Assessment of a Portable Spectrophotometer for Measuring Color of Automotive Paint Trace Evidence

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National Institute of Standards and Technology

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*Certain instruments or materials are identified in this presentation in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for experimental procedure
Why Engineering Laboratory?

*Integrating Sphere-Based UV Chamber*

- Simulated Photodegradation via High Energy Radiant Exposure (SPHERE)
- 2 m integrating sphere
- High power mercury lamps
  - ~170 W/m² (295 nm - 400 nm)
  - *Up to 10 x the outdoor exposure*
- 95% exposure uniformity
- Shorter wavelengths (<295 nm) removed
- Visible and infrared radiation removed
- Exposure conditions for 32 chambers, individually controlled (UV, RH, T)
- Capability of mechanical loading

*Martin and Chin, U.S. Patent 6626053
Outline

• Background and Purpose
  – Color measurements of paints
  – Handheld colorimeter vs microspectrophotometer (MSP)

• Experimental

• Results

• Summary

• Future Directions
Interactions between Light and Object

Three types of cone cells responsible for color vision: short (420-440 nm), middle (530-540 nm) and long (560-580 nm)

Rod cells are light intensity receptors

From BYK Additives and Instruments 2016 Catalog
Anatomy of Automotive Paint

- **Clearcoat 45 um (micrometer)**
  - Gloss, protects basecoat from UV light
- **Basecoat 10-20 um**
  - Color, metallic flakes
- **Primer 25 um**
  - Smoothes E-coat, protects E-coat from light, promotes adhesion
- **Electrocoat 20um**
  - Provides corrosion protection
- **Phosphate 5 um**
  - Provides corrosion protection
- **Substrate (EG Steel, Aluminum, CRS…)**

Note: Some commercial vehicles use monocoat paint systems for solid colors.

*From M. Nichols, Ford*
Color in Characterization of Paint Trace Evidence

• History of visual comparison
  – Subjective and color sensitivity dependent
  – Microscopy guidelines for illumination and background

• Visual color description/color-order systems
  – Classify colors in 3D color space
    • Munsell color coordinate system
    • Standard color chart DIN 6164
    • Natural color system
    • Methuen Handbook of Colors
Munsell Color Coordinate System

- **Human perception basis**
- Color assigned values for
  - Hue (H): color
  - Value (V): light or darkness
  - Chroma (C): saturation
- Visual comparison of samples to standard chips in Munsell Book of Color (X-Rite)
  - Gloss and matte
- ASTM 1535-14
- Color of effect (*pearlescent, special flakes or particles*) cannot be adequately analyzed

Designative System for Munsell Hue
from ASTM 1535-14: Standard Practice for Specifying Color by the Munsell System

Achromatic (neutral) = N
Chromatic: R, Y, G, B, P
Color notation: 4.5R 4.2/6.4
Commission Internationale de L’Eclairage (CIE)- L*a*b* System

• Mathematical basis
• Color is appearance using three components
  – **Illuminant**: spectral power distributions
  – **Observer**: standard 2° or 10° field of view functions
    • Relative response vs wavelength curves for red (r), green (g) and blue (b) response
  – **Object**: spectral reflectance distribution from spectrophotometer
• CIE color spaces combine r, g, and b spectra into color values
  – Accounts ratios of long, medium and short cones in the eye
• r, g, b converted to tristimulus values \((X, Y, Z)\), which are then converted to \(L^*, a^*, b^*\) values
• Differences between two colors, \(DE^*\)
  – \(DE^* = \sqrt{(dL^*)^2 + (da^*)^2 + (db^*)^2}\)

\(L^* = \) lightness, luminosity or luminance
\(a^* = \) red-green chromaticity
\(b^* = \) yellow-blue chromaticity
Measurements

- **Measurements**
  - 400 nm – 700 nm, 10 nm resolution
  - Illuminated diffusely, 8° observation angle
  - **11 mm aperture size**
  - Calibrate monthly with color standards; green used as a check
  - Color using L*a*b* (and X,Y,Z)
    - illuminant/observer settings
  - reflective mode
  - 10° observation fcn for CIE tests

- **Data Analysis** *(ASTM E1345-14)*
  - Sample to standard comparison
  - Modify input tolerances
  - Data processed using a PC
Colorimeter Example Data

Illuminants

Spectral Curve

From BYK Additives and Instruments 2016 Catalog
Measurements

- Transmission mode
- Xenon arc source
  - 200 nm- 900 nm
- Array detector
- 15x and 36x reflecting objectives
- (677 x 567) µm field of view
- Aperture sizes
  - (4.2 x 4.2) µm to (79 x 79) µm for 15x objective
- Sample preparation
  - Hand section (thin peel) versus microtome (cross section)
  - Quartz slip and coverslip with glycerin media
- Dark and reference spectra collected for each new location
Experimental

• **Color Standards**
  – Metal plates (20 mm x 30 mm)
  – 3 plates examined
  – beige, black, blue, cinnabar, gray, green, white, and yellow

• **Automotive Samples**
  – Metal and plastic substrates
    • Chips and plates
    • Black, blue, red, and white
  – Ford production panel (blue)

**Color Standards**

• **Colorimeter**
  – 20 measurements/plate
  – Average L*a*b* values for each plate used to calculate DE* between plates

• **MSP**
  – Sectioned samples from 3 plates
  – 10 locations from each sample
  – L*a*b* values from normalized average spectra used to calculate DE* between plates
MSP Results

Cinnabar (C): flat dark red (3-0158-0)
15x, aperture (8.6 x 8.6) μm

Optical Image

Standards

Notable peaks: 514 nm, 551 nm, 604 nm

Transmission

Wavelength (nm)
MSP Results

Bright Blue (BB): metallic medium blue (5-0231-0)
15x, aperture (8.6 x 8.6) µm

Notable peaks: 455 nm (shoulder), 529 nm, 658 nm

Optical Image
MSP Results

Dark Green (DG): metallic dark green (7-0147-0)
15x, aperture (8.6 x 8.6) μm

Standards

Notable peaks: 503 nm (shoulder), 579 nm, 711 nm

Optical Image
MSP Results

Medium Gray (MGr): metallic medium gray (2-0140-0)
15x, aperture (8.6 x 8.6) μm

Optical Image

Standards

Transmission

MGr1
MGr2
MGr3

Broad peak: 409 nm-560 nm

Wavelength (nm)
### DE* for different colored standards

**compare similar colors**

**Colors:** cinnabar (C), bright blue (BB), dark green (DG), medium gray (MGr)

#### Color meter:

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>stdev L*</th>
<th>stdev a*</th>
<th>stdev b*</th>
<th>Sample 2</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>stdev L*</th>
<th>stdev a*</th>
<th>stdev b*</th>
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<th>Da</th>
<th>Db</th>
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**Rule of Thumb:** Above 5 units is significant

*DE* never greater than 0.1 between the same colors;

Uncertainty = error of propagation using standard deviations

#### MSP:

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>L*</th>
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<th>b*</th>
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<th>b*</th>
<th>stdev L*</th>
<th>stdev a*</th>
<th>stdev b*</th>
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<th>Da</th>
<th>Db</th>
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<th>error</th>
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*DE* less than 3; microtoming would improve repeatability

*DE* errors not calculated due to limited number of replicates
DE* between different color standards

Colors: cinnabar (C), bright blue (BB), dark green (DG), medium gray (MGr)

• Comparing plate 1 of each color:

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>DE* (MSP)</th>
<th>DE* (CM)</th>
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</thead>
<tbody>
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<td>BB1</td>
<td>12.94</td>
<td>31.03</td>
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</table>

DE* values are larger when comparing completely different colors

Rule of Thumb:
Above 5 units is significant

• DE* between different colors generally smaller when determined by MSP versus colorimeter
  – Low transmission from MSP samples give near zero L*a*b* values
MSP Results

Metallic royal blue, metal/plastic substrates
Same car, different locations
15x, aperture (8.6 x 8.6) µm

Optical Image

Automotive samples

Shoulder at 550 nm
in 2nd layer indicates repaint

#34: 1st layer
#34: 2nd layer
#35
MSP Results

Automotive samples

Cross Section versus Thin Peel

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>Sample 2</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
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DE* uncertainty not calculated due to limited number of replicates.
MSP Results

Thin Peel Repeatability on Basecoats

Automotive Samples

DE* uncertainty not calculated due to limited number of replicates.
Summary

• CIE L*a*b* system has a quantitative mathematical foundation to analyze colors in trace evidence samples
  – The DE* values can be used to distinguish between samples
  – Handheld colorimeter and MSP can accommodate measurements

• Samples must be measured in reflective mode

• The handheld colorimeter has portable advantage for field measurements
  – Minimum aperture size is limited to 10 mm and so small trace samples cannot accurately be examined
Future Directions

• Add reflective measurement capabilities to the MSP

• Contact NIST Statistical Engineering Division to better examine test color standards

• Compare Ford production panels to current Ford paint samples
Acknowledgments

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• Amanda Forster and Julie Bitter, Project Team (MML)
Questions

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