Low Commitment Spectrophotometer Care

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Like all instruments used for measuring physical quantities, spectrophotometers need to be calibrated and characterized periodically. In this paper we give an overview of simple procedures that require a low commitment from the metrologist, yet ensure some control over the data obtained from the measurements and allow the certification of the measurement's quality. We give some advice on handling the material and on how to take into consideration thermal effects such as thermochromism.

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Abstract

Like all instruments used for measuring physical quantities, spectrophotometers need to be calibrated and characterized periodically. The procedure itself must be certified, also periodically, to validate the use of the instrument. ISO 9000 — a series of quality management and quality assurance standards — recommends the documentation of these procedures to maintain a history trail of a process.

In the literature several techniques are described for modeling spectrophotometer errors. These techniques allow to obtain very accurate measurement results. However, these techniques also require a very high commitment from the metrologist. In practice many spectrophotometer users are so intimidated by such techniques that they forgo any calibration. This behavior is further encouraged by the simple exterior design and sophisticated graphical user interface of modern instruments.

In this paper we give an overview of simple procedures that require a low commitment from the metrologist, yet ensure some control over the data obtained from the measurements and allows the certification of the measurement's quality. We give some advice on handling the material and on how to take into consideration thermal effects such as thermochromism.

Introduction

Most research in spectrophotometer characterization has been to improve the calibration of instruments. The techniques (see e.g., [1, 8]) consist in modeling the various errors, such as gain, offset, wavelength, and bandpass errors. A set of reference samples characterized with an absolute instrument by a standards body is measured with the instrument under consideration. The obtained data is used to estimate the parameters for the error model. The analyst can then measure a sample and apply the model to the measurement data to obtain a characterization that is traceable to a primary standard.

Fortunately in practice it is not necessary to achieve this high degree of accuracy. For example, in digital imaging an accuracy of slightly better than 1 CIELAB unit is often all that is required. In process control, accuracy is often less important than precision and repeatability.

A spectrophotometer is qualified in four stages [2]:

- design qualification (the instrument it fit for the task at hand)
- installation qualification (the instrument is compliant with the manufacturer's specifications)
- operational qualification (the instrument is used correctly for the specific applications)
- performance qualification (the instrument continues to work in the intended manner)

We are not interested in the first two qualifications, because they are specific to the various applications. The operational qualification includes most of all proper training of the staff, for example in the details of ASTM E1349–90 when an instrument with 45˚/0˚ geometry is used. The instructions for the procedures in this paper are also part of the operational qualification.

The performance qualification covers topics such as a regular service program, performance monitoring, logging in databases, peer review, and change procedures. In this paper we present some procedures for performance qualification that are very simple and require only a low commitment from the metrologist.

Procedures

WHITE CALIBRATION

The white calibration must be performed when one of the following events has occurred:

- begin a new measurement session
- end of a pause
- a number of consecutive measurements have been performed
- the ambient temperature has changed by more than 5˚C

Frequent white calibration is important in the case of process control, because a drift in the instrument might be interpreted as a drift in the process. When an automatic stage is used, the controller software must be programmed to perform the periodic calibration automatically.

The number of consecutive measurements between white calibrations depends on the time interval between measurements. If this interval is sufficient for the instrument to cool down completely, several hundred measurements can be made before recalibrating. For example, in a printer characterization situation we measure patches on a sheet of paper. When the measurements are performed at the maximum rate possible with an instrument based on a tungsten light source that is switched on for each measurement, the calibration becomes invalid after a few measurements, mainly because the physical dimensions of the diffraction grating change when it warms up from the lamp. In this case, the white calibration should be performed each 10 measurements, or after a row of patches in a printer characterization situation.

Today the white calibration reference is often a ceramic tile. Before the calibration, the reference should be checked for cleanliness. Especially with ceramic tiles, it is necessary to ensure that the reference is always measured in exactly the same spot, because ceramic tiles are never completely uniform. Refer to the manufacturer's instructions for the exact procedure for your instrument.

QUARTERLY CERTIFICATION

Instrument error is not the only source of incorrect measurements. More often the error is in the measurement procedure. This can have many causes, such as documentation error, personnel changes, etc. The best insurance against this type of problems is to participate in the *CTS Collaborative Reference Program for Color and Appearance*.

Collaborative Testing Services Inc. (CTS)[1] is an organization that conducts interlaboratory tests. In such a test, the performance of a laboratory is not compared to an absolute reference. Instead, multivariate comparative statistical methods developed in conjunction with the National Institute of Standards and Technology (NIST) are used to gauge performance.

With these techniques a consensus value among a large number of participating laboratories using a variety of instruments and methods is determined. The values of each laboratory are then compared with this consensus value. Such an analysis is also known as a “real world” analysis.

Analysts measure a set of three opaque color paint chips made by Munsell Color, Macbeth Division. The colors are selected from throughout the full color spectrum. The chips consist of a metameric and nonmetameric match with small color differences.

The measurements are performed according to the ASTM procedure for the particular instrument geometry immediately after opening the sealed moisture-free barrier bag containing the specimens. Each specimen is backed with the other specimens when making measurements. Each specimen is measured twice, rotating the specimen 90˚ for the second measurement. This latter step is very important for some spectrophotometers, because they are based on 45˚/0˚ geometry, which is susceptible to polarization.

In the report from CTS, each instrument’s data is marked one of two data flags: 0 or X. If the data flag is 0, the results are consistent with those of the other participants and work may proceed. If the data flag is X, work should stop immediately and an expert should be consulted to review the data and the testing procedure. This review can consist of four steps, as delineated in the decision tree in Fig. 1.

In the first step the performance test is repeated to verify that the results in the report can approximately be reproduced. This is a check for gross errors, such as using the paint chips from an old test or measuring the chips from the back side.

In the second step the relative certification procedure described in Section “Accuracy check” is performed. If this test fails, the instrument is probably defective and the CTS test should be repeated with the backup instrument. If the test would have passed with the backup instrument, the defective instrument needs to be replaced.

If the certification with the relative reference tile passes, we proceed with step three. We obtain a tile that has been calibrated absolutely and perform an absolute certification. If this certification passes, a procedural error occurred in performing the CTS test. Training in the appropriate ASTM procedure and the CTS test in particular should be taken. All procedures in the laboratory should be reviewed by an expert.

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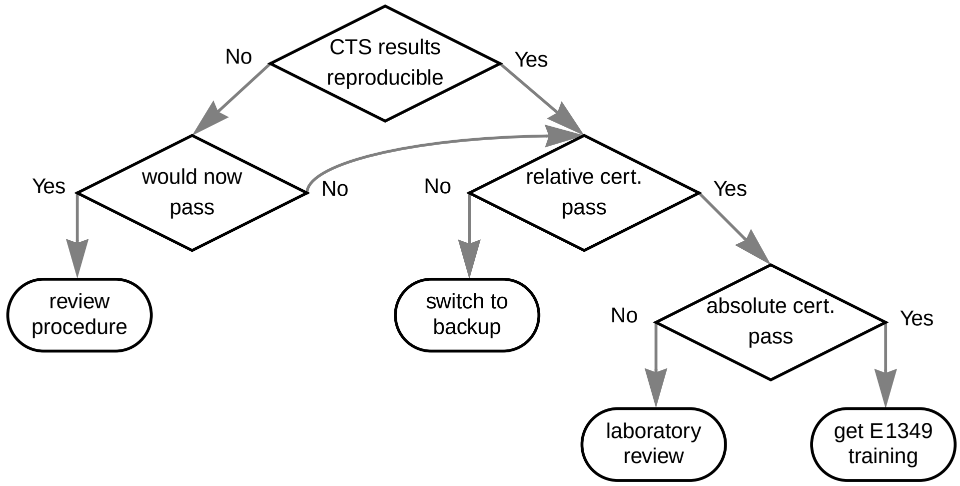
FIGURE 1. Decision tree in case of a CTS test failure



Step four. If the absolute certification fails and the relative certification failed, the laboratory may be set up incorrectly and an expert should review all operations.

Returning to the CTS report, after reviewing the data flag, the column labelled $\Delta E*$ is examined. If the result is followed by an * the ΔE is greater than 2 but less than 3 standard deviations from the grand mean. The procedure should be reviewed and the relative certification procedure should be performed to establish if it is safe to continue working.

If the result is followed by an X, the ΔE is greater than 3 standard deviations from the grand mean. In this case the decision tree in Fig. 1 should be followed.

YEARLY CALIBRATION

Once a year the instrument should be sent to the manufacturer to install hardware and firmware updates that may have become available, and to characterize the instrument with a full set of color ceramic tiles such as the BCRA-NPL[2] Ceramic Color Standards, Series II (CCS II). Although it is possible to purchase such a set of color tiles and have them characterized with a traceable instrument, this characterization requires a very high commitment. It is usually more cost effective to contract this work out to a laboratory specializing in such a service.

ACCURACY CHECK

The accuracy check is the cornerstone of an ISO 9000-compliant procedure that requires low commitment. How often this procedure is performed depends on the particular application. At very least, the accuracy check should be performed each three months. In a process control situation, where precision is very important and trend analysis is performed on the data, the accuracy check should be performed at least at each shift change.

In the accuracy check we measure a single color reference tile and establish that the measured color is within a certain tolerance of the tile's color. If the tile's color can be

2. BCRA: British Ceramic Research Association. NPL: National Physical Laboratory

traced to an absolute standard, the certification is *absolute*. If this is not the case and the tile can not be traced, then the certification is *relative*.

In a relative certification, the nominal colorimetry of the tiles is not known and the performance of an instrument is compared to an aim value obtained with the instrument itself. Ceramic tiles that have not been characterized following procedures for traceability to a primary standard are relatively inexpensive.

Although an absolute color tile is not necessary, it is useful to have access to one in the case of an emergency, like in the third step of the decision tree in Fig. 1, when it is necessary to establish if the instrument ever worked correctly. Such a "panic" reference tile can usually be provided by one of the established color laboratories or the instrument manufacturer, but a relation should be established in advance, before the panic situation occurs.

Initial characterization. When a new spectrophotometer is put into service, it is first necessary to measure the relative green reference tile. The measured color will be the aim value. Because a color tile can be used for several years, it is suggested to measured it under a number of viewing conditions, i.e., for a number of illuminants and both CIE Standard Observers. If the instrument can be fitted with filters, e.g., a polarizing filter for measuring wet inks, all viewing condition and filter combinations should be measured. To help diagnose instrument failures, it is useful to record also the reflectance spectrum.

The color reference is measured like the white reference. However, it is recommended to average a small number of measurements performed at a 10 second[3] interval. The current ambient temperature must also be recorded. If the tile is stored in a closed container, the container should be opened half an hour prior to use.

Accuracy check. The accuracy check consists in measuring the color reference and calculating the color difference to the aim value. If the check is absolute, the tolerance will be generous, like for example $\Delta E = 0.6$. If the check is relative, the tolerance can be much tighter, like $\Delta E = 0.2$. These tolerances are just examples; actual values depend on the tolerance required by the application and the realistic performance of the instrument checked. Usually the tolerance is decided in the design qualification following the practice described in ASTM3134–89 and the accuracy check provides the performance qualification.

The color difference is evaluated with the CIE 1994 total color difference formula [4] with symbol ΔE^*_{94} and abbreviation CIE94

$$\Delta E^*_{94} = \sqrt{\left(\frac{\Delta L^*}{k_L \cdot S_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{k_C \cdot S_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{k_H \cdot S_H}\right)^2} \qquad \text{(EQ 1)}$$

with

3. Modern portable spectrophotometers usually cool off after 10 seconds

$$S_L = 1$$
$$S_C = 1 + 0.045 \cdot C^*_{ab} \quad \text{(EQ 2)}$$
$$S_H = 1 + 0.015 \cdot C^*_{ab}$$

and

$$k_L = k_C = k_H = 1 \quad \text{(EQ 3)}$$

In formulæ (EQ 2), the value for chroma is the one from the reference measurement in the initial characterization (not the geometric mean of the two chroma values, as is customary). The only difficulty it the calculation of the hue difference.

The CIE hue-difference in the CIE publication [4] is a theoretical formula that is not usable in practice, because it is sensitive to rounding (CIELAB is not a perfect perceptually uniform color space) and to numerical cancellation when floating point arithmetic is used. Several notes have addressed this problem [3, 9, 10, 11], and the alternate formula in the CIE publication addresses the rounding problem. However, numerical cancellation can be avoided only when floating point additions are replaced with multiplications, because this avoids normalization. Hence, we recommend Sève's formula from [9]:

$$\Delta H^*_{ab}{}^2 = 4C^*_1 C^*_2 \left(\sin \frac{\Delta h°}{2} \right)^2 \quad \text{(EQ 4)}$$

This formula yields the square of the hue-difference, which is the quantity required for the CIE94 formula (EQ 1) and for the instrument certification. In other applications, it is often useful to know the difference for the perceptual correlates, not just the total color difference. When the hue-difference is needed, then the sign σ can be computed with the formula proposed by Stokes and Brill [11]:

$$\sigma = (a^*_1 \cdot b^*_2 > a^*_2 \cdot b^*_1) \quad \text{(EQ 5)}$$

Material

DATABASE

The ASTM standard practice E805–94 gives guidance on how to record color measurements. To fulfill ISO9000 requirements, especially the more stringent ISO9001 recommendations, record keeping in a log book is not sufficient. Spreadsheet programs have the advantage of computer storage and easy implementation of calculations. However, a spreadsheet has no structure and it is not easy to enforce data integrity.

Simple relational database programs such as FileMaker for Windows are the best applications to log the results of the various procedures in the previous section. These programs have a graphical user interface to design screen forms for data entry, queries, and statistical calculations. If the spectrophotometer has a serial interface, the spectrophotometer can be driven from the database application, avoiding data entry errors.

In our laboratory we use a simple relational database consisting of four tables. The first table is used to store the reference tile color data under the various viewing conditions and for a number of instruments. A second table contains the data from a single measurement, and a third table aggregates a number of related measurements by computing the mean and variance for each colorimetric variable. Practice ASTM E1345–90 is used to determine the number of measurements to average.

The main table and user interface is a fourth table, in which the actual certifications are managed. It contains relations to the first three tables, verifies that all measurement conditions are correct, calculates the total color difference between the aim color and the current check, makes a pass/fail decision, and issues a calibration certificate.

WHITE TILES

Each spectrophotometer has its own *white reference tile*. The absolute spectrum of the tile is stored in the instrument; during the calibration the spectral response is adjusted so that it matches the stored spectrum within a specified tolerance. A white calibration tile is “married” to an instrument; if a white tile is lost or damaged, the instrument must be returned to the manufacturer to marry the instrument with a new white tile.

The white reference tile can be used for ten years from the date the manufacturer has performed the absolute spectral characterization. The ceramic surfaces must not be scratched and shall not be exposed to permanent direct sunlight.

The tiles should be protected from soiling. Avoid all chemical substances that attack plastics, because they change the reflectance properties. In practice the most dangerous substance is acetone, because it is widely used for cleaning purposes. Acetone will destroy the calibration target. If a reference tile is soiled, it can be cleaned with a soft cloth and a mild soap water or ethanol.

COLOR TILES

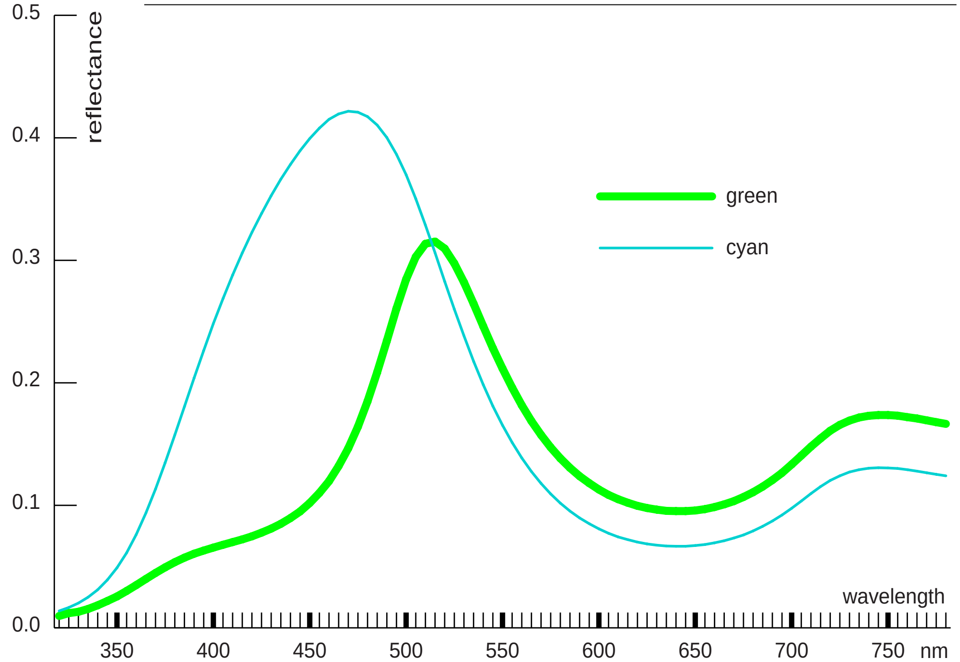
For the color reference tile there is a wide choice of colors from the CCS II set mentioned earlier. The neutral tiles are useful to test photometric linearity, but are not useful as a reference color. We can also eliminate the tiles that have a pronounced lateral diffusion problem, are very dark, or have a strong thermochromism effect. This leaves us with two choices, cyan and green.

We recommend green. Other authors have suggested the cyan CCS II tile because of its range of reflectance factor, multiple well-defined inflection points, and low sensitivity to temperature changes [1]. Fig. 2 shows the spectral reflectance data for the green and cyan master tiles measured at 25˚C over the wavelength range 320–780 nm for 0˚/45˚ geometry, published in [7]. The green tile has more inflection points than the cyan tile. As Fig. 2 illustrates, the green tile has also steeper slopes, which are in a more sensitive spectral range and improve the detection of spectral shifts in the instrument’s scale.

A single color tile can be used for all instruments at a location. In our laboratory we have mounted the tile in a holder like the one supplied by the instrument maker for the white reference tile. This ensures that the tile is always measured at exactly the same location and that the instrument is not tilted.

Colored ceramic tiles usually have a recommended calibration life time of 5 years. Handling and cleaning is the same as for the white reference tile.

FIGURE 2. **Spectral reflectance curves of two NPL master tiles [7]**



THERMOMETER

The spectral reflectance of ceramic tiles changes linearly with temperature, an effect known as thermochromism. For this reason we keep the tiles at the same ambient temperature as the instrument during its normal use; if the tiles are kept in a box or drawer, it should be opened half an hour prior to use [7].

Usually any thermometer with a tolerance of 2˚C is sufficient. A calibrated mercury in glass thermometer graduated in 0.5˚C intervals and placed near the instrument will be adequate for normal operation. For each measurement performed for certification purposes, we record both the current temperature and the thermometer's tolerance.

When ink on paper is measured, it is also necessary to record the current humidity, because humidity changes the way ink interacts with paper. The change of color with humidity is known as hygrochromism.

Thermal issues

INSTRUMENT ISSUES

CCDs have a temperature-dependent leakage current that flows even when no light impinges upon the element. This signal is called *dark current*. Heat also causes the optics in the instrument to expand. A common device used as a monochromator is a holographic diffraction grating. When the grating expands, the spectrum interval detected by the sensor moves and the instrument's calibration is no longer valid. For this reason we never make a long sequence of measurements at the maximal speed allowed by an instrument, but always wait for a short cool down time of a few seconds.

The lamp in an instrument can also heat the sample being measured. We took a spectrophotometer with a tungsten lamp and measured 30 times at the instrument's maximal firing rate a green CCS II tile cut to a 7 mm diameter. With a precision thermometer we determined that the tile's temperature increased by 0.2˚C, which introduces an error of approximately 0.01 CIELAB units due to thermochromism.

THERMOCHROMISM

Thermochromism refers to a color change with temperature change. Among others, it occurs with some tiles that contain selenium. Compton [5] reported that when a tile is heated from 25˚C to 35˚C — a typical temperature change in the instruments using prolonged polychromatic irradiaton common at that time — the effect is a small reduction in reflectance with an increase in temperature. She observed that in general thermochromism occurs on steep spectral profiles.

Fairchild and Grum [6] conducted a similar experiment with an instrument of 0˚/45˚ geometry. For the same temperature change they observed a ΔE^*_{ab} value of 0.7 for a green tile. However, they observed much larger changes for the orange (1.6) and red (1.5) BCRA Series II (CCS II) tiles. More recently the National Physical Laboratory (NPL) has released a comprehensive collection of spectral reflectance and thermochromism data [7] on the NPL Master Set of the BCRA CCS II tiles.

If the temperature is stable for a period of 30 minutes (the time for a ceramic tile to adapt to a small temperature change) or longer, and an accurate thermometer is available, for example a mercury in glass thermometer graduated in 0.1˚C intervals, then highly accurate measurements can be made by correcting the spectral data for the temperature difference before the colorimetric quantities are computed. The correction data is listed in reference [7].

Fig. 3 shows the spectral reflectance data of our green reference tile measured at 24.4˚C±0.7˚C. The gray curve plots the NPL data for the difference in reflectance caused by a 10˚C (25˚C to 35˚C) change in temperature (units on right axis).

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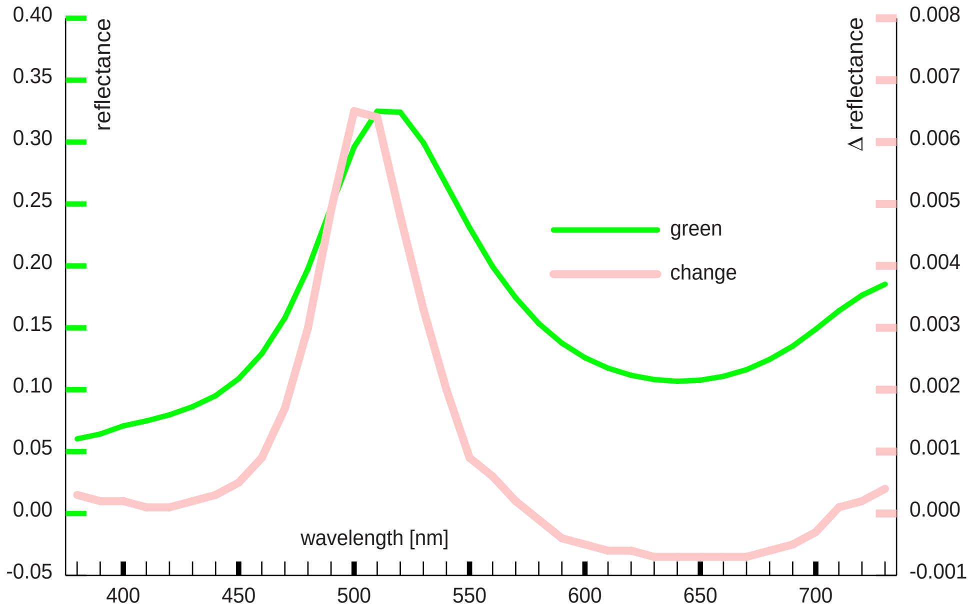
FIGURE 3. **Difference in reflectance due to thermochromism**



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