Evaluating Spectrophotometric Uncertainty

Hugh S. Fairman*, *Resource III, Inc.*, Tatamy, PA USA
Jack A. Ladson, *Color Science Consultancy*, 1000Plowshare Road, Yardley, PA19067, Jack.Ladson@verizon.net

Abstract

Ideally, manufacturer specifications provide performance characteristics and specifications that can be used to evaluate the suitability of colorimeter and spectrometer measuring and test equipment for a given application. However, understanding specifications and using them to compare equipment from different manufacturers, the quality of products, and its adherence to specifications can be a perplexing task. This primarily results from inconsistent terminology, units, and methods used to develop and report equipment performance specifications.

This paper discusses the continuation of work that was carried on since Hugh Fairman's ISCC presentation in October 2012 and the ASTM adoption of the standard test method referenced herein in 2013.

We review how to determine if manufacturer specifications are adequate for the intended purpose, and how to interpret and assess colorimeter and spectrometer performance and reliability. Recommended practices are presented and an illustrative example is given for combining components values into a specification.

Introduction

Approximately two years ago, in 2009, ASTM International[1] undertook to study this problem and to define a procedure that would assist the color measuring community in obtaining international accreditation. This paper describes the results of that study and the procedure finally standardized for the assessment of the uncertainty of spectrophotometric and colorimetric measurements; such as reflectance and transmittance measurements.

Instruments, as the term is used in this paper, mean spectrometers, spectrophotometers, abridged spectrometers, colorimeters, spectro-colorimeters, and other color measuring instruments. This includes whatever data processors are used to collect, process and compute the colorimetric values, color difference values and total color difference metrics.

Manufacturer specifications should provide detailed information about colorimeter and spectrometer performance characteristics. Some of the manufacturers may only provide a single specification for overall accuracy. None of the classical manufacturers provide ample information detailing individual performance

1 ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania, USA, www.astm.org, (610) 832-9500

specifications; such as uncertainty. In some instances, specifications can be complex, including numerous time and range dependent characteristics and values. And, since specification documents are also a means for manufacturers to market their products, they often contain additional information about features, operating condition limits, or other qualifiers that are not relevant to this paper.

There are various published approaches to the estimation of uncertainty and/or variability in testing. ISO/IEC 17025[2] does not specify any particular approach; rather laboratories are encouraged to use statistically valid approaches. The concept here is to provide a reasonable estimate of the appropriate uncertainty data according to known parameters within the industry. For instance, both the intermediate precision and reproducibility (from interlaboratory comparisons) described in ISO 57255[3] (see clause 5.4.6.3, note 3 of ISO/IEC 17025) may be used in estimating measurement uncertainty. However, these may omit some uncertainty sources that should also be identified.

Manufacturers publish colorimeter and spectrometer specifications in a variety of places. For instance, on their web pages, in product data sheets, technical notes, control drawings, and operating manuals. In some instances, manufacturers will only provide information about colorimeter and spectrometer specifications and data upon formal request by phone, fax or email. What is worse is that some manufacturers do not provide meaningful or interpretable data! In general, however, published specifications are relatively easy to find via an internet search or by phone. In specifications for spectrometry, it is helpful for one to know the relevant industry-specific terminology and jargon.

Definitions

There are several definitions and concepts that may be new to the reader. Uncertainty is defined as a property of measurement in a laboratory, not at a national standardization laboratory. Since uncertainty has been developed expressly for spectrometry and colorimetry and have different meanings, they are presented here.

a. **Uncertainty-n**, a parameter associated with a measurement result or test result that reasonably characterizes the dispersion of results attributable to the particular quantity being measured of the particular characteristic being tested.

b. **Instrument uncertainty conditions-n,** of a measurement, conditions wherein the measurements are made repetitively and carefully over a short timescale, without replacement of the specimen being measured in the specimen port of the instrument.

Note: Instrument uncertainty conditions always include potential specimen drift due to causes such as theromchromism, photochromism, or bleaching of the specimen.

---

2 ISO/IEC 17025:2005, *General requirements for the competence of testing and calibration laboratories*

3 ISO 5725-5:1998, *Accuracy (trueness and precision) of measurement methods and results - Part 5: Alternative methods for the determination of the precision of a standard measurement method* by ISO TC 69/SC 6/WG

While these may be thought of as characteristics of the specimen, their effects will be picked up here under instrument uncertainty conditions.

c. **Operator uncertainty conditions**-*n, of a measurement*, conditions wherein the measurements are made repetitively and carefully over a short timescale, with replacement of the specimen being measured by the operator completely withdrawing the specimen from the specimen port and replacing the specimen back in the specimen port prior to the ensuing measurement so that the specimen aperture samples the same location on the specimen, and the specimen has the same orientation as previous, to the best of the operator‘s ability to accomplish.

d. **Uniformity uncertainty conditions**-n, of a measurement, conditions wherein the measurements are made repetitively and carefully over a short timescale, with replacement of the specimen being measured to an entirely new location on the face of the specimen with the intent of sampling the entire surface of the specimen, or as much of the surface as is practical, by the end of the repetitive sampling run.

e. **Instrument uncertaint**y-n, the results of an uncertainty analysis of a measurement system made under instrument uncertainty conditions.

f. **Operator uncertainty**-n, the results of an uncertainty analysis of a measurement system made under operator uncertainty conditions.

g. **Uniformity uncertainty**-n, the results of an uncertainty analysis of a measurement system made under uniformity uncertainty conditions.

h. **Expanded uncertainty**-n, uncertainty reported as a multiple of the standard uncertainty.

i. **Measurement system**-n, the entirety of variable factors that could affect the precision, accuracy, or uncertainty of a measurement result. These include the instrument, the operator, the environmental conditions, the quality of the transfer standard, the specimen aperture size, as well as other factors.

j. **Standard uncertainty**-n, uncertainty reported as the standard deviation of the estimated value of the quantity subject to measurement.

k. **95% confidence interval**-n, the 95 percentile value of an ascending-ordered distribution of differences between multiple measurement results of a derived parameter characterized by a color measurement system.

Discussion: This value is the cumulative distribution between zero and the stated value of the measurand that contains 95% of all the measurement results made by this procedure.

Gaussian distribution

Laboratories that make spectrophotometric measurements for others are required by ISO 17025 to furnish an assessment of the uncertainty of the measurement with the result if they wish to obtain international accreditation of the measurement. Until recently all procedures for assessment of this value assumed that the uncertainty of the measurand was distributed normally as a two-sided symmetrical distribution. This is a Gaussian distribution and it is a continuous probability function. It is also known as the Bell curve because of its shape.

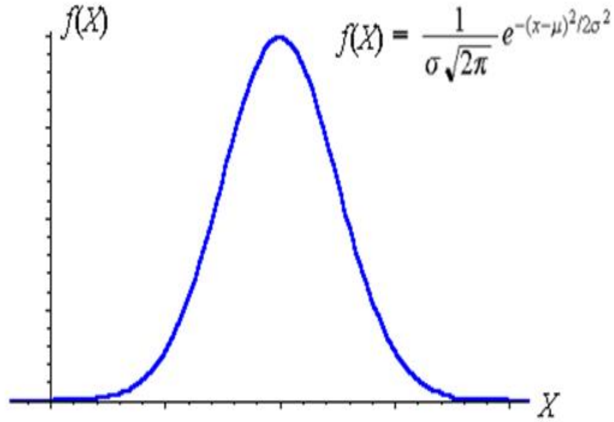

Figure 1 - *The Standard Normal Distribution*

This random variable X is said to be normally distributed when the mean, μ, is equal to zero (0.0) and the square of the standard deviation, σ^2, called the variance, is equal to one (1). This distribution is the first approximation to describe random variables that center around the mean value. The probability distribution function, *f(x)*, is given by the following equation

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2} \qquad (1)$$

Where:

u = mean value or expectation
σ = Standard Deviation

The properties of the Standard Deviation probability distribution function are:

1. The normal curve is symmetrical about the mean μ;
2. The mean is at the middle and divides the area into halves;
3. The total area under the curve is equal to 1;
4. It is completely determined by its mean and standard deviation σ (or variance σ2)

The distribution of color differences is, however, not such a distribution. It is, under ideal conditions, a Chi distribution. The Chi distribution is a continuous probability distribution function. It is the distribution of the square root of the sum of squares of independent random variables, and it is assumed that each underlying variable has a standard normal distribution. The Chi distribution is one-sided and asymmetrical; thus, presenting difficulty in determination of the coverage factor *k*, also required to be stated in the measurement report.

The Chi Distribution

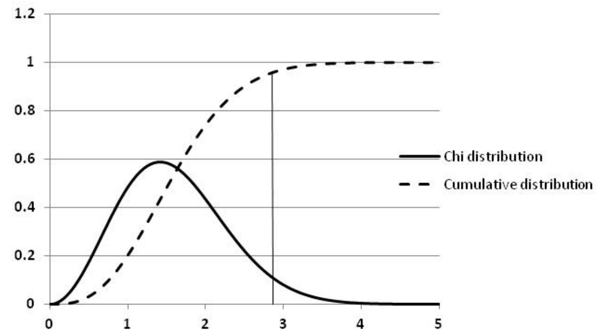

Figure 2 – *The Chi Distribution*

Figure 2 shows the Chi distribution of df = 3 and the cumulative distribution function.

The exact shape of the Chi distribution is dependent upon how many degrees of freedom, df, are present in the data. Figure 3 presents the graphical representation of the Chi distribution showing one (1) to four (4) degrees of freedom.

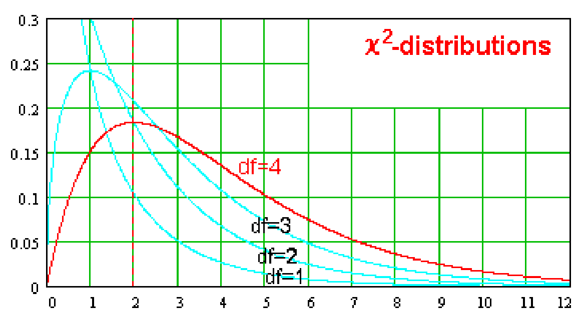

Figure3: Chi distributions as a function of degrees of freedom

In our case we have three degrees of freedom, df = 3. These three degrees of freedom are the component values of CIELAB, L*, a*, b*. It is interesting to note that, as the degrees of freedom increase, the chi distribution function appears to become more Gaussian.

The Chi distribution has the following properties:

- The Chi distribution is non-negative.
- The Chi distribution is non-symmetric.
- There are many different chi distributions, one for each degree of freedom.

The ASTM Method

ASTM derived a method of measuring uncertainty of measurement as follows: Assume that the components of uncertainty consist of the instrument, the operator, and the uniformity of the sample surface. Make 30 measurements of the sample under consideration under instrument uncertainty conditions, 30 measurements under operator uncertainty conditions, and finally 30 measurements under conditions that will discover the lack of uniformity of the surface of the sample. Each of these three conditions is defined in the standard as to exact procedure to follow to separate these contributions from each other.

Number of differences = n * (n - 1) / 2 (2)

There are differences among these 30 measurements. There are 435 differences when each measurement has been differenced with each other measurement. When the differences are sorted in ascending order, the 413^{th} value of these differences is the 95% confidence interval.

The differences may be appropriately subtracted from each other by treating the components as if they were a square-root of the sum of the squares. Thus, one may determine magnitudes of the sources of uncertainty for the purpose of assessing where effort may need to be placed to reduce or minimize uncertainty.

Caution must be exercised in separating these components from each other as the 95% confidence intervals do not subtract from each other under quadrature unless the distributions of the differences are nearly that of the Chi distribution, which many times they are not.

Results

Typical results would be as is contained and presented in the following tables. The first group of data is the experimentally determined 95% confidence values, but each of these is determined under conditions wherein the previously determined component is also present. That is, having determined the instrumental component, that component is also present when the operator uncertainty is determined. Similarly, the instrument and the operator components are present when the uniformity component is determined. These must be separated from each other as has been done in the second group of data, Table 2.

Table 1: Instrument, operator and uniformity uncertainty for a set of repetitive measurements of a white paper specimen

Experimental values	
Instrument	0.0513
Operator	0.0529
Uniformity	0.4091

Table 2: Separated values of uncertainty *for a white paper specimen*

Instrument	0.0513
Operator	0.0129
Uncertainty	0.4059 ΔE^*_{ab} 10°- D65

Uses for the Assessment of Uncertainty

Uncertainty can be used to decide whether there is a difference between results from different laboratories, or if the results from the same laboratory at different occasions (time trends etc.) are different from one another.

Uncertainty is also necessary when comparing results to allowable values, e.g. tolerance limits or allowable (legal) specifications. To make a correct decision one needs the uncertainty value which is the range of total color difference, DE. In this case, DE means DEab*[4], DEcmc[4], DE94[4], DE2000[4]. The DE used in the specification or reporting must be clearly specified by subscript notation. Users are cautioned that a DE specification may not be an adequate specification for acceptable product color control. It may be necessary or desirable to access one or more of the component values of CIELAB. For instance, the metric DE assumes that the error between the sample and the standard are equally distributed between the variables. However, if the error is only in the chromatic plane and even worse only in one axis, such as CIE a*, and the DE is equal to or slightly less than the specification, many times the product is unacceptable, even though the DE is acceptable by definition, since it is less than the specification.

In the example worked above, the data reports the range of the total combined uncertainty as 0.41 total color difference unit. Therefore the range of uncertainty is equal to $\geq$ 0.01 $\leq$ 0.41 total color difference unit, DE. Remember that DE means DEab*, DEcmc, DE94, DE2000 and the total color difference must be properly denoted.

Reporting Statement

The form of the reporting statement is important to all parties with an interest. In reporting uncertainty, a statement such as the following may be useful:

"The uncertainty of the value reported was found to be X.XX (here report the uncertainty value.) This value was determined using XX (here report the number of measurements made in the assessment of uncertainty; ninety, for instance) measurements categorizing the instrument, operator and uniformity uncertainty. This value is the combined expanded standard uncertainty in color difference units according to the (here name the color difference equation used) equation calculated from D65 and the CIE 10° Observer, which defines the uncertainty of the measured value to a confidence level of 95 percent.

---

4 ASTM E2244, *Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates*

The following measurement parameters shall be defined and specified in the uncertainty expression:

1) The identity of the measured sample being reported,

2) The color difference equation used in the uncertainty assessment,

3) The values of *l* and *c*, only for DECMC,

4) The Illuminant–Observer combination used,

5) The number of measurements in each of the uncertainty component assessments,

6) The level expressed as a percentage to which the coverage factor raises the confidence.

Conclusions

The laboratory desiring to obtain uncertainty values should identify all the significant components of uncertainty for each test. A component with an uncertainty of less than one –fifth (1/5) of the total measurement uncertainty will usually have little impact on the total measurement uncertainty. However, if there are several or more of such components, their combined contribution to the total measurement uncertainty may become significant and should not be ignored. Laboratories should make every endeavor to identify error sources. Even where reliance is to be made on overall precision data or where note 2 of clause 5.4.6.2 of ISO/IEC 17025[i], *General requirements for the competence of testing and calibration laboratories* is evoked. These data will provide information to confirm that all reasonable and significant components have been identified and accounted for.

Flowcharting the steps of the test method and using fish-bone diagrams to present the uncertainty components provide useful approaches to understanding and minimizing or eliminating error sources. In some cases, groups of steps in a test method may be common to several different test methods, and once an estimate of uncertainty has been obtained for that group of steps, it may be used in estimates of uncertainty for all methods where that group of steps applies.

Recommendations

It is recommended by the authors that laboratories, equipment manufacturers, product manufactures, specifiers and suppliers follow, and comply with the ASTM E2867-135, *Standard Practice for Estimating Uncertainty of Test Results Derived from Spectrophotometry*

---

5 Available from ASTM International January 2013

Acknowledgements

The authors wish to thank Dr. Michael Brill for his engaging discussions and suggestions throughout the development of the ASTM standard and this paper.

References

1. Wyszecki G, Stiles WS. Color Science, Concepts and Methods, Quantitative Data and Formulae. New York: John Wiley & Sons; 1982. p 293
2. Thornton WA. Toward a More Accurate and Extensible Colorimetry, Part II: Discussion. Color Res Appl 1992; 17:162-186
3. Fairchild MD. Colour Appearance in Image Displays. In: Proceedings of the ISCC/CIE Expert Symposium '06, 75 Years of the CIE Standard Observer. Ottawa; 2006. p 91-95

Author Biography

Hugh S. Fairman is a partner at Resource III. Hugh is a graduate of Princeton University in New Jersey, where he majored in analytical chemistry. While in the coatings industry with John L. Armitage & Co., he obtained expertise in color and appearance science. His current interests include metamerism, tristimulus integration, scotopic vision, and the study of error detection and correction in spectrophotometry, as well as in colorimetry. Hugh has been active in the ISCC and ASTM International. He was awarded the ISCC's Nickerson Service Award in 2000 and ASTM E-12's Fred W. Billmeyer Award in 2007.