METHODS OF SAMPLING AND TESTING
MT 548-16
METHOD OF TEST FOR ANALYSIS OF TRAFFIC PAINT
(*Montana Method*)

1. Scope

1.1 This method describes the procedures for analyzing physical and chemical properties of traffic paint samples including:

1.1.1 Color and Contrast Ratio – Modified ASTM D2805 and E1347

1.1.2 Viscosity – ASTM D562

1.1.3 Density – Modified ASTM D1475

1.1.4 Freeze-Thaw – primarily Modified ASTM D562 and D2243

1.1.5 Static Heat Stability

1.1.6 Bleeding Ratio – primarily Modified ASTM D868

1.1.7 Skinning and Lumps

1.1.8 Settling

1.1.9 Skinning

1.1.10 FTIR Spectra Verification – Modified ASTM D7588

1.1.11 Cracking

1.1.12 Determination of Heavy Metals

1.2 This standard involves hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM Standards

D562 Standard Test Method for Consistency of Paints Measuring Krebs Unit (KU) Viscosity Using a Stormer-Type Viscometer
D660 Standard Test Method for Evaluating Degree of Checking of Exterior Paints
D661 Standard Test Method for Evaluating Degree of Cracking of Exterior Paints
D823 Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels
D868 Standard Practice for Determination of Degree of Bleeding of Traffic Paint
D1193 Standard Specification for Reagent Water
D1475 Standard Test Method for Density of Liquid Coatings, Inks, and Related Products
D2243 Standard Test Method for Freeze-Thaw Resistance of Water-Borne Coatings
D2805 Standard Test Method for Hiding Power of Paints by Reflectometry
D7588 Standard Guide for FTIR Fingerprinting of a Non-Aqueous Liquid Paint as Supplied in the Manufacturer's Container
E77 Standard Test Method for Inspection and Verification of Thermometers
E1347 Test Method for Color and Color-Difference Measurement by Tristimulus Colorimetry

3 Summary of Test Methods

3.1 The Static Heat test involves storing paint at an elevated temperature for a week then conducting a viscosity test on the paint.

3.2 The Skinning and Lumps test involves storing paint at ambient conditions then straining the paint with a 100 mesh screen.

3.3 The Settling test involves centrifuging paint to produce a separation of the paint components.

3.4 The Skinning test involves partially filling a container with paint and inspecting it after two days to see if the paint has formed a skin.

3.5 The Cracking test involves casting a paint film over asphalt saturated felt and examining the film for cracks after it has dried.

3.6 For the determination of heavy metals, the paint is analyzed for the presence of antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), mercury (Hg), and tin (Sn). Paint samples are prepared through a microwave digestion system using nitric and fluoroboric acids. The samples are then analyzed for mercury with a cold vapor technique using a vapor generation assembly (VGA) outfitted onto a flame atomic absorption spectrometer (FAAS) and for the remainder of the analytes by an inductively coupled plasma optical emission spectrometer (ICP-OES).

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for traffic paint used within the Montana Department of Transportation's oversight.

5 Apparatus

5.1 *Analytical Balance* – Capable of measuring to 0.0001 g.

5.2 *Microwave digestion system* – Capable of heating samples to 200°C and maintaining that temperature for at least 10 minutes. The system must use sealable vessels that prevent the escape of vapors.

5.3 *ICP-OES* – Capable of measuring trace elements to low parts per billion (ppb) levels.

5.4 *FAAS* – Outfitted with a hollow cathode lamp (HCL) for measuring Hg and capable of being outfitted with a VGA.

5.5 *VGA* – Capable of cold vapor techniques for detecting mercury at low ppb to high parts per trillion (ppt) levels.

5.6 *Plasticware* – Suitable for trace element analysis. Properly cleaned and stored filled with dilute nitric acid solution (1 – 5%) for at least 2 days.

5.7 *Centrifuge* – Capable of a centrifugal force of 1112 Newtons.

5.8 *Asphalt Felt Paper* – 15 pound saturated asphalt felt paper.

5.9 *Cans* – Pint sized, lined and unlined.

5.10 *Screens* – 100 mesh screen capable of accommodating paint.

5.11 *Leneta 5C form* – an opacity chart containing a white section and a black section paint films can be applied to.

5.12 *Oven* – Capable of maintaining 60°C ± 1°C.

6 Reagents and Materials

6.1 *Trace metal grade (TMG) hydrochloric acid (HCl)* – Any commercially available brand at a concentration of 32-38%.

6.2 *TMG nitric acid (HNO_3)* – Any commercially available brand at a concentration of 63-70%.

6.3 *Fluoroboric acid (HBF_4)* – Any commercially available brand at a concentration of 46-54%.

6.4 *Stannous chloride ($SnCl_2$) solution* – 10% stannous chloride w/v and 20% TMG hydrochloric acid.

6.5 *1+1 hydrochloric acid* – Made with TMG HCl (e.g., Add 500 ml TMG HCl to 400 ml reagent water and dilute to 1 L).

6.6 *Reagent Water* – Purified water that meets ASTM Type II specifications or better (ASTM D1193)

7 Calibration and Standardization

7.1 Follow manufacturer's instructions for calibrating and standardizing the ICP-OES. Appendix A provides parameters for a Varian Axial ICP-OES used by MDT.

7.2 Follow manufacturer's instructions for calibrating and standardizing the FAAS and VGA. Appendix A provides parameters for a Varian FAAS used by MDT.

7.3 Check the calibration of the oven every 6 month with a thermometer verified in accordance with ASTM E77.

PROCEDURES

8 Color and Contrast Ratio

8.1 The paint shall be tested in accordance with ASTM D2805 and ASTM E1347 except for the following stipulations.

8.1.1 Rescind ASTM D2805 Sections 7.1.3 through 7.8 and replace with "15 mil films shall be cast on Leneta 5C opacity charts or equivalent and dried for a minimum of 2 hours." Use a colorimeter to determine coordinates per ASTM E1347. Use Y, x, and y coordinates with illuminant and observer settings of C and 2° when collecting readings. Record Y, x and y coordinates. Use these coordinates to calculate contrast ratio via ASTM D2805.

9 Viscosity

9.1 The paint shall be tested in accordance with ASTM D562.

10 Density

10.1 The paint shall be tested in accordance with ASTM D1475 including the following modification.

10.1.1 Add "Stir the sample until homogeneous." at the beginning of ASTM D1475 Section 9.1.

11 Freeze-Thaw

11.1 The paint shall be tested in accordance with ASTM D2243. Repeat procedures for 3 freeze-thaw cycles (ASTM D2243 Section 7.3). MDT does not require a control sample as described in ASTM D2243 Section 7.1.

11.2 After completion of the freeze-thaw procedures, visually examine the sample and note any signs of livering, hard settling, coagulating, lumps or coarse particles. Then determine the viscosity of the freeze-thaw sample per ASTM D562. Compare the original viscosity to the freeze-thaw viscosity and determine if there was an increase or decrease in viscosity.

12 Static Heat Stability

12.1 Pour paint into a pint container to within 6.4 mm (0.25 inches) of the top. Close the container, seal it with tape, and place the container in an oven maintained at 60°C ± 1°C (140°F ± 2°F) for 7 days.

12.2 After 7 days, remove the container from the oven. Equilibrate the paint at standard conditions and gently stir the paint for a minimum of 5 minutes. Visually examine the sample and note any signs of livering, hard settling, coagulating, lumps or coarse particles. Then determine the viscosity of the static heat sample per ASTM D562. Compare the original viscosity to the static heat viscosity and determine if there was an increase or decrease in viscosity.

13 Bleeding Ratio

13.1 The paint shall be tested in accordance with ASTM D868, except in section 7.4.1.1, replace the CIE L* value with the reflectance coordinate Y.

14 Skinning and Lumps

14.1 Fill a pint container ¾ full and seal it tightly. Allow the container and sample to sit for 72 hours at ambient laboratory conditions then strain the paint through a 100 mesh screen. Note if any lumps or skin is retained on the screen.

15 Settling

15.1 Fill a centrifuge tube with paint and revolve it for 2 hours at laboratory ambient conditions at a speed producing a centrifugal force of 1112 Newtons (250 pound-force). Note the amount of separation of the components; there shouldn't be more than 13 mm of separation.

16 Skinning

16.1 Fill a lined paint can ¾ full with paint and seal tightly. Invert the can momentarily, and then turn it upright. Place the can in an area where the temperature is 21°C to 32°C for 48 hours. Do not agitate or disturb the sample. After 48 hours, open the can and inspect the paint for the presence or absence of a skin.

17 FTIR Spectra Verification

17.1 The paint shall be tested in accordance with ASTM D7588. Compare the acquired absorbance spectrum to a previously measured spectrum or one provided by the manufacturer. Note any significant differences between the spectra. For multicomponent paints, determine a spectrum for each component separately.

18 Cracking

18.1 The film shall be cast with a 380 micron (15 mil) drawdown blade on 15-pound saturated asphalt felt paper. Allow the film to dry for 24 ours then examine the paint for cracking. Cracking is understood to be any break extending through the paint film to the surface it is applied to. Partial breakthroughs known as checking are not categorized as cracking and are not addressed in this test. Consult ASTM D660 and ASTM D661 to better understand definitions of cracking and checking.

19 Heavy Metals Determination

19.1 Procedure

19.1.1 Weigh 0.50 g of paint or a paint component into a Teflon insert of a high pressure sample rotor system for microwave digestion. Make note of the mass to 0.0001 g.

19.1.2 In a properly functioning ventilation hood add 8 mL TMG nitric acid and 2 mL of fluoroboric acid to the Teflon inserts. Place the Teflon insert in the carousel.

19.1.3 Assemble all components required for proper microwave digestion according to the manufacturer's instructions and then run the digestion. MDT's parameters for a Milestone Ethos EZ microwave digestion system are in Appendix A.

19.1.4 Following the manufacturer's instructions, remove and cool the digestion vessel and open it. Rinse the sample into a clean Teflon beaker or other suitable cleaned container. Tare an appropriate storage container on the analytical balance. Rinse the sample into the storage container. Place the storage container back onto the analytical balance and dilute with reagent water to a mass of 100 g. Record the mass to nearest 0.01 g.

Note – If titanium dioxide is present in the sample, the sample should be filtered with a syringe filter prior to analyzing in order to remove small particles that could block the nebulizer.

19.1.5 Once all the samples have been prepared, analyze them on an ICP-OES and a FAAS outfitted with a VGA.

19.2 Calculation or Interpretation of Results

19.2.1 For elements Sb, As, Cd, Cr, Co, Pb, and Sn measured in mg/kg on the spectrometer, the sample concentration is calculated by multiplying the measured value by the ratio of the solution weight and then dividing by the sample weight.

19.2.2 For Hg measured in µg/kg on the spectrometer, the sample concentration (mg/kg) is calculated by multiplying the measured value by the ratio of the solution weight then dividing by the sample weight then dividing by 1000.

19.3 Report

19.3.1 Elements Sb, As, Cd, Cr, Co, Pb, Hg, and Sn are to be reported in the units mg/kg.

APPENDIX A

Varian Axial ICP-OES configuration parameters

Equipment Configuration

a. Nebulizer: Sea Spray
b. Spray chamber: cyclonic
c. Sample pump tubing: White/White
d. Waste pump tubing: Blue/Blue
e. Rinse Solution: 3% Nitric Acid
f. Torch: High solids with sheath gas
g. Sheath gas: Argon at 10mL/min
h. Power: 1.40 kW
i. Plasma flow: 15.0 L/min
j. Auxiliary flow: 1.50 L/min
k. Nebulizer flow: 0.55 L/min
l. Replicate Read time: 10.00 s
m. Instrument stabilization delay: 15.00s
n. Sample uptake delay: 30.00s
o. Pump rate: 15 rpm
p. Rinse time: 100s
q. Fast pump: yes
r. Replicates: 3

Line Selection for Standard, Samples, and Blanks

a. As 188.980, 193.696
b. Cd 214.439
c. Co 230.786, 231.160
d. Cr 267.716
e. Pb 220.353
f. Sb 217.582, 231.146
g. Sn 189.925, 283.998

Calibration Varian Axial ICP-OES

a. Type: Linear for all elements
b. Linear-Maximum percent error of 5% except Cd that can be 15% and confidence limit of 0.99%
c. Calibration standards: Prepare calibration standards and blanks so that the sample matrices are being mimicked by compensating for the content of acids in the case of analyzing the amine component of two component paints. Prepare a total of one standard blank and three standards with varying concentrations of each desired analyte. For other paint types or components standard additions will need to be made by adding 3 differing spikes to a known portion of sample solution kept at a constant portion of each solution followed by a dilution with no spike.

An example for a stock solution taken to 500 g for standard addition spikes is as follows:

Analyte	Starting Concentration (mg/kg)	Mass Added (g)	Standard Concentration (mg/kg)
As	1000	0.5	1.0
Cd	1000	0.01	0.02
Co	1000	0.5	1.0
Cr	1000	0.1	0.2
Pb	1000	0.5	1.0
Sb	1000	0.5	1.0
Sn	1000	0.5	1.0

40 mL of TMG nitric acid and 10 mL of fluoroboric acid would added to keep the analytes stable.

Varian AA 240FS and VGA configuration parameters

Equipment configuration

a. Measurement time: 10.00s
b. Read delay: 115s
c. Sample tubing: Purple/black
d. Acid and reductant tubing: black/black
e. Replicates standards: 3
f. Replicates samples: 3
g. Precision % standards: 1.0
h. Precision % samples: 1.0
i. Lamp Current: Recommended current on Hg lamp
j. Slit width: 0.5R nm
k. Reslope rate: 50
l. Reslope standard: number 2

Wavelength selection for standards, samples, and blanks

a. 253.7 nm

Calibration Varian AA 240FS and VGA

a. Type: Linear
b. Calibration standards: Prepare calibration standards and blanks so that the acid content of the sample matrices are mimicked. However do not compensate for hydrogen peroxide as it seems to keep the analysis from working properly. Prepare a total of one standard blank and three standards with varying concentrations of each desired analyte

Milestone Ethos EZ microwave digestion system

Heat and time: Heat to 200°C and hold temperature during a 20 minute interval. Followed by a 10 minute cooling period

Microwave power: 1200W (500 W for 3 vessels or less)

Rotor: SK-10

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