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

Stephanie Watson, Li-Piin Sung and Kimberly Kha
Engineering Laboratory
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*

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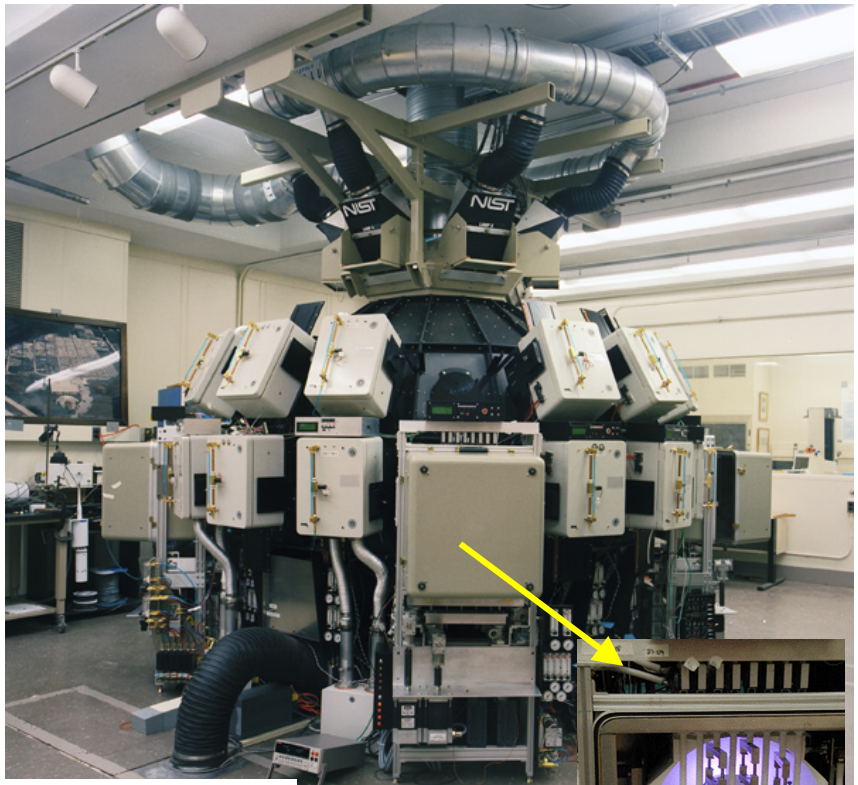
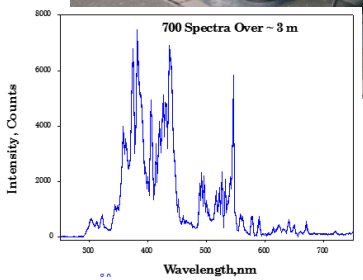
Why Engineering Laboratory?

Integrating Sphere-Based UV Chamber





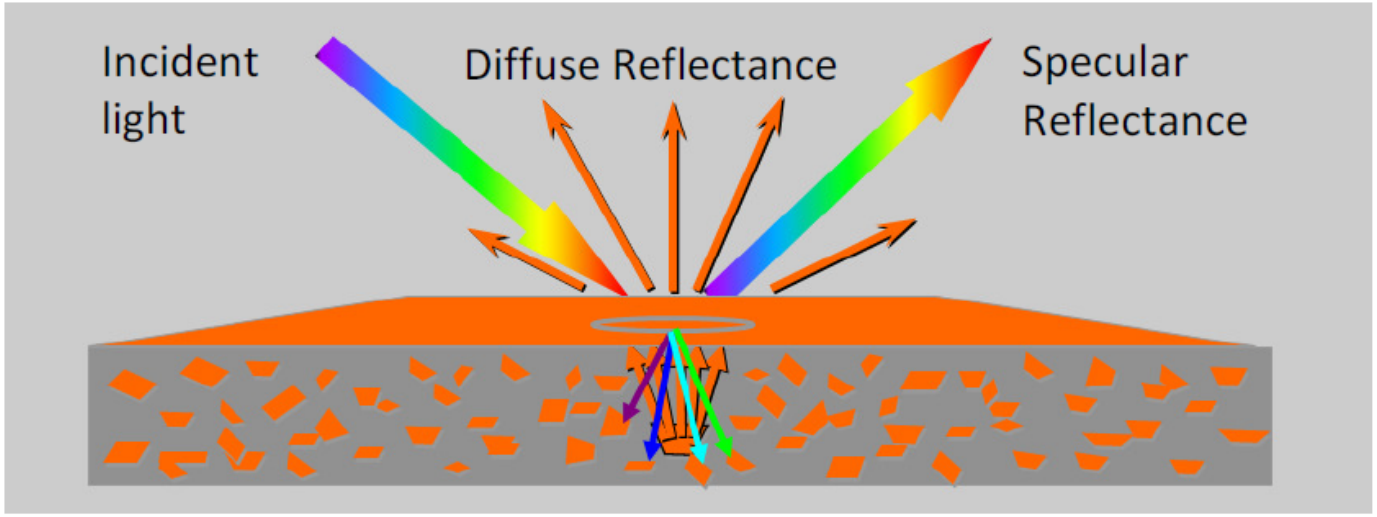
- Simulated Photodegradation via High Energy Radiant Exposure (SPHERE)
- 2 m integrating sphere
- High power mercury lamps
  - ~170 W/m^2 (295 nm - 400 nm)
  - *Up to 10 x the outdoor exposure*
- 95% exposure uniformity
- Shorter wavelengths (<295 nm) removed
- Visible and infrared radiation removed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

- ***Martin and Chin, U.S. Patent 6626053***
- ***Chin et al, Review of Scientific Instruments, 75(11), 4951-4959, 2004.***

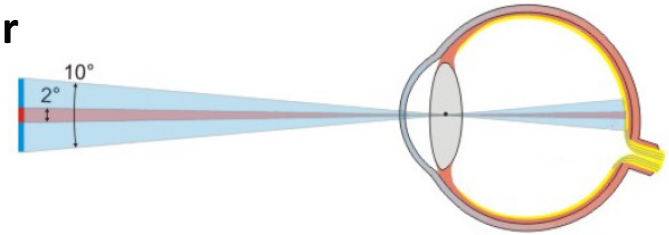
Outline

- Background and Purpose
  - Color measurements of paints
  - Handheld colorimeter vs microspectrophotometer (MSP)
- Experimental
- Results
- Summary
- Future Directions

Interactions between Light and Object



Standard Observer



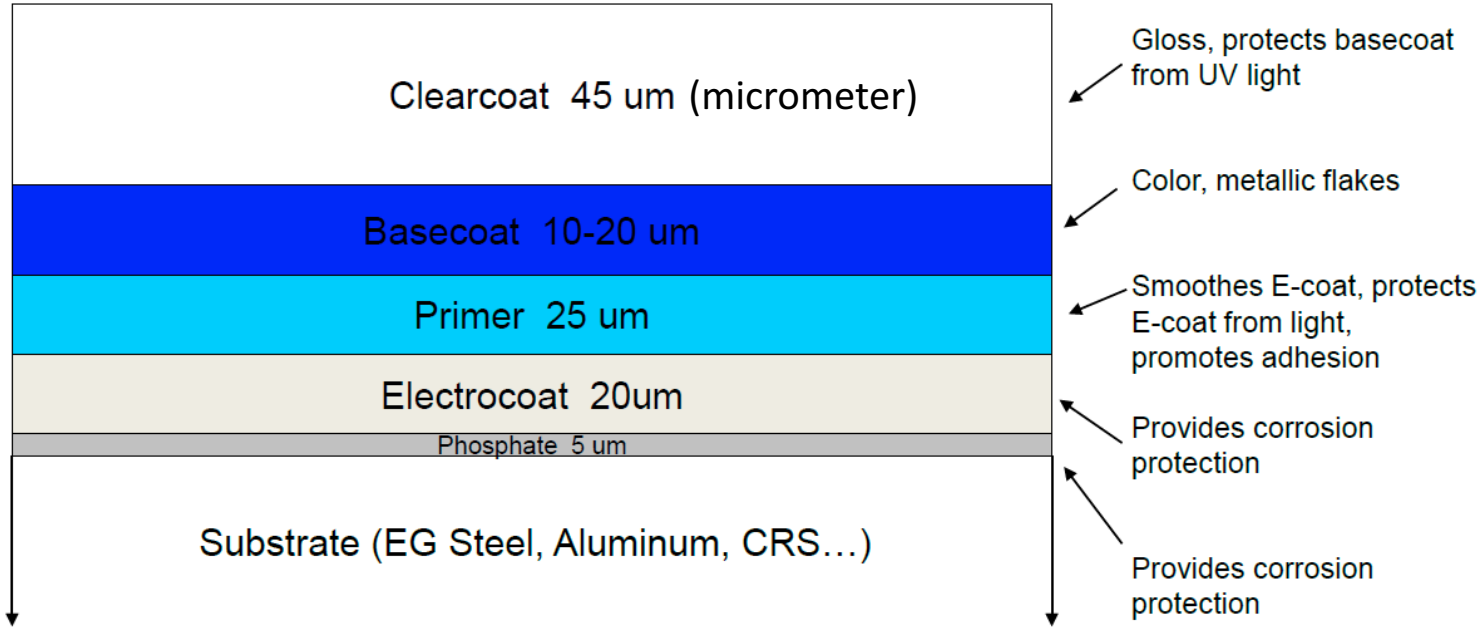
Human Eye

Rod cells are light intensity receptors

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

From BYK Additives and Instruments 2016 Catalog

Anatomy of Automotive Paint



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

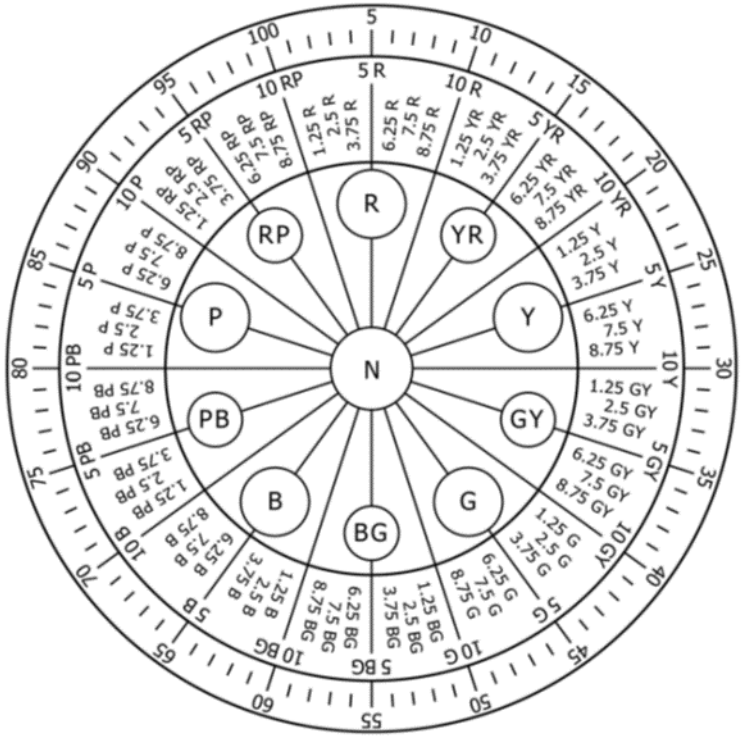
From M. Nichols, Ford

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

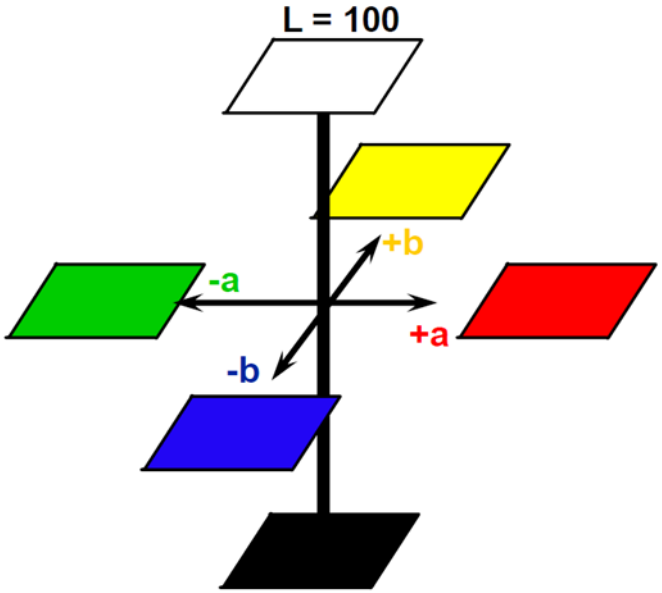
Achromatic (neutral) = N

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*
  - $DE^* = \sqrt{(dL^*)^2 + (da^*)^2 + (db^*)^2}$



From BYK Additives and Instruments 2016 Catalog

L* = *lightness, luminosity or luminance*

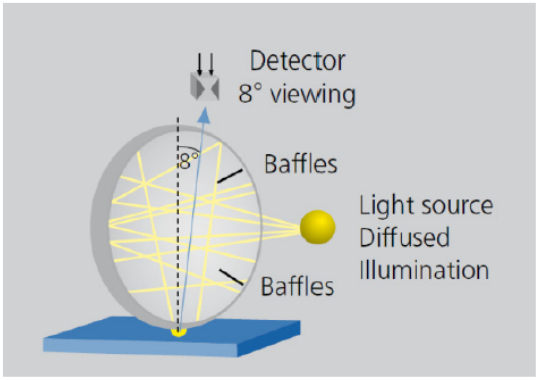
a* = *red-green chromaticity*

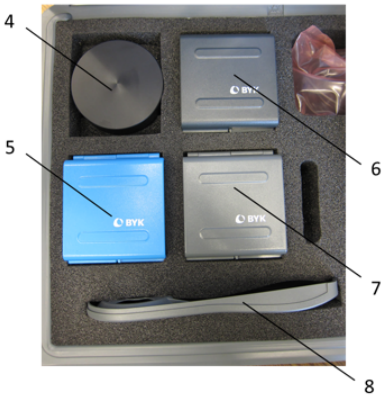
b*= *yellow-blue chromaticity*

Measurements

Colorimetry

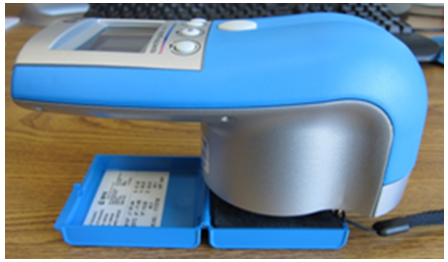
- Measurements
  - 400 nm – 700 nm, 10 nm resolution
  - Illuminated diffusely, 8° observation angle
  - *11 mm aperture size*
  - Calibrate monthly with color standards; green used as a check
  - Color using L*a*b* (and X,Y,Z)
    - illuminant/observer settings
  - reflective mode
  - 10° observation fcn for CIE tests
- Data Analysis (ASTM E1345-14)
  - Sample to standard comparison
  - Modify input tolerances
  - Data processed using a PC





4. Black Standard
5. Green Standard
6. High gloss
7. White gloss
8. Sample Area Locator

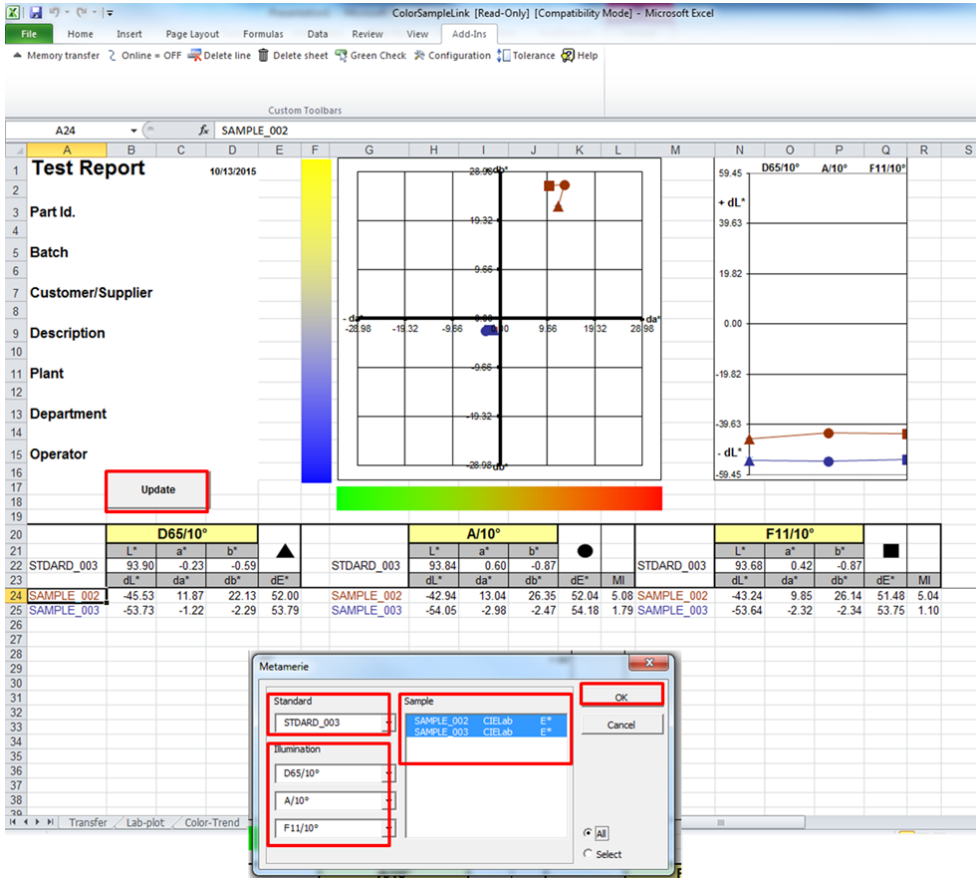
Sample Holder Small Parts



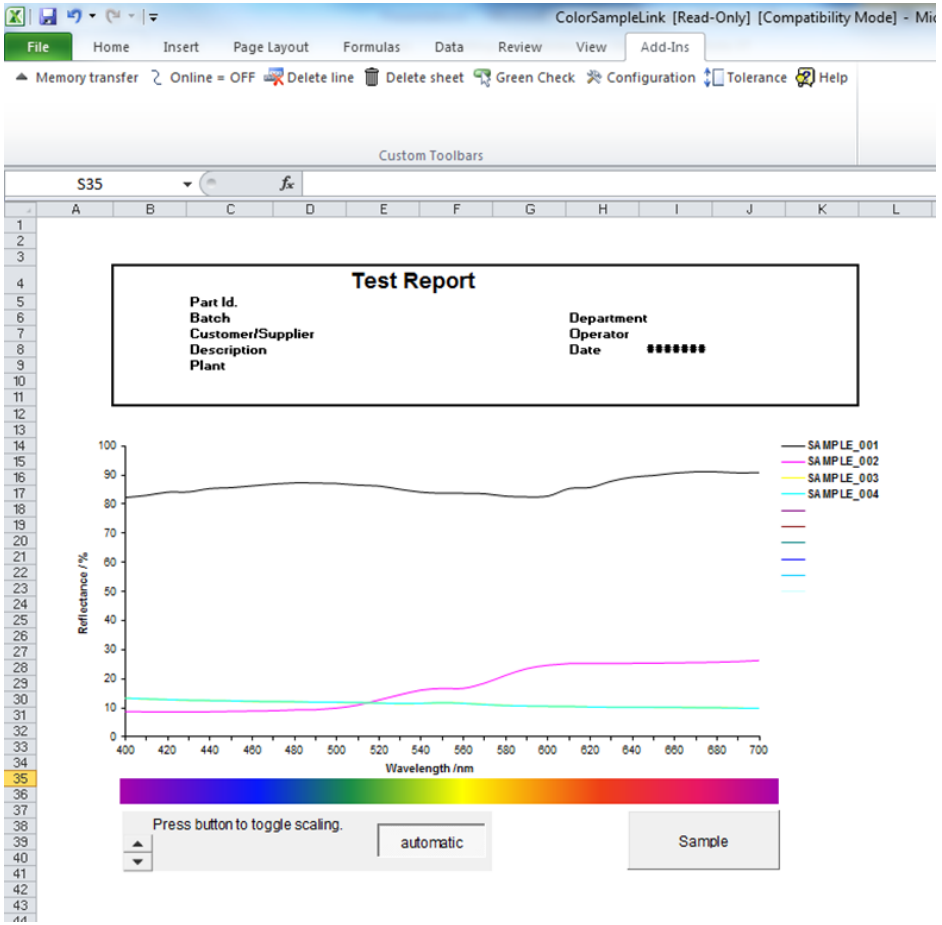
From BYK Additives and Instruments 2016 Catalog

Colorimeter Example Data

Illuminants



Spectral Curve



From BYK Additives and Instruments 2016 Catalog

Measurements

microspectrophotometry

MSP121

- 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

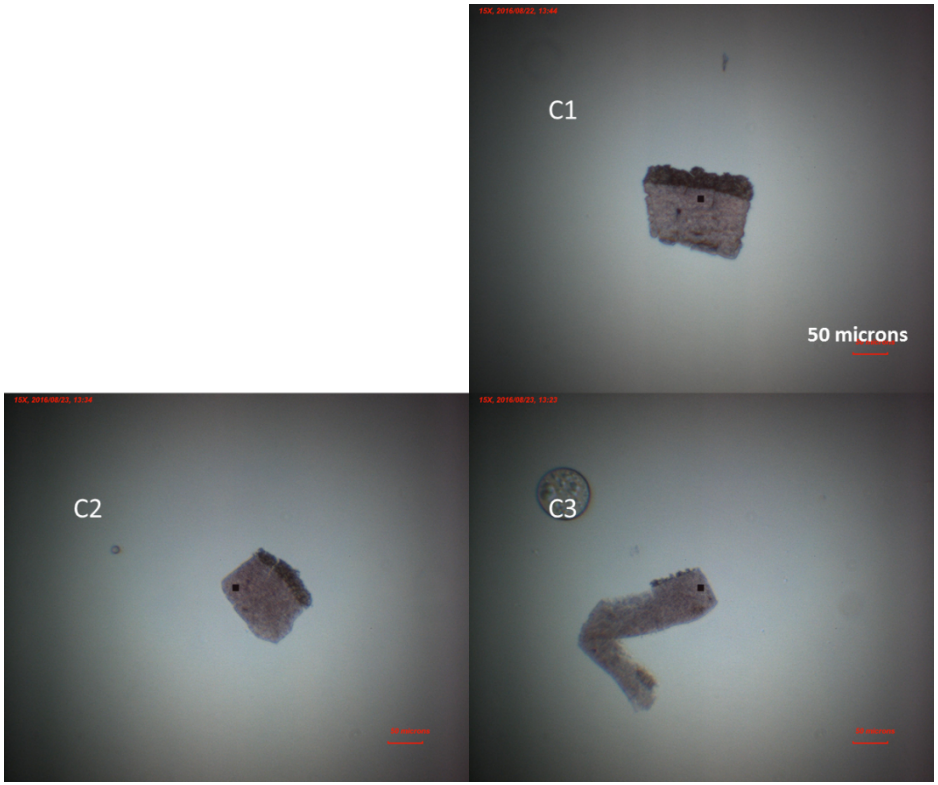
- *Color Standards*
  - Metal plates (20 mm x 30 mm)
  - 3 plates examined
  - beige, black, blue , cinnabar, gray, green, white, and yellow
- *Automotive Samples*
  - Metal and plastic substrates
    - Chips and plates
    - Black, blue, red, and white
  - Ford production panel (blue)

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

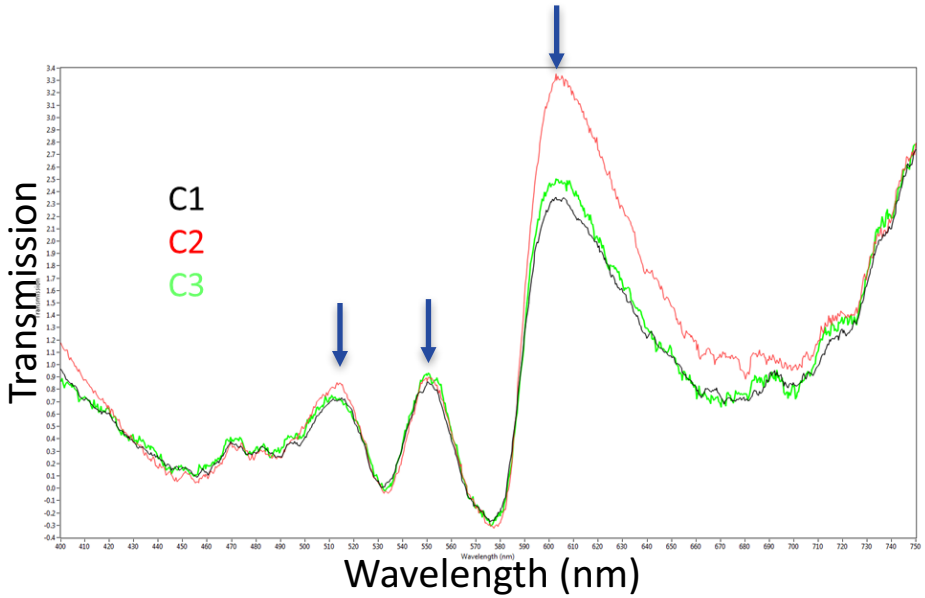
MSP Results

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



Optical Image

Standards

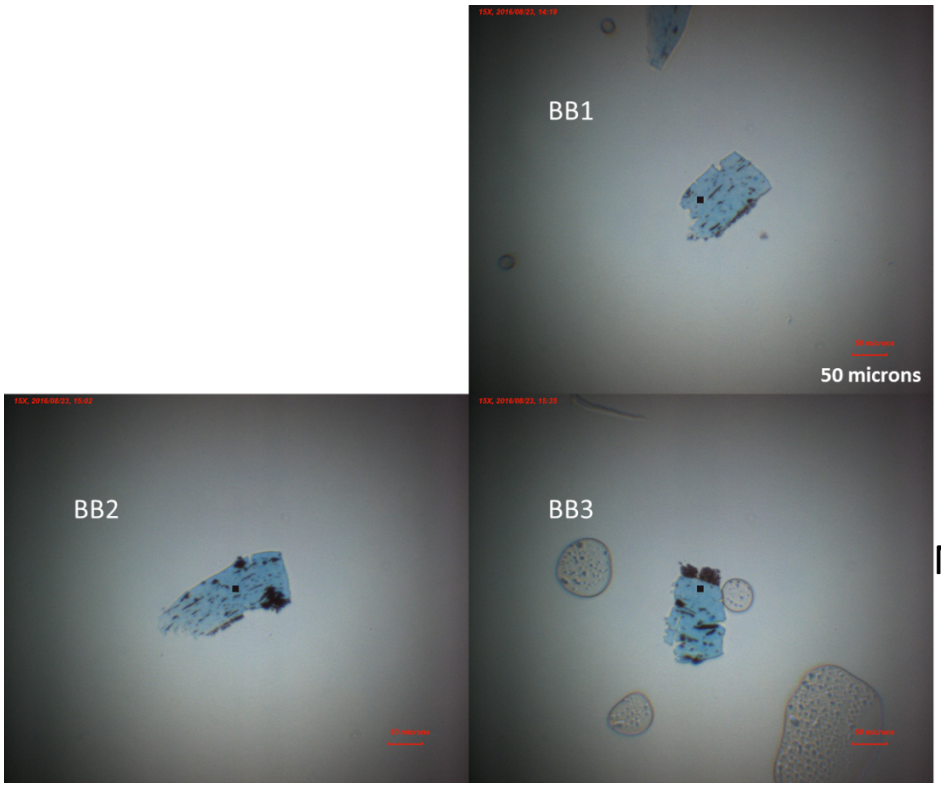


Notable peaks: 514 nm, 551 nm, 604 nm

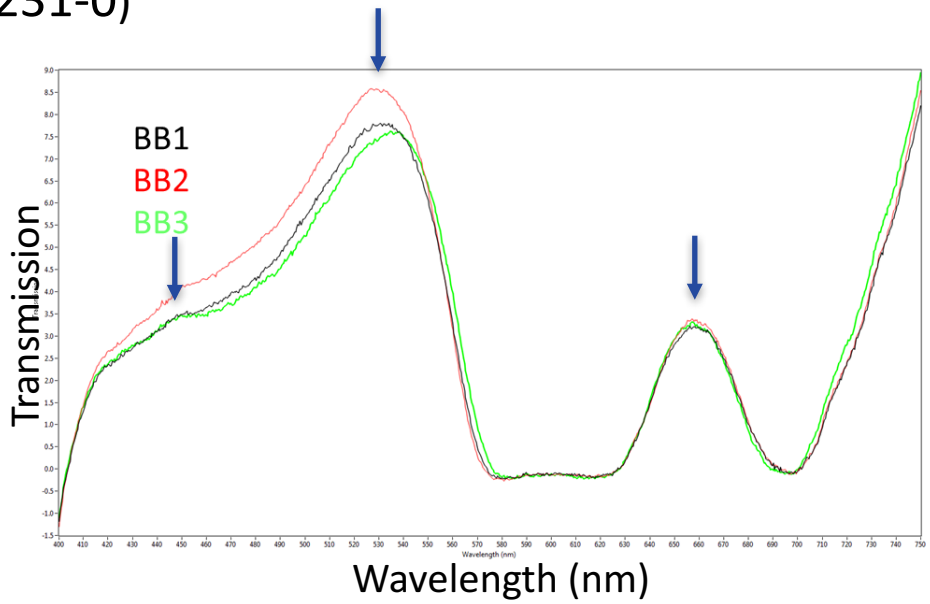
MSP Results

Standards

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



Optical Image

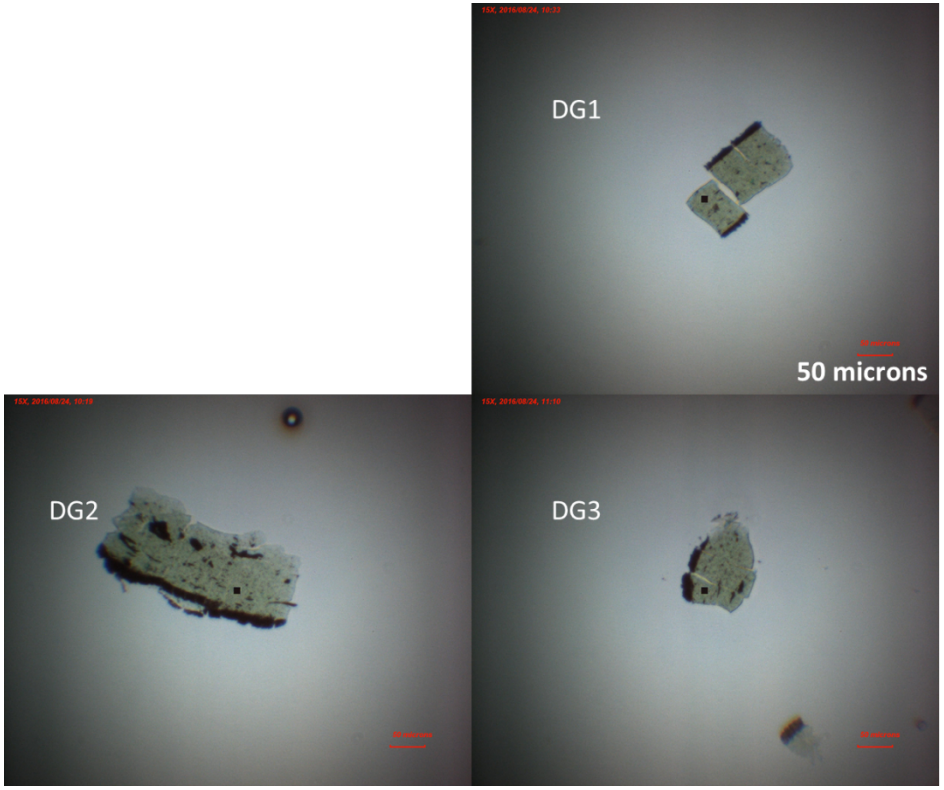


Notable peaks: 455 nm (shoulder), 529 nm, 658 nm

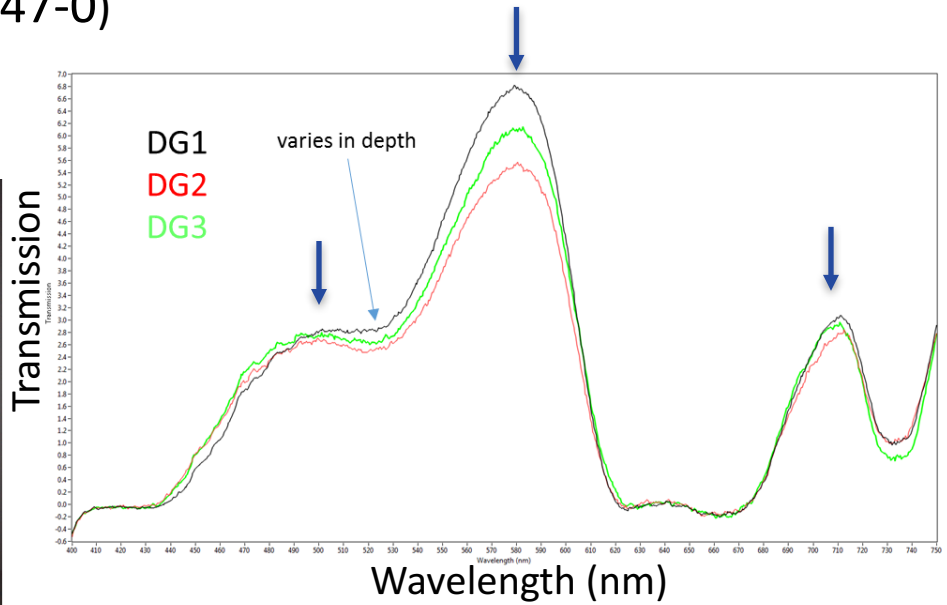
MSP Results

Standards

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



Optical Image

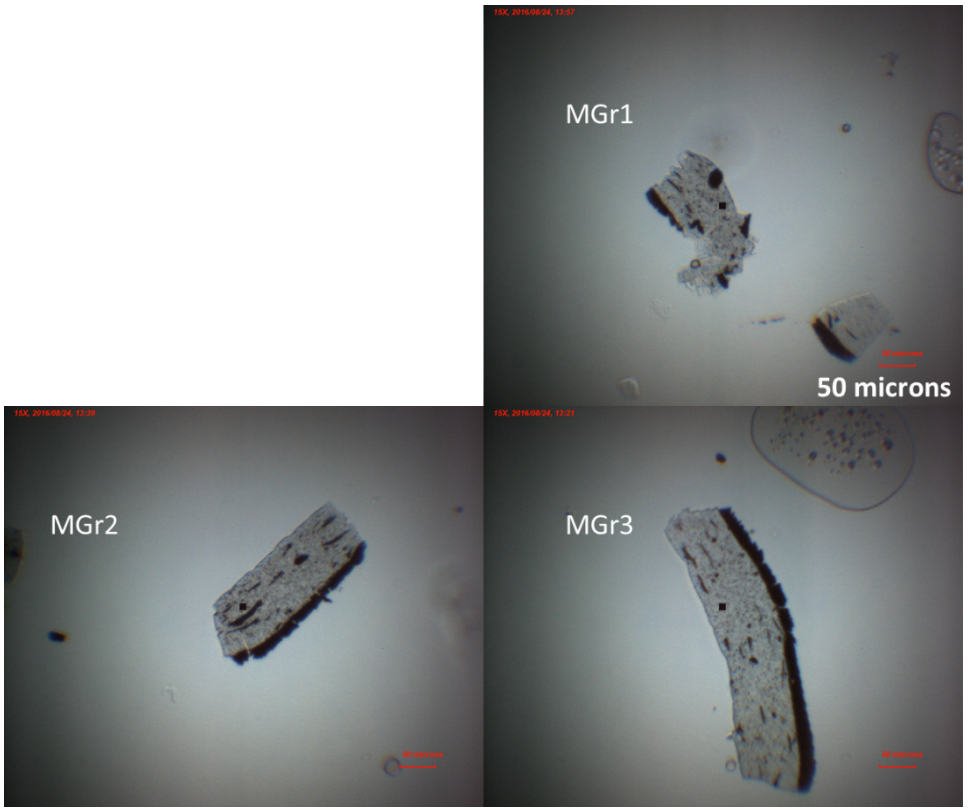


Notable peaks: 503 nm (shoulder), 579 nm,711 nm

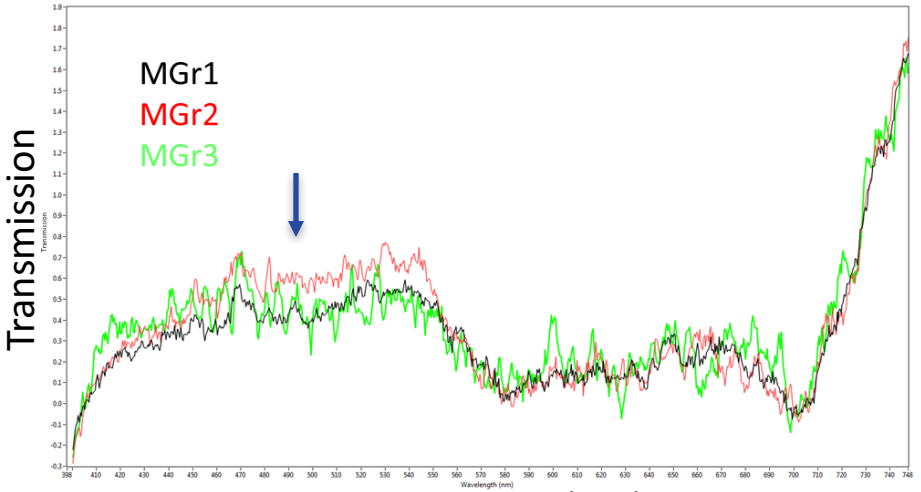
MSP Results

Standards

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



Optical Image



Broad peak: 409 nm-560 nm

DE* for different colored standards

compare similar colors

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

- **Color meter**:

Sample 1	L*	a*	b*	stdev L*	stdev a*	stdev b*	Sample 2	L*	a*	b*	stdev L*	stdev a*	stdev b*	DL	Da	Db	DE	error
C1	37.51	31.11	19.61	0.01	0.02	0.04	C2	37.52	31.15	19.65	0.02	0.02	0.02	0.02	0.04	0.04	**0.06**	0.03
C1	37.51	31.11	19.61	0.01	0.02	0.04	C3	37.52	31.18	19.66	0.02	0.03	0.02	0.01	0.07	0.05	**0.08**	0.04
C2	37.52	31.15	19.65	0.02	0.02	0.02	C3	37.52	31.18	19.66	0.02	0.03	0.02	-0.01	0.03	0.01	**0.03**	0.03
DG1	34.87	-4.52	6.32	0.12	0.03	0.06	DG2	34.66	-4.51	6.19	0.11	0.03	0.08	-0.21	0.01	-0.13	**0.25**	0.14
DG1	34.87	-4.52	6.32	0.12	0.03	0.06	DG3	34.54	-4.50	6.16	0.11	0.02	0.05	-0.33	0.03	-0.16	**0.37**	0.15
DG2	34.66	-4.51	6.19	0.11	0.03	0.08	DG3	34.54	-4.50	6.16	0.11	0.02	0.05	-0.12	0.02	-0.03	**0.12**	0.15
MGr1	44.28	-0.60	0.60	0.19	0.03	0.04	MGr2	44.30	-0.61	0.60	0.14	0.02	0.04	0.02	-0.01	0.00	**0.02**	0.21
MGr1	44.28	-0.60	0.60	0.19	0.03	0.04	MGr3	42.33	-0.55	0.67	0.15	0.02	0.03	-1.95	0.04	0.07	**1.95**	0.24
MGr2	44.30	-0.61	0.60	0.14	0.02	0.04	MGr3	42.33	-0.55	0.67	0.15	0.02	0.03	-1.97	0.05	0.07	**1.97**	0.21
MGr1	44.28	-0.60	0.60	0.19	0.03	0.04	MGr4	43.53	-0.50	0.50	0.17	0.02	0.03	-0.74	0.09	-0.10	**0.75**	0.25
BB1	55.43	-18.72	-21.98	0.12	0.05	0.04	BB2	55.54	-18.63	-21.91	0.14	0.06	0.07	0.11	0.09	0.07	**0.16**	0.14
BB1	55.43	-18.72	-21.98	0.12	0.05	0.04	BB3	55.52	-18.78	-21.98	0.17	0.05	0.04	0.09	-0.05	0.00	**0.10**	0.18
BB2	55.54	-18.63	-21.91	0.14	0.06	0.07	BB3	55.52	-18.78	-21.98	0.17	0.05	0.04	-0.02	-0.14	-0.07	**0.16**	0.09

DE* never greater than 0.1 between the same colors;

Uncertainty= error of propagation using standard deviations

Rule of Thumb:

Above 5 units is significant

- **MSP:**

Sample 1	L*	a*	b*	stdev L*	stdev a*	stdev b*	Sample 2	L*	a*	b*	stdev L*	stdev a*	stdev b*	DL	Da	Db	DE	error
C1	-1.11	9.96	6.67				C2	-0.75	10.98	8.70				0.36	1.02	2.03	**2.30**	
C1	-1.11	9.96	6.67				C3	-1.88	9.52	6.70				-0.77	-0.44	0.03	**0.88**	
C2	-0.75	10.98	8.70				C3	-1.88	9.52	6.70				-1.13	-1.46	-2.01	**2.72**	
DG1	4.71	-5.34	11.87				DG2	4.72	-5.76	11.93				0.01	-0.42	0.06	**0.42**	
DG1	4.71	-5.34	11.87				DG3	4.68	-5.29	12.20				-0.03	0.05	0.33	**0.34**	
DG2	4.72	-5.76	11.93				DG3	4.68	-5.29	12.20				-0.04	0.47	0.27	**0.55**	
MGr1	-2.59	-5.93	-0.28				MGr2	-1.43	-8.28	-0.97				1.16	-2.36	-0.69	**2.72**	
MGr1	-2.59	-5.93	-0.28				MGr3	-1.82	-4.54	-2.50				0.77	1.38	-2.22	**2.73**	
MGr2	-1.43	-8.28	-0.97				MGr3	-1.82	-4.54	-2.50				-0.39	3.74	-1.53	**4.06**	
BB1	3.07	-17.49	1.04				BB2	3.17	-17.40	-0.08				0.10	0.09	-1.12	**1.13**	
BB1	3.07	-17.49	1.04				BB3	2.87	-16.37	0.76				-0.19	1.12	-0.28	**1.17**	
BB2	3.17	-17.40	-0.08				BB3	2.87	-16.37	0.76				-0.30	1.03	0.84	**1.36**	

DE errors not calculated due to limited number of replicates*

DE* less than 3;microtoming would improve repeatability

DE* between different color standards

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

- Comparing plate 1 of each color:

Sample 1	Sample 2	DE* (MSP)	DE* (CM)
C1	DG1	17.17	38.12
C1	MGr1	17.40	37.59
C1	BB1	28.33	67.34
DG1	MGr1	14.18	11.69
DG1	BB1	16.36	37.76
MGr1	BB1	12.94	31.03

DE values are larger when comparing completely different colors*

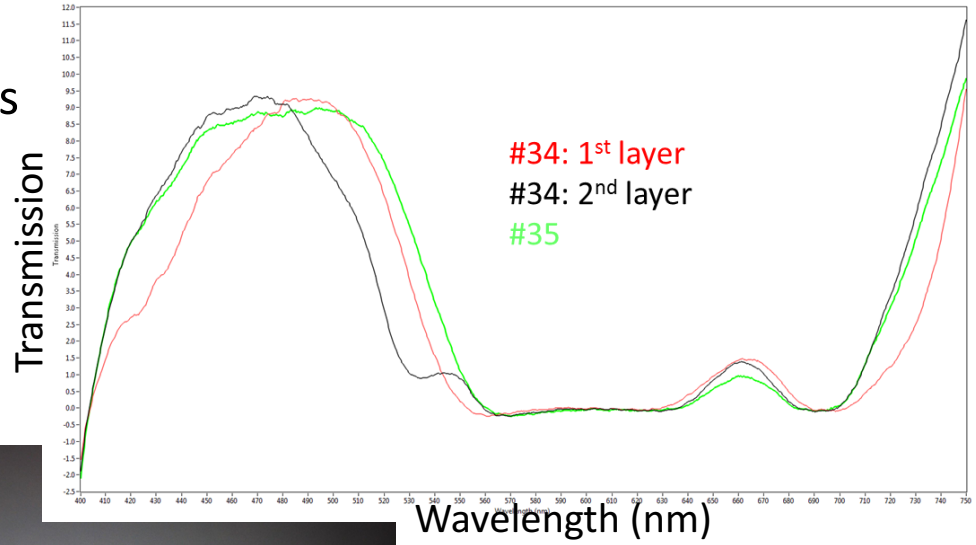
Rule of Thumb:
Above 5 units is significant

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

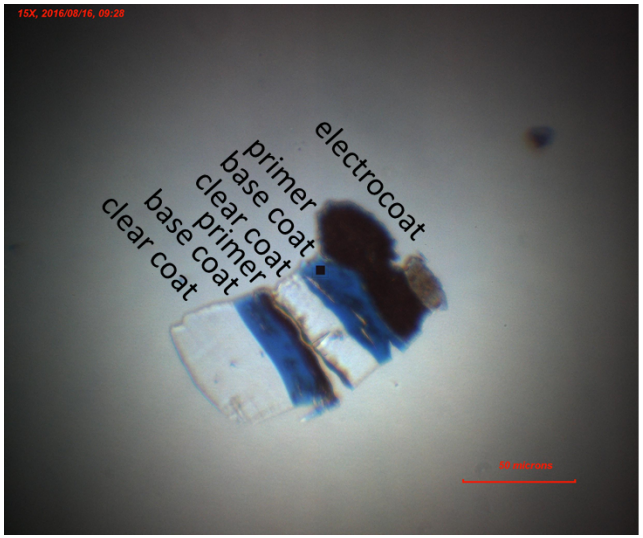
MSP Results

Automotive samples

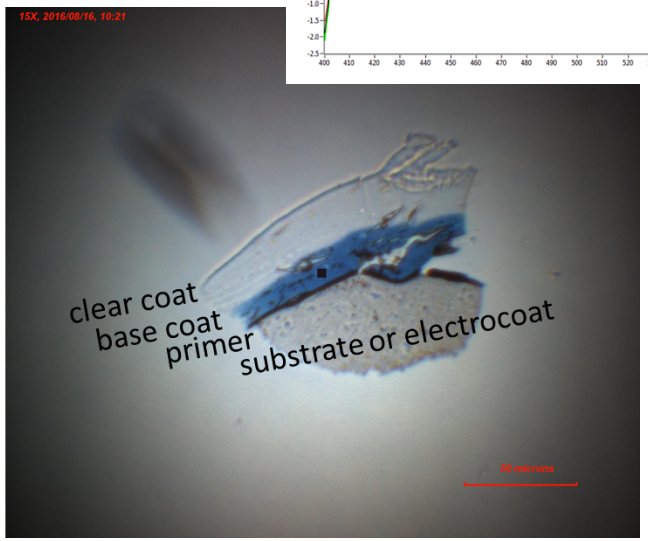
Metallic royal blue, metal/plastic substrates
Same car, different locations
15x, aperture (8.6 x 8.6) μm



Optical Image



#34: 15X, A5



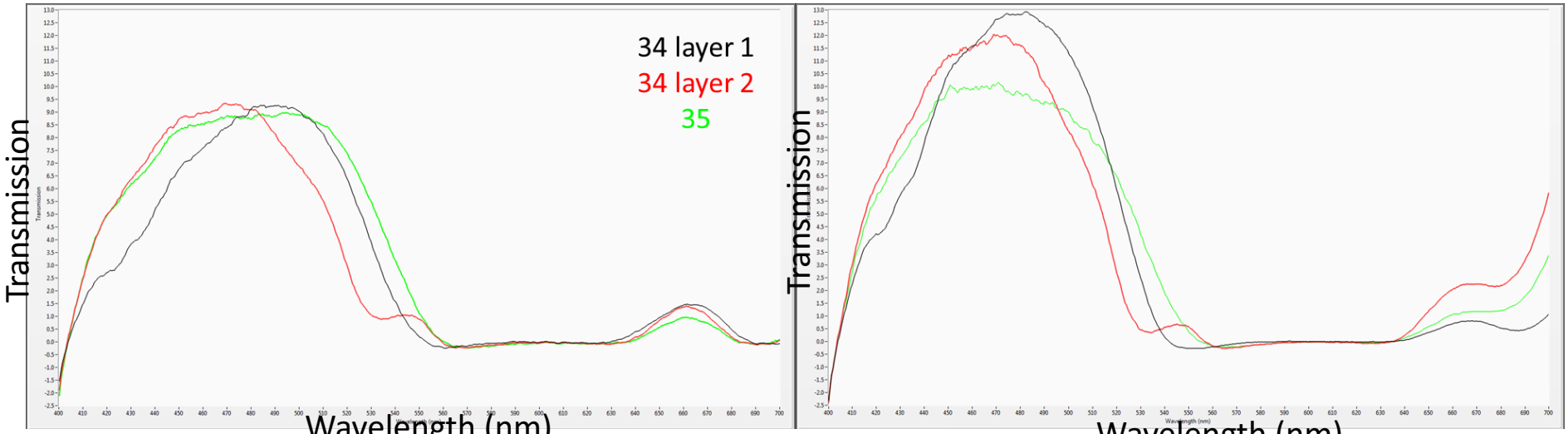
#35: 15X, A5

shoulder at 550 nm
in 2nd layer indicates repaint

MSP Results

Automotive samples

Cross Section versus Thin Peel



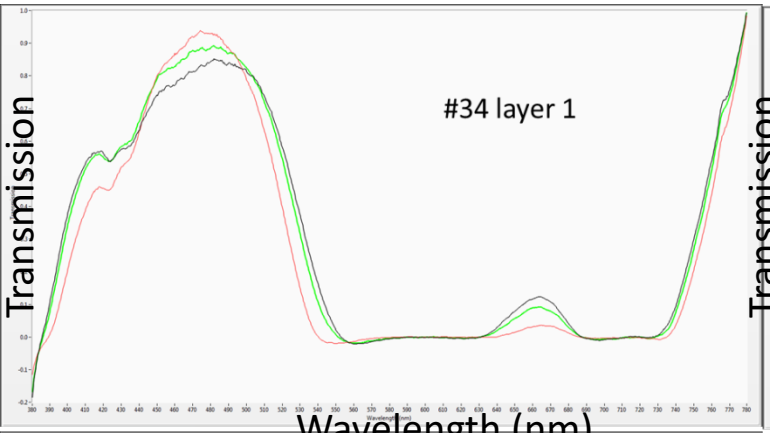
Sample 1	L*	a*	b*	Sample 2	L*	a*	b*	DL	Da	Db	DE
34 layer 1 CS	-0.50	-8.65	-12.27	34 layer 2 CS	-2.73	2.62	-18.49	-2.23	11.28	-6.22	**13.07**
34 layer 1 CS	-0.50	-8.65	-12.27	35 CS	0.38	-8.50	-13.13	0.88	0.15	-0.86	**1.24**
34 layer 2 CS	-2.73	2.62	-18.49	35 CS	0.38	-8.50	-13.13	3.11	-11.12	5.36	**12.73**
34 layer 1 TP	-0.37	-12.85	-9.21	34 layer 2 TP	-2.27	-3.72	-13.85	-1.91	9.13	-4.65	**10.42**
34 layer 1 TP	-0.37	-12.85	-9.21	35 TP	0.90	-12.13	-10.13	1.27	0.71	-0.93	**1.73**
34 layer 2 TP	-2.27	-3.72	-13.85	35 TP	0.90	-12.13	-10.13	3.18	-8.41	3.72	**9.73**
34 layer 1 CS	-0.50	-8.65	-12.27	34 layer 1 TP	-0.37	-12.85	-9.21	0.14	-4.19	3.06	**5.20**
34 layer 2 CS	-2.73	2.62	-18.49	34 layer 2 TP	-2.27	-3.72	-13.85	0.45	-6.34	4.64	**7.87**
35 CS	0.38	-8.50	-13.13	35 TP	0.90	-12.13	-10.13	0.52	-3.63	3.00	**4.74**

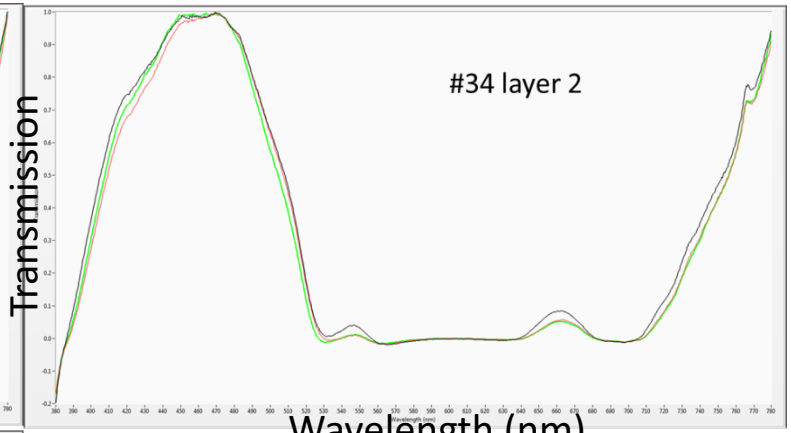
DE uncertainty not calculated due to limited number of replicates*

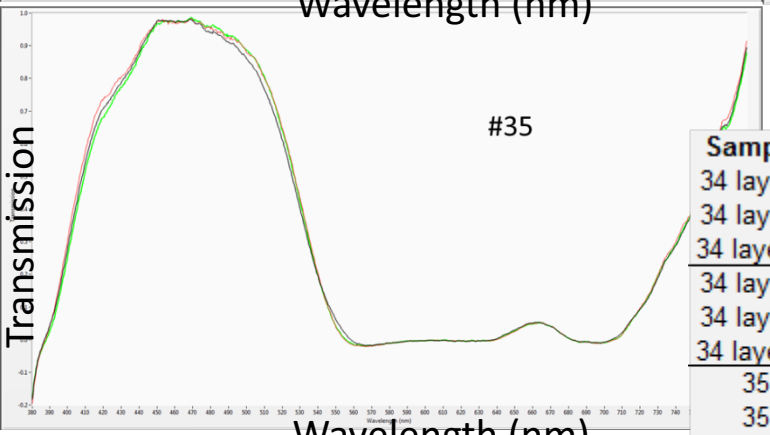
MSP Results

Automotive Samples

Thin Peel Repeatability on Basecoats







Sample 1	L*	a*	b*	Sample 2	L*	a*	b*	DE
34 layer 1 I	-0.50	-8.65	-12.27	34 layer 1 II	-1.39	-6.69	-13.61	**2.54**
34 layer 1 I	-0.50	-8.65	-12.27	34 layer 1 III	-0.31	-9.61	-11.34	**1.35**
34 layer 1 II	-1.39	-6.69	-13.61	34 layer 1 III	-0.31	-9.61	-11.34	**3.86**
34 layer 2 I	-2.73	2.62	-18.49	34 layer 2 II	-2.45	0.98	-17.76	**1.82**
34 layer 2 I	-2.73	2.62	-18.49	34 layer 2 III	-2.22	0.98	-17.75	**1.88**
34 layer 2 II	-2.45	0.98	-17.76	34 layer 2 III	-2.22	0.98	-17.75	**0.23**
35 I	0.38	-8.50	-13.13	35 II	0.40	-8.23	-13.30	**0.31**
35 I	0.38	-8.50	-13.13	35 III	0.26	-7.78	-13.39	**0.77**
35 II	0.40	-8.23	-13.30	35 III	0.26	-7.78	-13.39	**0.48**
34 layer 1 I	-0.50	-8.65	-12.27	34 layer 2 I	-2.73	2.62	-18.49	**13.07**
34 layer 1 I	-0.50	-8.65	-12.27	35 I	0.38	-8.50	-13.13	**1.24**
34 layer 2 I	-2.73	2.62	-18.49	35 I	0.38	-8.50	-13.13	**12.73**

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

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Questions

stephanie.watson@nist.gov
National Institute Standards and Technology
Engineering Laboratory
100 Bureau Drive, Stop 8615
Gaithersburg, MD 20899
301-975-6448

https://www.nist.gov/topics/forensic-science