page 15)

The most suitable didymium glass for the purpose, considering type of curve and availability, is a Corning 5120 glass of 3.0 mm thickness. While it is not known how much the wavelengths of maximum absorption of this 5120 glass might vary from melt to melt, glasses from at least three melts have been measured and there has never been any certain variation among the samples tested. For much work it is probably safe to use the values given in table 2.

While the use of a didymium glass for checking the wavelength calibration of recording spectrophotometers is highly recommended, as noted above, there are two other uses of the didymium glass which are not recommended. First, the didymium glass is not well suited for checking the photometric scale of any spectrophotometer, recording or nonrecording. Transmittances at the peaks of the absorption bands are too dependent on slit widths, and transmittances on the steep parts of the curve are too dependent on slight wavelength errors, both as illustrated by figure 8. Second, the use of a didymium glass to check the wavelength calibration of a nonrecording spectrophotometer is considered much inferior from the standpoints of time, convenience, and reliability to the direct use of line sources as described above. The National Bureau of Standards has consistently refused to accept didymium glasses for calibration for either of these two purposes.

Table 2. *Wavelengths of maximum absorption for Corning 5120 glasses at 3.0 mm as obtained at the National Bureau of Standards for the slit widths indicated*

Wavelength of maximum absorption	Over-all uncertainty	Approximate spectrum interval transmitted by slits
$m\mu$	$m\mu$	$m\mu$
$441._0$	±1	10
$475._5$	1	10
$528._7$	1	10
$585._0$	1	10
$684._8$	1	10
$743._5$	1	10
745	2	20
808	2	20
883	2	20
1,067	2	20

IV. Photometry

Another of the principal parts of a spectrophotometer is the photometric system, whereby the desired ratios of energy or flux may be determined at the various wavelengths isolated by the spectrometric system. Important parts of the photometric system are the source and detector of radiant energy, and these will be considered before discussing the photometric devices themselves.

1. Spectral Characteristics of Sources and Detectors

Various sources of radiant energy have proved adequate for spectrophotometry in the range from 200 to 1,000 mμ. From 350 or 400 mμ to beyond 1,000 mμ the incandescent filament lamp is by far the most suitable source for most purposes, either as a standard of spectral energy distribution when measuring the distribution of other sources or as the source for spectral transmission and reflection measurements. Its advantages relate to the facts that (1) its radiant intensity under normal operating conditions is adequate for the purpose, (2) its intensity can be readily kept constant, to a high degree if necessary, (3) having a continuous spectrum it enables measurements to be made at any wavelength over its useful range.

In figure 9 are shown the relative spectral energy distributions of an incandescent source at color temperatures of 2,600 and 3,000° K. Most incan-

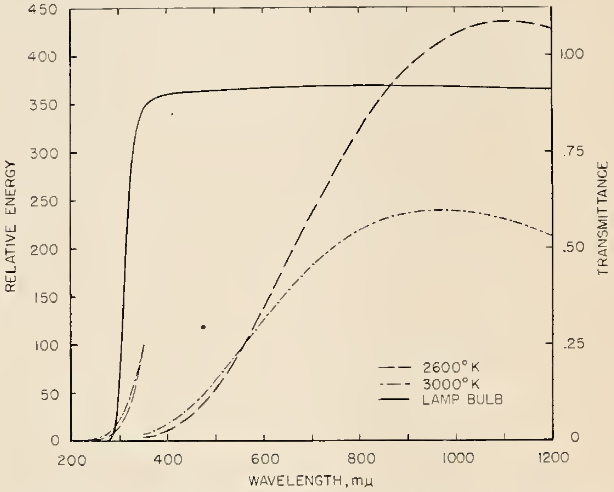


Figure 9. *Spectral energy distribution curves of blackbody at 2,600° and 3,000° K, adjusted to 100 at 560 and 350 mμ.*

These curves are closely like those from the incandescent lamp filaments used on spectrophotometers, except that in the ultraviolet below 350 mμ they are notably reduced by the transmittance of an ordinary glass bulb. The spectral transmittance curve (continuous line) of such a bulb is shown.

Figure 8. *Spectral transmittance curves of a didymium glass recorded on a General Electric photoelectric spectrophotometer at the National Bureau of Standards with nominal slit widths equivalent to 4 and 8 mμ of spectrum, as shown.*

For the two slit widths, note (1) shifts of the wavelengths of maximum absorption for the 480 and 513 mμ bands and (2) differences in recorded transmittances at all regions of sharp curvature.

descent lamps used on spectrophotometers operate within or close to this range. The data plotted are those from Planck's equation for the theoretical black body at these temperatures [44, 45, 46], but it is known that they closely represent the relative distributions of lamps at these color temperatures [47, 48]. Below 350 mμ, however, absorption of the ordinary glass bulb rapidly reduces the energy to zero near 300 mμ. This is apparent from the spectral transmittance curve shown in figure 9 for a piece of glass cut from a 200-watt incandescent lamp bulb.

The quartz mercury lamp is useful not merely for wavelength calibration of spectrophotometers; at certain wavelengths the radiant intensity is sufficiently great that it may also be used as the source for photometric measurements. The advantages of such use are that the results cannot be affected by wavelength or slit-width errors, as is possible with an incandescent lamp as source.

The Hg lines that have been found useful for such purpose at the National Bureau of Standards are (1) visually, on the König-Martens spectrophotometer, those at 404.7, 435.8, 546.1, and 578.0 (576.9+579.0) mμ, and (2) photoelectrically, on the Beckman spectrophotometer, those at 365.0, 334.2, 302.2 and 253.6 mμ in addition to those listed above in the visible spectrum. The relative intensities among various of these lines vary considerably from one type of lamp to another. One such set of intensities is shown in figure 10. In this figure the intensities below 400 mμ are taken without change from table XVII of reference [49]. Above 400 mμ, however, they have been adjusted to fit the individual lines. The data of figure 10 are for a "hot" quartz lamp. The relative intensities for a low-pressure, "cold-cathode" mercury lamp are much different, the intensity of the line at 253.6 mμ exceeding all the others.

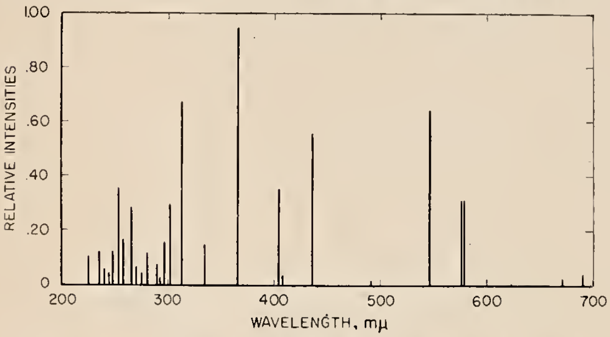


FIGURE 10. *Relative intensities of the various spectral "lines" in a quartz mercury arc.*

Such a source may be used for the wavelength calibration of spectrophotometers, and the stronger lines may be used also for photometric measurements. The relative intensities differ with the operating conditions and types of arcs. Those shown are for a "hot" quartz arc. For a low-pressure "cold-cathode" arc the major portion of the intensity is concentrated in the 253.6 mμ line. Wavelengths are given in table 1. The intensities shown are based on data by Luckiesh [49] (copyright by D. Van Nostrand Company, Inc.) and are reproduced by permission.

The most commonly used source of radiant energy for spectrophotometry in the ultraviolet spectral region is probably now the hydrogen arc. Under certain operating conditions of pressure and current a nearly continuous spectrum can be obtained, of adequate intensity for use over the range from 200 to above 400 mμ. Hydrogen arcs are suitable for use in both photoelectric and photographic spectrophotometers.

Other sources widely used in photographic spectrophotometry, but too unsteady for the usual type of photoelectric spectrophotometer, are (1) the under-water high-voltage spark discharge and (2) various arcs or sparks where the electrodes have been especially selected to yield a great number of closely spaced spectral lines. The underwater spark spectrum has long been used at the National Bureau of Standards and its appearance is shown later in figure 16. The spectrum is perfectly continuous without superposed lines and covers the range from 500 to 220 mμ and perhaps beyond. Examples of arc or spark spectra in air, as used widely by various investigators in ultraviolet absorption spectra, may be found in various publications [3, 11].

The detectors commonly used with spectrophotometric equipment over some part of the range from 200 to 1,000 mμ are (1) the eye, (2) the photographic plate, (3) the photoelectric cell (the vacuum or gas-filled electron-emission type, or the barrier-layer type) and (4) the thermopile or other form of radiometric device. Only the first three types of detectors will be considered here, since the thermopile and other radiometers are mostly used in infrared work.

The relative sensitivity (luminosity) curve of the human eye—that is, the photometric response of the eye to an equal-energy spectrum—has been determined by various investigators. It varies considerably from one individual to another and is widely different at low luminances (scotopic vision) [50] and at high luminances (photopic vision) [51]. In figure 11, curves A and B, are

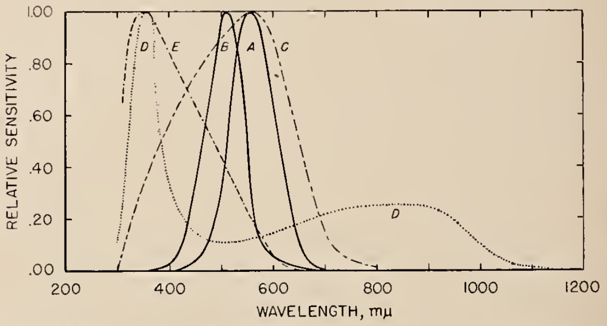


FIGURE 11. *Relative sensitivities of various detectors used in spectrophotometry.*

A and B are the photopic (light adapted) and scotopic (dark adapted) average luminosity curves of the human eye. C is more or less representative of barrier-layer photocells, D and E of certain "red sensitive" and "blue sensitive" electron-emission phototubes. The sensitivity of E continues adequate to at least 200 mμ. Differing greatly from these curves are the response curves of the respective detectors at the exit slits of spectrophotometers resulting from energy distribution of source, prism dispersion (if not compensated by varying slits), and instrumental transmittance.

shown the average photopic and scotopic luminosity curves plotted to unit maxima. The shift of the curve towards the shorter wavelengths with decreasing brightness is known as the Purkinje effect. In most visual spectophotometry the eye of the observer is probably in varying states of adaptation between the two extremes, depending on the part of the spectrum in which measurements are being made and the room luminance within his field of view.

The spectral responses of various types of photocells, including various types of sensitive surfaces, vary enormously [6, 52]. Even for photocells of a given type and surface the responses may vary considerably, somewhat similarly to the luminosity curves of different individuals. In figure 11 are shown spectral sensitivity curves of certain types of photoelectric cells that have been commonly used in spectrophotometers. These are plotted relative to unit maxima and give no indication of the absolute sensitivity of the cell. They indicate relative response to an equal-energy spectrum.

Curve C is more or less typical of the barrier-layer cells used in the Cenco-Sheard and Coleman spectrophotometers. Curve D represents more or less the so-called "red sensitive" electron-emission type of phototube used in the General Electric recording spectrophotometer, the Coleman universal spectrophotometer, and the Beckman quartz spectrophotometer. Curve E represents the "blue sensitive" phototube also used in the Beckman instrument.

It should be remembered that curves C, D, and E of figure 11 do not represent the relative responses of these photoelectric cells at the exit slits of actual instruments. The response will be considerably affected by the spectral energy distribution of the source used, by the spectral dispersion (for prism instruments) unless compensated by varying slit widths, and by the spectral transmittance of the spectrophotometer.

Similarly the luminosity curves, A and B, of figure 11 do not represent the relative field luminances in a visual spectrophotometer, nor does the plate sensitivity curve of a photographic plate represent the relative spectral densities obtained in any photographic spectrophotometer. In both cases the response curves (luminance or density) depend on the instrumental dispersion and transmission and the energy distribution of the source as well as on the spectral sensitivity of the detector.

The photographic plate has rarely been used for spectrophotometry above 500 mμ, this being the effective limit for unsensitized emulsions. Absorption of the gelatine prevents adequate sensitivity below about 220 mμ. If it is desired to use photographic methods below this wavelength, special plates must be used. These may use fluorescent dyes in the emulsion or may use non-gelatine suspensions [4, 6, 11]. A recent publication [54, fig. 34] gives relative spectral sensitivity curves of four typical photographic materials.

2. Photometric Principles and Devices

The design of the photometric part of a spectrophotometer depends directly upon the detector or receptor used. It may be recalled that spectrophotometry consists always of measuring the ratio of two radiant energies (or radiant fluxes) at a specified frequency or wavelength, this measurement being repeated at other frequencies or wavelengths as often as desired over the spectral range of interest. With a photoelectric cell this ratio may be determined by measuring the ratio of currents evoked by the two radiant fluxes, provided a closely linear relation can be established between the irradiance on the photocell and the current evoked in the cell and indicated in the galvanometer or other measuring device. In such cases the photometric system is mostly electrical.

A similar direct measurement of the spectrophotometric ratio by the photographic plate is difficult and by the eye impossible. In nearly all photographic spectrophotometers and in all visual spectrophotometers, therefore, this ratio is measured by some auxiliary optical system, often incorporated in the instrument, the setting being indicated by equality of luminance or of photographic density in a 2-part photometric field.

(a) Visual Photometry

While the eye can estimate only roughly the absolute magnitudes of photometric quantities, it can determine with considerable precision when the two properly juxtaposed parts of a photometric field are equally bright—provided, of course, that the two parts of the field are of the same chromaticity, as is usually the case in visual spectrophotometry.

In a visual spectrophotometer, therefore, the photometric part of the instrument includes (1) means for securing a uniformly bright 2-part photometric field and (2) means for varying the luminance of one or both parts of this field in a continuous, easily adjustable, and known manner, so that when the eye indicates equality of match the desired spectrophotometric ratio can be determined.

Various types of photometric field have been used; these are shown in figure 12, taken from the O. S. A. Spectrophotometry Committee report [1]. In type I of this figure the two parts of the field consist of two juxtaposed spectra formed at the exit slit of the instrument and viewed by a magnifying eyepiece; the other fields illustrated in figure 12, type II, are formed or projected in or between the telescope and collimator lenses and

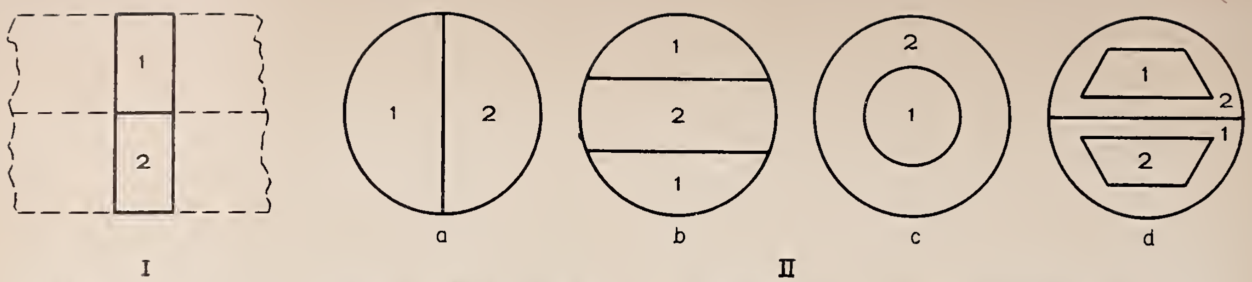


Figure 12. *Various types of photometric fields used on visual spectrophotometers. Type I, juxtaposed spectra; type II, monochromatic field.*

The eye can equate two properly juxtaposed brightnesses with considerable precision.

are viewed by the eye placed (usually) close to the exit slit. The trapezoids of type II–d are usually about 8 percent darker than their surroundings (being produced by reflection from clear glass plates), and equality of contrast rather than equality of brightness is the criterion for photometric match.

Various methods have been used to vary the luminance in one or both parts of the field. (1) When two collimators are used the slit width of one may be varied and the luminance is taken as proportional to the width. The method conserves light but its accuracy is limited. (2) Rapidly rotating sectors have been used, having variable aperture while rotating. (3) Polarization methods have often been used, probably more than other means. An instrument using this method of luminance variation is illustrated in section V–1.

Still other methods are possible and have occasionally been employed. However, the fundamental inverse-square relation has been little used in visual spectrophotometry because of the resulting low luminances. For further information regarding various phases of visual photometry or spectrophotometry reference may be made to section V–1 below or to some of the publications already listed [1, 5, 35].

When properly used, a visual spectrophotometer can give results of high accuracy. Under the best conditions the uncertainty of the mean of several settings is some fraction of 1 percent of the value. However, the necessity of making repeated settings to obtain adequate reliability makes the method tedious and time-consuming. As an independent method in measuring standards of spectral transmittance and for certain other special problems, the König-Martens visual spectrophotometer at the National Bureau of Standards is still of great utility, but for most transmission measurements and for practically all reflection measurements the instrument and method have been superseded by more rapid photoelectric spectrophotometers.

(b) Photographic Photometry

When a photographic plate is exposed to radiant energy and developed, the well known blackening occurs, and the relation between the photographic (optical) density of the developed plate and the exposure to which the plate is subjected is more or less as shown in figure 13 [6]. Density and exposure are terms widely used in photographic photometry, the former being defined usually as the negative logarithm of the transmittancy (ratio of luminous flux transmitted by the silver deposit to that incident upon it) of the developed photographic material, the latter representing the logarithm of the product of illuminance (light units) and the time of exposure. Photographic or optical density is thus analogous to absorbancy as defined in section II–2, above.

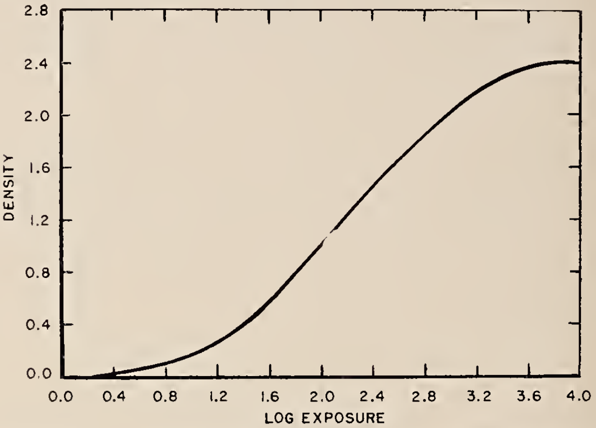


Figure 13. *Typical density-exposure curve of photographic emulsions.*

Photographic spectrophotometers are usually designed in such a way as not to be dependent on this and certain other characteristics of photographic materials. This curve is derived from figure 164 of reference [6] (copyright by McGraw-Hill Book Company, Inc.) and is reproduced by permission.

The relation shown in figure 13 is the basis for much photographic photometry. However, the many variables involved in the preparation, exposure, and development of photographic emulsions render accurate photographic spectrophotometry by this relation very difficult. Accordingly in such work it has become almost universal to ignore the characteristic relation shown in figure 13, and instead to design the photometric system such that two juxtaposed spectra are simultaneously photographed for each exposure and the only photometric observation required is the determination of points of density match along the juxtaposed spectra. Thus all worries regarding type of emulsion, factors of development, and uniformity of the plate, are eliminated.

In one of the two juxtaposed spectra the radiant energy has passed through the sample (for example, the solution), and in the other spectrum it has passed through the comparison sample (for example, the solvent) and been reduced in known amount by the photometric system. In general, a series of juxtaposed spectra is taken on each plate, the reduction of the comparison beam being made in known steps in the respective exposures. Measurement of the developed plate then consists in determining the precise frequencies or wavelengths at which the match-points occur, these being the frequencies or wavelengths at which the transmittancy of the solution has the predetermined value at which the photometer was set for that particular pair of spectra. The match points may be determined visually or photoelectrically. Further details are given in section V–2.

Perhaps the principal advantage of the photographic method of spectrophotometry is the permanent record obtained, and for a long time it was the only method commercially available for the ultraviolet.

(c) Photoelectric Photometry

As already noted, a photoelectric cell, with appropriate meter, contains within itself the possibility of direct spectrophotometric measurement, something wholly untrue of the eye and practically unfeasible with the photographic plate. If there be adequate sensitivity, the question of primary importance in direct photoelectric photometry is whether there is a linear relation between the irradiance on the photoelectric cell and the resulting indication on the meter or other device by which the photoelectric current is indicated. Lacking such linearity there must be adequate calibration or resulting error.

For a long time such linearity for the electron-emission type of cell, now usually called a phototube, appeared to be the exception rather than the rule [52]. For many modern phototubes, however, particularly the vacuum type, and at irradiances of the order of those used in spectrophotometry, the linear relation is closely if not exactly followed. Some of the photoelectric spectrophotometers now on the market are based on the linearity of the irradiance-current relation. In another type of spectrophotometer this linear relation is of no importance; the phototube is merely a balancing indicator and the photometric system is based on polarization principles similar to those in certain visual spectrophotometers.

The barrier-layer photocell, not requiring external voltage, has also been used in spectrophotometry. The question of linearity is likewise of importance with this photocell, and here as always the reliability of the photometric scale should be checked in one way or another if results of the highest accuracy are desired.

(d) Sample Holders

Four of the five principal constituents of every spectrophotometer—namely the source, the spectrometer, the photometer, and the detector—have been considered above. There remains only the sample container and the holder, carrier, or other device by which the sample may be moved in or out of the beam or from one beam to another, or interchanged with the standard or comparison sample, or merely held in place. Space is lacking to illustrate the numerous devices that have been designed for this purpose, these designs varying in turn with the type of measurement to be made, whether it be the transmittance of a glass, the transmittancy of a solution, or the directional reflectance of a textile, powder, or other type of material.

Glass or quartz cells of varying types for holding solutions and solvents are described in detail in many of the publications listed [3, 4, 11, 35, 53]. Several important considerations relate to the use of such cells. The end plates used in the solution and solvent cells should be identical in every respect; the internal dimensions of the cells should be accurately known; and all parts of the cells with which the solution and solvent are in contact should be capable of being thoroughly cleaned.

Another important factor in both transmission and reflection measurements relates to the mechanical stability of the sample holder or carrier, and the precise reproducibility of positioning when the sample is replaced by the standard, or when sample and standard are interchanged. Closely related to this in reflection measurements is the problem of the positioning of a sample such as a textile which is apt to "bulge" so that it is not in the same plane as the standard or comparison sample. Putting both samples under a cover glass may remedy this, but may introduce multiple reflection errors [55].

V. Typical Instruments and Methods

1. Visual

It is believed that the only visual spectrophotometer commercially available at present in this country is that manufactured and sold by the Gaertner Scientific Corporation [56]. Since this is somewhat similar to the visual spectrophotometers sold by Adam Hilger, Ltd. [3] and formerly sold by the Bausch and Lomb Optical Company [57], and also is similar in principle to the König-Martens spectrophotometer [35] in use at the National Bureau of Standards, it has been chosen for illustration. Where the other instruments have special points of difference, these will be noted.

The photometric part of the Gaertner spectrophotometer is outlined in figure 14, which is based on advertising circulars of the company. In this instrument, as shown, and in the Hilger and Bausch and Lomb instruments, the photometer is a separate unit from the spectrometer, whereas in the König-Martens spectrophotometer the two parts are incorporated into one instrument.

The source of radiant energy shown in the illustration is one designed for both transmission and reflection measurements. (A source designed solely for transmission measurements can be obtained if desired.) It is a white-lined sphere, 10 inches in diameter, in which 16 incandescent 6-volt lamps are mounted around the vertical equator. For reflection measurements the two samples being compared, *A* and *B*, are held against openings in the sphere as shown in the upper part of figure 14.

Specially designed diffusing screens near each lamp shield the sample and standard from direct irradiation without casting shadows. Multiple reflections from the walls of the sphere then combine to produce diffuse irradiation. This irradiation fails to be perfectly diffuse principally because of the sphere opening through which the reflected energy is taken to the instrument. Collimating lenses are placed at *L*. The type of directional reflectance measured is designated as $R_{d,o}$ (section II–3).

For transmittancy measurements a single diffusing plate, *C*, is used, as shown in the lower part of figure 14. The radiant energy reflected from this plate is split into two beams by the pair of rhombs, *R*, and led through the solution and solvent cells, *T* and *T′*, into the photometer.

For both reflection and transmission measurements the two beams are passed by suitable optical means through the photometer and the spectrometer, and the eye placed at the ocular slit of the spectrometer sees a photometric field of type IIa, figure 12, with dividing line horizontal.

The photometer *P* is the polarization type known as the Martens photometer [58], although

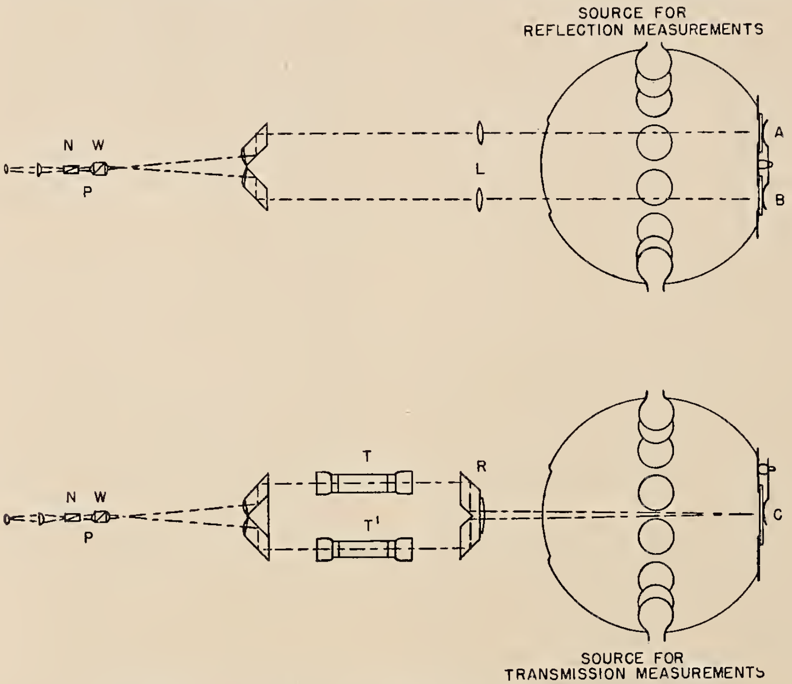


Figure 14. *Optics of the Gaertner visual spectrophotometer.*

The spectrometer is not shown. With this equipment the samples are irradiated before the radiant energy is dispersed in the spectrometer.

the internal optics of the German and American designs are not identical. The two beams entering the instrument are led to form the two halves of the photometric field, the dividing line of which is the edge of a biprism. The light in the two halves of the field is polarized in mutually perpendicular planes by means of a wollaston prism, W, the planes of polarization being respectively parallel to and at right angles to the dividing line of the field (the edge of the biprism). A nicol prism, N, is mounted at the left of the wollaston prism, and by turning this nicol the two halves of the field may be precisely matched in brightness.

If the transmittancy of a solution is being measured, let α_o be the angle of match with both beams blank (or containing identical solvent cells), and α_1 be the angle of match when the respective cells containing solution and solvent are placed in the beams. Then

$$T_s=\frac{\tan^2 \alpha_1}{\tan^2 \alpha_o}$$

The derivation of this formula and many other things of interest in this connection may be found in the papers by Martens [58] and McNicholas [35]. If the solution and solvent are interchanged, a similar relation is obtained. That is,

$$T_s=\frac{\cot^2 \alpha_2}{\cot^2 \alpha_o}$$

By combining these two relations it follows that

$$T_s^2=\frac{\tan^2 \alpha_1 \cot^2 \alpha_2}{\tan^2 \alpha_o \cot^2 \alpha_o}$$

or

$$T_s=\tan \alpha_1 \cot \alpha_2$$

The $\tan^2$ relation is useful if one wishes to put direct-reading scales on the photometer and this has been done by both Gaertner and Bausch and Lomb. In this case it is essential (unless correction be made) that α_o be exactly 45° (so that $\tan^2 \alpha_o=1.000$).

It may easily be overlooked in this connection that a substitution or interchange method should always be used in spectrophotometry. In a substitution method the test sample and its reference standard should be compared in the same beam by way of a third or comparison sample in the second beam. This is true in both transmission and reflection measurements. It is often convenient to have the comparison sample identical with the reference standard but except in direct-reading instruments this is not essential.

On the König-Martens spectrophotometer at the National Bureau of Standards the interchange method is used and T_s is computed from the $\tan \times \cot$ relation. This is equivalent to a substitution method, but the value of α_o is immaterial and no measurement is made of it. A reference standard is necessary but no comparison sample.

On the Bausch and Lomb spectrophotometer means were provided for passing the beam through solution and solvent cells in which the thickness of absorbing layer could readily be varied without removing the cells.

On the Hilger Industrial and Research Spectrophotometer a similar $\tan^4 \alpha$ relation is used [59, 3], resulting in a more open scale at high absorbancies.

Auxiliary equipment designed and constructed at the National Bureau of Standards [35] for use with the König-Martens spectrophotometer includes the following features:

1. Hemispherical irradiation of the sample and standard for reflection measurements, by means of which the irradiation is in effect almost perfectly diffused. The type of directional reflectance measured is thus in effect $R_{D,0}$, which is equal to R_0 by the reciprocal relation.
2. Installation of mercury and helium sources which can be readily interchanged with the incandescent source and are valuable for use in transmission measurements as well as in wavelength calibration.
3. The installation of accurately calibrated rotating sectors by means of which (1) the photometric scale can be readily checked over the range from $T=0.80$ to $T=0.00883$ and (2) the transmission scale can be greatly extended at low transmissions. This extension is effected by placing the sector ($T=0.09945$ or 0.00883) in the blank beam and measuring the transmittance of the sample relative to that of the sector.

Many other types of visual spectrophotometers have been designed and used during the past 100 years. These are described in other publications [1, 3, 5, 6, 11] or in papers to which these publications refer.

2. Photographic

Major contributions to the science of photographic spectrophotometry have been made by Adam Hilger, Ltd., of London. Their rotating sector photometer introduced about 1910 for use with suitable source and spectrograph was apparently the first commercially available equipment for reliable ultraviolet spectrophotometry, and such equipment was shortly thereafter in use in the United States [60].

The National Bureau of Standards equipment is described in B. S. Sci. Paper 440 [53], and the optics of the apparatus are outlined in figure 15. Radiant energy from the source, E, passes through cells T and T', containing solution and solvent placed in a constant-temperature inclosure. The respective beams are deviated and focused by the wedge lenses at L, then further redirected by the biprism, B, in front of the spectrograph slit;

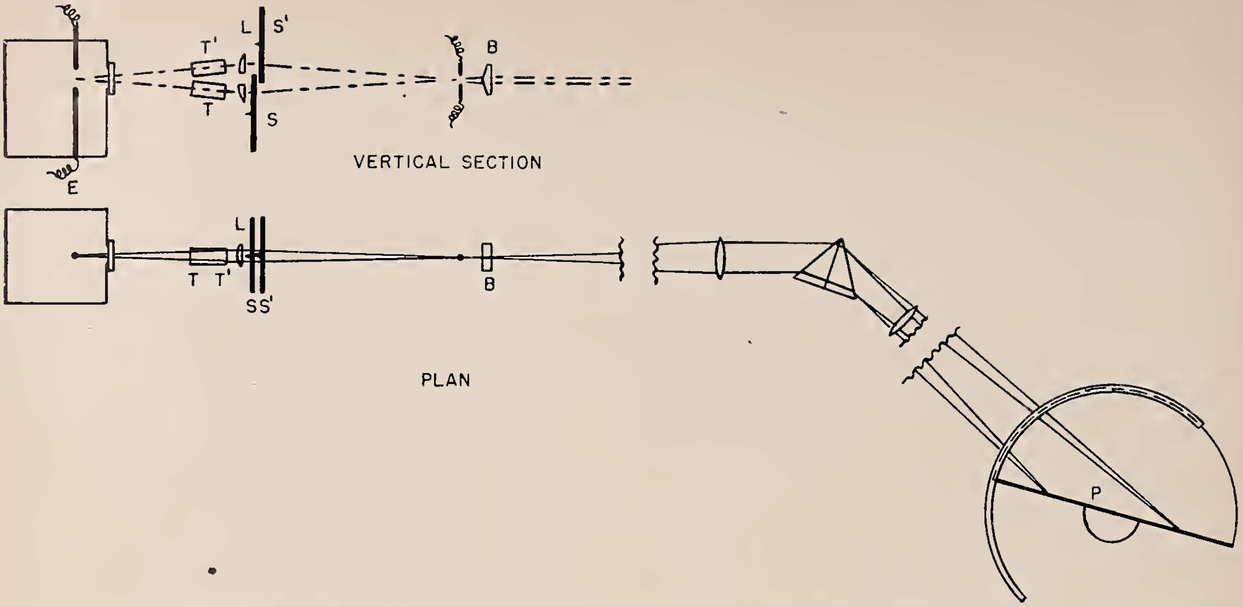


Figure 15. *Optics of the Hilger sector-photometer, photographic spectrophotometer as installed at the National Bureau of Standards.*

With this equipment the samples are irradiated before the radiant energy is dispersed in the spectrograph.

finally the two beams are made to form a pair of juxtaposed spectra on the photographic plate at *P*, the dividing line between the two spectra being the spectral image of the horizontal edge of the biprism, *B*. All optical parts are of crystalline quartz. Rotating sectors are placed at *S* and *S'*. The sector in the solution beam is kept at maximum opening, designated as 1.000 on the transmittancy scale; the sector in the solvent beam may be set at any transmittancy value between 1.000 and 0.000, this value being different for each exposure.

There results, when the plate is developed, a series of exposures as shown in figure 16. By determining for each exposure the frequencies or wavelengths at which the two juxtaposed spectra are of equal density, the transmittancy or absorbancy curve may be derived. On the plate at top and bottom may be seen the aluminum spark spectra used for wavelength calibration (the lines at the shorter wavelengths do not show well in figure 16) and the comparison spectra taken with both beams blank and both sectors set at 1.000. On this plate it will also be noted that

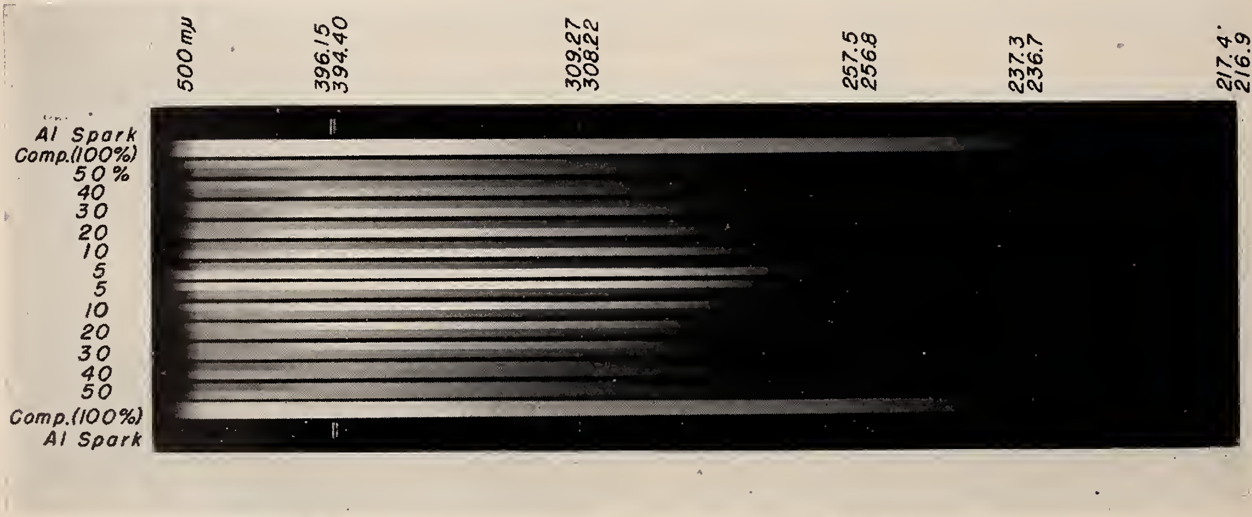


Figure 16. *Typical set of exposures made with equipment shown in figure 15.*

Note continuous spectrum extending from 500 to 220 mμ produced by high-voltage Tesla-coil spark in distilled water. For details see text.

the spectra in the lower half are a reverse repetition of the spectra taken in the upper half. On the National Bureau of Standards instrument both sectors were made adjustable and scales attached. To eliminate the effect of possible slight lack of match in the two halves of the comparison or 100 percent spectra, the solution and solvent cells are interchanged in the two beams at the middle of the plate and the reverse set of exposures made. Averaging the wavelengths obtained from the respective pairs of exposures tends to eliminate error from this cause.

The soundness of the principle involved in this method of photographic photometry is open to question, although at the Bureau of Standards consistent deviations in results from those by other methods were never noted [53]. The matter has been considered by various investigators but it is sufficient here to refer to the chapter by Jones in Measurement of Radiant Energy [6]. He discusses in detail the various factors involved in photographic photometry by various methods and concludes in this instance "that results are valid provided the sector speeds are sufficiently high." He further states, "It is impossible, of course, to make a general statement as to how fast sectors should be run to eliminate reciprocity-intermittency errors, but under the majority of conditions 30 interruptions per second are adequate." Since in the Hilger sector photometer both beams are interrupted by rotating sectors it is probable that error from this cause is not appreciable even at somewhat slower speeds.

However, to eliminate this uncertainty the Hilger Company put on the market another photographic photometer designated as the "Spekker" photometer [61, 3]. This design eliminated the rotating sectors and changed the optics to avoid the vertical dispersion introduced by the wedge-lenses and biprism (a more concentrated source can thus be used) and to produce a more nearly collimated beam through the solution and solvent. Instead of the rotating sectors, rectangular diaphragms are placed at appropriate places in the beams and the aperture in the solvent beam can be reduced by known amounts to compensate for the absorption of the solution in the other beam. Of course, for accurate work, this requires uniformity of radiant flux per unit area across the diaphragm. A similar photometer was previously designed by Lewis [62], except that vanes were used in place of the diaphragms. The methods are otherwise similar to the sector-photometer method.

In this country sector photometers are made and sold by the Bausch & Lomb Optical Co. [63] and the Gaertner Scientific Corp. [64] for use with certain of their spectrographic equipment. The principle in each case is the same as that of the Hilger sector photometer, but the sectors are synchronized so that variations in intensity of the source are much more certainly eliminated than with the Hilger sector equipment. Absorption tubes up to 70- or 100-mm length can be accommodated.

Perhaps the principal defect of the above methods is the time involved in the measurements. The series of exposures usually takes a half hour or more, to which must be added the time involved in development and reading of the plate. Various schemes have been devised to speed up this process, the principal objective being to obtain the whole series of calibrated spectra at one exposure, so that unstable solutions can be recorded in a very short time interval. In a design by O'Brien [65, 11] a Lummer-Brodhun cube with up to 20 silvered strips alternating with the same number of clear regions is combined with a rotating logarithmic step sector, all placed just in front of the spectrograph slit and with dimensions determined by the length of the slit. Juxtaposed spectra are obtained, absorption in the solution being balanced by the reduced apertures in the step sector. In this manner the spectrogram obtained provides a direct plot of photographic density against wavelength with any value of exposure.

In another design by Twyman, a pair of Hilger echelon cells [3, 61] having variable internal thicknesses are combined to give a series of juxtaposed spectra on the photographic plate. Absorption in the solution is balanced by a suitable rotating sector. Again the dimensions are determined by the length of the spectrograph slit.

3. Photoelectric

Numerous photoelectric spectrophotometers have been designed by various investigators but not until the 1930's did any type become commercially available and have extensive usage. The two photoelectric spectrophotometers that have been chosen for illustration are the General Electric recording spectrophotometer and the Beckman quartz spectrophotometer. Spectral reflection as well as spectral transmission measurements can be made on both of these, and they are both commercially available.

(a) General Electric Recording Spectrophotometer

The present model of the General Electric recording spectrophotometer [42] originally designed by Hardy [40, 41], gave great impetus to colorimetric analysis and specification because (1) there was great increase in speed over previous nonrecording spectrophotometers, (2) it could make spectral reflection measurements just as readily as spectral transmission measurements, and (3) its precision and reliability were adequate for most types of measurement. The recording

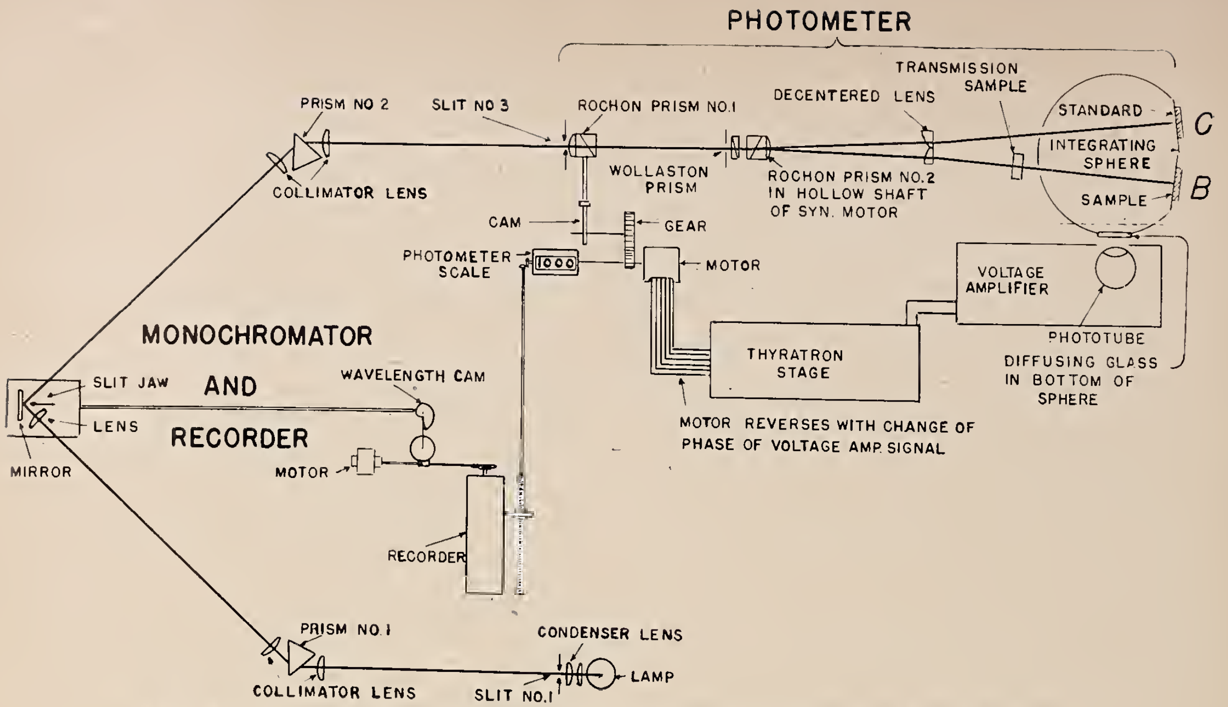


FIGURE 17. *Schematic diagram of General Electric photoelectric recording spectrophotometer.*

On this instrument the radiant energy is spectrally dispersed before incidence upon the samples.

feature is also of great importance in many kinds of work.

A schematic diagram of the instrument is shown in figure 17 which is a reproduction (with slight changes) of figure 1 of Michaelson's paper [42]. Radiant energy from the lamp forms a prismatic spectrum in the plane of the mirror at the left of the figure. A second slit here isolates a small part of the spectrum and passes it on through prism No. 2. This second dispersion spreads the stray energy into a secondary spectrum in the plane of slit No. 3. This third slit obstructs most of this stray energy but transmits most of the spectral band isolated by the second slit. Thus there passes into the photometer a spectral band of width determined by the slits used, and almost wholly free of stray energy from other spectral regions. As the spectrum is traversed the mechanical widths of the slits are continually changed by cams so as to transmit a constant amount of spectrum expressed in terms of millimicrons. The usual nominal width is 10 mμ over the range from 400 to 700 mμ but instruments with 4, 5, and 8 mμ widths have been made and the wavelength range has occasionally been extended to 750 mμ (and with wider slits to above 1,000 mμ), as on the National Bureau of Standards instruments.

The radiant energy transmitted by slit No. 3 passes in turn through (1) the balancing rochon prism No. 1, (2) the wollaston prism, where it is split into two beams polarized at right angles to each other, (3) the rotating rochon prism No. 2, mounted in the hollow shaft of a synchronous motor, (4) the separating decentered lenses, (5) the transmission compartment and (6) the sphere openings, and is finally incident upon the reflecting samples at B and C.

As rochon No. 2 rotates, the respective radiant energies incident upon B and C alternately go through successive maxima and minima, each maximum on B coinciding in time with the minimum on C. The instantaneous values of these alternating components are given in the following expressions [40]:

$$I=I_1R_1+I_2R_2=A^2(R_1\sin^2\alpha\sin^2\omega t+R_2\cos^2\alpha\cos^2\omega t)$$

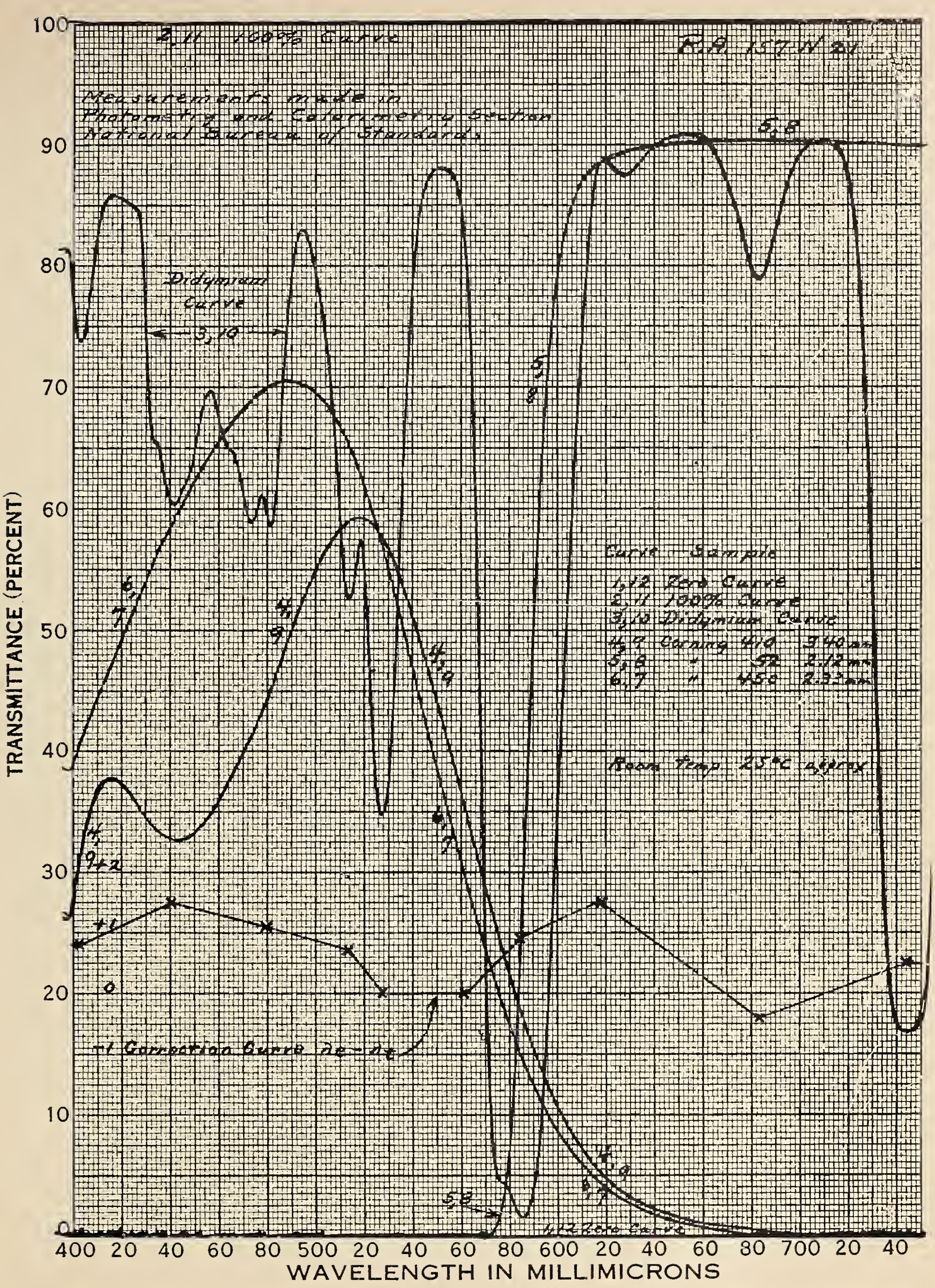
Let $A^2=2$, for convenience; then

$$I=(R_1\sin^2\alpha+R_2\cos^2\alpha)-(R_1\sin^2\alpha-R_2\cos^2\alpha)\cos^2\omega t.$$

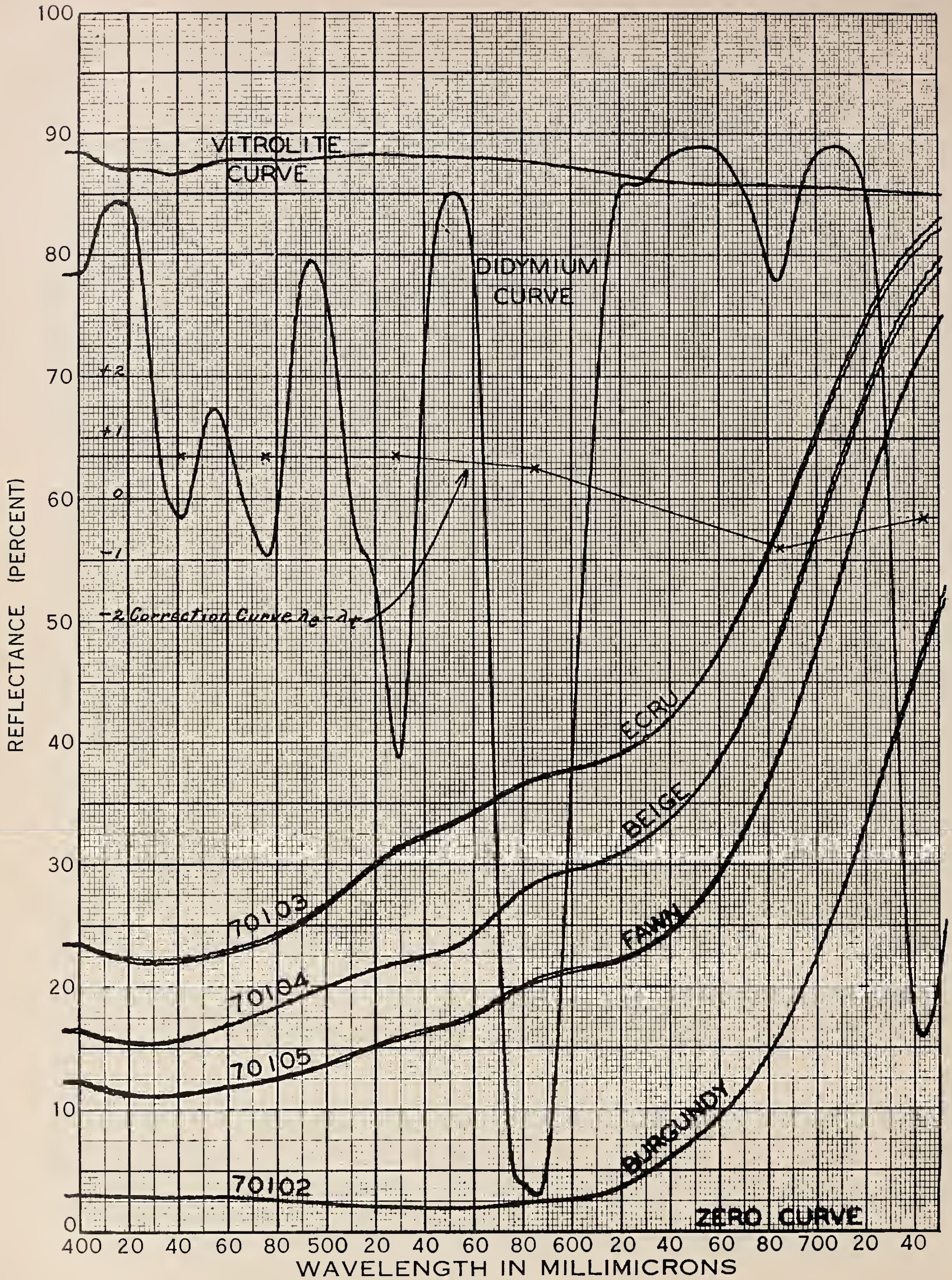
"Since the photoelectric current is a linear function of the light intensity, at least over a small range, this equation, when multiplied by a

FIGURE 18. *Typical spectral transmittance curves recorded on a General Electric spectrophotometer at the National Bureau of Standards.*

Zero, 100%, and didymium calibration curves are also shown. The didymium glass transmittance curve is used for wavelength calibration of the sheet, and the wavelength correction curve is shown plotted. Nominal slit widths used are equivalent to 4 mμ of spectrum.



(Legend on page 24)



(Legend on page 27)

suitable proportionality constant, represents the instantaneous value of the cell current. It will be seen that the cell current consists of a steady component proportional to $R_1 \sin^2 \alpha + R_2 \cos^2 \alpha$ and an alternating component of frequency 2f $(=\omega/\pi)$ and amplitude proportional to $R_1 \sin^2 \alpha - R_2 \cos^2 \alpha$. Since the prism (rochon prism No. 2) rotates at 1,800 rpm the frequency of the alternating component is 60 cycles per second" [40].

A photoelectric cell of the cesium-oxide type is placed just beneath a ground-glass window in the bottom of the sphere. This phototube is connected, through an a–c voltage amplifier and a "thyratron stage", so that any alternating current from the photocell will in effect drive the balance motor, the direction of turn of the motor depending on the phase of the current. This phase will, in turn, depend on which of the two radiant energies reflected from *B* and *C* is the greater.

The motor is geared through a cam arrangement so that, as the armature turns, it turns rochon prism No. 1 and always in the direction that will balance the two radiant energies reflected from *B* and *C*. When these two reflected radiant energies are equal, there is no torque on the motor and the motor and rochon are at rest.

In operation, another motor (at the left) runs steadily; through cams it changes the wavelength of the radiant energy passing slit No. 3 by moving the second slit through the spectrum, and at the same time it turns the wavelength drum on which the recording paper is placed. The final connection is made by translating through levers and cams the amount that rochon No. 1 turns so as to operate a recording pen that moves up and down on the paper. This pen moves linearly with the transmittance or reflectance of the sample and thus the respective curve is steadily traced through the spectrum. In addition to the normal cam, cams giving "×5," "log," and "loglog" curves can be used.

Typical sheets of such recordings as regularly run at the National Bureau of Standards are shown in figures 18 and 19. Figure 18 is the record of three transmittance curves run for certain glasses as indicated. The slits for this recording were equivalent to approximately 4 mμ of spectrum. In this figure will be noted first the three calibration curves. (1) The "zero-curve" is run with the sample beam blocked off. (2) The "100-percent curve" is run with no sample in either beam. (3) The "didymium curve" is run with a calibrated didymium glass in the sample beam; this curve is for wavelength calibration of the sheet as explained in section III–2. After the three calibration curves, the curves for the samples tested are successively run; then the whole series of sample curves and calibration curves are repeated in reverse order. This repetition insures against undetected erratic or gradual changes in conditions during the run. Each curve takes 2½ or 5 minutes, at the choice of the operator, depending on the selectivity.

Figure 19 shows a similar graph sheet for directional reflectance measurements made on the other recording spectrophotometer at the National Bureau of Standards, this instrument having slits equivalent to approximately 10 mμ of spectrum. (For reflectance measurements the "transmission sample" is of course removed.) The order and purpose of the respective curves is the same as in figure 19, except that a "Vitrolite curve" is run instead of the 100-percent curve. The purpose of the Vitrolite curve is to enable all of the reflectance curves to be corrected so as to be truly relative to freshly prepared MgO, the accepted standard for such work; see section VII–3. This is done as follows.

In transmission measurements it does not matter what the reflecting materials *B* and *C* (fig. 17) are, provided they will give a "100-percent" curve entirely on the network part of the sheet. (The cams are reliable for extrapolation above the network to only about 100.5 percent.) They can be fresh or old MgO, $MgCO_3$, white glass, white paper, etc. However, it is a matter of importance that the reflectance be high, to avoid loss of sensitivity; and it is a matter of convenience that *B* and *C* be essentially identical, so that the 100-percent curve will lie closely if not exactly on the 100-percent coordinate line. The substitution principle is fully complied with when at any wavelength the transmittance is computed from the ratio of ordinates of the transmission sample curve to the 100-percent curve (correcting each for the zero curve if necessary).

For spectral reflection measurements (transmission sample removed), if one is willing to prepare identical fresh MgO standard surfaces each day, the operation is similar to that for transmission measurements, except that by the substitution principle the MgO surface at *B* is *the* standard surface; the other MgO at *C*, identical or not, is merely the comparison sample. Because of the slight decrease in reflectance of the MgO (see section VII–3), it is necessary that each MgO sample be newly prepared each day. If *B* is not newly prepared it is no longer standard; if *C* is not newly prepared (and *B* is), the 100-percent curve will rise off the network below 500 mμ. Of course if it is known by experience that the 100-percent

FIGURE 19. *Typical spectral directional-reflectance curves recorded on a General Electric spectrophotometer at the National Bureau of Standards.*

Zero, Vitrolite, and didymium calibration curves are also shown. The didymium glass serves for wavelength calibration as in figure 18, but the shapes of the correction curves on the two instruments are different. Nominal slit widths equivalent to 10 mμ of spectrum are used on this second instrument. The Vitrolite curve replaces the 100% curve and enables the reflectance data to be reduced relative to freshly prepared magnesium oxide.

curve is "on the line" and one wishes to take the chance, he can omit the 100-percent curve and simply prepare sample *C* each morning for the day's operation.[2]

This is risky, however, for certain kinds of work, for experience has indicated that newly prepared MgO samples may vary slightly (0.1 or 0.2 percent) for unknown reasons. At the National Bureau of Standards it has been considered better to calibrate a working standard of directional reflectance (placed at *B*) by comparison with several different new preparations of MgO and to repeat this check occasionally to detect any possible change in the working standard.

The "Vitrolite curve" in figure 19 represents such a calibrated standard of directional reflectance [43]. By its use, comparison sample *C* can be any sample of high enough reflectance to keep the recording within the network; however, in order to keep the recordings close to their true values (which has several advantages), it is well for sample *C* to be a reasonably fresh surface of MgO. At any wavelength, the correct value of the directional reflectance of the sample (placed at *B*), relative to that of fresh MgO, is obtained by dividing the recorded ordinate for the sample by the ratio of the recorded ordinate of the Vitrolite to the correct value for the Vitrolite relative to fresh MgO.

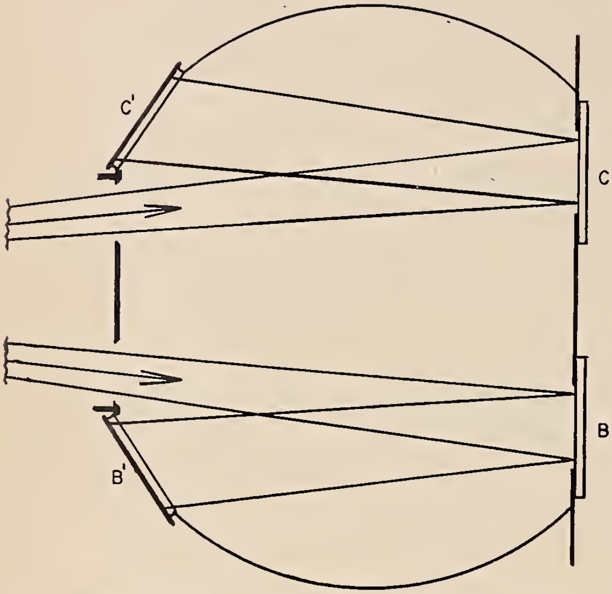


FIGURE 20. *Design of sphere used on newer models of General Electric spectrophotometer.*

The energy is incident at 6° and if the surface of B is plane and polished the specular component of the reflected energy is received at B' as shown. B' may be a "light trap" to absorb and thus exclude this specular component from the measurements, or it may be an MgO surface to reflect and thus include this component. In the older design of sphere, shown in figure 17, the energy is incident at right angles to B and part, but not all, of the specular component is reflected out through the entrance aperture.

The type of directional reflectance measured is $R_{0,d}$ with the type of sphere illustrated in figure 17; part of the specular component of the energy reflected from a plane polished surface at *B* goes back through the entrance aperture. With the newer design of sphere, shown in figure 20, the radiant energy is incident upon samples *B* and *C* at approximately 6° and the specular component of the reflected energy is returned to the sphere apertures at *B'* and *C'* as shown. If the surface of the test sample placed at *B* is plane and polished, this specular component can be wholly excluded from or included in the measurements by either placing a completely absorbing "light trap" at *B'* or filling the aperture with a sample of fresh MgO. The respective directional reflectances may be designated as $R_{6,d}$ and $R_{6,D}(=R_6)$. However, two things of importance should be noted in this connection:

1. *Specular component included* ($R_{6,D}$). If the sample at *B* is 96 percent diffusing and only 4 percent specularly reflecting (approximated by a plane, polished white glass), the error involved (in $R_{6,D}$) if the reflectance of *B'* does not quite equal that of fresh MgO is of second order, a small fraction of the 4 percent. However, if the sample at *B* is a polished mirror, so that the whole of the reflected beam is first incident upon *B'* before being diffused throughout the sphere, the error is of first-order importance and should be carefully considered.

2. *Specular component excluded* ($R_{6,d}$). If the surface of the sample is not plane but is mottled or irregular in flatness, such, for example, as a piece of enameled iron may be, some of the specularly reflected energy may not be caught in the light trap at *B'*, and the specular component is thereby not completely excluded from the measurements.

The wavelength correction curves for the graphs of figures 18 and 19 are shown in the graphs. The method of applying this correction is simply to read the values of transmittance or directional reflectance at $\lambda+(\lambda_e-\lambda_t)$ instead of at λ. The most effective method of reading such values is usually decided for himself by each reader; equipment facilitating the curve reading has been designed by Reimann [66].

Many other details relating to the General Electric or similar recording spectrophotometers may be found in papers issued from the National Bureau of Standards [38, 10, 67] and in papers published by Pineo [68], Stearns [69], and Buc and Stearns [70, 39, 71]. Discussion of the error possible with fluorescent samples is given in section VI–5.

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[2] It has been the Bureau's experience that the MgO may decrease perceptibly in the violet in a day or so after preparation. Others seems to have found somewhat greater stability, perhaps due to different ways of preparing the surface. How often one might need to prepare new surfaces will depend on his experience in the matter and on the accuracy of the work he is attempting to do. See also section VII–3.

(b) Beckman Quartz (Nonrecording) Spectrophotometer

The Beckman quartz photoelectric spectrophotometer, model DU, has several features not found in other commercial spectrophotometers: (1) It covers the wavelength range from 210 to 1,000 mμ approximately, (2) transmission measurements in the ultraviolet from 210 to 400 mμ are made as readily as in the visible spectrum, (3) directional reflectance measurements over the range from 350 to 1,000 mμ can be made under conditions closely equivalent to those recommended by the International Commission on Illumination in 1931 for colorimetric work.

The optics of the apparatus for transmission measurements are as shown in figure 21, taken from the paper by Cary and Beckman [37]. Radiant energy from an incandescent lamp or other source, *A*, is focused on the slit, *D*, by means of the concave mirror, *B*, and the plane mirror, *C*. The beam entering the slit is collimated by the mirror, *E*, and passes through the quartz prism to the reflecting surface, *F*. After reflection at *F* the beam returns along nearly the same path to the same slit, *D*, where it emerges slightly above the entrance beam and the mirror, *C*. After passage through the sample or sample compartment, *G*, the beam is incident on the phototube, *H*.

Two phototubes are supplied installed in the instrument, either of which may be inserted in the beam at will. One is a "cesium oxide" phototube ("red sensitive") for use primarily above 620 mμ. The other is a special "cesium antimony" phototube ("blue sensitive") for use primarily below 620 mμ. If incandescent lamp and common glass phototube are used, this range terminates at about 320 mμ. If the tube has an envelope of Corning 9740 glass, and if a hydrogen lamp with a window of the same type of glass is used as source (all supplied with the instrument when desired), the transmission range extends to nearly 200 mμ.

The photometric scale is based on electrical rather than optical principles. The photoelectric current from the irradiated phototube produces across the load resistor a voltage drop that is balanced by a potentiometer. While this null setting is being made, any imbalance is amplified electronically and is indicated by a milliammeter on the instrument. Accuracy of the photometric scale depends among other things on conformity of the phototube load resistor to ohm's law and on the linearity of the irradiance-current relationship. Since vacuum phototubes are used, the relation should hold closely. Linearity is still further assured by the use of a frame-type anode in the phototube.

Various details regarding the instrument and its operation in spectral transmission measurements may be found in a recent paper from the National Bureau of Standards [33] as well as in the original paper. The following points may be noted here:

1. The slits are narrower than usual on commercial spectrophotometers, normally isolating spectral regions of only 0.5 to 1.5 mμ within the range from 220 to 950 mμ. This feature of the instrument serves three useful purposes. It enables the spectral transmittance of samples having high selectivity to be determined with an accuracy unattainable with instruments having wider slits. It makes possible the precise and accurate comparison of nearly identical samples, even those having high absorption, without the use of slits unduly wide. It also makes possible the reliable determination of very low transmittances by a "step-down" procedure using samples of intermediate transmittance.
2. No error was detected in the photometric scale on an instrument obtained at the National Bureau of Standards in 1945. These tests were made by measuring and comparing the spectral transmittances of certain glass standards on the Beckman, the König-Martens, and the Gibson spectrophotometers, and together with many other details are described in the recent publication [33].
3. Residual wavelength errors found on two Beckman spectrophotometers are shown later in figure 27, curves 1 and 2. A screw adjustment provides for bringing any desired wavelength into perfect alinement. The mercury wavelength 546.1 mμ has been found suitable for this purpose.
4. The quartz mercury arc supplied with the instrument serves not only for wavelength calibration but can be used at certain wavelengths for photometric measurements (section IV–1).

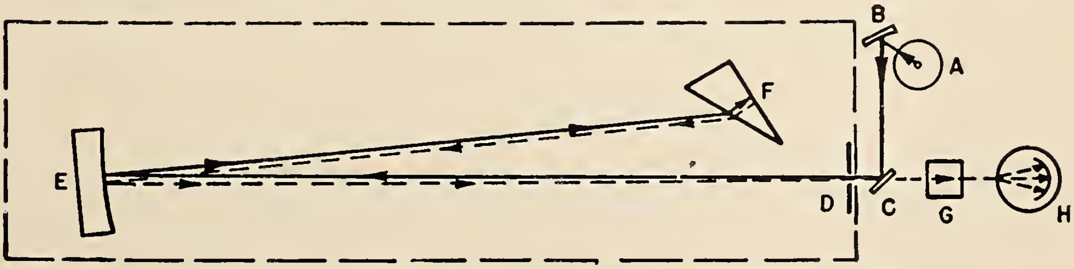

FIGURE 21. *Optics of the Beckman quartz nonrecording spectrophotometer.*

In this instrument the energy is spectrally dispersed before incidence on the sample.

5. The hydrogen arc supplied with the instrument gives a sufficiently continuous spectrum that transmission measurements can be made at any wavelength from 210 to 400 mμ.

6. Trouble has been experienced in the measurement of polarizing materials if the quartz plate over the entrance slit is not cut with faces perpendicular to the axis [33]. At the National Bureau of Standards this plate has been removed.

7. The instrument has the usual amount of stray energy present for single-dispersion spectrophotometers. The purple filter supplied with the instrument should always be used with incandescent source below 400 mμ, and other stray-energy filters should be obtained and used under certain circumstances (section VI–3).

8. Any deviation of the beam by the sample (if wedge-shaped or lens-shaped, for example) may cause error in the measurements.

Directional reflectance measurements can readily be made on the Beckman spectrophotometer by means of special attachments obtained from the manufacturer. The optics of such measurements are shown in figure 22. The radiant energy transmitted through the exit slit, D, is directed downward by means of the mirror, M, and is incident approximately at right angles upon the sample or standard at S. The irradiated area is about 8×17 mm. A carrier enables either the sample or the reflectance standard with which it is being compared to be placed in turn in the beam.

The energy reflected from the sample or standard at approximately 45° in all directions is reflected and focused by the ellipsoidal metallic mirror ring at R onto the ground-glass plate at P. The phototube compartment is mounted on top of the attachment so that the phototube, H, is just above the diffusing glass.

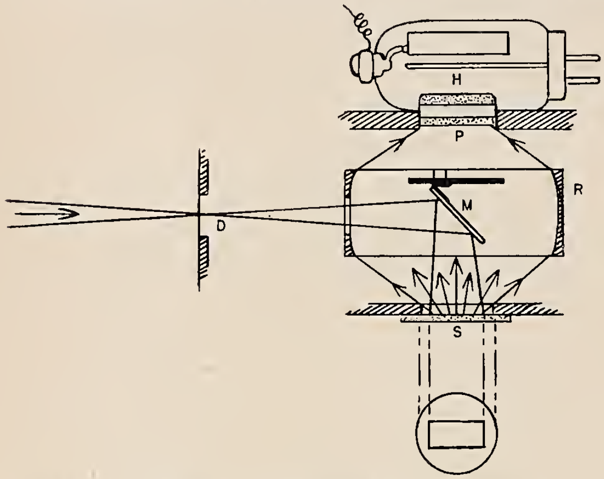

Figure 22. *Optics of the reflectance attachment to the Beckman quartz spectrophotometer.*

The incident energy from the exit slit, D, is directed by the mirror, M, so as to be incident at right angles on the sample or standard placed at S. The energy reflected from S at approximately 45° in all directions is focused by the ellipsoidal mirror ring, R, onto the diffusing glass, P, immediately under the phototube, H.

The operation of the instrument for reflection measurements is similar in all respects to that for transmission measurements. The following points may be noted, however:

1. The slit widths necessary for normal operation are much wider than for transmission measurements. They vary from 3 to 4 mμ in the region near 530 mμ to about 8 mμ at 350 mμ, and 15 mμ at 650 mμ. These widths may be made to vary considerably by adjustment of the sensitivity dial, however, or by operation solely at the ".1" position of the selector switch.

2. While the axis of the reflected energy is closely at 45°, the angular spread of the beam is approximately 20° (35° to 55°). The directional reflectance, $R_{0,45}$, thus measured, is numerically equivalent to that, $R_{45,0}$, recommended by The International Commission on Illumination, as noted above, except that the ICI recommendation implies that the spread of the reflected beam should be zero.

3. In reflection measurements of fluorescent materials the values obtained are liable to the same sort of error as with the General Electric spectrophotometer (section VI–5).

(c) Other Instruments and Methods

In addition to the General Electric and the Beckman spectrophotometers, there are many other photoelectric spectrophotometers of various designs that may be noted here. Some of these are commercial instruments: (1) The Cenco-Sheard spectrophotometer, 325 to 750 mμ, using concave reflection grating and barrier-layer photocell [72]; (2) the Coleman "double monochromator" spectrophotometer, 350 to 1,000 mμ, using transmission gratings instead of prisms [73]; (3) the Coleman "universal" spectrophotometer, 300 to 800 mμ, using single grating with barrier-layer cell, and designed primarily for chemical analysis in the industrial laboratory [73]; (4) the Coleman "junior clinical" spectrophotometer, 400 to 700 mμ, designed solely for clinical analysis [73]; (5) a Gaertner instrument using two spectrometers and a Martens photometer, 450 to 820 mμ [74].

Two new instruments now appearing on the market are the Cary recording quartz spectrophotometer, 200 to 700 mμ [75] and the Beckman model B spectrophotometer, 320 to 1,000 mμ [76].

Among those designed and used by various investigators since 1930, but so far as known not put on the market (those before 1930 are listed in reference [2]), may be noted instruments or equipment by Preston and Cuckow [77], Hogness, Zscheile, and Sidwell [78], Schlaer [79], Zworykin [80], Harrison and Bentley [81], Brode and Jones [82], Gillod [83], Drabkin [84], Little [85], Studer [86], Hardy [87], and Zscheile [88].

Some of these papers treat the subject of photoelectric spectrophotometry in considerable detail, describing methods of wavelength calibration, slit-width and stray-energy errors, absorption cells, treatment of data, and other matters of interest and importance. Examination of them should be of great benefit to those who wish to study the numerous possibilities in the design of such instruments and the use and reliability of the data obtained.

4. Filter Photometers

For certain kinds of work it has been found adequate to isolate desired spectral regions by means of optical filters, each of which will transmit a more or less narrow region of the spectrum. Since the selection of spectral regions is dependent upon the filters at hand, the method has sometimes been referred to as abridged spectrophotometry [89]. Instruments incorporating such means of spectrum variation are known as filter photometers, chemical photometers, or chemical colorimeters, and by various trade names. The present section deals primarily with the filters available for such instruments.

In general, of course, what is desired is a filter that will transmit freely over a narrow range of wavelengths and absorb or reflect completely at all other wavelengths at which (1) the source emits radiant energy in important amounts, and (2) the detector gives appreciable response. If either (1) or (2) is negligible over a given spectral range the spectral transmittance of the filter is unimportant over the same range.

The most suitable filter, or series of filters, for use in any particular instrument or type of work depends, therefore, not only on the spectral range of direct interest but also on the spectral characteristics of the source, detector, and filter over a much wider range. Filters that might be adequate for use with a mercury arc might be wholly unsuitable with an incandescent source. Filters that might be satisfactory for photographic or visual use might give highly inaccurate results if used with a phototube or thermopile as detector.

Several types of filters are available for general use. These are (1) glasses, usually two or more in combination, (2) two or more dyes in solution or incorporated into gelatine or other medium, (3) interference filters, and (4) miscellaneous types.

General information regarding the spectral transmission characteristics of such filters, or of the individual components or selectively absorbing constituents of such filters, may be found in various publications from the National Bureau of Standards [90, 91, 92, 93], in advertising circulars of the Corning Glass Works [94], the Eastman Kodak Company (the Wratten dyed gelatine filters) [95], and the Farrand Optical Company and Baird Associates (the interference filters) [96, 97], and in various other publications [98, 99, 100]. Special sets of filters are also often supplied with the various instruments on the market, and information

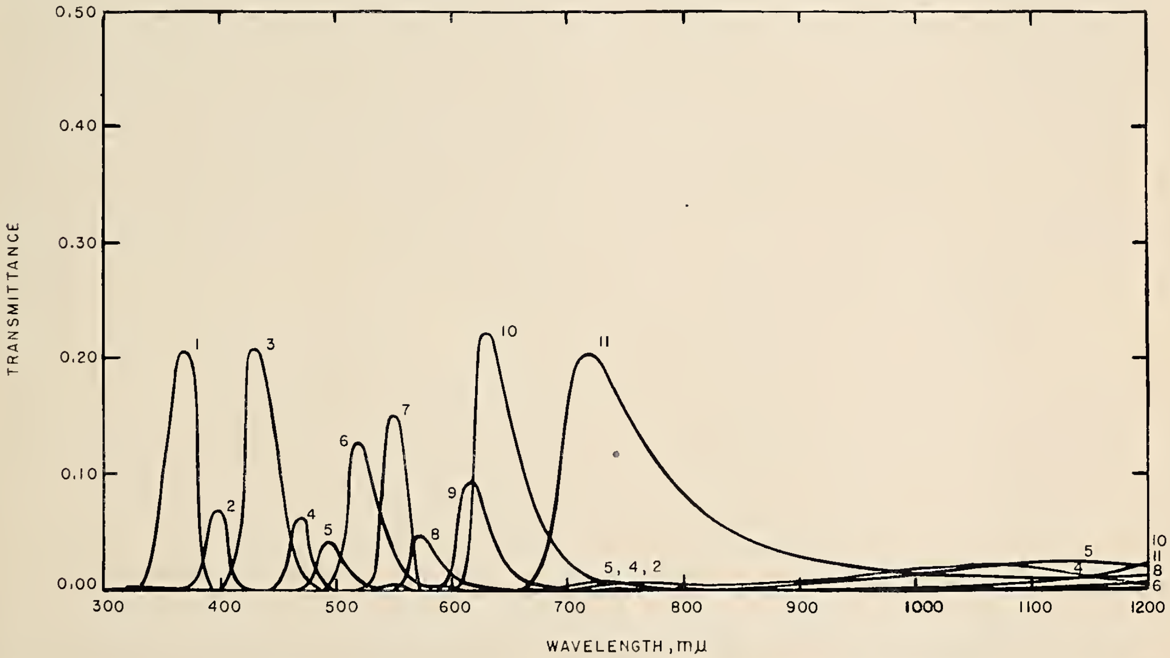

FIGURE 23. *Spectral transmittance curves of Corning glass filters (or filter combinations) which may be used for wavelength isolation in filter photometers.*

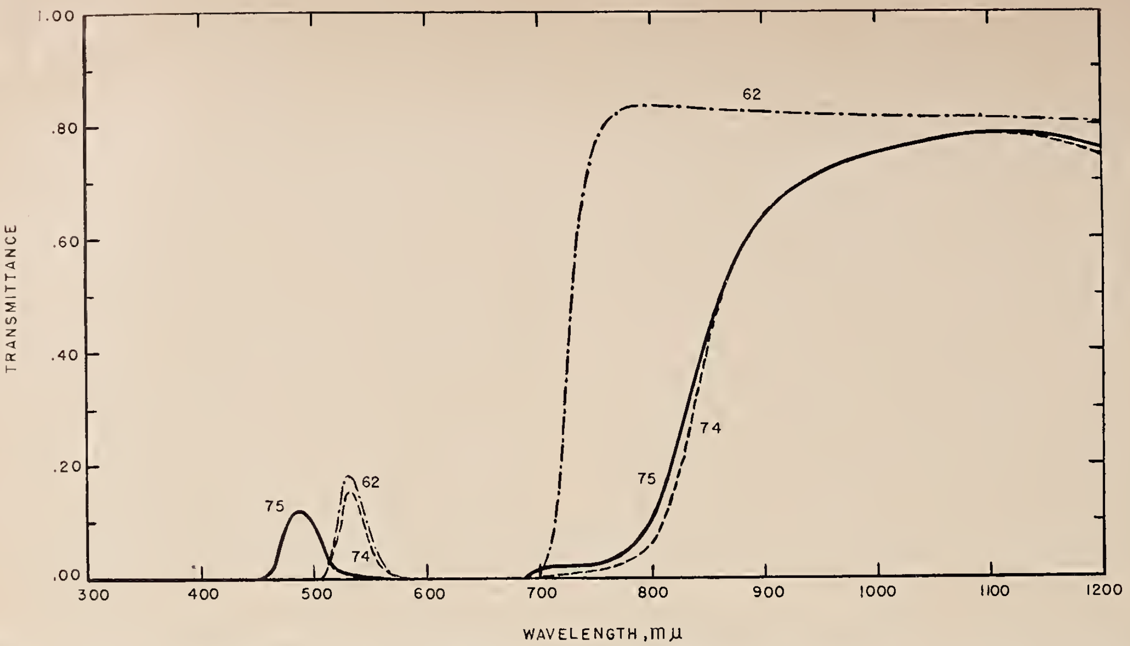

FIGURE 24. *Spectral transmittance curves of Eastman Wratten (dyed gelatine) filters which may be used for wavelength isolation in filter photometers.*

regarding the spectral transmittances of such filters may doubtless be obtained from the makers or sellers of the instruments.

In figure 23 are shown certain typical curves obtainable with glass filters sold by the Corning Glass Works, in figure 24 similar curves of certain Wratten filters, in figure 25 curves for certain interference filters, and in figure 26 curves for miscellaneous filters. All of the data for the curves of these four figures were obtained at the National Bureau

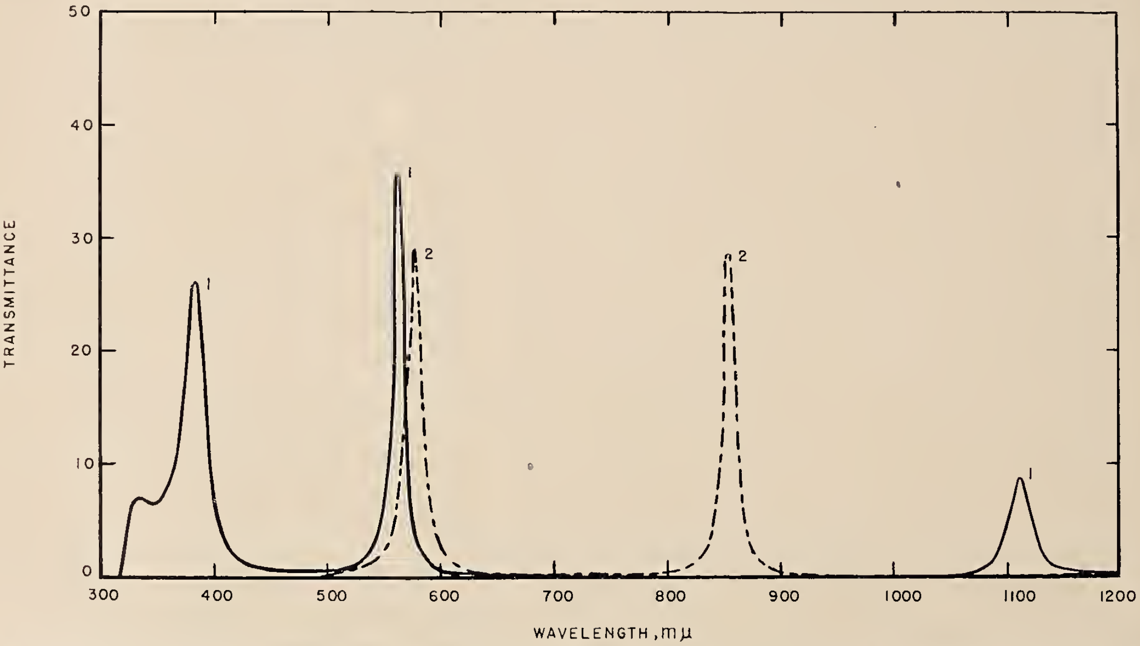

FIGURE 25. *Typical spectral transmittance curves of Baird (curve 1) and Farrand (curve 2) interference filters which may be used for wavelength isolation in filter photometers.*

Filters are obtainable with transmittance bands at nearly any desired wavelengths.

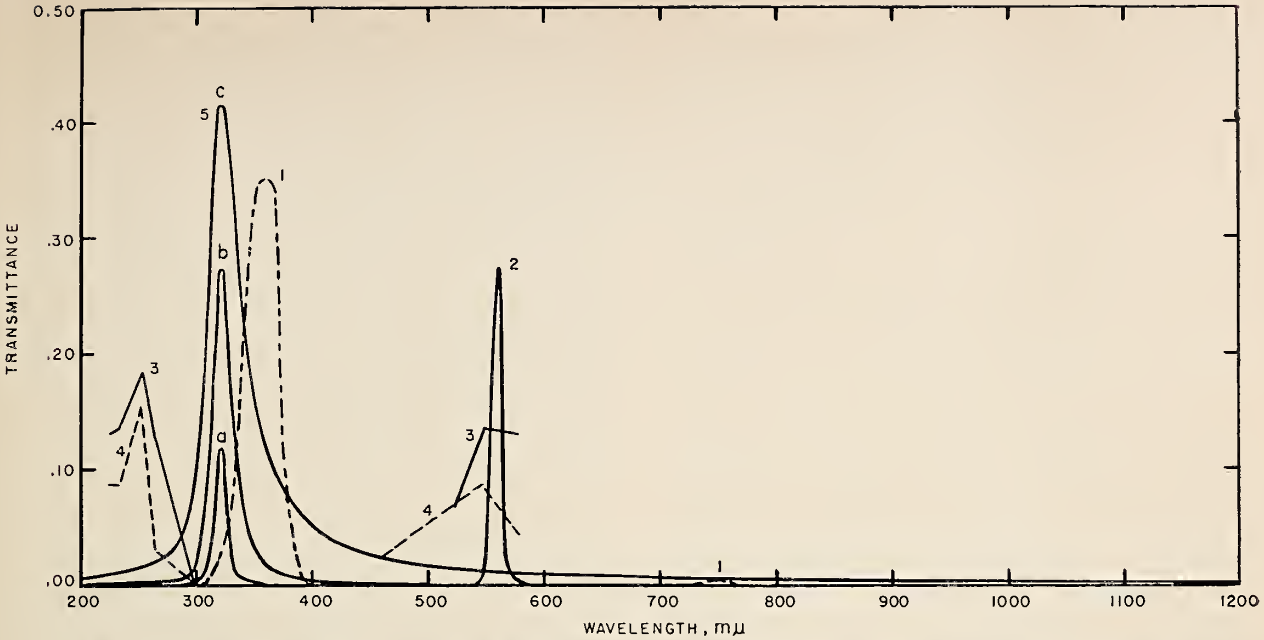

FIGURE 26. *Spectral transmittance curves of miscellaneous filters which may be used for wavelength isolation in filter photometers.*

1. Corning 5860 glass. 2. Gibson 4-component glass filter. 3. Quartz cell containing mixture of chlorine and bromine gas. 4. Quartz cell containing chlorine gas. 5. Fused quartz plates carrying silver films of the following thicknesses: (a) 0.0552 micron, (b) 0.0326 micron, (c) 0.0217 micron.

of Standards on samples purchased from the manufacturers, with the following exceptions: (1) The silver films of figure 26 were prepared on fused quartz by L. W. Scott of the National Bureau of Standards; (2) the data of curves 3 and 4 of figure 26 were taken from reference [92] originating with Peskov, J. Phys. Chem. **21,** 382 (1917), and these papers should be consulted for further details. Both the Farrand Optical Company and the Baird Associates advertise filters similar to those shown over the range from 400 to 700 mμ; in this range with these filters, there is no inherent limitation on the wavelength region that may be isolated. It is understood that similar interference filters for use in the ultraviolet or infrared are in process of development.

Two things of importance should be considered in connection with the selection and use of filters for abridged spectrophotometry, in addition to factors discussed elsewhere. One of these is the wavelength to be assigned to the photometric value obtained by use of the filter with incandescent source; the other is an expression for the effectiveness of such filters, with respect to their transmittance at the nominal or desired wavelength and their exclusion of radiant energy at all other wavelengths. In this connection the shape of the transmittance curves shown in figures 23 to 26 may be compared with the shape of the slit-width "curves" of figure 6. In effect, the use of filters is more or less equivalent to the use of wide slits on a spectrophotometer, although the generality and precision of wavelength settings are missing with the filters.

If the photometric values obtained with a series of filters are to be used to plot a transmittance or reflectance curve, the correct wavelength at which to plot any particular value is, of course, the one for which the same value would be obtained in accurate spectrophotometry.

The photometric value obtained by use of the filter is

$$R=\frac{\int_0^\infty S_\lambda I_\lambda T_\lambda R_\lambda d\lambda}{\int_0^\infty S_\lambda I_\lambda T_\lambda d\lambda},$$

where

S_λ=spectral response of the detector (eye, phototube, thermopile, etc.) for an "equal-energy" spectrum,
I_λ=relative spectral energy of the illuminant,
T_λ=spectral transmittance of the filter,
R_λ=spectral distribution of the measured quantity, and
λ=wavelength.

Since, in general, R_λ is unknown, this relation is not useful. As a first approximation to the correct wavelength at which to plot R, it is customary to use the spectral centroid, λ_c, as defined in the following relations:

$$\lambda_c=\frac{\int_0^\infty S_\lambda I_\lambda T_\lambda \lambda d\lambda}{\int_0^\infty S_\lambda I_\lambda T_\lambda d\lambda}$$

or

$$\lambda_c=\frac{\int_0^\infty S_\lambda I_\lambda T_\lambda R_\lambda \lambda d\lambda}{\int_0^\infty S_\lambda I_\lambda T_\lambda R_\lambda d\lambda}.$$

Values of λ_c by the second equation need be used only for highly selective materials (R_λ varying widely over the range of T_λ), and for such cases the values of λ_c by the other equation must first be obtained and R plotted as a function of λ_c yielding approximate values of R_λ. For nearly achromatic materials such as white or near-white enamels, papers, etc., the variation in R_λ is usually so small as to be negligible for the purpose, and values of λ_c by the first equation may be used. In general, it is much more important to know the values of T_λ accurately than the values of S_λ and I_λ; and the narrower is the spectral region transmitted by the filter, that is, the more restricted is the range of T_λ, the less accurately will the values of S_λ and I_λ need to be known. The integrations are usually made by summations at every 10 mμ; but if the filter is very restrictive, 5 mμ intervals are necessary.

The effectiveness of a filter for use in abridged spectrophotometry is often given in terms of its maximum transmittance and its "half-width." By the latter term is meant the wavelength interval between the two sides of the transmittance curve, taken at a transmittance equal to half the maximum. These specifications are good as far as they go, but they ignore the radiant energy transmitted at wavelengths near the base of the transmittance curve or at some other wavelength region perhaps far removed from λ_c.

An expression for the effectiveness, E, of a filter for transmitting and isolating radiant energy at any specified wavelength, λ', has been suggested [93]:

$$E_{\lambda'}=T_{\lambda'}-\frac{\sum S_\lambda I_\lambda T_\lambda|\lambda-\lambda'|\Delta\lambda}{\sum S_\lambda I_\lambda|\lambda-\lambda'|\Delta\lambda}$$

where the symbols have the same meanings as above and the absolute value signs (| |) indicate that the differences are to be taken all greater than zero. Other relations for expressing the various characteristics of a filter are given in the same publication.

If, instead of an incandescent source, a mercury arc or other source is used having intense lines at suitably spaced wavelengths, the filter photometer can give photometric values at these wavelengths with all the reliability and certainty of a true spectrophotometer. The problem is simpler than with the incandescent source in that the wavelength isolated by the filter is more definite, and in many cases the exclusion of unwanted energy is less difficult. Filters designed specifically for use with the mercury arc in abridged spectrophotometry have been developed by various investigators [91, 94, 95, 96, 97, 101, 102, 103].

Numerous designs of filter photometers are on the market. Examination of such instruments will show that they combine all of the essential parts of a spectrophotometer except that the series of filters replaces the more costly prism (or grating), lenses (or mirrors), and slits of the conventional instrument.

All of the types of errors that are listed in sections VI–1 to VI–7 may be present in measurements made with filter photometers. The wavelengths to be assigned to measurements with the filters were considered above. Reliability of the photometric scale is dependent on the same principles as in a true spectrophotometer; on many of the photoelectric instruments the linearity of the irradiance-current relationship must be carefully considered, and on visual instruments the soundness of the photometric device should be established in one way or another. Stray energy depends directly upon the spectral transmittance of the respective filters over the whole range of sensitivity, as already explained. Temperature effects must be carefully considered not only from the standpoint of the temperature of the sample, but also because the response of a barrier-layer cell varies so markedly with temperature. The magnitudes of errors resulting from fluorescence of the sample will depend on whether the radiant energy passes first through the sample or through the filters; but will always be less important in transmission measurements of nondiffusing materials than in reflection measurements of diffusing materials (see section VI–5). Slit-width errors can be very large because of the width of spectrum band passed by most of the filters; in some cases the error might be interpreted as a wavelength error; in either case the magnitude will depend importantly on the second derivative of the spectral transmission curve across the spectral range isolated by the particular filter being used (see section VI–6). Other errors, such as deviation of the beam when the sample is inserted, the effects of multiple reflections, electrical or mechanical instability, and so on, all must be carefully considered if the most reliable work is to be done with such instruments.

In this connection it may be noted that the types of filters desired for filter photometers in abridged spectrophotometry, such as here considered and illustrated in figures 23 to 26, are radically different from those necessary when the filter photometer is used for tristimulus colorimetry. In this colorimetric use, filters are desired that adequately duplicate the tristimulus functions of the human eye. Such filters cover a wide spectral range and would give only the crudest sort of spectrophotometric analysis.

VI. Errors—Discussion and Elimination

Numerous types of errors may be present in spectrophotometric measurements, and only the most careful calibration and operation of the instrument will render such errors negligible if the highest all-around reliability is desired. However, the importance of spectrophotometric errors varies greatly with the purpose of the measurements. One general statement is always true: The greater is the deviation between the spectral distributions of sample and standard, the more likely is the measured ratio of sample to standard to be in error.

Sometimes these errors may result from a fundamental defect in design or operation of the instrument; sometimes they result directly from carelessness or lack of training of the operator; sometimes they result from uncontrolled variables such as temperature and humidity. Whatever the cause, it is repeated here for emphasis that the importance of spectrophotometric errors depends on the purpose of the measurements. This is true for each type of error to be discussed but will not be noted further. Rather, what will be considered will be the causes of the errors and their magnitudes.

1. Wavelength

Two errors are to be distinguished, the error in the wavelength scale or calibration and the error thereby produced in the measured ratio. For any given wavelength error, the error induced in the ratio will depend directly on the spectral selectivity of the sample relative to the standard. This is fairly obvious; if the sample is nonselective at any wavelength or wavelengths, a wavelength error at those wavelengths induces no error in the measured ratio, but if the sample is highly selective, such as a selenium or didymium glass at certain wavelengths, an error of even 0.1 mμ has a measurable effect on the transmittance obtained. It is a simple matter for each investigator to determine the magnitude of this effect on the sample being measured.

It is believed that all commercially available spectrophotometers now have direct-reading wavelength scales. It is perhaps a matter of interest to note the residual errors found on various of the direct-reading wavelength scales of spectrophotometers in the Photometry and Colorimetry Section of the National Bureau of Standards. These are shown in figure 27, and give an idea of what to expect in a direct-reading instrument when put into such adjustment that the sum of these residual errors is kept close to a minimum. The deviations seldom exceed ±1.0 mμ. It is to be emphasized, however, that wavelength errors as small as shown are dependent on optimum adjustment of the instrument. It is easily possible for an instrument to get badly out of adjustment, and continual check is strongly advised.

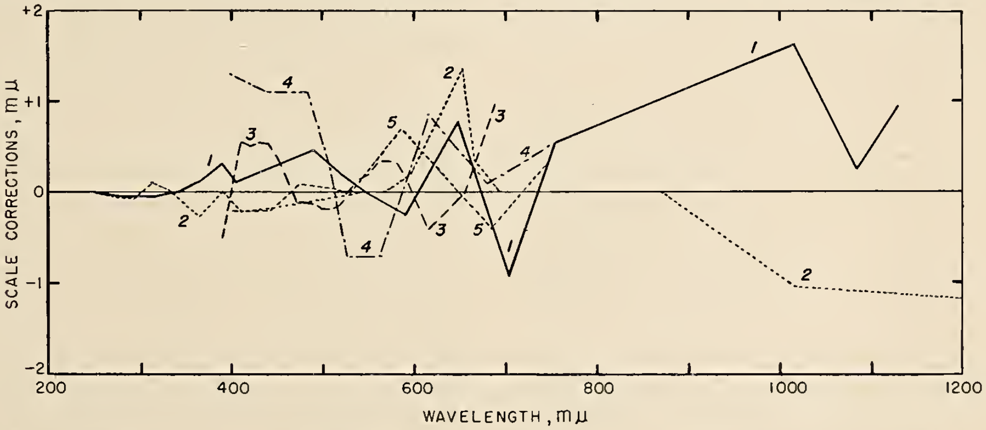

Figure 27. *Wavelength correction curves of various spectrophotometers in the Photometry and Colorimetry Section of the National Bureau of Standards.*

All of the instruments are direct-reading in wavelength and are adjusted so that corrections are close to minimum. Curves 1 and 2 are for Beckman spectrophotometers, curve 3 for a Hilger spectrometer used in the Gibson spectrophotometer, curves 4 and 5 from typical recordings for General Electric spectrophotometers.

2. Photometric Scale

A check of the photometric scale of a spectrophotometer independent of all other sources of error is difficult or impossible to make on most spectrophotometers. Useful for this purpose would be a series of samples whose respective transmittances do not vary with wavelength, which do not reflect highly, which will not displace the beam, and for which the transmittances can be independently determined with high accuracy. No such glasses or other suitable materials are available, however. Reflection samples are not good for such purpose because the directional reflectances are affected by the geometrical irradiating and receiving conditions. The use of thin metallic films does not seem advisable from the standpoints of permanence and effect of multiple reflections.

However, on visual spectrophotometers such a check is possible by means of rapidly rotating sectors. If such sectors are properly made, the angle of the total opening relative to 360°—that is, the effective transmittance of the sector—can be measured on a circular dividing engine with uncertainties only in the fifth decimal place. Of course, the use of such rotating sectors is based on the validity of Talbot's law. Throughout the spectrum, no certain deviations from this relation are known, however. In addition to published data bearing on this [104, 35] are extensive unpublished data at the National Bureau of Standards obtained over a period of many years on the König-Martens spectrophotometer. These data, obtained with sectors having transmittances over the range from 0.80 to 0.009, approximately, but principally at 0.50 and 0.10, prove both the validity of Talbot's law at the various wavelengths and the reliability of the instrument over most of the photometric scale, or else there is a remarkable balancing of errors. (The only consistent deviations are near the extinction points and are caused by stray unpolarized light, as explained in the next section.)

On photoelectric and photographic spectrophotometers similar checking of the photometric scale by rotating sectors is in general not feasible for one reason or another. Accordingly, shortly after the advent of commercial photoelectric spectrophotometers, the National Bureau of Standards instituted the service of issuing glass standards of spectral transmittance [105, 33]. To date, over 140 of these filters have been issued with accompanying certificates.

The spectral transmittances of these filters are approximately as shown in figure 28. A single filter thus covers a considerable part of the transmittance scale. In one sense these may be considered inferior to strictly neutral filters in that a deviation from the true value may be due to causes other than inaccuracy of the photometric scale. On the other hand, they are superior to the neutral filters in detecting errors resulting from stray energy, wide slits, and wavelength inaccuracies.

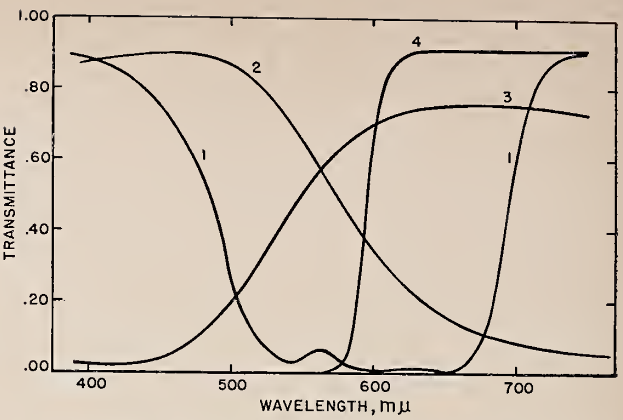

Figure 28. *Typical spectral transmittance curves of glass filters issued by the National Bureau of Standards for use in checking the photometric scale of spectrophotometers.*

Curves: 1—cobalt blue; 2—copper green; 3—carbon yellow; 4—selenium orange.

A similar check of the photometric scale can be made by means of the standard solutions, whose spectral transmittancies are given in section VII–2. An additional means of checking the scale is afforded by measuring the transmittancy of solutions in different thicknesses or, if Beer's law is known to be followed, at different concentrations in the same thickness. The relation, from the equations of section II–2, is

$$-\log_{10} T_s/bc = a_s$$

If, at each wavelength tested, a_s is found to be constant at the various thicknesses and/or concentrations, in all probability the photometric scale of the instrument is accurate.

3. Stray Energy

Stray energy is often a source of important error in spectrophotometry and is produced by a variety of causes. Some of these causes are as follows:

1. The stray energy emerging from the exit slit along with the spectral energy may be a general admixture of energy of all wavelengths emitted by the source and transmitted by the spectrophotometer. It may be caused by dust, scratches, or other optical imperfections on the prism, lenses, mirrors, or other optical parts of the instrument.
2. The stray energy may be reflected from the insides of collimator tubes, the edges of diaphragms, or from other places. This may be a general admixture of all wavelengths or may be

more or less localized in some other region of the spectrum than that being measured.

3. On a polarization spectrophotometer the stray energy may be manifested as unpolarized energy, and may therefore not be affected by rotation of the nicol or other device by means of which the photometric value is obtained. This may produce relatively large errors near the extinction points.

4. In a grating spectrophotometer, stray energy may come from orders of the spectrum other than that nominally used.

5. If the instrument or detector is not properly shielded, stray radiant energy from the room in which the spectrophotometer is used may cause error.

The spectrophotometric ratio measured is, in general, given by the following relations:

$$T_{\lambda+x}=\frac{mI_\lambda+nI_x}{mI_{o\lambda}+nI_{ox}},$$

where I and I_o have the usual significance, λ and x refer to the spectral and the stray energy, respectively, and m and n are weighting factors dependent on the spectral sensitivity of the detector and the spectral energy of the source. Also let

$$T_\lambda=I_\lambda/I_{o\lambda}$$

and

$$T_x=I_x/I_{ox}.$$

Then the above equation can be rearranged to give

$$T_\lambda=T_{\lambda+x}+\frac{nI_{ox}(T_\lambda-T_x)}{mI_{o\lambda}+nI_{ox}}.$$

This shows that the correct transmittance, T_λ, may be greater or less than the measured ratio, depending on whether the transmittance of the sample for the spectral energy is greater or less than its transmittance for the stray energy. The error will be zero if $T_\lambda=T_x$ or if n or I_{ox} is zero.

The proportion of nI_{ox} to $mI_{o\lambda}+nI_{ox}$ has been evaluated in certain cases [1, 78]. On a visual spectrophotometer it increases rapidly in the end regions of the spectrum and becomes 100 percent in the ultraviolet and infrared. On the Beckman spectrophotometer with present type of phototube, it becomes nearly or wholly 100 percent above 1,200 mμ. The most difficult part of the ratio to evaluate is often the quantity T_x, that is, the fraction of the stray energy transmitted by the particular filter being measured.

However, a little study of the relation will usually give one an idea of whether or not the stray energy is of importance with any particular sample and wavelength. For example, suppose that a filter of the selenium-orange type, figure 28, is being measured at 560 mμ (where T_λ is in reality zero) with a photoelectric single-dispersion spectrophotometer containing a phototube highly sensitive to the red and infrared where the transmittance of the filter is about 0.9. The value of $nI_{ox}/(mI_{o\lambda}+nI_{ox})$ at 560 mμ might well be equal to 0.02. By inserting values in the above equations, $T_{\lambda+x}$ is found to be of the order of 0.018, an apparent transmittance of 1.8 percent. This type of error often occurs at various wavelengths in measuring this type of glass.

Two methods are commonly used to eliminate stray energy from causes 1, 2, and 4 above.

1. The stray energy transmitted through the exit slit may be dispersed by means of a second spectrometer so that if the first instrument transmitted 2 percent of stray energy at any particular wavelength, the second similar instrument will probably transmit about 0.02×0.02, or roughly only 0.04 percent. This scheme has been used in certain photoelectric spectrophotometers, as noted in section V–3.

2. With a single-dispersion instrument the stray energy may be reduced by an appropriate filter placed at some suitable location in the optical path, which will transmit freely at the wavelengths at which it is used but absorb strongly at all other wavelengths to which the detector is highly sensitive. They are usually not needed in the regions of high response of the receiver but should usually be used when the spectral response becomes less than 10 or 15 percent of the maximum. Even in regions of fairly high response they may be needed when measuring the low transmittance of a filter that has high transmittance in other spectral regions. The subject is considered in greater detail in various publications [1, 5, 6, 78].

In the use of stray-energy filters, care should be taken to avoid the introduction of multiple-reflection errors. This can usually be effected by mounting the filter so that its surfaces are not quite at right angles to the axis of the beam.

The effect of stray unpolarized light, cause 3 above, is avoided on the König-Martens visual spectrophotometer by not taking measurements too near the extinction points (0° and 90°). When low transmittances are measured, rotating sectors are placed in the blank beam, as already explained, bringing the match points back towards the center of the scale.

On the Hilger Industrial and Research Spectrophotometer [3, 59], stray unpolarized light is reduced to negligible proportions by the second pair of nicols.

The effect of unpolarized energy on the General Electric recording spectrophotometer has been discussed by Pineo [68].

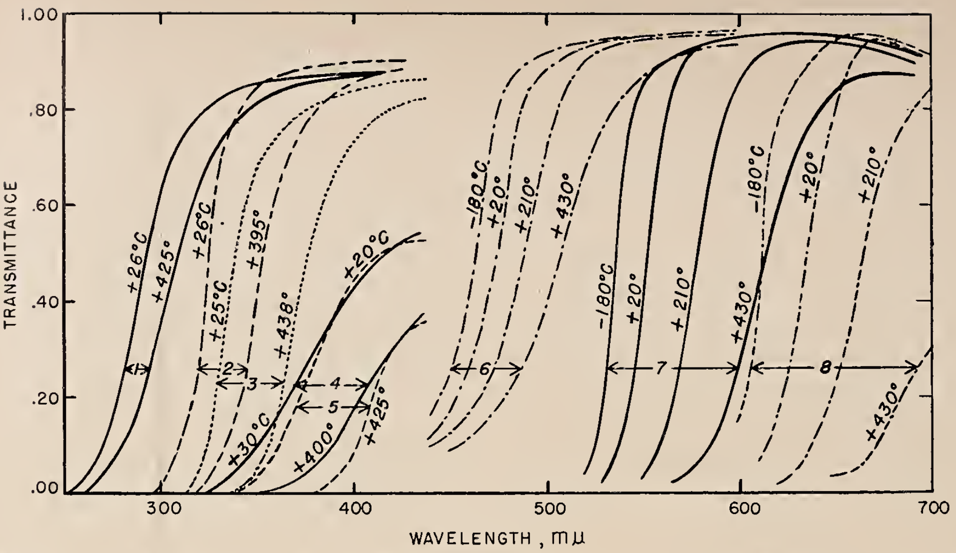

Figure 29. *Effect of temperature on the spectral transmittance (or internal transmittance) of certain glasses.*

Curves 1, 2, and 3 are for certain clear glasses, curves 4 and 5 for certain amber glasses, curves 6 for a Noviol yellow glass, curves 7 and 8 for selenium orange and red glasses. Curves 1 to 5 from Meyer [109], curves 6 to 8 from Gibson [107].

4. Temperature Effects

The effects of temperature on the spectral transmission characteristics of many kinds of glasses and other materials have often been studied and are in many cases well-known [106, 107, 108, 46, 109, 110]. Some typical examples are given in figures 29 and 30.

It can readily be seen that with certain samples at certain wavelengths the effect is so great that the transmittance is measurably affected by room temperature variations or by heating of the sample in the instrument. On the same samples at other wavelengths and on other samples, the effect is immeasurably small unless studied over large temperature ranges. The effect is usually, though not always, small in the infrared, at least for glasses.

Some generalizations can be made. The transmittance at any wavelength usually decreases as the temperature is increased, provided the spectral transmittance is increasing with wavelength; and the greater the slope of the transmittance curve, the greater the temperature effect usually is. If

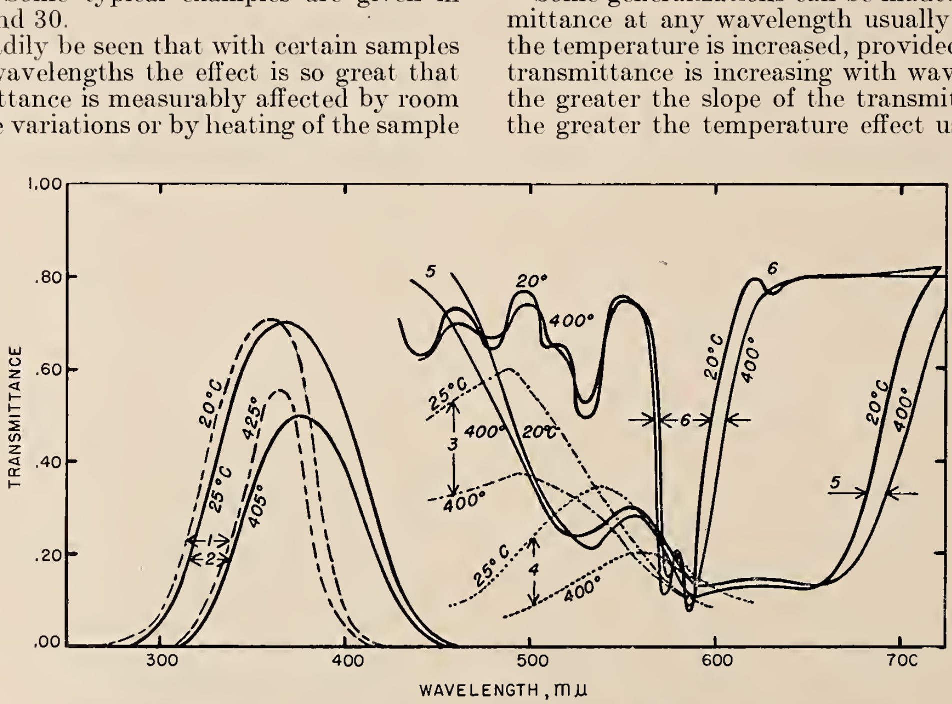

Figure 30. *Effect of temperature on the spectral transmittance of certain glasses.*

Curves 1 and 2 are for certain violet or blue-violet glasses, curves 3 for a copper green glass, curves 4 for a chrome green glass, curves 5 for a cobalt blue glass, curves 6 for a didymium glass. Curves 1 and 2 from Meyer [109], curves 3 and 4 from Gibbs [106], curves 5 and 6 from Holland and Turner [110].

the spectral transmittance curve is not varying much with wavelength the temperature effect is usually very small. If the spectral transmittance is decreasing from shorter to longer wavelengths, the effect is usually small and often of opposite sign.

The effects just described are elastic in that the sample always returns to a specified transmittance at a specified temperature. Corresponding changes in the spectral reflectance curves of certain samples have been observed at the National Bureau of Standards, but no quantitative study of the effect has been made.

Differing from the above are the permanent changes in the spectral reflectances of various materials (papers, dyed textiles, etc.) under strong and continued irradiation and the "solarization" of glasses when exposed to intense ultraviolet radiant flux [111], but such effects are not within the scope of this paper.

5. Fluorescence

The accurate measurement of the spectral transmittance or reflectance of strongly fluorescent materials has not yet been satisfactorily treated from the standpoint of instrument design, especially for reflecting materials. In the various types of instruments illustrated above, it may have been noted that, in some designs, the samples were mounted between the source of radiant energy and the spectrophotometer. In other designs, the samples are mounted between the instrument and the receptor. In the first type, the full flood of undispersed radiant energy is incident upon the sample and may cause temporary or permanent changes in the sample during the measurements. In the second design, the radiant energy is dispersed in the instrument and energy from only the small spectral region isolated by the exit slit falls upon the sample, thus, in general, avoiding the excessive temperature or fading effects of designs of the first type. For nonfluorescent samples the two designs are inherently equivalent and will give the same results under otherwise identical conditions.

With strongly fluorescent samples this may not be true, however. Both methods may produce erroneous results, but the second type of instrument is subject to much the greater error. In evaluating this error, one must define what is to be understood as the correct result. Where the effect has been most notable are in instances in which it was desired to derive colorimetric specifications of strongly fluorescent reflecting materials from the spectrophotometric data [112]. In such cases the correct result is considered to be a spectral curve or set of data consisting of (1) the true spectral directional reflectance, to which has been added (2) the spectral distribution of the fluorescent energy when excited by a source having the same spectral distribution of energy (ultraviolet, visible, infrared), as is used in the specified visual examination of the sample. This latter restriction is essential because the amount and distribution of the fluorescent energy may vary considerably with different irradiants.

If the colorimetric specification of the fluorescent sample is desired for an incandescent irradiant, a spectrophotometer of the first type (such as the Gaertner visual) can give a correct result. If it is desired for artificial daylight a correct result can be obtained if the artificial daylight is used as source in place of the bare incandescent light. If it is desired for natural daylight, it cannot be accurately obtained unless the illumination sphere be discarded and the sample and standard be actually irradiated by natural daylight. (Natural daylight and artificial daylight may differ considerably in the ultraviolet region.)

On spectrophotometers of the second type the fluorescent sample is irradiated by the continually

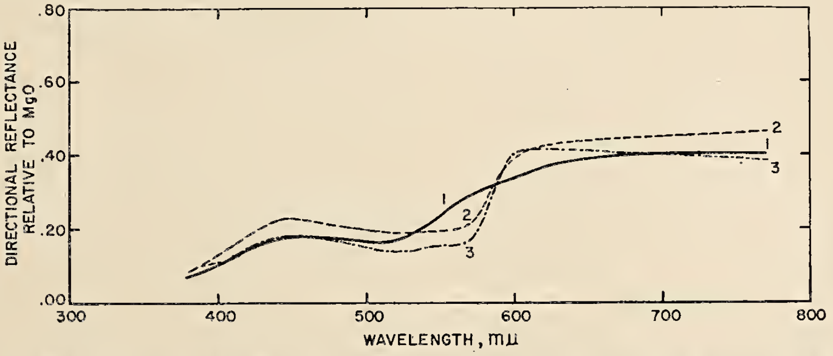

FIGURE 31. *Effect of fluorescence on the measured values of spectral directional reflectance.*

The sample was a pink phenolformaldehyde that fluoresced strongly to green and yellow energy but weakly or none at all to blue, violet, and ultraviolet energy. Curve 1 (R_0, d) was obtained on a photoelectric spectrophotometer in which the energy was spectrally dispersed before incidence on the sample; the high values from 500 to 580 mμ result from the reddish fluorescence excited by the green and yellow energy. Curves 2 ($R_{D,0}$) and 3 ($R_{45,0}$) were obtained with visual spectrophotometers (data extrapolated at ends) in which the sample is irradiated directly by the source, and the fluorescence excited is spectrally dispersed before measurement. Colorimetric comparison of the sample with nonfluorescent standards of nearly the same color, showed that colorimetric values derived from curve 1 were much more in error than those derived from curves 2 or 3.

changing region of the spectrum isolated by the exit slit, and is therefore subject to widely varying irradiances during the measurements, probably none of which are of any particular interest in the actual use of the fluorescent sample. The magnitude of such an error is shown in figure 31, these curves relating to the sample for which the effect was first noticed [113].

Explanation of the effect is readily seen. The sample in figure 31 exhibited a strong reddish fluorescence when excited by energy in the green and yellow-green parts of the spectrum. The sample was run on the General Electric recording spectrophotometer, which uses a phototube that responds freely to the red and near infrared. When the sample is irradiated by energy in the green and yellow parts of the spectrum (500 to 580 mμ), the strong reddish fluorescent energy evoked falls directly (undispersed) upon the red-sensitive phototube and is added to that truly reflected at the respective wavelengths in the green or yellow. The resulting reflectance curve, No. 1 of figure 31, is thus erroneosuly high in the green region. The same type of error occurs on the Beckman spectrophotometer, although the choice of two phototubes for the measurement can reduce the error somewhat in some cases.

The effect is much greater in reflection measurements of diffusing materials than in transmission measurements of nondiffusing samples. In the latter the fluorescent energy is emitted in all directions, only a small fraction being incident upon the phototube, and this can be reduced by moving the sample as far as possible from the phototube, or by a judicious use of filters. In reflection measurements of diffusing specimens, the proportion (geometrically) of the fluorescent energy accepted for measurement is the same as that of the diffusely reflected energy.

6. Slit Width

The magnitudes of slit-width errors depend primarily upon two things: (1) the effective width of the entrance and exit slits with a continuous spectrum source, and (2) the curvature (not the slope) of the spectral distributions under consideration. The principle can readily be seen from the simple illustrations in figure 32. Let *a* and *b* be the edges of a slit of width, $2\Delta\lambda$, and let λ be the nominal wavelength at which the spectrophotometer is set. Furthermore, let *c* and *d* represent two energy distributions that are being evaluated for wavelength, λ, by a nonselective detector such as a thermopile. This will integrate the energy transmitted by the slit over the range $2\Delta\lambda$, and the value obtained will be taken as for λ. It is apparent that for distribution *c* a value of *c′* is obtained, which is the correct value. For distribution *d*, on the other hand, a value of *d′* is obtained, which is different from the true value d″.

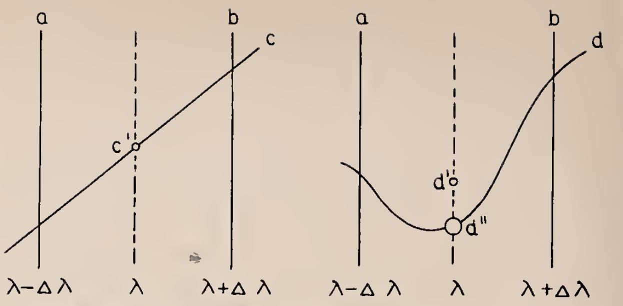

FIGURE 32. *Showing that slit-width errors depend on the curvature, not the slope, of the distribution curve across the slit.*

The slit width extends from a to b, λ±Δλ. At the left the measured and true values coincide at c′. At the right the measured value is at d′, the true value at d″. See also the effect of slit width in figure 8.

The effect of slit widths is easily shown on a recording spectrophotometer with a didymium glass. Two such curves are recorded in figure 8, one for 4-mμ slits and one for 8-mμ slits. Note that the differences are greatest where the curvatures are sharpest, and that at certain places on the steep sides of the bands (where the curves cross) the differences are zero.

Mathematical expressions to evaluate slit-width errors have been derived by various investigators. Among the first were Runge [114], Paschen [115], and Hyde [116]; these are discussed on pages 182 to 188 (by Weniger) and 349 to 351 of Measurement of Radiant Energy [6]. Equation 80, page 349, from that book is useful for spectrophotometry, namely,

$$T=\frac{\phi_T(\theta)}{\phi(\theta)}=\frac{F_T(\theta)-K\Delta^2F_T(\theta)+L\Delta^4F_T(\theta)+\ .\ .\ .}{F(\theta)-K\Delta^2F(\theta)+L\Delta^4F(\theta)+\ .\ .\ .},$$

where T is the correct transmittance or reflectance of the sample at the wavelength under consideration, θ is the angle of deviation at this wavelength, $\phi_T(\theta)$ and $\phi(\theta)$ are the relative intensities of the pure spectra with and without the sample in the beam, $F_T(\theta)$ and $F(\theta)$ represent the relative intensities, as evaluated by the detector, of the corresponding impure spectra resulting from the use of finite slit widths, the Δ^2 and Δ^4 functions relate to the second and fourth derivatives of the spectral distributions, and K and L are constants, L much smaller than K.

Note the absence of functions dependent on the first derivatives and the major importance of the second derivatives in this relation, consistent with figures 8 and 32. Hyde's paper [116] should be consulted for a more complete presentation of the relations, including the definitions of the Δ^2 and Δ^4 functions and indications of how to apply the corrections.

For a given sum of entrance and exit slits, the errors or corrections are least when the two slit widths are equal. For this case K=1/12 and L=1/90.

The obvious difficulty or bother of applying this slit-width correction, which at best is only an approximation, illustrates the desirability of keeping the slits sufficiently narrow that correction is unnecessary for the purpose at hand. It also illustrates the value of having auxiliary sources, such as the Hg arc, for use on a spectrophotometer, eliminating any possibility for slit-width errors at the wavelengths available.

More recent investigators of slit-width errors include Hogness, Zcheile, and Sidwell [78], Van den Akker [117], Buc and Stearns [70], and Hardy and Young [118]. The most general case of a nonsymmetrical "pass band" is treated in this last paper, and the authors derive a formula including a first-order correction term that may be considered as a wavelength correction and that becomes of importance with wide slits and an unsymmetrical pass band, as illustrated by Van den Akker. Hardy and Young also suggest a novel procedure for determining the second-order correction, and propose a definition for the effective slit width of a spectrophotometer.

7. Miscellaneous

Various other errors are possible in spectrophotometric work, some related to particular types of measurements, some related to particular instruments.

One that is often present is a multiple-reflection error, occurring especially when the transmittance of a sample is measured relative to the blank beam. The introduction of the sample being measured in effect changes the value of I_1 in the defining relation

$$T=I_2/I_1$$

This can happen in various ways. The energy reflected from the sample, which should not reach the detector, may have a small part of it redirected toward the detector by another optical part. The energy reflected from a shiny slit head may have a small part of it redirected by the sample into the slit (sample between source and slit) or the energy reflected from a phototube may have a small part of it redirected by the sample back onto the phototube (sample between slit and phototube). The error can usually be discovered, if present, by measuring the transmittance of a thin piece of crown glass placed first in its normal position at right angles to the beam and then at some small angle from this position. In this second position the reflected energy is directed out of the beam without affecting the true transmittance appreciably. The remedy will then depend on circumstances but should be such that the sample being measured can be inserted at right angles to the beam without introducing the error.

In polarization instruments the extinction points should be carefully checked and adjusted if in error. In direct-reading instruments the 100-percent point or curve should be checked (and evaluated if not precisely 100.0) to insure that the substitution method is being in effect employed.

If the transmittance sample is wedge-shaped, lens-shaped, or merely thick (in a converging or diverging beam), its introduction into the beam may in effect change the I_1 reading. The possibility and magnitude of this error depends on the design of the instrument.

VII. Standard Data

Standards of spectral transmittance or transmittancy are of importance in checking the photometric scale of spectrophotometers, as already explained, and such standards are useful whether the instruments are used for spectral transmission measurements or for measurements of spectral directional reflectance or spectral energy distribution. In general, no further standards are needed for transmission measurements, since practically all measurements are made on nondiffusing materials relative to the blank beam or to a solvent cell.

Reference or "100-percent" standards are needed, however, for spectral reflection or spectral energy measurements. While it might be possible to design an "absolute" spectroreflectometer for diffusely reflecting materials, such has not been done, and a diffusely reflecting sample or standard of known spectral directional reflectance is accordingly necessary. For spectral energy measurements a standard of known spectral distribution is likewise necessary if values for the unknown source are to be evaluated from the spectrophotometric ratio.

1. Spectral Energy Standards

A suitable standard of spectral energy distribution through the visible spectrum is the incandescent-filament electric lamp operated at a specified color temperature. The color temperature of such a source is defined as the temperature at which the Planckian radiator or "black body" would have to be operated to give the same color as the incandescent-filament lamp. When the incandescent lamp is thus operated at a specified color temperature, the relative spectral energy distribution through the visible spectrum is given by Planck's equation to a considerable degree of accuracy. This relation is [6]

$$I_\lambda = \frac{AC_1\lambda^{-5}}{e^{\frac{C_2}{\lambda\theta}} - 1},$$

in which

I_λ=spectral radiant intensity (or some quantity proportional thereto),
e=base of natural logs,
θ=absolute temperature in degrees Kelvin,
A, C_1, and C_2=constants.

In the visible spectrum differences between the measured relative energy distribution from an incandescent-filament lamp operated at a specified color temperature and the relative energy distribution derived from Planck's equation are so slight [47, 48] as to border on the uncertainties of measurement, and it has become customary therefore to accept incandescent-filament lamps as adequate standards of spectral energy distribution through the visible spectrum. Numerous publications have been issued in which these distributions have been computed and tabulated so that one does not need to derive the values for himself [44, 45, 46].

In table 3 is shown the relative energy distribution of the Planckian radiator at 2,848° K (C_2=14,350 micron degrees). The same distribution is given by 2,842° K (C_2=14,320) on the former international temperature scale, and by 2,854° K (C_2=14,380) on the new international temperature scale. This energy distribution was recommended in 1931 by the International Commission on Illumination as one of three standard illuminants for colorimetery and has come to be known as ICI standard illuminant *A*. It is perhaps as suitable as any other as a standard of spectral energy distribution. At lower color temperatures the radiant intensities become too low, particularly at the shorter wavelengths, to serve as a suitable standard. At higher color temperatures the lamp ages more and more rapidly, and the assumed spectral energy distribution may become inaccurate.

Incandescent-filament lamp standards of color temperature are issued by the National Bureau of Standards at 2,848° K and at other color temperatures.

Table 3. *Relative energy distribution of Planckian (black body) radiator at 2,848° K (C_2=14,350 micron degrees), ICI Standard Illuminant A*

The same distribution is given by 2,842° K (C_2=14,320) on the former international temperature scale, and by 2,854° K (C_2=14,380) on the new international temperature scale

Wavelength	Relative energy distribution	Wavelength	Relative energy distribution
$m\mu$		$m\mu$	
380	9.79	600	129.04
90	12.09	10	136.34
		20	143.62
400	14.71	30	150.83
10	17.68	40	157.98
20	21.00		
30	24.67	650	165.03
40	28.70	60	171.96
		70	178.77
450	33.09	80	185.43
60	37.82	90	191.93
70	42.87		
80	48.25	700	198.26
90	53.91	10	204.41
		20	210.36
500	59.86	30	216.12
10	66.06	40	221.66
20	72.50		
30	79.13	750	227.00
40	85.95	60	232.11
		70	237.01
550	92.91	80	241.67
60	100.00		
70	107.18		
80	114.44		
90	121.73		

2. Spectral Transmission Standards

Reference has already been made (section VI–2 and fig. 28) to the glass standards of spectral transmittance issued by the National Bureau of Standards for use in checking the photometric scale of spectrophotometers. These standards have a high degree of permanence if the surfaces are kept undamaged and if they are not exposed to sunlight or other excessive radiant flux. However, they are not precisely reproducible from specification and each glass must be independently calibrated before issuance. Accordingly, no transmittance values for the glasses are tabulated.

However, the spectral transmittancies of certain solutions have been measured with sufficient care, and the solutions themselves are sufficiently stable, that they may be accepted as suitable standards for checking the photometric scale of spectrophotometers. These are:

1. The aqueous solutions of copper sulfate and cobalt ammonium sulfate used in the series of filters developed at the National Bureau of Standards for reproducing the colors of sunlight and daylight and for the determination of color temperatures [46].

The published values for absorbancy and transmittancy are given in tables 4 and 5, together with the composition and certain other pertinent information. Many additional details are given in M114 [46] including the changes in absorbancy with temperature. Both solutions obey Beer's law over a considerable range. The values given for the eight Hg and He wavelengths are considered the most reliable, with an uncertainty in A_s not exceeding 0.001 for the particular chemicals used. Spectrophotometric reproducibility of the chemicals is also considered in the paper. By increasing the thickness or concentration, a wide range of the photometric scale can be covered, except at the shorter wavelengths.

Table 4. *Values of spectral absorbancy, A_s, and transmittancy, T_s, for standard copper sulfate solution as specified, unfiltered, thickness 10.00 mm, temperature 25° C, having the following composition:*

Copper sulfate ($CuSO_4.5H_2O$) [a]	20.000 g
Sulfuric acid (specific gravity 1.835)	10.0 ml
Water (distilled) to make	1,000 ml

Wavelength	A_s	T_s [b]	Wavelength	A_s	T_s [b]
mμ			mμ		
350	0.0090	0.979	600	0.0680	0.855
60	.0063	.986	10	.0885	.816
70	.0046	.989	20	.1125	.772
80	.0035	.992	30	.143	.719
90	.0028	.994	40	.180	.661
400	.0023	.995	650	.224	.597
10	.0019	.996	60	.274	.532
20	.0016	.996	70	.332	.466
30	.0014	.997	80	.392	.406
40	.0012	.997	90	.459	.348
450	.0011	.997	700	.527	.297
60	.0011	.997	10	.592	.256
70	.0012	.997	20	.656	.221
80	.0014	.997	30	.715	.193
90	.0018	.996	40	.768	.171
500	.0026	.994	750	.817	.152
10	.0038	.991			
20	.0055	.987	Hg 404.7	.0021	.995
30	.0079	.982	Hg 435.8	.0013	.997
40	.0111	.975	Hg 491.6	.0019	.996
			He 501.6	.0028	.994
550	.0155	.965			
60	.0216	.951	Hg 546.1	.0135	.969
70	.0292	.935	Hg 578.0	.0368	.919
80	.0390	.914	He 587.6	.0487	.894
90	.0518	.888	He 667.8	.319	.480

[a] Analysis showed the copper sulfate to have 99.7 percent of the theoretical copper content.
[b] Values of T_s are derived from values of A_s. $A_s=-\log_{10} T_s$

2. An aqueous solution of potassium chromate, K_2CrO_4 (0.04g/l) in 0.05N KOH. This solution has been studied by many investigators here and abroad, for example, Hogness, Zscheile, and Sidwell [78], and is considered one of the most suitable as a standard of spectral transmittancy and absorbancy in the ultraviolet. Its absorption in the violet is also useful because the copper and cobalt solutions have too little absorption in this region to be of much value. Accordingly, an extensive series of measurements was initiated in 1940 by Geraldine Walker Haupt of the Photometry and Colorimetry Section of the National Bureau of Standards to obtain standard spectral transmittancy and absorbancy data for a specified potassium chromate solution of known stability. This work was interrupted before completion, but sufficient data had been obtained that a tentative set of spectral transmittancy values could be adopted, and Mrs. Haupt has made these tentative values available for use herein. They are given in table 6. It is expected that this work will be completed and final values published. Pending this, the following details are of interest and importance in connection with the use of table 6.

Table 5. *Values of spectral absorbancy, A_s, and transmittancy, T_s, for standard cobalt ammonium sulphate solution, unfiltered, thickness 10.00 mm, temperature 25° C, having the following composition:* [a]

Cobalt ammonium sulphate ($CoSO_4.(NH_4)_2SO_4.6H_2O$) [b]	14.481 g
Sulphuric acid (specific gravity 1.835)	10.0 ml
Water (distilled) to make	1,000 ml

Wavelength	A_s	T_s	Wavelength	A_s	T_s
mμ			mμ		
350	0.0038	0.991	600	0.0137	0.969
60	.0040	.991	10	.0124	.972
70	.0050	.989	20	.0115	.974
80	.0065	.985	30	.0112	.975
90	.0088	.980	40	.0110	.975
400	.0125	.972	650	.0105	.976
10	.0168	.962	60	.0097	.978
20	.0224	.950	70	.0087	.980
30	.0340	.925	80	.0076	.983
40	.0522	.887	90	.0066	.985
450	.0773	.837	700	.0054	.988
60	.1031	.789	10	.0046	.989
70	.1213	.756	20	.0038	.991
80	.1349	.733	30	.0032	.993
90	.1472	.713	40	.0030	.993
500	.1635	.686	750	.0028	.994
10	.1742	.670			
20	.1689	.678	Hg 404.7	.0144	.967
30	.1452	.716	Hg 435.8	.0437	.904
40	.1113	.774	Hg 491.6	.1497	.708
			He 501.6	.1661	.682
550	.0775	.837			
60	.0496	.892	Hg 546.1	.0901	.813
70	.0308	.932	Hg 578.0	.0219	.951
80	.0207	.953	He 587.6	.0167	.962
90	.0158	.964	He 667.8	.0089	.980

[a] These data apply accurately also from 400 to 750 mμ to a similar solution made up with 10.3 g of cobalt sulphate ($CoSO_4.7H_2O$).
[b] Chemical analysis showed a cobalt (plus nickel) content of 100.0 percent of the theoretical, the ratio of nickel to cobalt (metals) being 1 to 200.

All of the potassium chromate solutions were prepared by S. Clabaugh of the National Bureau of Standards, Chemistry Division, under the direction of E. Wichers. The data of table 6 were obtained from solutions prepared in the following ways:

(1) A solution of K_2CrO_4 stock material, reagent grade, 0.0400 g per liter, in 0.05N KOH.

(2) A solution of K_2CrO_4 of the same concentration and alkalinity as (1) but prepared from 0.0303 g of $K_2Cr_2O_7$ which when neutralized gave 0.0400 g of K_2CrO_4 per liter.

Both solutions were found to remain stable (in transmittancy) for the two years during which the measurements were being made, if stored in ordinary storeroom glass bottles. "Flaking" may occur during this time and any sediment should be allowed to settle to the bottom of the bottle. It is recommended that alkali-resistant ware, now available, be used for storing the solutions.

In the values of T_S given in table 6 there is considerable uncertainty in the third decimal where three significant figures are used. Where but two significant figures are used there is some uncertainty in the last figure.

Table 6. *Tentative values of spectral transmittancy, T'_s, and absorbancy, A_s, for standard potassium chromate solution, unfiltered, thickness 10.00 mm, room temperatures (usually close to 25° C), having the following composition:*

0.0400 g per liter of potassium chromate (K_2CrO_4) in 0.05 normal potassiu m hydroxide solution [a]

Wavelength	T_s [b]	A_s [c]	Wavelength	T_s [b]	A_s [c]
mμ			*mμ*		
210	0.000	----	350	.28	.5528
15	.037	1.4318	55	.202	.6946
20	.35	.4559	60	.148	.8297
			65	.115	.9393
225	.60	.2218	70	.102	.9914
30	.68	.1675			
35	.62	.2076	375	.103	.9872
40	.509	.2933	80	.118	.9281
45	.408	.3893	85	.152	.8182
			90	.207	.6840
250	.319	.4962	95	.30	.5229
55	.268	.5719			
60	.232	.6345	400	.41	.3872
65	.201	.6968	404.7	.52	.2840
70	.180	.7447	410	.635	.1972
			20	.748	.1261
275	.173	.7620	30	.824	.0841
80	.189	.7235	435.8	.861	.0650
85	.254	.5952	40	.884	.0535
90	.372	.4295			
95	.527	.2782	450	.928	.0325
			60	.961	.0173
300	$.70_5$	.1518	70	.981	.0083
05	.83	.0809	80	.992	.0035
10	.90	.0458	90	.998	.0009
15	$.90_5$	.0434	500	1.000	.0000
20	.867	.0620			
325	.810	.0915			
30	$.71_5$	.1457			
35	$.60_5$	.2182			
40	$.48_5$	.3143			
45	.38	.4202			

[a] This solution of potassium hydroxide can be prepared with sufficient accuracy by dissolving 3.3 g of potassium hydroxide sticks (85% KOH) of reagent quality in sufficient distilled water to make 1 liter.

[b] Tentative values. See text.

[c] These values of A_s derived from the values of T_s.

3. Spectral Reflection Standards

As a fundamental standard of spectral directional reflectance nothing has as yet been found more suitable than freshly prepared magnesium oxide. Its (total) luminous reflectance is high, 0.97 or 0.98, and nothing has been found of certainly higher reflectance. Its directional luminous reflectance, $R_{0,45}$, is 1.00, and its spectral selectivity throughout the visible spectrum appears to be less than 1 percent. These data are based on work by Priest [119], McNicholas [24], and Preston [120], and are summarized in National Bureau of Standards Letter Circular LC547 [121]. In recent publications, Benford and others [122, 123] give the spectral reflectance of MgO and $MgCO_3$ in the ultraviolet and visible spectrum obtaining a value of about 0.99 for the luminous reflectance of MgO, with a selectivity of about 2 percent in the visible spectrum.

Other agencies besides the Bureau have also recommended MgO for the same or similar purpose. In 1931, the International Commission on Illumination adopted a resolution which may be translated as follows: "For the colorimetric measurement of opaque materials the luminance of the specimen studied ought to be expressed as a function of the luminance of a surface of the oxide of magnesium considered under the same conditions of illumination and observation" [124]. In 1944, this method was incorporated in ASTM Standard Method of test for spectral characteristics and color of objects and materials [125].

While these characteristics make fresh MgO an excellent fundamental standard, it has other characteristics that are undesirable and that make the calibration and use of a secondary working standard a very advisable procedure. An MgO surface is extremely fragile and thus is not very suitable for continued handling. A more serious defect is that its spectral reflectance may change perceptibly within a short time after preparation.

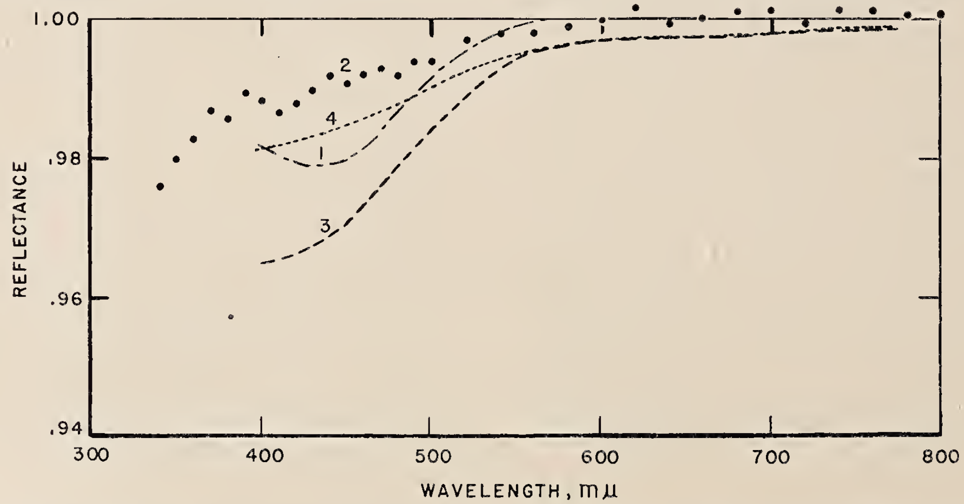

Figure 33. *Effect of age, and probably other factors, on the spectral reflectance of magnesium oxide.*

Values are plotted relative to the reflectance of freshly prepared MgO. Curves 1, 3, and 4 were obtained with the General Electric spectrophotometer, curve 2 with the Beckman spectrophotometer. The ages of the samples were: curve 1, 2½ weeks; curve 2, 5 months; curve 3, 20 months; curve 4, 2 years.

The nature of the change is shown in figure 33; the reflectance decreases below 550 mμ as shown. Furthermore the nature and extent of the changes are variable. A third reason for use of a working standard is that slight variations in reflectance (0.1 or 0.2 percent) have been noted for different preparations of freshly prepared MgO. By calibrating the working standard against several different MgO preparations, a more representative standard is obtained than would be any single MgO surface by itself.

White structural glass by the name of Vitrolite, with polished surface, has proved the most suitable for working standards of spectral directional reflectance, although the material is not uniformly good for this purpose and must be selected with care. A considerable supply of suitable Vitrolite has been obtained by the National Bureau of Standards, and standards are now calibrated and issued for either the General Electric recording spectrophotometer or the Beckman quartz spectrophotometer. Further information regarding these is given in NBS Letter Circular LC929, Standards for checking the calibration of spectrophotometers (200 to 1,000 mμ) [126].

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VIII. References

[1] Spectrophotometry, report of O. S. A. Progress Committee for 1922–23, K. S. Gibson, Chairman, J. Opt. Soc. Am. & Rev. Sci. Inst. **10,** 169 (1925).

[2] K. S. Gibson, The use of the photoelectric cell in spectrophotometry, Photo-electric Cells and Their Applications, pp. 157 to 173 (The Physical and Optical Societies, Great Britain, Cambridge University Press, 1930).

[3] F. Twyman and C. B. Allsopp, The practice of absorption spectrophotometry with Hilger instruments, 2d ed. (Adam Hilger, Ltd., London, 1934).

[4] G. R. Harrison, Current advances in photographic photometry, J. Opt. Soc. Am. **24,** 59 (1934).

[5] K. S. Gibson, Visual spectrophotometry, J. Opt. Soc. Am. **24,** 234 (1934). (Also chapter 11 of ref. 6.)

[6] W. E. Forsythe, editor, Measurement of Radiant Energy (McGraw-Hill Book Company, Inc., New York, N. Y., and London, 1937).

[7] M. G. Mellon, The role of spectrophotometry in colorimetry, Ind. Eng. Chem. Anal. Ed. **9,** 51 (1937).

[8] R. H. Müller, Photoelectric methods in analytical chemistry, Ind. Eng. Chem. Anal. Ed. **11,** 1 (1939).

[9] S. E. Q. Ashley, Spectrophotometric methods in modern analytical chemistry, Ind. Eng. Chem. Anal. Ed. **11,** 72 (1939).

[10] K. S. Gibson, Survey of spectrophotometers, pp. 475–479 of A Symposium on Spectrophotometry in the Pulp and Paper Industries, Tech. Assoc. Papers **23,** 473 (1940), also Paper Trade J., Tech. Sec. **111,** 135 (1940).

[11] W. R. Brode, Chemical Spectroscopy, 2d ed. (John Wiley & Sons, Inc., New York, N. Y.; Chapman & Hall, Ltd., London, 1943).

[12] L. Heilmeyer, translated by A. Jordan and T. L. Tippell, Spectrophotometry in medicine (Adam Hilger, Ltd., London, 1943).

[13] J. S. Preston, Photoelectric photometers: Their properties, use and maintenance, Trans. Ill. Eng. Soc. London **8–9,** 121 (1943).

[14] D. L. Drabkin, Photometry and spectrophotometry Medical Physics, pp. 967 to 1008 (The Year Book Publishers, Inc., Chicago, 1944).

[15] J. W. Stillman, Bibliography of photoelectric spectrophotometric methods of analysis for inorganic ions (covering the analytical edition of Ind. & Eng. Chem., Vol. **1** to Vol. **16,** and the Analyst, Vol. 62 to Vol. 69), A. S. T. M. Proceedings of the 47th Annual Meeting, New York, N. Y., June 26–30, 1944. (A. S. T. M., Philadelphia, Pa., 1945.)

[16] G. F. Lothian, Absorption spectrophotometry (Adam Hilger, Ltd., London, 1949).

[17] W. R. Brode, Spectrophotometry and colorimetry. A chapter in Physical methods in chemical analysis (Academic Press, New York, N. Y., in press).

[18] G. R. Harrison, R. C. Lord, and J. R. Loofbourow, Practical Spectroscopy (Prentice-Hall, Inc., New York, N. Y., 1948.)

[19] Illuminating Engineering Nomenclature and Photometric Standards. American Standard, approved February 27, 1942 by American Standards Association, ASA Z7.1–1942. Prepared under the direction of and issued by the Illuminating Engineering Society. Published also as Report of I. E. S. Committee on Nomenclature and Standards, E. C. Crittenden, Chairman, Illum. Eng. **36,** 813 (1941).

[20] Report for 1920–21 of Optical Society of America Committee on Colorimetry, L. T. Troland, Chairman, J. Opt. Soc. Am. & Rev. Sci. Inst. **6,** 527 (1922).

[21] Chapters from the forthcoming report of the Optical Society of America Committee on Colorimetry, L. A. Jones, Chairman, J. Opt. Soc. Am., as follows:
  Chapter 2, The concept of color, **33,** 544 (1943).
  Chapter 5, Physical concepts: Radiant energy and its measurement, **34,** 183 (1944).
  Chapter 6, The psychophysics of color, **34,** 245 (1944).
  Chapter 7, Quantitative data and methods for colorimetry, **34,** 633 (1944).
  Chapter 8, Colorimeters and color standards, **35,** 1 (1945).

[22] Terminology and symbols for use in ultraviolet, visible, and infrared absorptometry, NBS Letter Circular LC857 (1947).

[23] Announcement of changes in electrical and photometric units, NBS Circular C459 (1947).

[24] H. J. McNicholas, Absolute methods in reflectometry, BS J. Research **1,** 29 (1928) RP3.

[25] D. B. Judd, with the collaboration of W. N. Harrison, B. J. Sweo, E. F. Hickson, A. J. Eickhoff, M. B. Shaw, and G. C. Paffenbarger, Optical specification of light scattering materials, J. Research NBS **19,** 287 (1937) RP1026.

[26] H. von Helmholtz, Handbuch der Physiologischen Optik, (1911), translated from the Third German Editon, Edited by J. P. C. Southall, and published by the Optical Society of America (1924), Volume II, The Sensations of Vision.

[27] C. S. French, G. S. Rabideau, and A. S. Holt, The construction and performance of a large grating monochromator with a high energy output for photochemical and biological investigations, Rev. Sci. Inst. **18,** 11 (1947).

[28] W. E. Forsythe and B. T. Barnes, A quartz monochromator and its spectral transmission, Rev. Sci. Inst. **1,** 569 (1930).

[29] K. K. Kay and H. M. Barrett, A new method for the determination of the transmission factor of a spectroradiometer, J. Opt. Soc. Am. **27,** 65 (1937).

[30] Beckman Bulletin 91–c, p. 12, National Technical Laboratories, South Pasadena, California (1947).

[31] Massachusetts Institute of Technology Wavelength Tables, measured and compiled under the direction of George R. Harrison (John Wiley & Sons, Inc., New York, 1939).

[32] N. C. Beese, Cesium vapor lamps, J. Opt. Soc. Am. **36,** 555 (1946).

[33] K. S. Gibson and M. M. Balcom, Transmission measurements on the Beckman quartz spectrophotometer, J. Research NBS **38,** 601 (1947) RP1798; also J. Opt. Soc. Am. **37,** 593 (1947).

[34] M. Garbuny, Relative Intensitäten und Übergangswahrscheinlichkeiten der rotgelben Neonlinien, Z. Physik **107,** 362 (1937).

[35] H. J. McNicholas, Equipment for routine spectral transmission and reflection measurements, BS J. Research **1,** 793 (1928) RP30.

[36] K. S. Gibson, Direct-reading photoelectric measurement of spectral transmission, J. Opt. Soc. Am. and Rev. Sci. Inst. **7,** 693 (1923); also described in J. Opt. Soc. Am. **21,** 564 (1931).

[37] H. H. Cary and A. O. Beckman, A quartz photoelectric spectrophotometer, J. Opt. Soc. Am. **31,** 682 (1941).

[38] K. S. Gibson and H. J. Keegan, Calibration and operation of the General Electric recording spectrophotometer of the National Bureau of Standards, J. Opt. Soc. Am. **28,** 372 (1938).

[39] G. L. Buc and E. I. Stearns, Uses of retardation plates in spectrophotometry, II. Calibration of wavelength, J. Opt. Soc. Am. **35,** 465 (1945).

[40] A. C. Hardy, A new recording spectrophotometer, J. Opt. Soc. Am. **25,** 305 (1935).

[41] A. C. Hardy, History of the design of the recording spectrophotometer, J. Opt. Soc. Am. **28,** 360 (1938).

[42] J. L. Michaelson, Construction of the General Electric recording spectrophotometer, J. Opt. Soc. Am. **28,** 365 (1938).

[43] H. J. Keegan and K. S. Gibson, On the use of working standards of didymium and Vitrolite glasses for spectrophotometric measurements, J. Opt. Soc. Am. **34,** 770 (1944).

[44] M. K. Frehafer and C. L. Snow, Tables and graphs for facilitating the computation of spectral energy distribution by Planck's formula, NBS Miscellaneous Publication M56 (1925).

[45] J. F. Skogland, Tables of spectral energy distribution and luminosity for use in computing light transmissions and relative brightnesses from spectrophotometric data, NBS Miscellaneous Publication M86 (1929).

[46] R. Davis and K. S. Gibson, Filters for the reproduction of sunlight and daylight and the determination of color temperature, BS Miscellaneous Publication M114 (1931).

[47] I. G. Priest, Measurement of the color temperature of the more efficient artificial light sources by the method of rotatory dispersion, BS Sci. Pap. **18,** 221 (1922–23); also J. Opt. Soc. Am. and Rev. Sci. Inst. **6,** 27 (1922).

[48] W. E. Forsythe, Color match and spectral distribution, J. Opt. Soc. Am. and Rev. Sci. Instr **7,** 1115 (1923).

[49] M. Luckiesh, Applications of germicidal, erythemal and infrared energy (D. Van Nostrand Co., Inc., New York, N. Y., 1946).

[50] K. S. Weaver, The visibility of radiation at low intensities, J. Opt. Soc. Am. **27,** 36 (1937); also W. S. Stiles and T. Smith, A mean scotopic visibility curve, Proc. Phys. Soc. **56,** 251 (1944).

[51] K. S. Gibson, Spectral luminosity factors, J. Opt. Soc. Am. **30,** 51 (1940).

[52] H. E. Ives and E. F. Kingsbury, The applicability of photoelectric cells to colorimetry, J. Opt. Soc. Am. **21,** 541 (1931).

[53] K. S. Gibson, H. J. McNicholas, E. P. T. Tyndall, M. K. Frehafer, Bureau of Standards, with the cooperation of W. E. Mathewson, Bureau of Chemistry, The spectral transmissive properties of dyes. I. Seven permitted food dyes, in the visible, ultraviolet, and near infrared. Sci. Pap. BS **18,** 121 (1922) S440.

[54] L. A. Jones and H. R. Condit, Sunlight and daylight as determinants of photographic exposure. II. Scene structure, directional index, photographic efficiency of daylight, safety factors, and evaluation of camera exposure, J. Opt. Soc. Am. **39,** 94 (1949).

[55] D. B. Judd and K. S. Gibson, Note on the effect of a cover glass in reflectance measurements, J. Research NBS **16,** 261 (1936) RP872.

[56] Gaertner spectrophotometers, Bulletin 142–74, The Gaertner Scientific Corporation, Chicago 14, Ill.

[57] Scientific instruments, catalogue D–111, Bausch & Lomb Optical Co., Rochester, N. Y. (1940).

[58] F. F. Martens, Über ein neues Polarisationsphotometer, Physik. Z. **1,** 299 (1900).

[59] J. H. Dowell, A new polarizing system for spectrophotometers, J. Sci. Inst. **8,** 382 (1931). A new industrial and research spectrophotometer, J. Sci. Inst. **10,** 153 (1933).

[60] H. E. Howe, On a modification of the Hilger sector photometer method for measuring ultraviolet absorption and its application in the case of certain derivatives of fluoran, Phys. Rev. **8,** 674 (1916).

[61] F. Twyman, The "Spekker" photometer for ultraviolet spectrophotometry, Trans. Opt. Soc. London **33,** 9 (1931–32).

[62] S. J. Lewis, A new sector spectrophotometer, Trans. J. Chem. Soc. **115**^{1}, 312 (1919).

[63] Bausch & Lomb spectrographic equipment, catalog D–20, p. 26 (1947), Bausch & Lomb Optical Co., Rochester, N. Y.

[64] Gaertner rotating sector photometer, Bulletin 149–44, The Gaertner Scientific Corporation, Chicago 14, Ill.

[65] B. O'Brien, Information supplied by letter. Description of the sector is given in reference 11.

[66] G. Reimann and E. J. Carmine, A device to facilitate the reading of spectrophotometric curves, J. Opt. Soc. Am **36,** 235 (1946).

[67] H. J. Keegan, On the measurement of the spectral apparent reflectance of low-reflecting materials, J. Opt. Soc. Am. **34,** 770 (1944).

[68] O. W. Pineo, Residual photometric errors in the commercial recording spectrophotometer, J. Opt. Soc. Am. **30,** 276 (1940).

[69] E. I. Stearns, Applications of near infra-red spectrophotometry, J. Opt. Soc. Am. **33,** 27 (1943).

[70] G. L. Buc and E. I. Stearns, Uses of retardation plates in spectrophotometry, I. Determination of slit shape and slit width, J. Opt. Soc. Am. **35,** 458 (1945).

[71] G. L. Buc and E. I. Stearns, Uses of retardation plates in spectrophotometry, III. Measurement of dichroic samples, J. Opt. Soc. Am. **35,** 521 (1945).

[72] C. Sheard and M. N. States, A concave grating photoelectric spectrophotometer, J. Opt. Soc. Am. **31,** 64 (1941). Also Bulletin 104A of the Central Scientific Company, Chicago 13, Ill.

[73] Coleman Electric Co., Chicago, Ill. Bulletin No. 104 and other advertising circulars.

[74] S. Jacobsohn, H. E. Bent, and A. J. Harrison, A precision spectrophotometer for use in the range 450 to 820 mμ, Rev. Sci. Inst. **11,** 220 (1940).

[75] Rev. Sci. Inst. **17,** 558 (1946). Also advertizing circulars of the Applied Physics Corporation, Pasadena, Calif.

[76] Advertizing circulars of the National Technical Laboratories, South Pasadena, Calif.

[77[J. S. Preston and F. W. Cuckow, A photoelectric spectrophotometer of high accuracy, Proc. Phys. Soc. **48,** 869 (1936).

[78] T. R. Hogness, F. P. Zscheile, Jr., and A. E. Sidwell, Jr., Photoelectric spectrophotometry; an apparatus for the ultraviolet and visible spectral regions: its construction, calibration, and application to chemical problems, J. Phys. Chem. **41,** 379 (1937).

[79] S. Schlaer, A photoelectric transmission spectrophotometer for the measurement of photosensitive solutions, J. Opt. Soc. Am. **28,** 18 (1938).

[80] V. K. Zworykin, An automatic recording spectroradiometer for cathodoluminescent materials, J. Opt. Soc. Am. **29,** 84 (1939).

[81] G. R. Harrison and E. P. Bentley, An improved high speed recording spectrophotometer, J. Opt. Soc. Am. **30,** 290 (1940).

[82] W. R. Brode and C. H. Jones, A recording spectrophotometer and spectropolarimeter, J. Opt. Soc. Am. **31,** 743 (1941).

[83] J. Gillod, Contribution a la solution spectrophotometrique du probléme de la mesure des couleurs, Publication No. 82, Republique Francaise Laboratoire d'Essais (1944).

[84] D. L. Drabkin, A new form of photoelectric spectrophotometer, J. Opt. Soc. Am. **35,** 163 (1945).

[85] E. P. Little, A photoelectric spectrophotometer for the Schumann region, J. Opt. Soc. Am. **36,** 168 (1946).

[86] F. J. Studer, A method for measuring the spectral energy distribution of low brightness sources, J. Opt. Soc. Am. **37,** 288 (1947).

[87] A. E. Hardy, A combination phosphorometer and spectroradiometer for luminescent materials, Publication No. ST–358, Tube Department, Radio Corporation of America (1947).

[88] F. P. Zscheile, Photoelectric spectrophotometry, the performance of a quartz double monochromator in an improved and more versatile photoelectric spectrophotometer, J. Phys. Colloid Chem. **51,** 903 (1947).

[89] J. A. Van den Akker, A survey of abridged spectrophotometers, Tech. Assoc. Papers (T. A. P. P. I.) **23,** 480 (1940); also Paper Trade J., Tech. Sec. **111,** 140 (1940).

[90] W. W. Coblentz, W. B. Emerson, and M. B. Long, Spectroradiometric investigation of the transmission of various substances, Bul. BS **14,** 653 (1918) S325.

[91] K. S. Gibson, E. P. T. Tyndall, and H. J. McNicholas, The ultraviolet and visible transmission of various colored glasses, Techn. Pap. No. 148 (1920) T148.

[92] K. S. Gibson, Spectral filters, J. Opt. Soc. Am. and Rev. Sci. Inst. **13,** 267 (1926); also Int. Crit. Tables **5,** 271 (1929).

[93] K. S. Gibson, A filter for obtaining light at wavelength 560 mμ, J. Research NBS **14,** 545 (1935) RP785; also J. Opt. Soc. Am. **25,** 131 (1935).

[94] Glass color filters, Corning Glass Works, Corning, N. Y. (1946).

[95] Wratten light filters, Eastman Kodak Co., Rochester, N. Y. (1938).

[96] Farrand interference filters, Farrand Optical Co., New York, N. Y. (1947).

[97] Baird Associates interference filters, Baird Associates, Cambridge, Mass. (1946).

[98] E. Pettit, Transmission properties of some filters, Astrophys. J. **66,** 43 (1927).

[99] W. C. Holmes, Monochromatic light filters for the visible spectrum, Am. Dyestuff Reptr. **17,** 31 (1928).

[100] L. A. Jones, Light filters for the isolation of narrow spectral regions, J. Opt. Soc. Am. & Rev. Sci. Inst. **16,** 259 (1928).

[101] E. J. Bowen, Light filters for the mercury lamp, J. Chem. Soc., London, part 2, p. 2236 (1932).

[102] C. Winther, Ein Filtersatz fur die Quartz-Quecksilberlampe, Z. Elektrochem. **43,** 691 (1937).

[103] E. M. Staats, The design of monochromatic filters for the type H–3 mercury lamp, J. Opt. Soc. Am. **28,** 112 (1938).

[104] E. P. Hyde, Talbot's law as applied to the rotating sectored disk, Bul. BS **2,** 1 (1906) S26.

[105] K. S. Gibson, G. K. Walker, and M. E. Brown, Filters for testing the reliability of spectrophotometers, J. Opt. Soc. Am. **24,** 58 (1934).

[106] R. C. Gibbs, The effect of temperature on fluorescence and absorption, Phys. Rev. **31,** 463 (1910).

[107] K. S. Gibson, The effect of temperature upon the coefficient of absorption of certain glasses of known composition, Phys. Rev., **7,** 194 (1916). See also Phys. Rev., **8,** 38 (1916).

[108] G. E. Grantham, The effect of temperature upon the infra-red absorption spectra of certain glasses, Phys. Rev., **16,** 565 (1920).

[109] S. Meyer, Über die Temperaturabhängigkeit der Absorption bei Gläsern in Ultrarot und Ultraviolett, Glastech. Ber., **14,** 305 (1936).

[110] A. J. Holland and W. E. S. Turner, An investigation into the variation with temperature of the spectral transmission of glasses. I. The transmission in the visual spectral region at temperatures from 20° to the softening point, J. Soc. Glass Tech., **25,** 164 (1941).

[111] W. W. Coblentz and R. Stair, Data on ultra-violet solar radiation and the solarization of window materials, J. Research NBS **3,** 629 (1929) RP113.

[112] G. Reimann, D. B. Judd, and H. J. Keegan, Spectrophotometric and colorimetric determination of the colors of the TCCA standard color cards, J. Research NBS **36,** 209 (1946) RP1700; also J. Opt. Soc. Am. **36,** 128 (1946).

113] K. S. Gibson and H. J. Keegan, On the magnitude of the error resulting from fluorescence in spectrophotometric measurements, J. Opt. Soc. Am. **28,** 180 (1938).

[114] C. Runge, Über die Differentiation empirischer Functionen, Z. Math. Phys. **42,** 205 (1897).

[115] F. Paschen, Ueber die Correction der Energiecurven wegen der Unreinheit des Spectrums, Wied. Ann. **60,** 712 (1897).

[116] E. P. Hyde, Slit-width corrections in spectrophotometry and a new form of variable sectored disk, Astrophys. J. **35,** 237 (1912).

[117] J. A. Van den Akker, Wavelength calibration of spectrophotometers, J. Opt. Soc. Am. **33,** 257 (1943).

[118] A. C. Hardy and F. M. Young, The correction of slit-width errors, J. Opt. Soc. Am. **39,** 265 (1949).

[119] I. G. Priest and J. O. Riley, The selective reflectance of magnesium oxide, J. Opt. Soc. Am. **20,** 156 (1930).

[120] J. S. Preston, The reflection factor of magnesium oxide, Trans. Opt. Soc. (London) **31,** 15 (1929–30).

[121] Preparation and colorimetric properties of a magnesium-oxide reflectance standard, NBS Letter Circular LC547 (1939).

[122] F. Benford, G. P. Lloyd, and S. Schwarz, Coefficients of reflection of magnesium oxide and magnesium carbonate, J. Opt. Soc. Am. **38,** 445 (1948).

[123] F. Benford, S. Schwarz, and G. P. Lloyd, Coefficients of reflection in the ultraviolet of magnesium carbonate and oxide, J. Opt. Soc. Am. **38,** 964 (1948).

[124] Proceedings, ICI, 8th Session, Cambridge, p. 23, 1931.

[125] ASTM standard method of test for spectral characteristics and color of objects and materials, ASTM D-307-44.

[126] Standards for checking the calibration of spectrophotometers (200 to 1,000 mμ), NBS Letter Circular LC 929 (1948).

[127] M. G. Mellon, editor, Analytical Absorption Spectroscopy. (John Wiley & Sons, Inc., New York, N. Y., in press.)

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