Standard Guide for
Microspectrophotometry and Color Measurement in Forensic Paint Analysis[1]

This standard is issued under the fixed designation E2808; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Color is one of the most important comparative characteristics of paints. The comparison of color is one of the first steps taken in a forensic paint comparison and it is essential to note that this guide does not propose the use of instrumental color comparison for objects that are distinguishable to the eye. Since the 1940s, analytical instruments have been able to discriminate colors that the average human eye cannot distinguish. Microspectrophotometers (MSPs), in particular, allow for an objective measurement of the color of small, millimetre or submillimetre samples and are more precise or quantitative compared to the more subjective results of visual microscopical color comparisons.

Suitable instruments with appropriate optics, sensitivity, resolution, and dynamic range can measure and produce spectral curves of light energy from small samples as that light is transmitted, absorbed, or reflected by the sample. These spectra are collected over small measurement steps or increments of one-half to a few nanometers each. MSPs typically operate in the visible spectral region (~380 to ~800 nm) and also in the ultraviolet region (~190 to ~380 nm). They should not be confused with broadband or absorption filter-based, tristimulus systems or low-resolution, large measurement step (5 nm or more) spectral analyzers.

The spectral limits of different instruments can vary in all of the above noted spectral regions and may also include the near infrared region from about 780 to 2100 nm. The usefulness of this last spectral region in the analysis and comparison of paint fragments is currently indeterminate and will not be covered in this guide.

Subjective terms such as "blue, "violet," or "purple" are inadequate descriptors of actual color. MSP instruments can be used to describe or numerically "name" an item's color by calculating the item's colorimetric values. These values, or chromaticity coordinates, can be expressed in any one of several coordinate systems and are useful in the development and maintenance of color comparison databases.

Colorimetric values are of limited use in actual color comparison of evidence samples because differing spectral curves can yield identical colorimetric values. This is commonly found in industrial or commercial paint-matching protocols in which the only requirement is to paint an item so it appears to be the same as others. The eye's perception and the colorimetric values of two items may indicate that they are the same color, but the spectral curves of those items may still be distinguished. This leads to the use of the MSP in the comparison of visually indistinguishable colored items.

1. Scope

1.1 This guide is intended to assist individuals and laboratories that conduct forensic visible and ultraviolet (UV) spectral analyses on small fragments of paint using Guide E1610.

1.2 This guide deals primarily with color measurements within the visible spectral range but will also include some details concerning measurements in the UV range.

1.3 This guide does not address other areas of color evaluation such as paint surface texture or paint pigment particle size, shape, or dispersion within a paint film that are evaluated by other forms of microscopy. Other techniques such as spectral luminescence, fluorescence, and near infrared (NIR) are not included in this guide because of their limited use, lack of validation, or established efficacy in forensic paint analysis.

1.4 This guide is directed at the color analysis of commercially prepared paints and coatings. It does not address the analysis or determination of provenance of artistic, historical, or restorative paints, but it may be found useful in those fields.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D16 Terminology for Paint, Related Coatings, Materials, and Applications
D1535 Practice for Specifying Color by the Munsell System
D2244 Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates
E179 Guide for Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers
E284 Terminology of Appearance
E308 Practice for Computing the Colors of Objects by Using the CIE System
E805 Practice for Identification of Instrumental Methods of Color or Color-Difference Measurement of Materials
E1610 Guide for Forensic Paint Analysis and Comparison

3. Terminology

3.1 *Definitions*—For definitions of paint-associated terminology used in this guide, see Terminologies D16, E284, and E1610.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorbance, n*—logarithm to the base 10 of the reciprocal of spectral transmittance, (*T*).

$$A = \log_{10}(1/T) = -\log_{10}T$$

3.2.1.1 *Discussion*—It is often expressed as a fraction or decimal value and may be referred to as optical density.

3.2.2 *absorption, n*—transformation of incident energy into longer wavelength energy.

3.2.3 *bandwidth, n*—optical width of the monochromator exit slit or the optical width of a semiconductor detector element that will vary with monochromator design.

3.2.3.1 *Discussion*—This term can also refer to the wavelength interval over which radiant energy is greater than 50 % of the maximum intensity.

3.2.4 *charge-coupled device (CCD), n*—a silicon-based semiconductor chip consisting of a two-dimensional matrix of photo sensors or pixels.

3.2.5 *chromaticity, n*—dimensions of a color stimulus, excluding luminous intensity, and expressed in terms of hue and saturation (Commission Internationale de l'Eclairage (CIE)) or redness-greenness and yellowness-blueness (L*, a*, b*).

3.2.5.1 *Discussion*—It is generally represented as a point in a constant luminance plane of a three-dimensional color space.

3.2.6 *chromaticity coordinates, CIE, n*—ratios of each of the three tristimulus values *X*, *Y*, and *Z* in relation to the sum of the three designated as *x*, *y*, and *z*, respectively.

3.2.6.1 *Discussion*—They are sometimes referred to as the trichromatic coefficients. When written without subscripts, they are assumed to have been calculated for Illuminant C and the 2° (1931) Standard Observer unless specified otherwise. If they have been obtained for other illuminants or observers, a subscript describing the observer or illuminant should be used. For example, x_{10D} and y_{10D} are chromaticity coordinates for the 10° observer and Illuminant D. A "standard observer" refers to specific numerical values that represent the nominal color response of the human eye to different wavelengths of light. It is based on a study of the average retinal response of the human population.

3.2.7 *chromaticity diagram, CIE, n*—two-dimensional graph that describes a color as the locus of chromaticity coordinates in a field of monochromatic light varying from 380 to 780 nm in wavelength where *X* is the abscissa of the coordinate system and *Y* is the ordinate and it is used to describe and compare the colors of both luminous and non-luminous materials.

3.2.8 *CIELAB Unit E, n*—(L*a*b*) color difference equation from Practice D2244.

3.2.8.1 *Discussion*—The color difference E between two samples is given by:

$$\Delta E_{\text{CIE}}(L^*, a^*, b^*) = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

where

L* (pronounced "L star") = where a color falls on a vertical scale from light to dark,
a* = where the color falls on the continuum of colors between red and green, and
b* = where the color falls on the continuum of colors between blue and yellow.

3.2.9 *colorimetry, n*—conversion of instrumental light measurements into psychophysical descriptions or numerical notations that can be correlated with visual evaluations of color and color differences.

3.2.10 *effect pigment, n*—any paint pigment that is designed to produce a significant change in color attribute(s) in a paint film when the film is viewed or illuminated from varied geometries.

3.2.11 *error ellipse (visual limits), n*—plotted limits of variation in visually indistinguishable color coordinate values that form an elliptical shape around a central color value when plotted in a chromaticity diagram.

3.2.12 *grating, n*—parallel set of linear, regularly repeating structures that, when illuminated, produces maxima and minima of light intensity as a consequence of interference.

3.2.12.1 *Discussion*—These maxima and minima vary in position with wavelength. This allows radiation of any given wavelength to be isolated from a complex mixture of wavelengths and allows the grating to be used as a monochromator.

3.2.13 *illumination aperture, n*—element in the optical path of a microspectrophotometric (MSP) system that limits the area of illumination reaching the sample focal plane.

3.2.14 *measuring aperture, n*—element in the optical path of a microspectrophotometric (MSP) system that limits the area of illumination reaching the detector focal plane.

3.2.15 *monochromator, n*—device designed to isolate narrow wavelength ranges of light from complex, broad-spectrum radiation.

3.2.16 *photomultiplier tube (PMT), n*—photosensitive vacuum tube device that quantitatively converts photons of light into electrical energy.

3.2.17 *reflectance, R, n*—the ratio of the radiant power reflected by the specimen to the radiant power incident on the specimen.

3.2.17.1 *Discussion*—In popular usage, it is considered as the ratio of the intensity of reflected radiant energy from a test sample to that reflected from a defined reference standard.

3.2.18 *significant difference, n*—difference between two specimens that indicates their possible common origin cannot be established.

3.2.19 *standard observer, CIE, n*—visual color perception data set adopted by CIE to represent the response of the average human eye when light adapted to an equal energy spectrum.

3.2.19.1 *Discussion*—Unless otherwise specified, the term applies to the data adopted in 1931 for a 2° field of vision. The data adopted in 1964, sometimes called the 1964 observer, were obtained for a 10° field of vision and are generally used in industrial measurements.

3.2.20 *standard illuminant, CIE, n*—standard sources for which the CIE specified the spectral energy distribution as follows:

3.2.20.1 *standard illuminant A, CIE, n*—tungsten filament lamp operated at a color temperature of 2856 K, approximating a blackbody operating at that temperature.

3.2.20.1.1 *Discussion*—It is defined in the wavelength range of 380 to 770 nm.

3.2.20.2 *standard illuminant C, CIE, n*—approximation of overcast daylight having a correlated color temperature of approximately 6770 K.

3.2.20.2.1 *Discussion*—This color of light can be obtained by using a combination of Illuminant A and a color-correcting filter. It is defined in the wavelength range of 380 to 770 nm.

3.2.20.3 *standard illuminant D, CIE, n*—approximation of bright daylight illumination having a correlated color temperature of 6504 K in the spectral range of 300 to 830 nm.

3.2.20.3.1 *Discussion*—The UV portion of Illuminant D, 300 to 380 nm, is necessary to describe correctly colors that contain fluorescent colorants or ultraviolet (UV) absorbers. The UV and visible portions are designated as UVD and VisD. Illuminant D is based on actual measurements of the spectral distribution of daylight and is the most commonly used standard illuminant for spectral measurements.

3.2.21 *thermochromy, n*—characteristic of some materials, including some pigments, to change color as temperature changes.

3.2.22 *step width, n*—distance between two points of wavelength measurement in a spectrum, not to be confused with resolution although it can have an impact on resolution.

3.2.23 *transmittance, T, n*—the ratio of radiant power transmitted by the specimen to the radiant power incident on the specimen.

3.2.23.1 *Discussion*—Both absorption and reflection influence total transmittance.

3.2.24 *tristimulus values, CIE, n*—amounts (in percent) of the three components necessary in a three-color additive mixture required for matching a color.

3.2.24.1 *Discussion*—These components are designated as *X*, *Y*, and *Z* in the CIE system. The illuminant and standard observer color-matching functions must be designated. If they are not, an assumption is made that the reported values are for the 1931 observer (2° field) and Illuminant C. The values obtained depend on the method of integration used, the nature of the sample surface, sample homogeneity, and the instrument design. Tristimulus values are therefore not absolute values for a sample, but relative values dependent on the method used to obtain them. Examples of calculations of tristimulus values in the CIE system can be found in Practice E308.

3.2.25 *Wood's anomaly, n*—effect caused by a polarization of diffracted energy as a result of non-uniform reflection as the angle of incidence varies on a holographically blazed monochromator.

3.2.25.1 *Discussion*—This effect can be observed as a distinct transmittance maximum within the spectrum.

4. Summary of Practice

4.1 One of the most obvious decorative properties of paint is its color. Usually, one or more major pigments are used in a paint together with one or more minor pigments whose purpose is to modify color or other film properties. The interaction of pigments with light is very complex with light being scattered, absorbed, and reflected within the paint layer.

4.2 The processes responsible for producing the color of pigments include: crystal-field effects with transition metal compounds (most of the inorganic pigments belong to this group), electron transitions between molecular orbitals in compounds with conjugated double bonds (organic pigments), electron transitions in compounds with conduction energy bands (metal pigments and pure semiconductors), and other processes caused by geometrical and wave optics (interference,

scattering, diffraction in optically variable pigments, liquid crystal pigments, and so forth). All of these processes are based on the interaction between ultraviolet-visible (UV-Vis) light waves themselves or with electrons in pigments and can be measured and compared using MSP.

4.3 The analysis of paint using MSP can be carried out using either transmission or reflectance techniques. However, be aware that paint color comparisons or pigment identifications using reflectance measurements are difficult tasks because of the effects of surface observation angle, surface texture, and sample curvature. This method is seldom used for detailed color comparison or pigment identification, but it can be useful in exclusionary comparisons of bulk colors.

4.4 *Basic Principles:*

4.4.1 A MSP can measure reflected or transmitted radiation at selected wavelengths. The resulting total spectral curve of a colored sample is produced by comparing the light reflected from a sample to the light reflected from a white reflectance standard or by comparing light transmitted by the sample to the light transmitted by a colorless background.

4.4.2 Paint colors are usually measured in transmission through thin sections. Reflectance techniques can also be used especially when fluorescence measurements in the UV range are desired. When performing measurements on UV-absorbing materials in the UV region, transmission techniques are recommended.

4.4.3 In reflectance measurements of paint color, a sample is illuminated and the fraction of light reflected in the visible range is recorded. The reflectance curve obtained provides a representation of the color. In transmission measurements, a paint thin section is illuminated and the fraction of light transmitted or absorbed in the Vis or UV range or both is recorded.

4.4.4 Transmittance spectra may be plotted in either percent transmittance or absorbance. Reflectance spectra may be plotted in either percent reflectance or absorbance.

4.5 *Colorimetry:*

4.5.1 To achieve accurate color values, a number of instrumental parameters have to be defined. In 1931, CIE defined the standard illuminants, measuring conditions and the three standard primary colors [X], [Y], and [Z]. The amount of each of these colors needed to match a specific color can be calculated. These calculations yield a mathematical representation of a color (tristimulus values). This is described in Practice D1535.

4.5.2 Using a mathematical equation, these tristimulus values can be converted into L*, a*, and b* coordinates. The Color Measurement Committee of the Society of Dyers and Colorists recommends this system for the description of color. From the values of L*, a*, and b*, color differences can be obtained in CIELAB units. See Practice E805.

4.6 *Metamerism*—Two samples can appear to have the same color under one type of illumination but may appear dissimilar under different lighting conditions. This phenomenon is one form of metamerism. A second form occurs when two samples appear to be the same color under all lighting conditions, yet their reflectance/transmittance curves are different. Both forms are a result of differences in their pigment compositions. Note

that two objects with different reflectance or transmittance curves can have identical colorimetric values (tristimulus values or chromaticity coordinates). Therefore, it is not recommended to use colorimetric values alone for detailed sample comparisons.

4.7 *Instrumentation:*

4.7.1 The MSP has been designed to meet the requirements of analyzing the color of a sample in situ. In scanning spectroscopy, a MSP consists basically of a research-grade microscope with a stabilized light source, a spectrometer, and a data-processing device. The main function of the microscope is to reflect or transmit light energy efficiently, uniformly, and reproducibly. The spectrometer contains a spectrally dispersive element, most commonly a diffraction grating, and a detector and measures intensity of light energy with respect to spectral position within a spectral range. All MSPs are single-beam instruments: a standard or a blank is measured, the result is stored, and a sample is measured and a ratio made to the blank to yield a transmittance or reflectance spectrum. MSP systems are generally used in forensic analysis because of the small sample sizes presented by paint film fragments, but instruments for color measurement from large samples (spectrometers) can also be used for compiling color databases. Large area measurements can differ from microscale measurements because of the effects of averaging. It can be difficult to compare data from a MSP to that of a macroscale spectrometer.

4.7.2 A monochromator produces monochromatic light of a certain spectral bandwidth. The sample is scanned step by step and a spectrum created point by point. This type of instrument is known as a scanning spectrometer and generally uses a photomultiplier tube (PMT) detector. In a multichannel spectrometer, however, all spectral regions are detected simultaneously and a semiconductor detector is commonly used.

4.7.3 The use of semiconductor detectors is relatively new in forensic analysis. Spectrometers using these devices are composed of a diffraction grating together with an array detector that acts as the photosensitive device. The detector's resolution will depend on the number of diodes or elements in the array, the dispersion and line spacing of the grating, and the distance between the grating and the array. Measurement time is drastically reduced compared to PMT systems because of simultaneous detection of the full spectral range.

4.7.4 Commercially available MSPs have incorporated the requirements of operational settings, data control, processing, and recording with the support of a computer processor. As such, they all carry their own software routines to cope with the tasks.

5. Significance and Use

5.1 Paint sample colors can be measured by reflectance (visible range) or transmission (UV-Vis) for comparison purposes. Transmission measurements are especially necessary for the analysis of UV absorbers in clear coats, the identification of pigments, and the detailed analysis of effect pigments that are not opaque.