CURRENT DATE OF REVISION
MT 500 SECTION
CHEMISTRY

Test Method No.	Title	Pages	Date of Publication or Revision
MT 501	pH, Insoluble Materials, Corrosion Rate, Percent Settleable Solids and Percent Passing a #10 Sieve of Brine Materials	1 pp	Jun 2016
MT 502	Elemental Chemical Analysis Of Brine Materials	7 pp	Sep 2016
MT 503	Vacant		
MT 504	Cyanide In Brine Material		Under Development
MT 505	Vacant		
MT 506	Vacant		
MT 507	Vacant		
MT 508	Vacant		
MT 509	Vacant		
MT 510	Vacant		
MT 511	Vacant		
MT 512	Vacant		
MT 513	Vacant		
MT 514	Vacant		
MT 515	Vacant		
MT 516	Vacant		
MT 517	Vacant		
MT 518	Vacant		
MT 519	Vacant		
MT 520	Determination of Wear Metals in Engine Oil		Under Development
MT 521	Testing Dyed Diesel	1 pp	Sep 2016
MT 522	Vacant		
MT 523	Vacant		
MT 524	Vacant		
MT 525	Mechanical Rocker Test for Ice Melting Capacity for Deicing Material	5 pp	Aug 2019
MT 526	Moisture Analysis of Clear Roads Category 8A, 8B, and 8C Solid Sodium Chloride	2 pp	Jun 2016
MT 527	Vacant		
MT 528	Vacant		
MT 529	Vacant		

CURRENT DATE OF REVISION
MT 500 SECTION
CHEMISTRY

Test Method No.	Title	Pages	Date of Publication or Revision
MT 530	Determination of Chloride in Bridge Deck Cement by Ion Chromatography	5 pp	Dec 2016
MT 531	Vacant		
MT 532	Determination of Sulfate Content in Soils by Ion Chromatography	4 pp	Dec 2016
MT 533	Chemical Analysis of Fly Ash and Pozzolans via Spectrophotometry	9 pp	Sep 2016
MT 534	Chemical Analysis of Portland Cement via Spectrophotometry	8 pp	Jun 2016
MT 535	Bridge Deck Crack Sealant IR Test		Under Development
MT 536	Chemical Analysis of Silica Fume	1 pp	Jun 2016
MT 537	Chemical Analysis of Ground Granulated Blast-Furnace Slag (GGBFS)	4 pp	Sep 2016
MT 538	Chemical Analysis of Blended Cement via Spectrophotometry	9 pp	Sep 2018
MT 539	Chemical Analysis of Portland Cement via X-Ray Fluorescence	17 pp	Jun 2023
MT 540	Chemical Analysis of Blended Cement via X-Ray Fluorescence	16 pp	Jun 2023
MT 541	Chemical Analysis of Fly Ash and Pozzolans via X-Ray Fluorescence	13 pp	Jun 2023
MT 542	Vacant		
MT 543	Vacant		
MT 544	Vacant		
MT 545	Vacant		
MT 546	Vacant		
MT 547	Vacant		
MT 548	Analysis of Traffic Paint	7 pp	Jun 2016

METHODS OF SAMPLING AND TESTING
MT 501-16
pH, INSOLUBLE MATERIAL, CORROSION RATE, PERCENT SETTLEABLE SOLIDS AND PERCENT PASSING A NO. 10 SIEVE OF BRINE MATERIALS
(*Montana Method*)

MT 501 is identical to the 2010 Clear Roads Snow and Ice Control Chemical Products Specifications and Test Protocols (https://clearroads.org/wp-content/uploads/12-10-Final-CR-SPECS-wCategory4.pdf) except for the following stipulations:

Test Method C

1 Perform a prescreening procedure for the Percent Total Settleable Solids methods.

1.1 Pour a well-mixed sample into a 50 ml conical bottom disposable vial to the 50 ml mark. Cap vial. Repeat for all samples. Place the vials in a freezer at the test temperature designated below for 168 hours:

- Sodium Chloride: -17.8°C ± 1°C (0°F ± 2°F)
- Magnesium Chloride: -17.8°C ± 1°C (0°F ± 2°F)
- Calcium Chloride: -29°C ± 1°C (-20°F ± 2°F)

Note 1 – Ensure the samples remain free from agitation or disturbance during the entire testing duration.

1.2 At the end of the testing time (168 hours), observe samples. If any noticeable hardening or crystallization of the deicer is observed, then perform additional testing in accordance with Clear Roads Test Method C. If the sample does not exhibit hardening or crystalizing the sample passes the test.

2 Report

2.1 Report settleable solids as a (V/V) percent ±0.1% in Site Manager.

2.2 Report solids passing through a number 10 sieve as a (V/V) percent ±0.1% in Site Manager.

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METHODS OF SAMPLING AND TESTING
MT 502-16
ELEMENTAL CHEMICAL ANALYSIS OF BRINE MATERIALS
(*Montana Method*)

1 Scope

1.1 This test method describes the procedures used to analyze brine materials for the following analytes: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), phosphorus (P), lead (Pb), mercury (Hg), selenium (Se), and zinc (Zn) in brine materials. Additionally the samples are analyzed for magnesium (Mg), sodium (Na), and sulfur (S) to determine the percentage of magnesium chloride, sodium chloride, and sulfates in the samples.

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
D1193 Standard Specification for Reagent Water

Milestone
Milestone Grease Digestion Application Note HPR-CH-16

3 Summary of Test Method

3.1 Samples are prepared using a microwave digestion technique based on Milestone Grease Digestion Application Note HPR-CH-16. Mercury is analyzed using a cold vapor technique with a vapor generation assembly (VGA) attached to a flame atomic absorption spectrometer (FAAS). All other analytes are analyzed using a inductively coupled plasma – optical emission spectrometer (ICP-OES).

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance and control for deicer materials and dust palliatives.

5 Apparatus

5.1 *Analytical Balance* – with a precision of 0.0001 g

5.2 *Microwave digestion system* – Capable of heating samples to 200°C and maintaining that temperature for at least 30 minutes. The system must use sealable vessels that prevent the escape of vapors.

5.3 *ICP-OES* – Capable of measuring analytes of interest at parts per million (ppm) levels and low parts per billion (ppb) levels

5.4 *Flame Atomic Absorption Spectrometer (FAAS)* – Equipped with a hollow cathode lamp (HCL) for measuring Hg and capable of operating with an attached VGA

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

5.6 *Labware* – Glassware, Teflon, and Plasticware containers that have been properly cleaned and stored filled with dilute nitric acid solution (1 – 5%) for at least 2 days.

6 Reagents and Materials

6.1 *Trace metal grade (TMG) hydrochloric acid (HCl)* – concentration of 32-38%

6.2 *TMG nitric acid (HNO_3)* – concentration of 65-70%

6.3 *Technical grade hydrogen peroxide (H_2O_2)* – concentration of 34-37%

6.4 *Stannous chloride solution* - 10% stannous chloride ($SnCl_2$) 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

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES and VGA. Appendix A provides calibrating and standardizing specifications for a Varian Axial View ICP-OES, an Agilent Radial View ICP-OES, and Varian VGA.

8 Procedure

8.1 Tare a clean microwave digestion vessel on the analytical balance. Use a transfer pipet to dispense a portion of the sample into a digestion vessel in accordance with the table below. Record the mass.

Material Being Analyzed	Amount of material (grams)
Corrosion Inhibitor	1.2
Sodium Chloride Magnesium Chloride Calcium Chloride	7.5

Note 1 – Use a small weighing dish in place of a microwave digestion vessel when static electricity prevents a stable measurement. Transfer contents to a microwave digestion vessel; use a small amount of water to rinse the contents of the weighing dish.

8.2 In a ventilation hood, add 1 mL of hydrogen peroxide and 9 mL of nitric acid to each of the digestion vessels. Assemble the digestion vessels and all other components required for proper microwave digestion in accordance with the manufacturer's instructions and then run the digestion program. MDT's parameters for a Milestone Ethos EZ microwave digestion system are in Appendix A.

8.3 After completion of the digestion program, allow the carousel to cool before removing. The carousel may be left overnight to cool.

8.4 Remove a 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 until a mass of 100.00 g ± 0.05. Record the mass to nearest 0.01 g. Repeat for all samples.

8.5 Label the sample bottles with the sample number, date, analyst initials, and as Brine Material stock solution.

8.6 Dilute the stock solutions with reagent water for the analysis of Mg, Na, and S to 1:100 by weight. Label the dilute samples with the sample number, date, analyst initials, and as Brine Material dilute solution.

8.7 Analyze the stock and dilute samples on the radial view ICP-OES, axial view ICP-OES, and VGA with FAAS, as appropriate.

9 Calculation or Interpretation of Results

9.1 Concentration Calculations

9.1.1 As, Ba, Cd, Cr, Cu, P, Pb, Se, and Zn (measured in mg/kg by the ICP-OES)

Sample concentration is calculated by multiplying the measured value by a ratio of the solution weight divided by the sample weight.

$$C = DM(\frac{L}{S})$$

Where:

C = sample concentration (mg/kg)

M = measured value (µg/kg)

L = solution mass

S = sample mass

D = dilution factor that is equal to 1 for final products or is equal to 100%/P where P is the percentage of the component of interest in the final product

Note – Concentration calculations for corrosion inhibitors requires the inclusion of a dilution factor based on the amount of inhibitor used in the product.

9.1.2 Hg (measured in µg/kg by the VGA)

Mercury concentration is calculated by multiplying the measured value by a ratio of the solution mass divided by the sample mass then divided by 1000.

$$C = \frac{ML}{1000S}$$

Where:

C = sample concentration in mg/kg

M = measured value in µg/kg

L = solution mass

S = sample mass

9.2 Percent Weight Calculations

$$P = \frac{LMNO}{10000STU}$$

Where:

P = percent weight of the desired compound

L = mass of the first solution

M = measured value of the analyte in mg/kg

N = mass of the second solution

O = molecular mass of the desired compound

S = sample mass

T = mass of the aliquot from the first solution

U = atomic mass of the measured analyte.

Elements and molecules	Atomic mass	Molecular mass
Na	22.99	
NaCl		58.44
Mg	24.31	
$MgCl_2$		95.21
S	32.066	
SO_4		96.066

10 Report

10.1 Elements As, Ba, Cd, Cr, Cu, Hg, P, Pb, Se, and Zn – report as mg/kg

10.2 $MgCl_2$, NaCl, and SO_4 – report as percent by weight of the product

APPENDIX A
ANALYTICAL INSTRUMENTATION CALIBRATION

Milestone Ethos EZ microwave digestion system

Digestion program used: motoroil.mpr

Heat and time: Heat to 200°C and hold temperature during a 30 minute interval. Follow by a 10 minute cooling period.

Rotor: SK-10

Varian Axial View ICP-OES configuration parameters for brines and non-inhibitors

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: 1.20 kW
i. Plasma flow: 15.0 L/min
j. Auxiliary flow: 1.50 L/min
k. Nebulizer flow: 0.70 L/min for $MgCl_2$ brines 0.80 L/min for NaCl brines
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 193.696
b. Ba 233.527
c. Cd 214.439
d. Cr 267.716
e. Cu 324.754
f. P 213.618
g. Pb 220.353
h. Se 196.026
i. Zn 213.857

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 and salts. Prepare a total of one standard blank and three standards with varying concentrations of each desired analyte.

Agilent Radial View ICP-OES configuration parameters for brines and inhibitors

Equipment configuration

a. Nebulizer: One Neb
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
g. Power: 1.15 kW $MgCl_2$ brines, 1.20 kW NaCl brines, and 1.10 kW for inhibitors.
h. Plasma flow: 15.00 L/min
i. Auxiliary flow: 1.50 L/min
j. Nebulizer flow: 0.80 L/min $MgCl_2$ brines, 0.75 L/min NaCl brines, and 0.70 L/min for inhibitors.
k. Viewing height: 11 mm $MgCl_2$ brines, 12 mm NaCl brines, and 9 mm for inhibitors.
l. Replicate read time: 10.00s
m. Instrument stabilization delay: 15s
n. Sample uptake delay: 30s
o. Pump rate: 15s
p. Rinse rate: 10s
q. Fast pump: yes
r. Replicates: 3

Line selection for standards, samples and blanks:

$MgCl_2$ brines

a. Mg 280.270
b. Na 589.592
c. S 181.972

NaCl brines

a. Na 589.592

Corrosion Inhibitors

b. As 188.980
c. Ba 455.403
d. Cd 226.502
e. Cr 205.560
f. Cu 324.754
g. P 213.618
h. Pb 220.353
i. Se 196.026
j. Zn 213.857

Calibration Agilent Radial ICP-OES

a. Type: Linear for all elements
b. Linear-Maximum percent error of 5% and confidence limit of 0.99%.
c. Calibration standards: Prepare calibration standards and blanks so that the inhibitor sample matrices are being mimicked by compensating for the acids and inhibitor components. For the brines only compensate for the acid content. Prepare a total of one standard blank and three standards with varying concentrations of each desired analyte.

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. Prepare a total of one standard blank and three standards with varying concentrations of each desired analyte.

Reagents

a. Acid: Described in 6.5
b. Reductant: Described in 6.4

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METHODS OF SAMPLING AND TESTING
MT 521-16
METHOD OF TESTING DYED DIESEL
(*Modified ASTM D6258*)

MT 521 is identical to ASTM D6258 except for the following stipulations:

1. Add the following to Section 9.2.1:

Volume of Stock Standard/100 ml	Approximate Concentration of Working Standards
6.0 mL	18 mg/L
7.0 mL	21 mg/L

2. Add to the end of Section 9.5:

"Also measure the amplitude difference between the peak and valley of 580 ± 20 nm and 561 ± 20 nm.

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METHODS OF SAMPLING AND TESTING
MT 525-19
MECHANICAL ROCKER TEST FOR ICE MELTING CAPACITY FOR DEICING MATERIAL
(Montana Method)

1 Scope

1.1 This procedure modifies the Mechanical Rocker Test for Ice Melt Capacity procedure developed by Nebraska Department of Transportation and the University of Nebraska-Lincoln to reflect research developments and improvements.

1.2 This document establishes a procedure for testing the ice melting capacity of liquid deicers and developing an ice melting curve over 90 minutes. The purpose is to provide a precise, accurate and repeatable test method to compare different liquid deicing products for effectiveness.

1.3 This procedure does not address the potential environmental impacts of liquid deicers such as pollution to roadside vegetation, soil, and run-off or damage to pavements due to corrosiveness of the deicers.

1.4 This procedure does not address the potential effects from natural conditions such as sunlight, wind speed, relative humidity, or other weather events experienced by field-applied deicers.

1.5 This procedure does not address detailed safety concerns of handling different deicer chemicals. It is the responsibility of the user to address any safety concerns that may arise.

2 Reference Documents

Nebraska Department of Transportation
Mechanical Rocker Test for Ice Melting Capacity (MRT or MRT-IMC), 2014
https://dot.nebraska.gov/media/5752/final-report-m322.pdf

3 Significance and Use

This test method describes procedures to be used for testing the ice melting capacities of chemical deicers to determine the effectiveness of different commercial deicing chemical products.

4 Apparatus and Materials

4.1 Mechanical Test Equipment

4.1.1 *Laboratory Freezer* – The freezer must be large enough to hold at least four thermoses, one sieve, two ice trays, one funnel, a spatula, and tweezers. The freezer must be able to maintain a temperature of 0°F (-17.8°C) with an accuracy of ±2°C.

4.1.2 *Mechanical Rocker* – The mechanical rocker must be able to rock with a frequency range of 60 to 120 rpm. It must be capable of a tilt angle of ±10°. It must be able to hold the weight of at least ten lbs.

4.1.3 *Digital Mass Balance* – A digital mass balance in a confined box with ± 0.001 gram accuracy. A confining glass box is important to eliminate the error caused by air flow within the room.

4.1.4 *Stopwatch* – A digital stopwatch is required to record the rocking duration.

4.2 Sampling Equipment

4.2.1 *Latex Gloves* – A pair of latex gloves should be worn during the experiment.

4.2.2 *Thermos* – Four stainless-steel vacuum-insulated thermoses (16 oz. each) labeled A, B, C and D. It is important that the thermos be vacuum insulated. This obtains the highest insulation possible. The thermos should also be stainless-steel to protect against corrosion from the deicer due to multiple uses.

4.2.3 *No.4 Sieve* – A No. 4 sieve allows particles no larger than ¼ inch (6.4 mm) pass through its mesh. A sieve of a courser value may allow ice cubes to pass through, and a sieve of finer value may collect liquid on its mesh, allowing for melting to continue. Using other sized sieves is not recommended.

4.2.4 *Plastic Spatula and Plastic Tweezers* – A plastic spatula and plastic tweezers will be used to collect the residual ice chunks on the sieve.

4.2.5 *Styrofoam cups* – Eight 8 oz. Styrofoam cups or dishes that easily contain 33 ice cubes and fit in the mass balance. Styrofoam as a material is important because of its insulation properties. Styrofoam was chosen as a material to eliminate the error caused by condensation when weighing the cup. If the reading of the mass balance increases significantly over time, the environment might be too humid such that the condensation on the cup or dish could cause significant error in the measurements.

4.2.6 *Two ice cube trays* – Ice cube trays must produce ice cubes that have a cross-section of 7/16 in × 7/16 in (1.1 cm × 1.1 cm) and a depth of 7/16 in (1.1 cm). The ice cube trays must be able to make 140 ice cubes total (33 ice cubes for 4 samples and at least 8 extras in case any are damaged or defective.)

4.2.7 *Micropipette* – The micropipette must be able to deliver 1.3 ml of water in a single delivery within the ±0.10 ml tolerance.

4.2.8 *Pipette* – A volumetric pipette must be able to deliver 30 ml of deicer chemical with a tolerance of ±0.03 ml.

4.2.9 *Funnel* – A working funnel must allow for the ice cubes to pass through its small-end hole. The funnel's small end diameter must not be less than 1 in (2.5 cm).

4.2.10 *Deicer Chemical* – Any deicer liquid that can stay in liquid form at or below 0°F (-17.8°C).

5 Testing Procedures

5.1 Put on latex gloves before testing.

5.2 Sample Preparation

5.2.1 Label eight Styrofoam cups: A, B, C, D and AA, BB, CC, DD.

5.2.2 Label four thermoses: A, B, C, and D.

5.2.3 Prepare ice cubes. Use the micropipette to dispense 1.3 mL of distilled/deionized water into the apertures of the ice cube trays to create 140 ice cubes. Thirty-three ice cubes are required for a single sample and four samples will be analyzed for each test. Eight extra ice cubes should be prepared in case some are damaged or do not freeze entirely.

5.2.4 After filling the ice cube trays, tap the sides of the tray gently to vibrate the liquid inside the tray. This breaks the surface tension of the water and ensures that all the ice cubes will freeze properly. Ice cubes that do not freeze properly will appear as unfrozen liquid or slush.

5.2.5 Prepare deicer sample. Use the pipette to dispense 30 mL of a given liquid chemical deicer into each of the four thermoses labeled A, B, C, and D. Make sure to shake or stir any container containing the liquid deicer chemical before dispensing into the thermoses.

5.2.6 Measure and record the mass of the eight Styrofoam cups labeled A, B, C, D and AA, BB, CC, DD using the digital mass balance.

5.2.6.1 Styrofoam cups A, B, C, and D will be used for the measurement of the mass of ice before rocking.

5.2.6.2 Styrofoam cups AA, BB, CC, and DD will be used to measure the mass of melted ice after rocking.

5.2.7 Place the thermoses and the ice cube trays in the freezer with the temperature set at 0°F (-17.8°C). Place the lids of the thermoses over the openings of the thermoses, but do not secure the lids. Place the No. 4 sieve with bottom pan, a funnel, tweezers, and a spatula in the freezer. Place the Styrofoam cups labeled A, B, C, and D in the freezer. **Do not place the Styrofoam cups labeled AA, BB, CC, and DD in the freezer.** Allow all materials to acclimate and the ice to freeze for 24 hours.

5.3 Testing

5.3.1 Working inside the freezer, place 33 ice cubes inside Styrofoam cup A. The plastic funnel may be used to guide the ice cubes to fall into the cup.

5.3.2 Remove Styrofoam cup A filled with the ice from the freezer and place it within the mass balance. Measure and record the mass of cup A and the ice and place cup A and the ice back into the freezer. The reading on the mass balance should be recorded quickly within 30 seconds from the time the cup leaves the freezer.

5.3.3 Repeat steps 5.3.1 and 5.3.2 for Styrofoam cups B, C, and D.

5.3.4 Set the mechanical rocker's tilt angle to 10° and the frequency to 90 rpm.

5.3.5 Working within the confines of the freezer, remove the lid of the Thermos A and pour the 33 ice cubes from Styrofoam cup A into Thermos A, using the funnel to guide the ice cubes. Secure the lid of the thermos. Verify all the ice cubes are in the thermos as the ice cubes may stick to the cup or the funnel. Also, make sure to tighten the lid securely to prevent leaking during the rocking motion. Repeat this step for Thermos B, C and D.

5.3.6 Remove Thermos A, B, C and D from the freezer and place them on the mechanical rocker perpendicular to the rocking axis. Start the rocker and the stopwatch immediately afterwards. This step should not take more than 15 seconds.

5.3.7 Let the thermoses rock for 15 minutes for Thermos A, 30 minutes for Thermos B, 60 minutes for Thermos C and 90 minutes for Thermos D.

5.3.8 At the end of 15 minutes, remove Thermos A from the rocker. Remove the lid from Thermos A and pour its contents onto the No.4 sieve within the confines of the freezer. This step will separate the liquid from the remaining ice. Verify all the ice is dispensed from Thermos A onto the sieve. Gently tap the sides of the thermos to remove excess ice, and/or use the plastic tweezers and spatula to remove trapped ice, if necessary.

5.3.9 Place cup AA within the confines of the freezer and use the tweezers and/or spatula to move the ice from the No. 4 sieve to the cup. If the spatula is used to slide the ice into the cup, move no more than two ice cubes at a time to reduce the amount of liquid carried to the cup. In order to reduce ice melting, the ice cubes should be moved off the sieve and into cup AA as quickly as possible. No more than 90 seconds should pass from the time the thermos is removed from the rocker in Step 5.3.8 to the time the melted contents are moved from the sieve to cup AA. Cup AA should not have been allowed to acclimate with the rest of the testing materials in the freezer. Once inside cup AA, any melting that occurs will not affect the final mass of the ice.

5.3.10 Measure and record the mass of cup AA with the remaining ice in the digital mass balance. Although the effect of condensation is low, the reading on the mass balance will increase as the

material remains on the balance. Cup AA should be removed from the freezer with its mass recorded in less than 30 seconds.

5.3.11 Repeat steps 5.3.8 to 5.3.10 for Thermos B, Thermos C, and Thermos D at their respective time intervals as stated in step 5.3.7. Styrofoam cup BB corresponds with Thermos B, Styrofoam cup CC with Thermos C, and Styrofoam cup DD with Thermos D.

5.3.12 Repeat the Testing Procedure in Section 5 at least two more times to obtain triplicate test data. Once the Testing Procedure has been completed at least three times, proceed to the calculations.

6 Calculations

6.1 Mass of Ice Melted (m_{xn}), grams ice

Calculate the mass of ice melted for each sample analyzed for each replicate test. The mass of ice melted is mass of the ice before rocking minus the mass of ice after rocking. This will be calculated from measurements taken in steps 5.2.6, 5.3.2, and 5.3.10.

m_{xn} = (mass cup X w/ice – mass of cup X) – (mass cup XX w/ice – mass of cup XX) (Equation 1)

Where:
X = sample (A, B, C, or D)
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

6.2 Ice Melting Capacity (IMC_{xn}), grams ice/mL deicer

Calculate the ice melting capacity for each sample analyzed for each replicate test.

$$IMC_{xn} = m_{xn} / 30 \text{ mL} \qquad \text{(Equation 2)}$$

Where:
X = sample (A, B, C, or D)
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

6.3 Average Ice Melting Capacity ($I\bar{M}C$) – *Optional*

$I\bar{M}C$ is the average of the replicate test IMC_{xn} (Equation 2) at each time interval. The averages of the four time intervals can be plotted to create a graph of the average ice melt capacity at each time interval.

$$I\bar{M}Cxn = \Sigma IMCxn / n \qquad \text{(Equation 3)}$$

Where:
X = sample (A, B, C, or D)
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

6.4 Average Ice Melting Capacity 90 ($I\bar{M}C_{90}$)

$I\bar{M}C_{90}$ is the average of the Sample D replicate results from Equation 2 (IMC_{xn}) at 90 minutes, the end of the rocking period.

$$I\bar{M}C_{90} = \Sigma IMC_{Dn} / n \qquad \text{(Equation 4)}$$

Where:
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

6.5 Initial Melting Velocity (IMV_n), grams ice melted/mL deicer*min

IMV_n measures the rate or velocity at which ice melts during the first 15 minutes and is calculated from sample A results from Equation 2 for each replicate test.

$$IMV_n = IMC_{An} / 15 \text{ min} \qquad \text{(Equation 5)}$$

Where:
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

6.6 Average Initial Melting Velocity ($I\bar{M}V_{avg}$)

$I\bar{M}V_{avg}$ is the average of the results from Equation 5.

$$I\bar{M}V_{avg.} = \Sigma IMVn / n \qquad \text{(Equation 6)}$$

Where:
n = replicate test number (i.e., n = 1, 2, 3*)
*Note – If more than triplicate testing is required, n will correspond to the number of tests performed.

7 Reporting

7.1 The Initial Melting Velocity IMVn (Equation 5). This indicates how fast a deicer product begins working.

7.2 The average ice melting capacity at 90 minutes $I\bar{M}C90$ (Equation 4). This indicates how much ice a deicer will melt 90 minutes after contact.

8 Precision and Bias

8.1 The Single-Operator Coefficient of Variation represents the expected variation of measured ice melting capacity of a sample prepared and tested in triplicate by one operator in a single lab. The Coefficient of Variation is 3.0%

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METHODS OF SAMPLING AND TESTING
MT 526-16
MOISTURE ANALYSIS OF CLEAR ROADS CATEGORY 8A, 8B, AND 8C SOLID SODIUM CHLORIDE
(*Modified ASTM E534*)

1 Scope

1.1 This method is utilized to determine the water insoluble residue of Clear Roads specified salt for product acceptance by the Montana Department of Transportation. This method will serve as the reference method for salt with an insoluble residue of 0.0% – 10.0% by mass.

2 Referenced Documents

ASTM Standards
E534 Standard Test Methods for Chemical Analysis of Sodium Chloride

Other Standards
Clear Roads Document - Clear Roads Snow and Ice Control Chemical Products, Specifications, and Test Protocols (https://clearroads.org/wp-content/uploads/12-10-Final-CR-SPECS-wCategory4.pdf).

3 Apparatus and Reagents

3.1 *Analytical Balance*

3.2 *Desiccator*

3.3 *Oven*

4 Procedure

4.1 Weigh 100g of salt to the nearest 0.01g (split or quartered from original sample) into a previously dried and weighed moisture dish or pan. Distribute the salt in the vessel such that it is not more than 1/4 of an inch in depth at any given location.

4.2 Dry at 110°C for 2 hours.

4.3 Cool to room temperature in a desiccator and weigh.

5 Calculation and Reporting

5.1 Calculate the percentage of moisture as follows:

$$moisture, mass\ \% = \frac{(I - F)}{I} * 100$$

where:

F = final mass of the dry salt
I = initial mass of the wet salt

5.2 Report the insoluble residue to the nearest 0.01%.

6 Validation Data

6.1 Precision and Bias

Moisture %	$\sigma_{(n-1)}$ %	n	95% CL %	Intra Laboratory $\sigma_{(n-1)}$ %	Intra Laboratory n	Intra Laboratory 95% CL %	Inter Laboratory $\sigma_{(n-1)}$ %	Inter Laboratory n	Inter Laboratory 95% CL %
0-5.0%	0.005	29	0.03	0.006	3	0.03	0.006	6	0.04
5.1%-10.0%	0.008	31	0.05	0.008	3	0.06	0.009	6	0.06

METHODS OF SAMPLING AND TESTING
MT 530-16
DETERMINATION OF CHLORIDE IN BRIDGE DECK CONCRETE BY ION CHROMATOGRAPHY
(*Montana Method*)

1 Scope

1.1 This method describes the procedure used to determine the concentration of acid-soluble chloride in bridge deck concrete via ion chromatography.

1.2 This method may involve hazardous materials, operations, and equipment. This method 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
D1193 Standard Specification for Reagent Water

MT Materials Manual
MT 114 Sampling for Chloride Content of Bridge Deck Concrete

Other
Method Tex-620-J, Determining Chloride and Sulfate Contents in Soil
(http://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/600-J_series/archives/620-0805.pdf)

3 Terminology

3.1 *Chromatography* – the separation and quantitative analysis of ions based on their affinity to the ion exchanger.

3.2 *Eluent* – A solution that transports the sample through the system and contributes to the selectivity of the separation in the ion chromatograph.

4 Summary of Test Method

4.1 The chloride ion is extracted from concrete samples, put into solution, centrifuged, filtered and injected into the Ion Chromatograph (IC). The sodium carbonate/bicarbonate eluent transports the sample through the column which is operating with a suppressed conductivity method. The ion chromatograph detects chloride ions which interface with the column and are read on the instrument's conductivity detector.

5 Significance and Use

5.1 This procedure is used to determine the concentration of the chloride ion in concrete samples collected from bridge decks. The chloride ion concentration is used to evaluate the level of corrosion and determine the maintenance requirement for bridge decks.

6 Apparatus

6.1 *Metrohm Basic Ion Chromatograph Plus 883* equipped with:

6.1.1 Autosampler

6.1.2 Metrosep A Supp 150/4.0 Column

6.1.3 Conductivity Detector

6.1.4 MagIC Net Software

6.2 *Centrifuge*

7 Reagents and Materials

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

7.2 *Suppressor Regenerant Solution*, 0.1 Molar Sulfuric Acid (H_2SO_4)

7.3 *Suppressor Rinse Solution,* 99.9% MeOH

7.4 *Neutralizing Solution*, 0.5 M Sodium Hydroxide (aqueous)

Add 500mL of reagent water to a 750 or 1000mL glass beaker and slowly add 9.99 g of solid NaOH pellets to the reagent water and mix.

7.5 *Eluent*, 3.2 M Sodium Carbonate, Na_2CO_3/1.0 M Sodium Bicarbonate, $NaHCO_3$ (aqueous); (stock eluent solution, A Supp 5 Eluent 100x, ordered from Metrohm). Shelf life of eluent is 2 days.

7.6 *Nitric Acid (HNO_3),* concentrated Trace Metal Grade, 65-75%

7.7 *Standard Stock Solution*, Dionex Five Anion Standard, chloride concentration of 30 ppm

7.7 *Glassware*: 50 mL beakers, 100mL volumetric flasks for dilution

7.8 *Auto-pipettes*

7.9 *Plastic Syringes*, 30 mL non-sterile

7.10 *Syringe filters* - particle retention of 0.2 µm

7.11 *Dry plastic bottles* that have been stored filled with a dilute HNO_3 acid solution (1 – 5%) prior to use

7.12 *Disposable IC vials*, 11 ml

8 Sampling

8.1 Bridge deck concrete samples are collected in accordance with MT 114 and pulverized in a Bico pulverizer with plates spaced between 1 and 2 mm.

9 Calibration and Standardization

9.1 *IC Instrumentation Settings:*

9.1.1 Flow rate on IC: 0.7 mL/min

9.1.2 Sample Loop: 20 µL

9.1.3 Run time: 20 minutes

9.2 *Calibration Curve Determination*

9.2.1 Prepare standards from a five anion standard. The Dionex Five Anion Standard with a chloride concentration of 30 ppm is commonly used.

9.2.2 Weigh indicated masses from the 5 anion standard bottle into a dry plastic bottle (See Table 1). Record weights to the thousandth decimal place.

9.2.3 Dilute with reagent water for a target total mass of 50 g (± 0.001)

Table 1: Standard calibration solutions and masses of components

Concentration, ppm	Mass of 5 anion standard, g	Mass of solution, g
0.5	0.834	50.000
1.0	1.667	50.000
2.0	3.334	50.000
4.0	6.667	50.000
5.0	8.334	50.000
10.0	16.668	50.000

Note 1 - The masses in Table 1 above have been developed for the Dionex Five Anion Standard which has a chloride concentration of 30 ppm, if another standard is used the weights in the table are not applicable

9.2.4 Determine concentration of each standard and enter into the IC software.

10 Procedure

10.1 *Preparation of Controls*

10.1.1 For each sequence to be analyzed on the IC, prepare and analyze a quality control (QC) sample. Use a QC sample with a concentration which is mid-range of the calibration curve. For example, chloride standard preparations range from 0.5 ppm to 10 ppm. A QC sample with a target of approximately 3 ppm is sufficient. Using a Portland cement with a qualified standard of 0.127% is an acceptable QC sample. Determine percent recovery per Section 11.5 below. Analysis is considered acceptable with a percent recovery on the quality control sample of ±10%.

10.2 *Sample Preparation and Analysis*

10.2.1 Weigh 0.25 g of sample into a 50 – 60 mL beaker using a balance with an accuracy of ± 0.0001 g. Record the sample weight to be used in final calculation (W_s). Add 1 mL of reagent water to the beaker to liquefy the cement sample.

10.2.2 In a fume hood, add 100 µL of concentrated HNO_3 to the cement paste and and swirl gently to mix well. CO_2 gas liberates from the reaction between the cement constituents and nitric acid. Wait roughly 10 minutes for the extraction to occur.

10.2.3 Neutralize the solution by adding approximately 1.5 mL of 0.5 M NaOH (2-4 mL may be needed). Test with litmus paper strips to make sure the solution is neutral.

10.2.4 Transfer the neutral solution into a 100 mL volumetric flask (V), rinsing the beaker to transfer the solids from the beaker to the flask. Dilute to the fill line with reagent water.

10.2.5 Pour approximately 10 mL of the solution into a plastic syringe equipped with a 0.2 µm nylon filter tip. Filter the solution into a plastic ion chromatography test tube.

Note 2 – If the turbidity of the sample is such that light cannot pass through it, then centrifuge the sample at 500 rpm for roughly 15 minutes in a plastic nunc tube prior to pouring the sample into the IC vial centrifuge.

10.6 Analyze the sample and the QC sample simultaneously on the IC to determine the chloride concentration. Shelf life of the sample is one week.

11 Calculation or Interpretation of Results

11.1 *Dilution Factor*

$$DF = \frac{Vf}{Vi}$$

Where:
DF = Dilution factor
Vf = Final volume (diluent and aliquot)
Vi = initial volume

11.1.1 Dilution Factor for Concrete Sample

The dilution factor (DF) for the concrete sample is the volume of the volumetric flask used in Section 10.2.4 (i.e., 100 mL).

11.2 *Chloride Concentration in Concrete*

$$Ccl = \frac{(Cic * DF)}{Ws}$$

Where:
C_{cl} = Concentration of the chloride in the original concrete, ppm
C_{ic} = Concentration of the chloride as determined by the IC, ppm
DF = Dilution factor
W_s = Weight of the sample, g

11.2.1 Example: C_{ic} = 2.78 mg/L (*or ppm)*
DF = 100
W_s= *0.2529 g*

C_{cl}= *(*2.78*100)/0.2529 = 1099 ppm

11.3 *Percent Chloride in Concrete*

$$\%Cl = \frac{Ccl}{10{,}000}$$

11.3.1 Example: C_{cl} *= 1099 ppm (from above)*

%Cl = 1099/10,000 = 0.1099%

11.4 *Pounds of Chloride per cubic yard of Concrete*

$$Pc = \frac{(Ccl * Dc)}{1{,}000{,}000}$$

Where:
P_c = Pounds of chloride per cubic yard of concrete
C_{cl} = Concentration of chloride ions in the original concrete sample, ppm
D_c = Density of concrete (4,000 lb/cy)

11.5 *Percent Recovery of Quality Control Sample*

$$\% \text{ Recovery} = [C_{IC(QC)} * DF / W_{QC} / 10{,}000 / C_{QC}] * 100\%$$

Where:
$C_{IC(QC)}$ = Concentration of the Quality Control Sample as determined by the IC, ppm
C_{QC} = Known value of the quality control sample
DF = Dilution factor
W_{QC} = Weight of the Quality Control Sample, g

11.5.1 Example: *$C_{IC(QC)}$ = 3.15 ppm*
DF = 100
W_{QC}= 0.2529g
C_{QC} = 0.127%

*% Recovery = [3.15*100/0.2529/10,000/0.127]*100 = 98.07%*

12 Report

12.1 Enter chloride analysis results in the following location:
X:\CHEMISTRY\LAB\Bridge Chlorides 20XX.xlsx

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METHODS OF SAMPLING AND TESTING
MT 532-16
DETERMINATION OF SULFATE CONTENT IN SOILS BY ION CHROMATOGRAPHY

1 Scope

1.1 This method describes the procedures used to determine water-soluble sulfate in soils through the use of the ion chromatograph (IC).

1.2 This method was developed as an alternative to the sulfate analysis in MT 232 and was validated June 2016.

1.3 This method may involve hazardous materials, operations, and equipment. This method 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
C1580 Standard Test Method for Water-Soluble Sulfate in Soil
D1193 Standard Specification for Reagent Water

MT Materials Manual
MT 232 Soil Corrosion Test

Other
TX DOT, Tex-620-J, Determining Chloride and Sulfate Contents in Soil (http://ftp.dot.state.tx.us/pub/txdot-info/cst/TMS/600-J_series/archives/620-0805.pdf)
Validation of Sulfate Method on the Ion Chromatograph, MDT, June 2016.

3 Summary of Test Method

3.1 Soils are dissolved in water and analyzed on the ion chromatograph. This method is substantially based on ASTM C1580 and the Texas Department of Transportation Method Tex-620-J. The method of analysis can be used for both solid soil and water samples. The samples are dissolved or diluted in water, filtered and injected into the IC instrument. A calibration curve is prepared on the IC using a five anion standard. Sulfate results are obtained in ppm as determined by the IC.

4 Significance and Use

4.1 This procedure is used to determine sulfate content in soil samples for pipe corrosion evaluation and soil survey samples.

5 Apparatus

5.1 *Metrohm Basic Ion Chromatograph Plus 883* equipped with:

5.1.1 Autosampler

5.1.2 Metrosep A Supp 150/4.0 Column

5.1.3 Conductivity Detector

5.1.4 MagIC Net Software

6 Reagents and Materials

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

6.2 *Suppressor Regenerant Solution*, 0.1M Sulfuric Acid, H_2SO_4 (aqueous)

6.3 *Suppressor Rinse Solution*, 99.9% MeOH

6.4 *Eluent*, 3.2 M Sodium Carbonate, Na_2CO_3/1.0 M Sodium Bicarbonate, $NaHCO_3$ (aqueous); (stock eluent solution, A Supp 5 Eluent 100x, ordered from Metrohm and kept in-house).

6.5 *Standard Stock Solution*, Dionex Five Anion Standard, Sulfate concentration of 150 mg/L

6.6 *Glassware*: 250 mL beakers and large glass centrifuge tubes

6.7 *Class A pipettes*, for secondary dilution

6.8 *Plastic Syringes*, 30 mL non-sterile

6.9 *0.20 µm nylon filters*, non-sterile

7 Sampling

7.1 Samples are prepared in accordance with MT 232. A 3 gram (g) sample is required for analysis.

8 Calibration and Standardization

8.1 *IC Instrumentation Settings*

8.1.1 Flow rate on IC: 0.7 mL/min

8.1.2 Sample Loop: 20 µL

8.1.3 Run time: 20 minutes

8.2 *Calibration Curve Determination*

8.2.1 Prepare six standards based on the indicated concentrations and masses in Table 1 using the Dionex Five Anion Standard. The values for the sulfate calibration curve range from approximately 2.5 ppm and 50 ppm.

8.2.2 Weigh the standard into a plastic bottle. Record weights to the thousandth decimal place.

8.2.3 Dilute the standard to a target total mass of 50 (±0.001g) with reagent water. Record the final weight.

Table 1: Standard calibration solutions and masses of components

Concentration, ppm	Mass of 5 anion standard, g	Mass of solution, g
2.5	0.834	50.000
5	1.667	50.000
10	3.334	50.000
20	6.667	50.000
25	8.334	50.000
50	16.668	50.000

Note 1 - The masses in Table 1 above have been developed for the Dionex Five Anion Standard which has a sulfate concentration of 150 ppm, if another standard is used the weights in the table are not applicable

8.2.4 Inject the six prepared standards and utilize the instrumentation on the IC to develop a calibration curve.

9 Procedure

9.1 *Preparation of Controls*

For each sequence to be analyzed on the IC, prepare a Quality Control (QC) sample in the target range of approximately 20 ppm. Use a qualified soil standard with a known concentration of 1630 ppm (±43.7 ppm) to prepare the control. Determine percent recovery per Section 10.4 below. Analysis is considered acceptable with a percent recovery on the control sample of ±10%.

9.2 *Sample Preparation and Analysis*

9.2.1 Weigh 3 grams of sample from the remaining material used for the conductivity preparation in MT 232 into a 250 ml glass beaker. Record the weight to the thousandth decimal place (W_s).

9.2.2 Add 150 mL of reagent water and mix with a stir bar for an hour.

9.2.3 Pour approximately 20 mL of the liquid extract into a syringe with attached 0.20 µm nylon filter. Filter this extract directly into plastic ion chromatography test tube and cap.

9.2.4 Analyze the sample and the QC sample simultaneously on the IC to determine the sulfate concentrations.

Note 2 – A secondary dilution may be necessary if concentration falls outside of the range determined by the calibration curve.

10 Calculation or Interpretation of Results

10.1 *Dilution Factor*

$$DF = \frac{Vf}{Vi}$$

Where:
DF = Dilution factor
Vf = Final volume (diluent and aliquot)
Vi = initial volume

10.1.1 Dilution Factor for Secondary Dilution

$$DF = \frac{Vd}{Vp}$$

Where:
DF = Dilution factor
Vd = Volume of the flask used for the dilution, mL
Vp = Volume of the pipette used to make the dilution, mL

10.2 *Concentration of sulfate ion in the original soil sample*

$$C_{SO4} = (C_{IC}*DF)/W_s$$

Where:
C_{SO4} = Concentration of the sulfate in the original soil sample, ppm
C_{IC} = concentration of sulfate ion in the sample run through the IC, ppm
DF = Dilution factor
W_s = Weight of the sample, g

10.2.1 Example: C_{IC} = 2.948 mg/L (*or ppm)*
DF = 150
W_s= *3.0041 g*

C_{SO4}= *(*2.948*150)/3.0041 = 147.2 ppm

10.3 *Percent Sulfate in Soil*

$$\% SO_4 = C_{SO4}/10{,}000$$

10.4 *Percent Recovery Quality Control Sample*

$$\% \text{ Recovery} = [C_{IC(QC)}*DF/W_{QC}/10{,}000/C_{QC}]*100\%$$

Where:
$C_{IC(QC)}$ = Concentration of the soil standard sample as determined by the IC, ppm
C_{QC} = Known value of the soil standard (soil standard typically is 1630 ppm SO_4), ppm
DF = Dilution factor
W_{QC} = Weight of the quality control sample, g

10.4.1 Example: $C_{IC(QC)}$ = 31.96 ppm
DF = 50
W_{QC}= *1.004 g*
C_{QC} = *1630 ppm*

% Recovery = [31.96*50/1.004/1630]*100 = 98.07%

11 Report

The concentration of the sulfate will be recorded in the soil corrosion spreadsheets and the Sitemanager data base as percent sulfate.

METHODS OF SAMPLING AND TESTING
MT 533-16
METHOD OF TEST FOR CHEMICAL ANALYSIS OF FLY ASH AND POZZOLANS VIA SPECTROPHOTOMETRY
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides and sulfur trioxide of fly ash and pozzolans for use in Portland Cement. Three test procedures are described in this document:

1.1.1 Spectroscopic Determination of Elemental Oxides in Fly Ash and Pozzolans

1.1.2 Spectroscopic Determination of Sulfur Trioxide in Fly Ash and Pozzolans

1.1.3 Spectroscopic Determination of Silicon Dioxide in Fly Ash and Pozzolans

1.2 This test method also denotes reference test methods:

1.2.2 Moisture of Fly Ash and Pozzolans – ASTM C311 Sections 11 and 12

1.2.1 Loss on Ignition of Fly Ash and Pozzolans – ASTM C311 Sections 13 and 14

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM

C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
C150 Standard Specifications for Portland Cement
C311 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
D1193 Standard Specification for Reagent Water
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Practice for Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus
STP 985 Rapid Methods for Chemical Analysis of Hydraulic Cement

FHWA

FHWA-RD-72-41 A New Method for Rapid Cement Analysis (Atomic Absorption Spectrophotometry)

MT Materials Manual

MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *Spectroscopic Determination of Elemental Oxides in Fly Ash and Pozzolans Summary of Test Method*

In this test method fly ash or pozzolans are dissolved in a combination of acids via a digestion in Teflon vessels secured in a microwave digestion system. The solution is diluted and analyzed by means of an Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES). The following analytes are quantified as oxides: calcium, magnesium, iron, aluminum, potassium, and sodium.

3.2 *Spectroscopic Determination of Sulfur Trioxide in Fly Ash and Pozzolan Summary of Test Method*
This test method is substantially based on the publications ASTM STP 985, FHWA-RD-72-41 and the reference test method of ASTM C114. In this method, sulfur is extracted from fly ash or pozzolans using nitric acid and hydrogen peroxide and then quantified via ICP-OES analysis. This procedure is valid for the analysis and reporting of sulfur trioxide.

3.3 *Spectroscopic Determination of Silicon Dioxide in Fly Ash and Pozzolans Summary of Test Method*
This test method is substantially based on the publications ASTM STP 985 and FHWA-RD-72-41. In this method, the fly ash or pozzolan is solubilized by fusion with a mixed lithium metaborate and lithium tetraborate powder. The molten glass bead is dissolved in a weak nitric acid solution and analyzed by ICP-OES.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the fly ash and pozzolan samples submitted by suppliers for inclusion on the MDT Qualified Product List as well as provide analytical information for design applications using fly ash or pozzolans.

5 Apparatus

5.1 *Inductively Coupled Plasma-Optical Emission Spectrophotometer* (ICP-OES)

5.2 *Microwave digestion system* – Capable of heating samples to 200°C and maintaining that temperature for at least 30 minutes.

5.3 *Labware* – Glassware, Teflon, and Plasticware containers that have been properly cleaned and stored filled with dilute nitric acid solution (1 – 5%) for at least 2 days.

5.4 *Analytical Balances* – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

5.5 *Muffle Furnace* – Capable of maintaining a temperature of 950°C ± 25° verified by clay pyrometric cones yearly.

6 Reagents and Materials

6.1 *Trace metal grade (TMG) Hydrochloric acid (HCl),* concentrated (32-38%)

6.2 *TMG Nitric acid (HNO_3),* concentrated (65-70%)

6.3 *Fluoroboric acid (HBF_4)*, concentrated (46-52%)

6.4 *Hydrogen Peroxide (H_2O_2)*, concentrated (30-38%)

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

6.6 *Filter paper* – Particle retention of 20 – 25 µm and a medium flowrate.

6.7 *Ultra-pure Grade Lithium Borate Flux* – composed of 66 ±10% Lithium tetraborate ($Li_2B_4O_7$), 33 ±10% lithium metaborate ($LiBO_2$) and 1 ±1% lithium bromide (LiBr)

7 Sampling

7.1 Fly ash or pozzolan samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN FLY ASH AND POZZOLANS

8 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix A provides calibrating and standardizing specifications for a Varian Axial ICP-OES for the determination of elemental oxides.

9 Procedure

9.1 Weigh 0.1000 g ± 0.0005 g of fly ash or pozzolan onto tared waxed paper or a small weighing boat. Record the mass.

9.2 Transfer the sample to a Teflon insert for microwave digestion. Reweigh the waxed paper or weighing boat and note the residual mass from the sample. Record the residual mass and calculate the mass transferred to the Teflon insert.

9.3 In a ventilation hood, add 10 mL TMG Hydrochloric acid, 4 mL TMG Nitric acid, and 4 mL Fluoroboric acid to the Teflon insert using autopipets with disposable tips. Place the Teflon insert in the carousel.

9.4 Once all samples have been prepared, place the carousel in the microwave digestion system. Begin the digestion process (see Appendix A for MDT digestion process). After completion of the digestion process, allow the carousel to cool before removing. The carousel may be left overnight to cool.

9.5 Remove a digestion vessel and open it. Rinse the sample into a clean Teflon beaker. Tare a dry 500 mL plastic volumetric flask. Rinse the solution from the beaker into the plastic volumetric flask. Place the plastic volumetric flask on the balance and add reagent water to a mass of 500.00 g ± 0.05 g. Cap the plastic volumetric flask and invert it several times to homogenize the solution.

9.6 Pour some of the solution into a plastic sample bottle for a stock solution. Label the container with the sample number, date, analyst initials, and as fly ash or pozzolan stock solution.

9.7 Dilute the stock solution by dispensing 1.50 g ± 0.03 g of the solution into a 15 mL centrifuge tube and add reagent water until the mass is 15.00 g ± 0.03 g. Label the centrifuge tube with the sample number, date, analyst initials, and as fly ash or pozzolan dilute solution.

9.8 Repeat Sections 9.5 to 9.7 for all samples.

9.9 Analyze the dilute solutions on an ICP-OES.

SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN FLY ASH AND POZZOLANS

10 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix B provides calibrating and standardizing specifications for a Agilent Radial ICP-OES for the determination of sulfur trioxide.

11 Procedure

11.1 Weigh 0.5000 g ± 0.0005 g fly ash or pozzolan directly into a dry 250 mL beaker.

Note – If a thick walled beaker is used that is too heavy for the balance, the cement can be weighed on waxed paper or a small weighing boat and transferred. Reweigh the waxed paper or weighing to account for any cement that may have stuck to it.

11.2 Add 5.0 mL of hydrogen peroxide using an autopipet to each beaker.

11.3 Bring the solution to the 100 mL mark on the beaker with reagent water.

11.4 Add 10.0 mL of nitric acid to the beaker using an autopipet.

11.5 Add a Teflon stir bar and place on a stir plate to agitate for a minimum of 60 minutes. A good stir rate is about two revolutions per second.

11.6 Quantitatively filter into a 500 mL glass volumetric flask and rinse many times with reagent water.

11.7 Bring to volume with reagent water.

11.8 Transfer the solution to a 500 mL HDPE bottle. Label with the sample number, the date, analyst initials, and analyte of interest.

11.9 Once all the samples are prepared, analyze the solutions using the ICP-OES.

SPECTROSCOPIC DETERMINATION OF SILICON DIOXIDE IN FLY ASH AND POZZOLANS

12 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix C provides calibrating and standardizing specifications for a ICP-OES for the determination of silicon dioxide.

13 Procedure

13.1 Weigh 0.8000 g ± 0.005 g of lithium borate flux into a graphite crucible.

13.2 Tare the flux and crucible and add 0.1000 g ± 0.0005 g fly ash or pozzolan on top of the flux.

13.3 Fuse the graphite crucible(s) containing the samples in the muffle furnace at 950°C for 5 minutes. Do not fuse more than two crucibles at a time. Swirl the crucible to consolidate all residual sample that may be sticking to the sides of the crucible. Continue fusing for an additional 15 minutes at 950°C.

13.4 Prior to or during the fusion process, prepare an adequate number of Teflon beakers (at least 200 mL) by rinsing them copiously with reagent water. Add 50 mL of 1 + 24 nitric acid to the beakers. Place a Teflon stir bar in each beaker and cover each with a watch glass. Place the beakers on a stir plate near the furnace and stir at a rate of about two revolutions per second.

13.5 At the completion of the fusion process, quickly transfer the fusion bead from the graphite crucible to one of the prepared Teflon beakers. Inspect the graphite crucible for any trace of sample or fusion material; discard the sample if either are present. Replace the watch glass on the beaker and stir for a minimum of 30 minutes or until all material is dissolved. More acid may be needed to completely dissolve the fusion bead; add the same amount of acid to each sample in order to maintain the same acid content. If additional acid results in material coming out of solution, the sample is not suitable for analysis; discard the sample.

13.6 Once all the material has dissolved, prepare the stock solution by transferring the solution to a 500 mL class A volumetric flask. Bring to volume with reagent water and add nitric acid such that the concentration of nitric acid will be 15 + 485. Cover the flask with Parafilm and invert a minimum of eight times to thoroughly mix.

13.7 Transfer the stock solution to a plastic sample bottle; discard any excess solution. Label the container with the sample number, fly ash or pozzolan, Si analysis, stock solution, date, and analyst initials.

13.8 Once all the samples are prepared, analyze the stock solutions on an ICP-OES.

14 Report

14.1 Data Reporting and Retention for fly ash or pozzolans will be reported as shown below:

Analyte	Report As	Significance
Ca	CaO	XX.XX
Al	Al_2O_3	X.XX
Fe	Fe_2O_3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
K	K_2O	X.XXX
Na	Na_2O	0.XXX
S	SO_3	X.XX
LOI	LOI	X.XX
Moisture	Moisture	X.XX

15 Validation

15.1 For validation data and quality control information consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN FLY ASH OR POZZOLANS

Varian Axial ICP-OES configuration parameters

Equipment Configuration
Nebulizer: Sea Spray
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids with sheath gas
Sheath gas: Argon at 10mL/min
Power: 1.20 kW
Plasma flow: 15.0 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.75 L/min
Replicate read time: 6.00s
Instrument stabilization delay: 15s
Sample uptake delay: 30s
Pump rate: 15 rpm
Rinse time: 120s
Fast pump: yes
Replicates: 5

Line Selection for Standards, Samples, and Blanks: Select the best line(s) and average for each element.
Al: 396.152, 394.401, 309.271, and 257.509.
Ca: 393.366, 370.602, 318.127, 317.933, 315.887, 219.779, and 210.324.
Fe: 273.358, 261.187, 260.709, 259.940, and 238.204.
Mg: 285.213, 280.270, 279.553, and 202.582.
K: 766.491 and 769.897.
Na: 589.592 and 588.995.

Calibration Varian Axial ICP-OES
Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL pozzolan standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

Milestone Ethos EZ microwave digestion system

Digestion program used: portcement.mpr

Heat and time: Heat to 200°C and hold temperature during a 30 minute interval. Followed by a 10 minute cooling period

Rotor: SK-10

APPENDIX B
SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN FLY ASH OR POZZOLANS

Agilent Radial ICP-OES configuration parameters

Equipment Configuration
Nebulizer: OneNeb
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids
Power: 1.00 kW
Plasma flow: 15.00 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.75 L/min
Viewing height: 10 mm
Replicate read time: 10.00 s
Instrument stabilization delay: 15s
Sample uptake delay: 30s
Pump rate: 15rpm
Rinse time: 10s
Fast pump: yes
Replicates: 3

Line Selection for Standards, Samples, and Blanks: Select the best line(s) and average for each element.
S : 180.669, 181.972

Calibration Agilent Radial ICP-OES
Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL pozzolan standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

APPENDIX C
SPECTROSCOPIC DETERMINATION OF SILICON DIOXIDE IN FLY ASH OR POZZOLANS

Agilent Radial ICP-OES configuration parameters

Equipment Configuration
Nebulizer: OneNeb
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids
Power: 1.10 kW
Plasma flow: 15.00 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.75 L/min
Viewing height: 10 mm
Replicate read time: 10.00 s
Instrument stabilization delay: 15s
Sample uptake delay: 45s
Pump rate: 15rpm
Rinse time: 10s
Fast pump: yes
Replicates: 3

Line Selection for Standards, Samples, and Blanks: Select the best line(s) and average for each element.
Si : 212.412

Calibration Agilent Radial ICP-OES
Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL pozzolan standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

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METHODS OF SAMPLING AND TESTING
MT 534-16
CHEMICAL ANALYSIS OF PORTLAND CEMENT VIA SPECTROPHOTOMETRY
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides and sulfur trioxide of Portland cement. Two test procedures are described in this document:

1.1.1 Spectroscopic Determination of Elemental Oxides in Portland Cement

1.1.2 Spectroscopic Determination of Sulfur Trioxide in Portland Cement

1.2 This test method also denotes reference test methods:

1.2.1 Loss on Ignition of Portland Cement – ASTM C114, Section 18

1.2.2 Insoluble Residue of Portland Cement – ASTM C114, Section 7

1.2.3 Carbon Dioxide Determination in Portland Cement – ASTM C114, Section 24

1.2.4 Sulfide Determination in Portland Cement – ASTM C114, Section 17

1.2.5 Halogen Determination in Portland Cement – No current validated method

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM

C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
C150 Standard Specifications for Portland Cement
D1193 Standard Specification for Reagent Water
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Practice for Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus
STP 985 Rapid Methods for Chemical Analysis of Hydraulic Cement

FHWA

FHWA-RD-72-41 A New Method for Rapid Cement Analysis (Atomic Absorption Spectrophotometry)

MT Materials Manual

MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *Spectroscopic Determination of Elemental Oxides in Portland Cement Summary of Test Method* In this test method, Portland cement is dissolved in a combination of acids via a microwave digestion system. The solution is then diluted and analyzed by an Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES). The following analytes are quantified as oxides: calcium, magnesium, silicon, iron, aluminum, potassium, titanium, sodium, manganese, zinc, chromium, and phosphorus.

3.2 *Spectroscopic Determination of Sulfur Trioxide in Portland Cement Summary of Test Method* This test method is substantially based on the publications STP 985, FHWA-RD-72-41, and ASTM C114. In this method, sulfur is extracted from Portland cement using nitric acid and hydrogen peroxide and then quantified via ICP-OES analysis. This procedure is valid for the analysis and reporting of sulfur trioxide.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the Portland cement submittals for suppliers on the MDT Qualified Product List as well as provide analytical information for design applications using Portland cement.

5 Apparatus

5.1 *Inductively Coupled Plasma-Optical Emission Spectrophotometer* (ICP-OES)

5.2 *Microwave digestion system* – Capable of heating samples to 200°C and maintaining that temperature for at least 30 minutes.

5.3 *Labware* – Glassware, Teflon, and Plasticware containers that have been properly cleaned and stored filled with dilute nitric acid solution (1 – 5%) for at least 2 days.

5.4 *Analytical Balances* – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

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 65-70%.

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

6.4 *Hydrogen Peroxide (H_2O_2)* – Any commercially available brand at a concentration of 30-38%.

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

6.6 *Filter paper* – Particle retention of 20 – 25 µm and a medium flowrate.

7 Sampling

7.1 Cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT

8 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix A provides calibrating and standardizing specifications for an Agilent Radial ICP-OES for the determination of elemental oxides.

9 Procedure

9.1 Weigh 0.2000 g ± 0.0005 g Portland cement onto tared waxed paper or small weighing boat. Record the mass.

9.2 Transfer the sample to a Teflon insert for microwave digestion. Reweigh the waxed paper or weighing boat and note the residual mass from the sample. Record the residual mass and calculate the mass transferred to the Teflon insert.

9.3 In a ventilation hood, add 10 mL TMG Hydrochloric acid, 4 mL TMG Nitric acid, and 4 mL Fluoroboric acid to the Teflon insert using autopipets with disposable tips. Place the Teflon insert in the carousel.

9.4 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.

9.5 After completion of the digestion process, allow the carousel to cool before removing. The carousel may be left overnight to cool.

9.6 Remove 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 until a mass of 100.00 g ± 0.05. Record the mass to nearest 0.01 g.

9.9 Label the sample bottle with the sample number, date, analyst initials, and as Portland cement stock solution.

9.10 Using the stock solution, prepare a dilute solution for the analysis of silicon and calcium oxides. In a centrifuge tube, dilute the stock solution at a ratio of 1:5 with reagent water. Label the centrifuge tube with the sample number, date, analyst initials, and as Portland cement dilute solution.

9.11 Once all the samples have been prepared, analyze the dilute and stock solutions on an ICP-OES.

SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN PORTLAND CEMENT

10 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix B provides calibrating and standardizing specifications for an Agilent Radial ICP-OES for the determination of sulfur trioxide.

11 Procedure

11.1 Weigh 0.5000 g ± 0.0005 g Portland cement directly into a dry 250 mL beaker.

Note – If a thick walled beaker is used that is too heavy for the balance, the cement can be weighed on waxed paper or a small weighing boat and transferred. Reweigh the waxed paper or weighing to account for any cement that may have stuck to it.

11.2 Add 5.0 mL of hydrogen peroxide using an autopipet to the beaker.

11.3 Bring the solution to the 100 mL mark on the beaker with reagent water.

11.4 Add 10.0 mL of nitric acid to the beaker using an autopipet.

11.5 Add a Teflon stir bar and place on a stir plate to agitate for a minimum of 60 minutes. A good stir rate is about two revolutions a second.

11.6 Quantitatively filter the sample into a 500 mL glass volumetric flask rinsing many times with reagent water.

11.7 Bring to volume with reagent water.

11.8 Transfer the solution to a 500 mL HDPE bottle. Label with the sample number, the date, analyst initials, and analyte of interest.

11.9 Once all the samples are prepared, analyze the solutions using the ICP-OES.

12 Calculation or Interpretation of Results

12.1 Portland Cement Potential Phase Composition Calculations

12.1.1 Refer to ASTM C150 Annex A1.

12.2 Portland Cement Limestone Content Calculation

12.2.1 Refer to ASTM C150 Annex A2.

12.3 Equivalent Alkalis Calculation for Portland Cement

12.3.1 Refer to ASTM C150 Section 4 Table 2.

13 Report

13.1 Data Reporting for Portland Cement will be reported as shown below:

Analyte	Reported As	Significance
Ca	CaO	XX.XX
Al	Al_2O_3	X.XX
Fe	Fe_2O_3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
Ti	TiO_2	0.XX
Cr	Cr_2O_3	0.0XX
K	K_2O	X.XXX
Mn	Mn_2O_3	0.XXX
Na	Na_2O	0.XXX
P	P_2O_5	0.XXX
Zn	ZnO	0.XXX
S	SO_3	X.XX
S-	S-	X.XX
LOI	LOI	X.XX
ISR	ISR	0.XX
CO_2	CO_2	X.XX
Lime Content	Lime Content	X.X
C_3S	C_3S	XX.X
C_2S	C_2S	XX.X
C_3A	C_3A	X.X
C_4AF	C_4AF	XX.X
Alkalinity	Alkalinity	X.XX
Cl-	Cl-	0.0XX
F-	F-	0.XX

14 Validation

14.1 For validation data quality control information consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT

Milestone Ethos EZ microwave digestion system

Digestion program used: portcement.mpr

Heat and time: Heat to 200°C and hold temperature during a 30 minute interval. Followed by a 10 minute cooling period

Rotor: SK-10

Agilent Radial ICP-OES configuration parameters

Equipment Configuration for Ca and Si

a. Nebulizer: One Neb
b. Spray chamber: cyclonic
c. Sample pump tubing: Gray/Gray
d. Waste pump tubing: Blue/Blue
e. Rinse solution: 5% Nitric acid
f. Torch: High solids
g. Power: 1.20 kW
h. Plasma flow: 15.00 L/min
i. Auxiliary flow: 1.50 L/min
j. Nebulizer flow: 0.60 L/min
k. Viewing height: 10 mm
l. Replicate read time: 1.00 s
m. Instrument stabilization delay: 15 s
n. Sample uptake delay: 30 s
o. Pump rate: 15 rpm
p. Rinse time: 10 s
q. Fast pump: yes
r. Replicates: 8

Equipment Configuration for all other analytes

a. Nebulizer: One Neb
b. Spray chamber: cyclonic
c. Sample pump tubing: White/White
d. Waste pump tubing: Blue/Blue
e. Rinse solution: 5% Nitric acid
f. Torch: High solids
g. Power: 1.15 kW
h. Plasma flow: 15.00 L/min
i. Auxiliary flow: 1.50 L/min
j. Nebulizer flow: 0.75 L/min
k. Viewing height: 8 mm
l. Replicate read time: 1.00 s
m. Instrument stabilization delay: 15 s
n. Sample uptake delay: 45 s
o. Pump rate: 15 rpm
p. Rinse time: 40 s
q. Fast pump: yes
r. Replicates: 5

Line Selection for Standards, Samples, and Blanks: Select the best line(s) and average for each element.

a. Ca : 210.324, 219.779, 315.887, 317.933, 318.127, 370.602, 393.366
b. Al: 309.271
c. Fe: 261.187
d. Mg: 280.270
e. Si: 185.005, 185.185, 250.690, 251.611, 251.920, 252.411, 252.851, 288.158
f. Ti: 334.941
g. Cr: 267.716
h. K: 766.491
i. Mn: 257.610
j. Na: 589.592
k. P: 213.618
l. Zn: 213.857

Calibration Agilent Radial ICP-OES

a. Type: Linear for all elements.
b. Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
c. Calibration Standard Selection: Pick NIST or CCRL Portland cement standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

APPENDIX B
SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN PORTLAND CEMENT

Agilent Radial ICP-OES configuration parameters

Equipment Configuration

a. Nebulizer: OneNeb
b. Spray chamber: cyclonic
c. Sample pump tubing: White/White
d. Waste pump tubing: Blue/Blue
e. Rinse solution: 5% Nitric acid
f. Torch: High solids
g. Power: 1.45 kW
h. Plasma flow: 15.00 L/min
i. Auxiliary flow: 1.50 L/min
j. Nebulizer flow: 0.55 L/min
k. Viewing height: 6 mm
l. Replicate read time: 3.00 s
m. Instrument stabilization delay: 15 s
n. Sample uptake delay: 30 s
o. Pump rate: 15 rpm
p. Rinse time: 10 s
q. Fast pump: yes
r. Replicates: 3

Line Selection for Standards, Samples, and Blanks: Select the best line(s) and average for each element

a. S : 180.669, 181.972

Calibration Agilent Radial ICP-OES

a. Type: Linear for all elements.
b. Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
c. Calibration Standard Selection: Pick NIST or CCRL Portland cement standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

METHODS OF SAMPLING AND TESTING
MT 536-16
CHEMICAL ANALYSIS OF SILICA FUME
(Montana Method)

1 Scope

1.1 This method describes the procedures to be used for determining chemical analytes in silica fume as recommended by AASHTO M 307 Standard Specification for Silica Fume Used in Cementitious Mixtures.

1.2 Spectroscopic Determination of Silicon Dioxide in Silica Fume – MT 533 Chemical Analysis of Fly Ash and Pozzolans

1.3 Moisture Content of Silica Fume – ASTM C311 sections 11 and 12

1.4 Loss on Ignition (LOI) of Silica Fume – ASTM C311 sections 13 and 14

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM
C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
C311 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete

AASHTO
M 307 Standard Specification for Silica Fume Used in Cementitious Mixtures

MT Materials Manual
MT 533 Chemical Analysis of Fly Ash and Pozzolans
MT 607 Procedure for Reducing Field Samples to Testing Size

3 Significance and Use

3.1 This procedure is primarily used to provide quality assurance for the silica fume submittals for suppliers on the MDT Qualified Product List as well as provide analytical information for design applications using silica fume.

4 Report

4.1 Data Reporting and Retention for Silica Fume will be reported as shown below:

Analyte	Report As	Significance
Si	SiO_2	XX.XX
Moisture	Moisture	X.XX
LOI	LOI	X.XX

5 Validation

5.1 For validation data and quality control information consult ASTM C114 and ensure all instruments meet its conditions.

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METHODS OF SAMPLING AND TESTING
MT 537-16
CHEMICAL ANALYSIS OF GROUND GRANULATED BLAST-FURNACE SLAG
(Montana Method)

1 Scope

1.1 This method describes the procedures to be used for determining chemical analytes of ground granulated blast-furnace slag (GGBFS) as recommended by AASHTO M 302 Slag Cement for Use in Concrete Mortars.

1.1.1 This method includes the procedures for the determination of chloride by Ion Chromatography (IC) and the following reference methods.

1.2 This test method also denotes reference test methods:

1.2.1 Spectroscopic Determination of Sulfur Trioxide – MT 533 Chemical Analysis of Fly Ash and Pozzolans

1.2.2 Sulfide Determination – Reference method in ASTM C114 Section 17.2.

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM
C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
D1193 Standard Specification for Reagent Water

AASHTO
M 302 Slag Cement for Use in Concrete Mortars

MT Materials Manual
MT 533 Chemical Analysis of Fly Ash and Pozzolans
MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 Chloride ions are extracted from GGBFS with nitric acid. The resulting sample solutions are analyzed on an Ion Chromatograph.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the GGBFS submittals by suppliers for inclusion on the MDT Qualified Product List as well as provide analytical information for design applications using GGBFS.

5 Apparatus

5.1 *Ion Chromatograph (IC)*

5.2 *Analytical Balance* – A balance with a precision of 0.0001 g should be used.

6 Reagents and Materials

6.1 *Trace metal grade (TMG) Nitric acid (HNO_3)*, concentrated (65-70%)

6.2 *Sodium Hydroxide (NaOH)*, concentration of 0.7 Molar

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

6.3 *Syringe filters* - particle retention of 0.2 µm

6.4 *Litmus paper* - capable of indicating basicity or acidity

7 Sampling

7.1 GGBFS samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

8 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the IC. Appendix A provides calibrating and standardizing specifications for a Metrohm 883 Basic IC plus for the determination of chloride.

9 Procedure

9.1 Weigh 0.2500 g ± 0.0005 g GGBFS into a 50 mL beaker. Record the mass.

9.2 Gently tap the materials to thinly spread it over the bottom of the beaker.

9.3 Mix 1 mL of reagent water and 200 µL of TMG Nitric Acid.

9.3 Add the acid/water mixture to the sample in a hood and gently break apart clumps using a glass rod.

9.4 Set the mixture on a warm hot plate for five minutes, intermittently grinding any clumps so the slag completely dissolves.

9.5 Remove the sample from the hot plate; let it cool for 10 minutes.

9.6 Add 1 mL of 0.7 M sodium hydroxide to the sample. Check the pH with litmus paper; continue adding sodium hydroxide or nitric acid until the pH is neutral.

9.7 Transfer the sample to a 100 mL volumetric flask and bring to volume with reagent water.

9.8 Using a syringe filter, transfer a sufficient amount of the sample to a vial for the IC.

9.9 Analyze the sample on the IC.

10 Report

10.1 Data Reporting and Retention for GGBFS will be reported as shown below:

Analyte	Report As	Significance
S	SO_3	X.XX
S-	S-	X.XX
Cl-	Cl-	0.0XX

11 Validation

11.1 For validation data and quality control information consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
CHLORIDE DETERMINATION IN GGBFS USING ION CHROMATOGRAPHY

Metrohm 883 Basic IC Plus configuration parameters

Equipment Configuration
Run time: 20 minutes
Injection volume: 20µL
Eluent: 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate

METHODS OF SAMPLING AND TESTING
MT 538-18
METHOD OF TEST FOR CHEMICAL ANALYSIS OF BLENDED CEMENT VIA SPECTROPHOTOMETRY
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides of blended cement samples.

1.1.1 Spectroscopic Determination of Elemental Oxides in Blended Cement

1.1.2 Spectroscopic Determination of Silicon Dioxide and Calcium Oxide in Blended Cement

1.1.3 Spectroscopic Determination of Sulfur Trioxide in Blended Cement

1.2 This test method also denotes reference test methods:

1.2.1 Loss on Ignition of Portland Cement – ASTM C114 Section 18

1.2.2 Standard Specification for Blended Hydraulic Cements – ASTM C595/C595M

1.2.3 Spectroscopic Determination of Elemental Oxides in Portland Cement

1.2.4 Insoluble Residue of Portland Cement – ASTM C114, Section 7

1.2.5 Sulfide Determination in Portland Cement – ASTM C114, Section 17

1.3 This standard does not purport to address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM

C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
C595/C595M Standard Specification for Blended Hydraulic Cements
D1193 Standard Specification for Reagent Water
E29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Standard Practice for Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus
STP 985 Rapid Methods for Chemical Analysis of Hydraulic Cement

FHWA

FHWA-RD-72-41 A New Method for Rapid Cement Analysis (Atomic Absorption Spectrophotometry)

MT Materials Manual

MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *Spectroscopic Determination of Elemental Oxides in Blended Cement Samples*

In this test method, blended cement samples are dissolved in a combination of acids via a digestion in Teflon vessels secured in a microwave digestion system. The solution is diluted and analyzed by means of an Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES). The following analytes are quantified as oxides: magnesium, iron, aluminum, potassium, manganese, titanium, zinc, chromium, phosphorus, strontium and sodium.

3.2 *Spectroscopic Determination of Silicon Dioxide and Calcium Oxide in Blended Cement Samples*

This test method is substantially based on the publications ASTM STP 985 and FHWA-RD-72-41. In this method, the blended cement is solubilized by fusion with a mixed lithium metaborate and lithium tetraborate powder. The produced molten glass bead is then dissolved in a weak nitric acid solution and analyzed by ICP-OES.

3.3 *Spectroscopic Determination of Sulfur Trioxide in Blended Cement*

This test method is substantially based on the publications ASTM STP 985, FHWA-RD-72-41 and the reference test method of ASTM C114. In this method, sulfur is extracted from blended cement using nitric acid and hydrogen peroxide and then quantified via ICP-OES analysis.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for blended cement samples submitted by suppliers for inclusion on the MDT Qualified Product List as well as provide analytical information for design applications using blended cement.

5 Apparatus

5.1 *Inductively Coupled Plasma-Optical Emission Spectrophotometer* (ICP-OES)

5.2 *Microwave digestion system* – Capable of heating samples to 200°C and maintaining that temperature for at least 30 minutes.

5.3 *Labware* – Glassware, Teflon, and Plasticware containers that have been properly cleaned and stored filled with dilute nitric acid solution (1 – 5%) for at least 2 days.

5.4 *Analytical Balances* – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

5.5 *Muffle Furnace* – Capable of maintaining a temperature of 950˚C ± 25º verified by clay pyrometric cones yearly.

6 Reagents and Materials

6.1 *Trace metal grade (TMG) Hydrochloric acid (HCl),* concentrated (32-38%)

6.2 *TMG Nitric acid (HNO_3),* concentrated (65-70%)

6.3 *Fluoroboric acid (HBF_4)*, concentrated (46-52%)

6.4 *Hydrogen Peroxide (H_2O_2)*, concentrated (30-38%)

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

6.6 *Filter paper* – Particle retention of 20 – 25 µm and a medium flowrate.

6.7 *Ultra-pure Grade Lithium Borate Flux* – composed of 66 ±10% Lithium tetraborate ($Li_2B_4O_7$), 33 ±10% lithium metaborate ($LiBO_2$) and 1 ±1% lithium bromide (LiBr)

7 Sampling

7.1 Blended cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT

8 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix A provides calibrating and standardizing specifications for an Agilent Radial ICP-OES for the determination of elemental oxides.

9 Procedure

9.1 Weigh 0.1000 g ± 0.0005 g of blended cement onto tared waxed paper or a small weighing boat. Record the mass.

9.2 Transfer the sample to a Teflon insert for microwave digestion. Reweigh the waxed paper or weighing boat and note the residual mass from the sample. Record the residual mass and calculate the mass transferred to the Teflon insert.

9.3 In a ventilation hood, add 10.0 mL TMG Hydrochloric acid, 4.0 mL TMG Nitric acid, and 4.0 mL Fluoroboric acid to the Teflon insert using autopipettes with disposable tips. Place the Teflon insert in the carousel.

9.4 Once all samples have been prepared, place the carousel in the microwave digestion system. Begin the digestion process (see Appendix A for MDT digestion process). After completion of the digestion process, allow the carousel to cool before removing. The carousel may be left overnight to cool.

9.5 Remove a digestion vessel and open it. Rinse the sample into a clean Teflon beaker. Tare a dry 125 mL plastic sample bottle. Rinse the solution from the beaker into the plastic sample bottle. Place the plastic sample bottle on the balance and add reagent water to a mass of 100.00 g ± 0.05 g. Cap the plastic sample bottle and invert it several times to homogenize the solution.

9.6 Label the container with the sample number, date, analyst initials, and as blended cement.

9.7 Repeat Sections 9.5 and 9.6 for all samples.

9.8 Analyze the solutions on an ICP-OES.

SPECTROSCOPIC DETERMINATION OF SILICON DIOXIDE AND CALCIUM OXIDE IN BLENDED CEMENT

10 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix B provides calibrating and standardizing specifications for an Agilent Radial ICP-OES for the determination of silicon dioxide.

11 Procedure

11.1 Weigh 0.8000 g ± 0.005 g of lithium borate flux into a graphite crucible.

11.2 Tare the flux and crucible and add 0.1000 g ± 0.0005 g blended cement on top of the flux.

11.3 Fuse the graphite crucible(s) containing the samples in the muffle furnace at 950°C for 5 minutes. Do not fuse more than two crucibles at a time. Swirl the crucible to consolidate all residual sample that may be sticking to the sides of the crucible. Continue fusing for an additional 15-25 minutes at 950°C.

11.4 Prior to or during the fusion process, prepare an adequate number of Teflon beakers (at least 200 mL) by rinsing them copiously with reagent water. Add no less than 60 ml of water into the beakers. Place a Teflon stir bar in each beaker and cover each with a watch glass. Place the beakers on a stir plate near the furnace and stir at a rate of about two revolutions per second.

11.5 At the completion of the fusion process, quickly transfer the fusion bead from the graphite crucible to one of the prepared Teflon beakers. Inspect the graphite crucible for any trace of sample or fusion material; discard the sample if either are present. Add 5 ml of nitric acid, replace the watch glass on the beaker, and stir for a minimum of 30 minutes or until all material is dissolved. More acid may be needed to completely dissolve the fusion bead; add the same amount of acid to each sample in order to maintain the same acid content. If additional acid results in material coming out of solution, the sample is not suitable for analysis; discard the sample.

11.6 Once all the material has dissolved, prepare the stock solution by transferring the solution to a 500-mL class A volumetric flask. Bring to volume with reagent water and add nitric acid such that the concentration of nitric acid will be 15 + 485. Cover the flask with Parafilm and invert a minimum of eight times to thoroughly mix. If needed, quantitatively filter the samples.

11.7 Transfer the stock solution to a plastic sample bottle; discard any excess solution. Label the container with the sample number, blended cement, Ca and Si analysis, date, and analyst initials.

11.8 Once all the samples are prepared, analyze the solutions on an ICP-OES.

SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN BLENDED CEMENTS

12 Calibration and Standardization

Follow manufacturer's specifications for calibrating and standardizing the ICP-OES. Appendix C provides calibrating and standardizing specifications for an Agilent Radial ICP-OES for the determination of sulfur trioxide.

13 Procedure

13.1 Weigh 0.5000 g ± 0.0005 g blended cement directly into a dry 250 mL beaker.

Note – If a thick-walled beaker is used that is too heavy for the balance, the cement can be weighed on waxed paper or a small weighing boat and transferred. Reweigh the waxed paper or weighing to account for any cement that may have stuck to it.

13.2 Add 5.0 mL of hydrogen peroxide using an autopipette to each beaker.

13.3 Bring the solution to the 100 mL mark on the beaker with reagent water.

13.4 Add 10.0 mL of nitric acid to the beaker using an autopipette.

13.5 Add a Teflon stir bar and place on a stir plate to agitate for a minimum of 60 minutes. A good stir rate is about two revolutions per second.

13.6 Quantitatively filter into a 500 mL glass volumetric flask and rinse many times with reagent water.

13.7 Bring to volume with reagent water.

13.8 Transfer the solution into a suitable clean container for analysis. Label with the sample number, the date, analyst initials, and analyte of interest.

13.9 Once all the samples are prepared, analyze the solutions using the ICP-OES.

14 Report

14.1 Data Reporting and Retention for blended cements will be reported as shown below:

Analyte	Reported As	Significance
Ca	CaO	XX.XX
Al	Al_2O_3	X.XX
Fe	Fe_2O_3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
Ti	TiO_2	0.XX
Cr	Cr_2O_3	0.0XX
K	K_2O	X.XXX
Mn	Mn_2O_3	0.XXX
Na	Na_2O	0.XXX
P	P_2O_5	0.XXX
Zn	ZnO	0.XXX
S	SO_3	X.XX
S-	S-	X.XX
LOI	LOI	X.XX
ISR	ISR	0.XX
CO_2	CO_2	X.XX

15 Validation

15.1 For validation data and quality control information, consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
SPECTROSCOPIC DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT

Agilent Radial ICP-OES configuration parameters

Equipment Configuration

Nebulizer: One Neb
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids
Power: 1.15 kW
Plasma flow: 15.0 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.75 L/min
Replicate read time: 1.00s
Instrument stabilization delay: 15s
Sample uptake delay: 45s
Pump rate: 15 rpm
Rinse time: 40s
Fast pump: yes
Replicates: 5
Viewing Height: 8mm

Line Selection for Standards, Samples, and Blanks

Al: 309.271
Cr: 205.560
Fe: 261.187
K: 766.491
Mg: 280.270
Mn: 257.610
Na: 589.592
P: 213.618
Ti: 334.941
Zn: 213.857

Calibration Agilent Radial ICP-OES

Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL blended cement standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

Milestone Ethos EZ microwave digestion system

Digestion program used: portcement.mpr

Heat and time: Heat to 200°C and hold temperature during a 30-minute interval. Followed by a 10-minute cooling period

Rotor: SK-10

APPENDIX B
SPECTROSCOPIC DETERMINATION OF SILICON DIOXIDE AND CALCIUM OXIDE IN BLENDED CEMENT

Agilent Radial ICP-OES configuration parameters

Equipment Configuration

Nebulizer: One Neb
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids
Power: 1.20 kW
Plasma flow: 15.0 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.60 L/min
Replicate read time: 1.00s
Instrument stabilization delay: 15s
Sample uptake delay: 45s
Pump rate: 15 rpm
Rinse time: 40s
Fast pump: yes
Replicates: 5
Viewing Height: 11mm

Line Selection for Standards, Samples, and Blanks

Ca: 317.933
Si: 212.412

Calibration Agilent Radial ICP-OES

Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL blended cement standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

APPENDIX C
SPECTROSCOPIC DETERMINATION OF SULFUR TRIOXIDE IN BLENDED CEMENTS

Agilent Radial ICP-OES configuration parameters

Equipment Configuration

Nebulizer: One Neb
Spray chamber: cyclonic
Sample pump tubing: White/White
Waste pump tubing: Blue/Blue
Rinse solution: 3% Nitric acid
Torch: High solids
Power: 1.00 kW
Plasma flow: 15.0 L/min
Auxiliary flow: 1.50 L/min
Nebulizer flow: 0.60 L/min
Replicate read time: 1.00s
Instrument stabilization delay: 15s
Sample uptake delay: 30s
Pump rate: 15 rpm
Rinse time: 40s
Fast pump: yes
Replicates: 5
Viewing Height: 11mm

Line Selection for Standards, Samples, and Blanks

S: 180.669, 181.972

Calibration Agilent Radial ICP-OES

Type: Linear for all elements.
Linear-Maximum percent error of 10% and Confidence limit of 0.99%.
Calibration Standard Selection: Pick NIST or CCRL blended cement standards that provide a range covering what would likely be expected of the samples being analyzed. Usually a minimum of four should be selected. If any samples fall outside the range of the selected standards more should be selected to expand the range.

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METHODS OF SAMPLING AND TESTING
MT 539-23
CHEMICAL ANALYSIS OF PORTLAND CEMENT VIA X-RAY FLUORESCENCE
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides of Portland cement. Two test procedures are described in this document:

1.1.1 WDXRF Determination of Elemental Oxides in Portland Cement using the Pressed Pellet method.

1.1.2 WDXRF Determination of Elemental Oxides in Portland Cement using the Fusion method.

1.2 This test method also denotes reference test methods.

1.2.1 Loss on Ignition of Portland Cement – ASTM C114, Section 18

1.2.2 Insoluble Residue of Portland Cement – ASTM C114, Section 7

1.2.3 Carbon Dioxide Determination in Portland Cement – ASTM C114, Section 24

1.2.4 Sulfide Determination in Portland Cement – ASTM C114, Section 17

1.2.5 Halogen Determination in Portland Cement – No current validated method

1.3 This standard does not purport to address all the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM
C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement
C150 Standard Specifications for Portland Cement
E29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Standard Practice for Gravimetric Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus
STP985 Rapid Methods for Chemical Analysis of Hydraulic Cement

MT Materials Manual
MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *WDXRF Determination of Elemental Oxides in Portland Cement using Pressed Pellet Summary of Test Method*

In this test method, Portland cement is mixed with a grinding, blending, and pelletizing additive and then pressed into a pellet using a 32 mm Die Set and Press. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, silicon, iron, aluminum, potassium, titanium, sodium, manganese, zinc, chromium, phosphorus, strontium and sulfur.

3.2 *WDXRF Determination of Elemental Oxides in Portland Cement using Fusion Summary of Test Method*

In this test method, Portland cement is mixed with a Lithium based flux, fused in a platinum crucible, and then poured into a platinum mold to form a glass bead. The bead is cooled at room temperature. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, silicon, iron, aluminum, potassium, titanium, sodium, manganese, zinc, chromium, phosphorus, strontium and sulfur.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the Portland cement submittals for suppliers on the MDT Qualified Products List as well as provide analytical information for design applications using Portland cement.

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT USING PRESSED PELLET

5 Apparatus

5.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

5.2 32 mm Pellet Press Die Set

5.3 Pellet Press – Capable of maintaining 10,000 pounds of pressure for 4 minutes

5.4 Analytical Mill (i.e., IKA A11 Basic S001)

5.5 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

6 Reagents and Materials

6.1 Grinding, blending, and pelletizing additive - Powder wax form (i.e., Chemplex Spectroblend)

7 Sampling

7.1 Cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

8 Calibration and Standardization

8.1 Follow manufacturer’s specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix A provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

9 Procedure

9.1 Weigh 5.0000 g ± 0.05 g Portland cement onto tared waxed paper or small weighing boat. Record the mass.

9.2 Weigh 1.2500g ± 0.05 g wax powder pelletizing agent onto tared waxed paper or small weighing boat. Record the mass.

9.3 Transfer the Portland cement and wax powder pelletizing agent to the grinder/mixer cup of the analytical mill.

9.4 Mix the sample for 30 seconds in the analytical mill.

9.5 Scrape down the sides of the mixing bowl to remove any sample/wax pelletizing additive that is stuck to the sides.

9.6 Repeat 9.4 and 9.5 three more times for a total of 2 minutes. At the end of the last mixing time scrape down the sides.

9.7 Assemble the die set according to Figure 1. Pour the sample/pelletizing additive mixture into the assembled die set.

9.8 Press the sample for 4 minutes at approximately 10,000 pounds.

9.9 Release the press and place the ejector sleeve on the die set and place it in the press to remove the pellet from the die set.

9.10 Label the side not being analyzed on the WDXRF with the sample ID.

9.11 Repeat steps 9.1 to 9.10 for additional samples.

9.12 Once all the samples have been prepared, analyze the pellets on the S8 Tiger WDXRF.

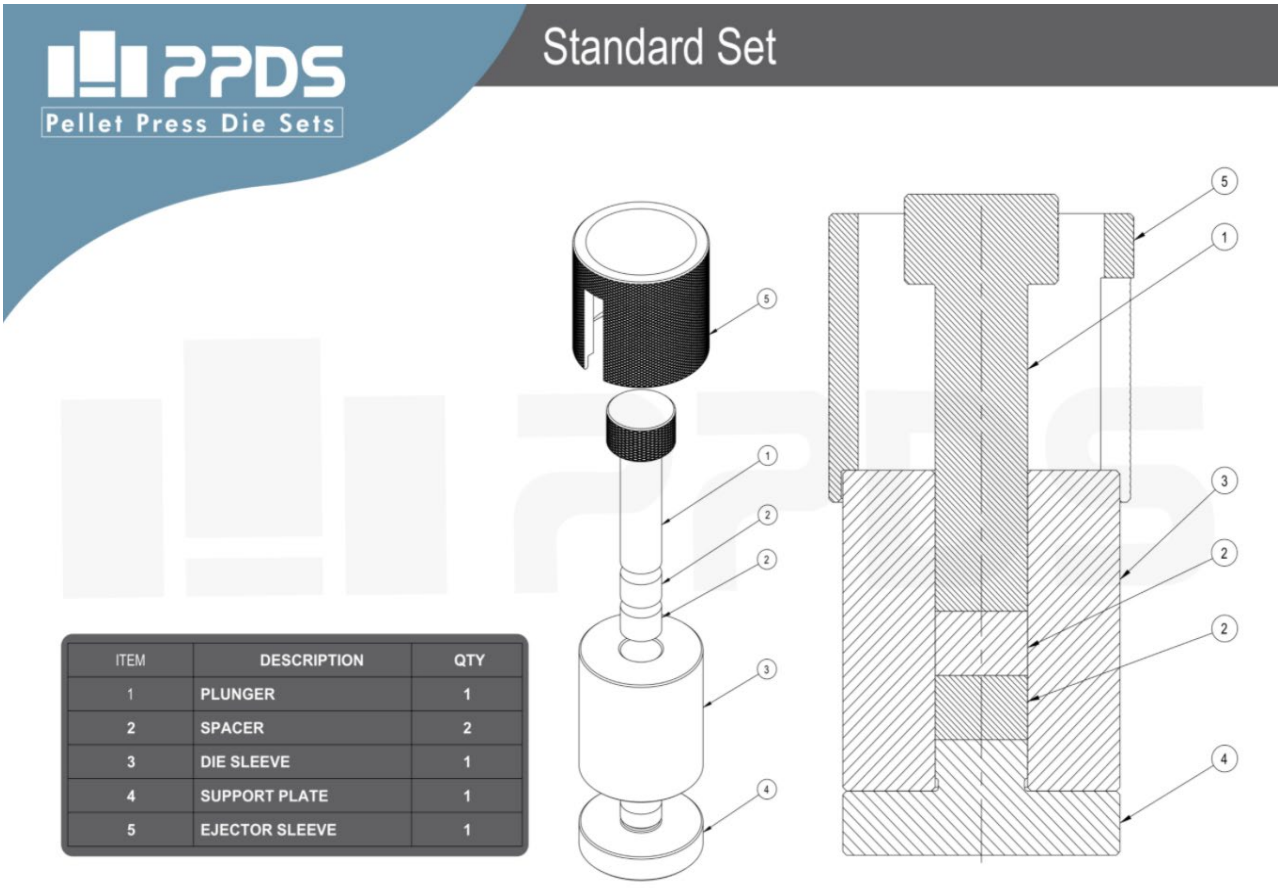


Figure 1. Die Set assembly for WDXRF

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT USING FUSION

10 Apparatus

10.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

10.2 Platinum crucible

10.3 32 mm platinum mold

10.4 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

10.5 Furnace - Capable of reaching 950ºC

11 Reagents and Materials

11.1 Fusion Flux (66.67% Lithium Tetraborate, 32.83% Lithium Metaborate, 0.5% Lithium Bromide)

12 Sampling

12.1 Cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

13 Calibration and Standardization

13.1 Follow manufacturer's specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix B provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

14 Procedure

14.1 Weigh 1.5000 g ± 0.05 g Portland cement into a small beaker or plastic cup. Record the mass.

14.2 Weigh 7.5000g ± 0.05 g Fusion Flux into a small beaker or plastic cup. Record the mass.

14.3 Mix the cement sample and Fusion Flux together and pour the mixture into the platinum crucible.

14.4 Place the crucible and mold into a furnace preheated to 550ºC.

14.5 Change the furnace temperature to 950ºC.

14.6 5 minutes after the furnace reaches 950ºC, mix the sample/flux mixture at a 45º angle.

14.7 Continue to fuse the sample for 5 minutes, mix the sample/flux mixture at a 45º angle.

14.8 Continue the fusing process for 10 minutes, mix the sample again at a 45º angle.

14.9 Continue to fuse the sample for an additional 5 minutes.

14.10 Remove the mold from the furnace and place it on a heat resistant surface. Remove the crucible from the furnace and quickly, but carefully pour the molten sample into the mold.

14.11 Allow the sample to cool for 25 minutes at room temperature.

14.12 Once cool, remove the sample from the mold and label the rounded side of the bead with a sticker.

14.13 Repeat steps 14.1 to 14.12 for additional samples.

14.14 Once all the samples have been prepared, analyze the fusion beads on the S8 Tiger WDXRF.

15 Report

Data Reporting for Portland Cement will be reported as shown below:

Analyte	Reported As	Significance
Ca	CaO	XX.XX
Al	Al_2O_3	X.XX
Fe	Fe_2O_3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
Ti	TiO_2	0.XX
Cr	Cr_2O_3	0.0XX
K	K_2O	X.XX
Mn	Mn_2O_3	0.XXX
Na	Na_2O	0.XXX
P	P_2O_5	0.XXX
Zn	ZnO	0.XXX
S	SO_3	X.XX
S-	S-	X.XX
LOI	LOI	X.XX
ISR	ISR	0.XX
CO_2	CO_2	X.XX
Lime Content	Lime Content	X.X
C_3S	C_3S	XX.X
C_2S	C_2S	XX.X
C_3A	C_3A	X.X
C_4AF	C_4AF	XX.X
Cl-	Cl-	0.0XX

16 Validation

For validation data quality control information, consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
WDXRF DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT USING PRESSED PELLET

Bruker Tiger S8 XRF configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 60, ULD = 147% of nominal peak
h. Adjusted peak: 17.139 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: 1 at 18.702 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: Intensity, (Si KA1-HR-Min) * (-0.1807)
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 235% of nominal peak
h. Adjusted peak: 45.168 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: 1 at 47.481 degrees 2-theta
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: Al, Si
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Cr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 66, ULD = 137% of nominal peak
h. Adjusted peak: 69.374 degrees 2-theta
i. Wavelength: 2.2897 Å
j. Background: None
k. Absorption correction: None

l. Intensity model: Raw peak intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 300 seconds
s. Background measurement time: NA

Equipment Configuration for Cr – Low Level

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 57, ULD = 148% of nominal peak
h. Adjusted peak: 69.364 degrees 2-theta
i. Wavelength: 2.2897 Å
j. Background: 1 at 70.883 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 13 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 300 seconds
s. Background measurement time: 60 seconds

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 47, ULD = 164% of nominal peak
h. Adjusted peak: 57.534 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: 1 at 60.207 degrees 2-theta
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: Variable
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 74, ULD = 136% of nominal peak
h. Adjusted peak: 136.693 degrees 2-theta

i. Wavelength: 3.7414 Å
j. Background: 1 at 139.503 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 20 seconds

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 48, ULD = 147% of nominal peak
h. Adjusted peak: 20.378 degrees 2-theta
i. Wavelength: 9.893 Å
j. Background: 1 at 21.956 degrees 2-theta
k. Absorption correction: Fixed alphas (theoretical values for average standard)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: 20 seconds

Equipment Configuration for Mn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 60, ULD = 150% of nominal peak
h. Adjusted peak: 63.005 degrees 2-theta
i. Wavelength: 2.1018 Å
j. Background: 1 at 65.353 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 20 seconds

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å

f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 138% of nominal peak
h. Adjusted peak: 24.600 degrees 2-theta
i. Wavelength: 11.91 Å
j. Background: 1 at 26.365
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: 40 seconds

Equipment Configuration for P

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 71, ULD = 134% of nominal peak
h. Adjusted peak: 89.430 degrees 2-theta
i. Wavelength: 6.157 Å
j. Background: 1 at 91.524 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 109.019 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: 1 at 110.786 degrees 2-theta
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: Fe
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for SO_3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA

c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 73, ULD = 132% of nominal peak
h. Adjusted peak: 75.741 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: 1 at 78.197 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: 20 seconds

Equipment Configuration for Sr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 72, ULD = 135% of nominal peak
h. Adjusted peak: 25.162 degrees 2-theta
i. Wavelength: 0.87526 Å
j. Background: 1 at 28.417 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Ti

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 74, ULD = 134% of nominal peak
h. Adjusted peak: 86.154 degrees 2-theta
i. Wavelength: 2.7485 Å
j. Background: 1 at 89.191 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 80 seconds
s. Background measurement time: 30 seconds

Equipment Configuration for Zn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 65, ULD = 150% of nominal peak
h. Adjusted peak: 41.817 degrees 2-theta
i. Wavelength: 1.4352 Å
j. Background: 1 at 43.006 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Cl

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: scintillation counter LLD = 49, ULD = 132% of nominal peak
h. Adjusted peak: 65.428 degrees 2-theta
i. Wavelength: 1.4352 Å
j. Background: 2 at 65.155 degrees 2-theta and 66.176 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 20 standards
n. Alphas: none
o. Line overlap correction: None
p. Corrected Intensity offset: On
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 10 seconds

Line Selection for Standards

a. Ca: KA1-ALT-Min
b. Al: KA1-ALT-Min
c. Fe: KA1-HS-Min
d. Mg: KA1-HR-Min
e. Si: KA1-HR-Min
f. Ti: KA1-HS-Min
g. Cr: KA1-HS-Min
h. K: KA1-HS-Min
i. Mn: KA1-HS-Min
j. Na: KA1-HS-Min
k. P: KA1-HS-Min
l. Zn: KA1-HS-Min
m. S: KA1-HS-Min
n. Sr: KA1-HS-Min
o. Cl: KA1-HR-Min

APPENDIX B
WDXRF DETERMINATION OF ELEMENTAL OXIDES IN PORTLAND CEMENT USING FUSION

Bruker Tiger S8 XRF configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 74, ULD = 138% of nominal peak
h. Adjusted peak: 144.699 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -31.28 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 71, ULD = 234% of nominal peak
h. Adjusted peak: 113.083 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Raw peak intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: Si
o. Line overlap correction: None
p. Corrected Intensity offset: On, -620.1 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Cr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 147% of nominal peak
h. Adjusted peak: 69.363 degrees 2-theta
i. Wavelength: 2.2897 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity

m. Minimization target: Absolute error, 14 standards
n. Alphas: B
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.05619 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: NA

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 56, ULD = 148% of nominal peak
h. Adjusted peak: 57.546 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: Variable
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.4309 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: NA

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 74, ULD = 139% of nominal peak
h. Adjusted peak: 136.651 degrees 2-theta
i. Wavelength: 3.7414 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.1314
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 47, ULD = 153% of nominal peak
h. Adjusted peak: 20.381 degrees 2-theta
i. Wavelength: 9.893 Å

j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: (Ca KA1-HR-Min) * (-0.002529)
p. Corrected Intensity offset: On, +0.6633 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Mn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 147% of nominal peak
h. Adjusted peak: 62.963 degrees 2-theta
i. Wavelength: 2.1018 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.7842 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: NA

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 137% of nominal peak
h. Adjusted peak: 24.609 degrees 2-theta
i. Wavelength: 11.91 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.04535 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for P

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees

g. Detector: flow counter LLD = 72, ULD = 150% of nominal peak
h. Adjusted peak: 89.445 degrees 2-theta
i. Wavelength: 6.157 Å
j. Background: 1 at 90.994 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.01465 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 70 seconds
s. Background measurement time: 30 seconds

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 50, ULD = 146% of nominal peak
h. Adjusted peak: 109.010 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 13 standards
n. Alphas: Na
o. Line overlap correction: None
p. Corrected Intensity offset: On, -351.4 kcps
q. Quadratic Correction: On
r. Sample measurement time: 80 seconds
s. Background measurement time: NA

Equipment Configuration for SO_3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 67, ULD = 144% of nominal peak
h. Adjusted peak: 75.732 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.2523 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 70 seconds
s. Background measurement time: NA

Equipment Configuration for Sr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 62, ULD = 139% of nominal peak
h. Adjusted peak: 25.158 degrees 2-theta
i. Wavelength: 0.87526 Å
j. Background: 1 at 23.776 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +1.598 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Ti

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 79, ULD = 134% of nominal peak
h. Adjusted peak: 86.176 degrees 2-theta
i. Wavelength: 2.7485 Å
j. Background: 1 at 86.176 degrees 2-theta
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: B, Si, Ca
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.006213 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: 30 seconds

Equipment Configuration for Zn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 59, ULD = 146% of nominal peak
h. Adjusted peak: 41.834 degrees 2-theta
i. Wavelength: 1.4352 Å
j. Background: 1 at 43.391 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.4181 kcps
q. Quadratic Correction: Off

r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Cl

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 85, ULD = 125% of nominal peak
h. Adjusted peak: 65.414 degrees 2-theta
i. Wavelength: 4.7278 Å
j. Background: 1 at 66.396 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: none
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.04806 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 20 seconds

Line Selection for Standards

a. Ca: KA1-HR-Min
b. Al: KA1-HS-Min
c. Fe: KA1-HS-Min
d. Mg: KA1-HR-Min
e. Si: KA1-HR-Min
f. Ti: KA1-HR-Min
g. Cr: KA1-HS-Min
h. K: KA1-HS-Min
i. Mn: KA1-HS-Min
j. Na: KA1-HS-Min
k. P: KA1-HS-Min
l. Zn: KA1-HS-Min
m. S: KA1-HR-Min
n. Sr: KA1-HS-Min
o. Cl: KA1-HR-Min

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METHODS OF SAMPLING AND TESTING
MT 540-23
CHEMICAL ANALYSIS OF BLENDED CEMENT VIA X-RAY FLUORESCENCE
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides of Blended cement. Two test procedures are described in this document:

1.1.1 WDXRF Determination of Elemental Oxides in Blended Cement using the Pressed Pellet method.

1.1.2 WDXRF Determination of Elemental Oxides in Blended Cement using the Fusion method.

1.2 This test method also denotes reference test methods.

1.2.1 Loss on Ignition of Blended Cement – ASTM C114, Section 18

1.2.2 Insoluble Residue of Blended Cement – ASTM C114, Section 7

1.2.3 Carbon Dioxide Determination in Blended Cement – ASTM C114, Section 24

1.2.4 Sulfide Determination in Blended Cement – ASTM C114, Section 17

1.2.5 Halogen Determination in Blended Cement – No current validated method

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM

C114 Standard Test Methods for Chemical Analysis of Hydraulic Cement C595/C59M Standard Specifications for Blended Hydraulic Cements
E29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Standard Practice for Gravimetric Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus
STP985 Rapid Methods for Chemical Analysis of Blended Hydraulic Cement

MT Materials Manual

MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *WDXRF Determination of Elemental Oxides in Blended Cement using Pressed Pellet Summary of Test Method*

In this test method, Blended Hydraulic cement is mixed with a grinding, blending, and pelletizing additive and then pressed into a pellet using a 32 mm Die Set and Press. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, silicon, iron, aluminum, potassium, titanium, sodium, manganese, zinc, chromium, phosphorus and sulfur.

3.2 *WDXRF Determination of Elemental Oxides in Blended Cement using Fusion Summary of Test Method*

In this test method, Blended cement is mixed with a Lithium based flux, fused in a platinum crucible, and then poured into a platinum mold to form a glass bead. The bead is cooled at room

temperature. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, silicon, iron, aluminum, potassium, titanium, sodium, manganese, zinc, chromium, phosphorus, strontium and sulfur.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the Blended cement submittals for suppliers on the MDT Qualified Products List as well as provide analytical information for design applications using Blended cement.

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT USING PRESSED PELLET

5 Apparatus

5.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

5.2 32 mm Pellet Press Die Set

5.3 Pellet Press – capable of maintaining 10,000 pounds of pressure for 4 minutes

5.4 Analytical Mill (i.e., IKA A11 Basic S001)

5.5 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

6 Reagents and Materials

6.1 Grinding, blending, and pelletizing additive - Powder wax form (i.e., Chemplex Spectroblend)

7 Sampling

7.1 Blended Cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

8 Calibration and Standardization

8.1 Follow manufacturer's specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix A provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

9 Procedure

9.1 Weigh 5.0000 g ± 0.05 g Blended cement onto tared waxed paper or small weighing boat. Record the mass.

9.2 Weigh 1.2500g ± 0.05 g wax powder pelletizing agent onto tared waxed paper or small weighing boat. Record the mass.

9.3 Transfer the Blended cement and wax powder pelletizing agent to the grinder/mixer cup of the analytical mill.

9.4 Mix the sample for 30 seconds in the analytical mill.

9.5 Scrape down the sides, and along the bottom of the mixing cup and around the blade to remove any sample/wax pellet that became stuck to the sides.

9.6 Repeat 9.4 and 9.5 three more times for a total of 2 minutes. At the end of the last mixing time scrape down the sides.

9.7 Assemble the die set according to Figure 1. Pour the sample/pelletizing additive mixture into the assembled die set.

9.8 Press the sample for 4 minutes at approximately 10,000 pounds.

9.9 Release the press and place the ejector sleeve on the die set and place it in the press to remove the pellet from the die set.

9.10 Label the side not being analyzed on the WDXRF with the sample ID.

9.11 Repeat steps 9.1 to 9.10 for additional samples.

9.12 Once all the samples have been prepared, analyze the pellets on the S8 Tiger WDXRF.

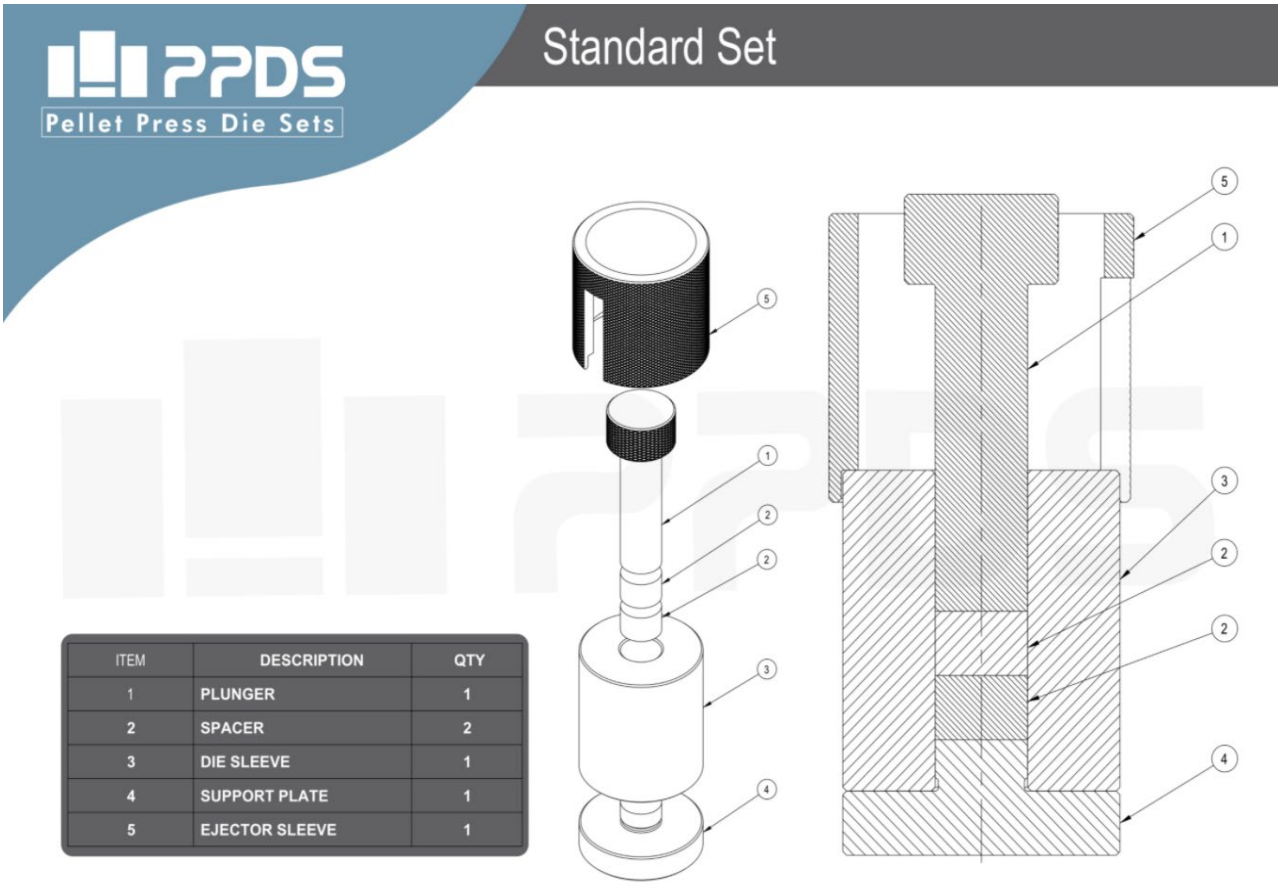


Figure 1. Die Set assembly for WDXRF

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT USING FUSION

10 Apparatus

10.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

10.2 Platinum crucible

10.3 32 mm platinum mold

10.4 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

10.5 Furnace - Capable of reaching 950ºC

11 Reagents and Materials

11.1 Fusion Flux (66.67% Lithium Tetraborate, 32.83% Lithium Metaborate, 0.5% Lithium Bromide)

12 Sampling

12.1 Cement samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

13 Calibration and Standardization

13.1 Follow manufacturer's specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix B provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

14 Procedure

14.1 Weigh 1.5000 g ± 0.05 g Blended cement into a small beaker or plastic cup. Record the mass.

14.2 Weigh 7.5000g ± 0.05 g Fusion Flux into a small beaker or plastic cup. Record the mass.

14.3 Mix the cement sample and Fusion Flux together and pour the mixture into the platinum crucible.

14.4 Place the crucible and mold into a furnace preheated to 550ºC.

14.5 Change the furnace temperature to 950ºC.

14.6 5 minutes after the furnace reaches 950ºC, mix the sample/flux mixture at a 45º angle.

14.7 Continue to fuse the sample 5 minutes, mix the sample/flux mixture at a 45º angle.

14.8 Continue the fusing process for 10 minutes, mix the sample again at a 45º angle.

14.9 Continue to fuse the sample for an additional 5 minutes.

14.10 Remove the mold from the furnace and place it on a heat resistant surface. Remove the crucible from the furnace and quickly, but carefully pour the molten sample into the mold.

14.11 Allow the sample to cool for 25 minutes at room temperature.

14.12 Once cool, remove the sample from the mold and label the rounded side of the bead with a sticker.

14.13 Repeat steps 14.1 to 14.12 for additional samples.

14.14 Once all the samples have been prepared, analyze the fusion beads on the S8 Tiger WDXRF.

15 Report

Data Reporting for Blended Cement will be reported as shown below:

Analyte	Reported As	Significance
Ca	CaO	XX.XX
Al	Al_2O_3	X.XX
Fe	Fe2O3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
Ti	TiO_2	0.XX
Cr	Cr_2O_3	0.0XX
K	K2O	X.XXX
Mn	Mn_2O_3	0.XXX
Na	Na_2O	0.XXX
P	P_2O_5	0.XXX
Zn	ZnO	0.XXX
S	SO_3	X.XX
S-	S-	X.XX
LOI	LOI	X.XX
ISR	ISR	0.XX
CO_2	CO_2	X.XX

16 Validation

For validation data quality control information consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
WDXRF DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT USING PRESSED PELLET

Bruker Tiger S8 configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 144.673 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 23 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.2853 kcps
q. Quadratic Correction: On
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 19mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 55, ULD = 220% of nominal peak
h. Adjusted peak: 113.102 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 23 standards
n. Alphas: Mg
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.8524 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Cr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 62, ULD = 143% of nominal peak
h. Adjusted peak: 69.391 degrees 2-theta
i. Wavelength: 2.2897 Å
j. Background: None
k. Absorption correction: None

l. Intensity model: Net Intensity
m. Minimization target: Absolute error, 15 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +1.046 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 300 seconds
s. Background measurement time: NA

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 57.528 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: None
t. Absorption correction: Fixed alphas (empirically adjusted values)
k. Intensity model: Net intensity
l. Minimization target: Absolute error, 24 standards
m. Alphas: Si, Ca
n. Line overlap correction: (Cr KA1-HS-Min) * (-8.552)
o. Corrected Intensity offset: On, +5.804 kcps
p. Quadratic Correction: Off
q. Sample measurement time: 40 seconds
r. Background measurement time: None

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 136.681 degrees 2-theta
i. Wavelength: 3.7414 Å
j. Background: 1 at 138.878 degrees 2-theta
u. Absorption correction: Variable alphas
k. Intensity model: Net intensity
l. Minimization target: Absolute error, 24 standards
m. Alphas: None
n. Line overlap correction: None
o. Corrected Intensity offset: On, -0.2407 kcps
p. Quadratic Correction: Off
q. Sample measurement time: 40 seconds
r. Background measurement time: 20 seconds

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 68, ULD = 157% of nominal peak
h. Adjusted peak: 20.384 degrees 2-theta

i. Wavelength: 9.893 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 25 standards
n. Alphas: None
o. Line overlap correction: (Na KA1-HS-Min) * (-1.035)
p. Corrected Intensity offset: On, +0.683 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: None

Equipment Configuration for Mn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 62.999 degrees 2-theta
i. Wavelength: 2.1018 Å
j. Background: 1 at 65.468 degrees 2-theta
v. Absorption correction: Fixed alphas (empirically adjusted values)
k. Intensity model: Net intensity
l. Minimization target: Absolute error, 24 standards
m. Alphas: Mg, Ca
n. Line overlap correction: (Cr KA1-HS-Min) * (-0.2186)
o. Corrected Intensity offset: On, +0.03243 kcps
p. Quadratic Correction: Off
q. Sample measurement time: 40 seconds
r. Background measurement time: 20 seconds

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 71, ULD = 145% of nominal peak
h. Adjusted peak: 24.629 degrees 2-theta
i. Wavelength: 11.91 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 24 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.06942 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: None

Equipment Configuration for P

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å

f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 77, ULD = 139% of nominal peak
h. Adjusted peak: 89.470 degrees 2-theta
i. Wavelength: 6.157 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 25 standards
n. Alphas: Mg
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.1273 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: None

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 66, ULD = 150% of nominal peak
h. Adjusted peak: 109.007 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 23 standards
n. Alphas: Al, Fe
o. Line overlap correction: None
p. Corrected Intensity offset: On, +183.6 kcps
q. Quadratic Correction: On
r. Sample measurement time: 30 seconds
s. Background measurement time: None

Equipment Configuration for SO_3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 68, ULD = 141% of nominal peak
h. Adjusted peak: 75.740 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 25 standards
n. Alphas: Fe
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.1217 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 100 seconds
s. Background measurement time: None

Equipment Configuration for Ti

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA

c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 83, ULD = 132% of nominal peak
h. Adjusted peak: 86.168 degrees 2-theta
i. Wavelength: 2.7485 Å
j. Background: None
t. Absorption correction: Fixed alphas (empirically adjusted values)
k. Intensity model: Net intensity
l. Minimization target: Absolute error, 25 standards
m. Alphas: Ca
n. Line overlap correction: None
o. Corrected Intensity offset: On, -0.7824 kcps
p. Quadratic Correction: Off
q. Sample measurement time: 80 seconds
r. Background measurement time: None

Equipment Configuration for Zn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 148% of nominal peak
h. Adjusted peak: 41.824 degrees 2-theta
i. Wavelength: 1.4352 Å
j. Background: 1 at 42.820 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 24 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.4159 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Line Selection for Standards

a. Ca: KA1-HS-Min
b. Al: KA1-HS-Min
c. Fe: KA1-HS-Min
d. Mg: KA1-HS-Min
e. Si: KA1-HS-Min
f. Ti: KA1-HS-Min
g. Cr: KA1-HS-Min
h. K: KA1-HS-Min
i. Mn: KA1-HS-Min
j. Na: KA1-HS-Min
k. P: KA1-HS-Min
l . Zn: KA1-HS-Min
m. S: KA1-HR-Min
n. Cl: KA1-HR-Min
o. Cr: KA1-HS-Min

APPENDIX B
WDXRF DETERMINATION OF ELEMENTAL OXIDES IN BLENDED CEMENT USING FUSION

Bruker Tiger S8 configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 52, ULD = 150% of nominal peak
h. Adjusted peak: 144.677 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: 1 AT 140.556 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, --0.1054 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: 20 seconds

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 70, ULD = 234% of nominal peak
h. Adjusted peak: 113.116 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -89.31 kcps
q. Quadratic Correction: On
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for Cr

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 145% of nominal peak
h. Adjusted peak: 69.367 degrees 2-theta
i. Wavelength: 2.2897 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity

m. Minimization target: Absolute error, 13 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.1925 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 57.534 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: 1 at 59.703 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +5.078 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 75, ULD = 143% of nominal peak
h. Adjusted peak: 136.648 degrees 2-theta
i. Wavelength: 3.7414 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.2396
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 65, ULD = 160% of nominal peak
h. Adjusted peak: 20.402 degrees 2-theta
i. Wavelength: 9.893 Å

j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.2929 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Mn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 54, ULD = 150% of nominal peak
h. Adjusted peak: 63.002 degrees 2-theta
i. Wavelength: 2.1018 Å
j. Background: 1 at 64.592 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.07747 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 70, ULD = 137% of nominal peak
h. Adjusted peak: 24.595 degrees 2-theta
i. Wavelength: 11.91 Å
j. Background: None
k. Absorption correction: Fixed alphas (theoretical values for average standard)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.1205 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for P

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees

g. Detector: flow counter LLD = 73, ULD = 134% of nominal peak
h. Adjusted peak: 89.476 degrees 2-theta
i. Wavelength: 6.157 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.02595 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 50, ULD = 146% of nominal peak
h. Adjusted peak: 109.017 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -6.211 kcps
q. Quadratic Correction: On
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for SO3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 70, ULD = 144% of nominal peak
h. Adjusted peak: 75.727 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.04943 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for Ti

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 81, ULD = 127% of nominal peak
h. Adjusted peak: 86.169 degrees 2-theta
i. Wavelength: 2.7485 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.03345 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 80 seconds
s. Background measurement time: NA

Equipment Configuration for Zn

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: scintillation counter LLD = 64, ULD = 143% of nominal peak
h. Adjusted peak: 41.810 degrees 2-theta
i. Wavelength: 1.4352 Å
j. Background: 1 at 42.831 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.3309 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: 10 seconds

Equipment Configuration for Cl

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 48, ULD = 128% of nominal peak
h. Adjusted peak: 65.363 degrees 2-theta
i. Wavelength: 4.7278 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 14 standards
n. Alphas: none
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.28 kcps
q. Quadratic Correction: Off

r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Line Selection for Standards

a. Ca: KA1-HS-Min
b. Al: KA1-HS-Min
c. Fe: KA1-HS-Min
d. Mg: KA1-HS-Min
e. Si: KA1-HS-Min
f. Ti: KA1-HR-Min
g. Cr: KA1-HS-Min
h. K: KA1-HS-Min
i. Mn: KA1-HS-Min
j. Na: KA1-HS-Min
k. P: KA1-HS-Min
l. Zn: KA1-HS-Min
m. S KA1-HS-Min
n. Cl KA1-HS-Min

METHODS OF SAMPLING AND TESTING
MT 541-23
CHEMICAL ANALYSIS OF FLY ASH AND POZZOLANS VIA X-RAY FLOURESCENCE
(Montana Method)

1 Scope

1.1 This test method describes the procedures used to determine the concentration of elemental oxides of fly ash and pozzolans. Two test procedures are described in this document.

1.1.1 WDXRF Determination of Elemental Oxides in fly ash and pozzolans using the Pressed Pellet method.

1.1.2 WDXRF Determination of Elemental Oxides in fly ash and pozzolans using the Fusion method.

1.2 This test method also denotes reference test methods.

1.2.1 Loss on Ignition of Pozzolan and Fly Ash Cement – ASTM C311, Sections 13 and 14

1.2.2 Moisture of Fly Ash and Pozzolans – ASTM C311 Sections 11 and 12

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Referenced Documents

ASTM

C311 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
E29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E542 Standard Practice for Gravimetric Calibration of Laboratory Volumetric Apparatus
E694 Standard Specification for Laboratory Glass Volumetric Apparatus STP985 Rapid Methods for Chemical Analysis of Hydraulic Cement

MT Materials Manual

MT 607 Procedure for Reducing Field Samples to Testing Size

3 Summary of Test Method

3.1 *WDXRF Determination of Elemental Oxides in Fly Ash or Pozzolans using Pressed Pellet Summary of Test Method*

In this test method, fly ash or pozzolans are mixed with a grinding, blending, and pelletizing additive and then pressed into a pellet using a 32 mm Die Set and Press. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, iron, aluminum, potassium, silicon, sodium, and sulfur.

3.2 *WDXRF Determination of Elemental Oxides in Fly Ash and Pozzolans using Fusion Summary of Test Method*

In this test method, fly ash or pozzolans are mixed with a Lithium based flux, fused in a platinum crucible, and then poured into a platinum mold to form a glass bead. The bead is cooled at room temperature. The pellet is then analyzed by S8 Tiger Wave Dispersive X-Ray Fluorescence Analyzer (WDXRF). The following analytes are quantified as oxides: calcium, magnesium, iron, aluminum, potassium, silicon, sodium, and sulfur.

4 Significance and Use

4.1 This procedure is primarily used to provide quality assurance for the fly ash or pozzolan cement submittals for suppliers on the MDT Qualified Products List as well as provide analytical information for design applications using Blended cement.

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN FLY ASH AND POZZOLANS USING PRESSED PELLET

5 Apparatus

5.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

5.2 32 mm Pellet Press Die Set

5.3 Pellet Press – Capable of maintaining 10,000 pounds of pressure for 4 minutes

5.4 Analytical Mill (i.e., IKA A11 Basic S001)

5.5 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

6 Reagents and Materials

6.1 Grinding, blending, and pelletizing additive - Powder wax form (i.e., Chemplex Spectroblend)

7 Sampling

7.1 Fly and pozzolan samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

8 Calibration and Standardization

8.1 Follow manufacturer's specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix A provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

9 Procedure

9.1 Weigh 5.0000 g ± 0.05 g fly ash or pozzolan cement onto tared waxed paper or small weighing boat. Record the mass.

9.2 Weigh 1.2500g ± 0.05 g wax powder pelletizing agent onto tared waxed paper or small weighing boat. Record the mass.

9.3 Transfer the fly ash or pozzolan cement and the wax powder pelletizing agent to the grinder/mixer cup of the analytical mill.

9.4 Mix the sample for 30 seconds in the analytical mill.

9.5 Scrape down the sides, and along the bottom of the mixing cup and around the blade to remove any sample/wax pellet that became stuck to the sides.

9.6 Repeat 9.4 and 9.5 three more times for a total of 2 minutes. At the end of the last mixing time scrape down the sides.

9.7 Assemble the die set according to Figure 1. Pour the sample/pelletizing additive mixture into the assembled die set.

9.8 Press the sample for 4 minutes at approximately 10,000 pounds.

9.9 Release the press and place the ejector sleeve on the die set and place it in the press to remove the pellet from the die set.

9.10 Label the side not being analyzed on the WDXRF with the sample ID.

9.11 Repeat steps 9.1 to 9.10 for additional samples.

9.12 Once all the samples have been prepared, analyze the pellets on the S8 Tiger WDXRF.

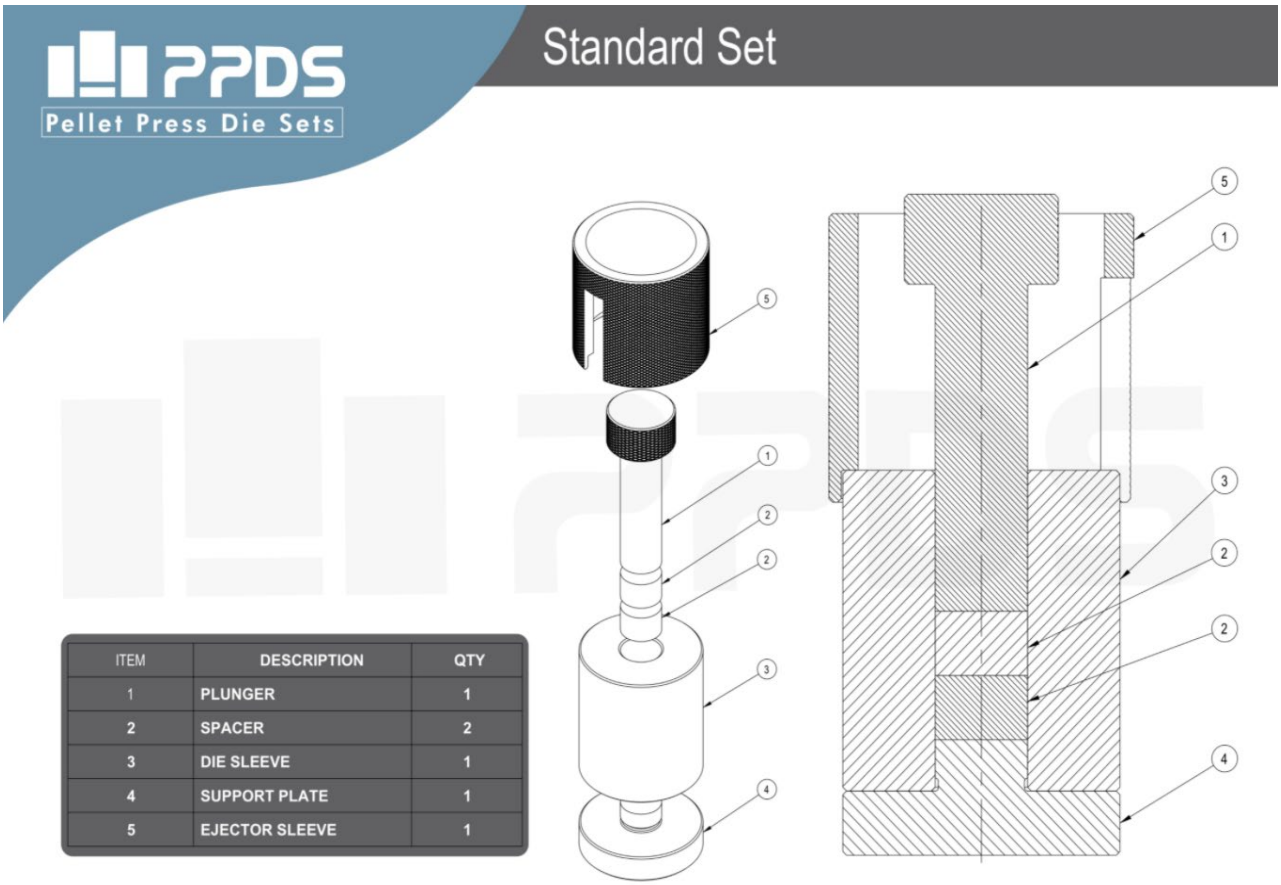


Figure 1. Die Set assembly for WDXRF

WDXRF DETERMINATION OF ELEMENTAL OXIDES IN POZZOLAN CEMENT USING FUSION

10 Apparatus

10.1 Wave Dispersive X-Ray Fluorescence (WDXRF) Analyzer

10.2 Platinum crucible

10.3 32 mm platinum mold

10.4 Analytical Balances – For the initial weighing of samples and standards, a balance with a precision of 0.0001 g should be used. For weighing material over 210 g, a balance with a precision of 0.01 g should be used.

10.5 Furnace - Capable of reaching 950ºC

11 Reagents and Materials

11.1 Fusion Flux (66.67% Lithium Tetraborate, 32.83% Lithium Metaborate, 0.5% Lithium Bromide)

12 Sampling

12.1 Fly ash and pozzolan samples are to be split in accordance with MT 607. A 50 mL sample should be provided to the Chemistry Lab for analysis.

13 Calibration and Standardization

13.1 Follow manufacturer's specifications for calibrating, standardizing and drift correcting the WDXRF. Appendix B provides calibration and standardization specifications for a Bruker Tiger S8 WDXRF for the determination of elemental oxides.

14 Procedure

14.1 Weigh 1.5000 g ± 0.05 g fly ash or pozzolan cement into a small beaker or plastic cup. Record the mass.

14.2 Weigh 7.5000g ± 0.05 g Fusion Flux into a small beaker or plastic cup. Record the mass.

14.3 Mix the cement sample and Fusion Flux together and pour the mixture into the platinum crucible.

14.4 Place the crucible and mold into a furnace preheated to 550ºC.

14.5 Change the furnace temperature to 950ºC.

14.6 5 minutes after the furnace reaches 950ºC, mix the sample/flux mixture at a 45º angle.

14.7 Continue to fuse the sample for 5 minutes, mix the sample/flux mixture at a 45º angle.

14.8 Continue the fusing process for 10 minutes, mix the sample again at a 45º angle.

14.9 Continue to fuse the sample for an additional 5 minutes.

14.10 Remove the mold from the furnace and place it on a heat resistant surface. Remove the crucible from the furnace and quickly, but carefully pour the molten sample into the mold.

14.11 Allow the sample to cool for 25 minutes at room temperature.

14.12 Once cool, remove the sample from the mold and label the rounded side of the bead with a

sticker.

14.13 Repeat steps 14.1 to 14.12 for additional samples.

14.14 Once all the samples have been prepared, analyze the fusion beads on the S8 Tiger WDXRF.

15 Report

Data Reporting for fly ash and pozzolans will be reported as shown below:

Analyte	Reported As	Significance
Ca	CaO	XX.XX
Al	Al_2O3	X.XX
Fe	Fe_2O_3	X.XX
Mg	MgO	X.XX
Si	SiO_2	XX.XX
K	K_2O	0.XX
Na	Na_2O	0.0XX
S	SO_3	X.XXX
LOI	LOI	0.XXX
Moisture	Moisture	0.XXX

16 Validation

For validation data quality control information consult ASTM C114 and ensure all instruments meet its conditions.

APPENDIX A
WDXRF DETERMINATION OF ELEMENTAL OXIDES IN FLY ASH AND POZZOLANS USING PRESSED PELLET

Bruker Tiger S8 configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 68, ULD = 141% of nominal peak
h. Adjusted peak: 144.680 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: None
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 21 standards
n. Alphas: Ca
o. Line overlap correction: None
p. Corrected Intensity offset: On, -3.3128 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 78, ULD = 230% of nominal peak
h. Adjusted peak: 113.109 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: none
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 21 standards
n. Alphas: Fe
o. Line overlap correction: None
p. Corrected Intensity offset: On, +45.71 kcps
q. Quadratic Correction: on
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: scintillation counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 57.521 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: none

k. Absorption correction: Variable alphas
l. Intensity model: net intensity
m. Minimization target: absolute error, 23 standards
n. Alphas: none
o. Line overlap correction: none
p. Corrected Intensity offset: on, -17.8 kcps
q. Quadratic Correction: off
r. Sample measurement time: 30 seconds
s. Background measurement time: NA

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 75, ULD = 136% of nominal peak
h. Adjusted peak: 136.655 degrees 2-theta
i. Wavelength: 3.7414 Å
j. Background: none
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 23 standards
n. Alphas: Ca
o. Line overlap correction: none
p. Corrected Intensity offset: on, 0.1985 kcps
q. Quadratic Correction: off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 153% of nominal peak
h. Adjusted peak: 20.381 degrees 2-theta
i. Wavelength: 9.893 Å
j. Background: none
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 25 standards
n. Alphas: K
o. Line overlap correction: (Al KA1-HS) * (-0.01484), (Ca KA1-HS) * (+0.008641)
p. Corrected Intensity offset: on, -1.37 kcps
q. Quadratic Correction: off
r. Sample measurement time: 50 seconds
s. Background measurement time: none

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak

h. Adjusted peak: 24.618 degrees 2-theta
i. Wavelength: 11.91 Å
j. Background: 1 at 27.230
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 25 standards
n. Alphas: K
o. Line overlap correction: none
p. Corrected Intensity offset: on, +0.08056 kcps
q. Quadratic Correction: off
r. Sample measurement time: 60 seconds
s. Background measurement time: 30 seconds

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 109.004 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: none
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 22 standards
n. Alphas: Al, K
o. Line overlap correction: none
p. Corrected Intensity offset: on, +8.5 kcps
q. Quadratic Correction: off
r. Sample measurement time: 40 seconds
s. Background measurement time: none

Equipment Configuration for SO_3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 49, ULD = 142% of nominal peak
h. Adjusted peak: 75.738 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: none
k. Absorption correction: Fixed alphas (empirically adjusted values)
l. Intensity model: net intensity
m. Minimization target: absolute error, 23 standards
n. Alphas: Mg
o. Line overlap correction: (Fe KA1-HR) * (+0.003027)
p. Corrected Intensity offset: on, -2.137 kcps
q. Quadratic Correction: on
r. Sample measurement time: 60 seconds
s. Background measurement time: none

Line Selection for Standards

a. Ca: KA1-HS-Min
b. Al: KA1-HS-Min
c. Fe: KA1-HR-Min
d. Mg: KA1-HS-Min
e. Si: KA1-HS-Min
f. K: KA1-HS-Min
g. Na: KA1-HS-Min
h. S: KA1-HS-Min

APPENDIX B
XRF FUSION DETERMINATION OF ELEMENTAL OXIDES IN FLY ASH AND POZZOLANS

Bruker Tiger S8 configuration parameters

Equipment Configuration for Al

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 59, ULD = 147% of nominal peak
h. Adjusted peak: 144.673 degrees 2-theta
i. Wavelength: 8.3393 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 17 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.971 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Ca

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 60, ULD = 232% of nominal peak
h. Adjusted peak: 113.083 degrees 2-theta
i. Wavelength: 3.3584 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 17 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.32 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 50 seconds
s. Background measurement time: NA

Equipment Configuration for Fe

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: scintillation counter LLD = 57, ULD = 150% of nominal peak
h. Adjusted peak: 57.522 degrees 2-theta
i. Wavelength: 1.936 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity

m. Minimization target: Absolute error, 17 standards
n. Alphas: Variable alphas
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.3622 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 30 seconds
s. Background measurement time: NA

Equipment Configuration for K

a. Mask: 28 mm
b. Mode: Vacuum with seal, 50kV, 20mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 4.026 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 136.630 degrees 2-theta
i. Wavelength: 3.7414 Å
j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 16 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.05864
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Mg

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 40, ULD = 160% of nominal peak
h. Adjusted peak: 20.366 degrees 2-theta
i. Wavelength: 9.893 Å
j. Background: 19.033 degrees 2-theta and 23.122 degrees 2-theta
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 17 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, +0.1882 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 40 seconds
s. Background measurement time: NA

Equipment Configuration for Na

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 55.9 Å
f. Collimator aperture (nominal): 0.23 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 24.612 degrees 2-theta
i. Wavelength: 11.91 Å

j. Background: None
k. Absorption correction: None
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 17 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.01355 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 60 seconds
s. Background measurement time: NA

Equipment Configuration for Si

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 109.022 degrees 2-theta
i. Wavelength: 7.1254 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity
m. Minimization target: Absolute error, 17 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -12.62 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 80 seconds
s. Background measurement time: NA

Equipment Configuration for SO_3

a. Mask: 28 mm
b. Mode: Vacuum with seal, 30kV, 33mA
c. Filter: None
d. Be: 75um
e. Crystal (nominal): 2d = 8.752 Å
f. Collimator aperture (nominal): 0.46 degrees
g. Detector: flow counter LLD = 50, ULD = 150% of nominal peak
h. Adjusted peak: 75.748 degrees 2-theta
i. Wavelength: 5.3722 Å
j. Background: None
k. Absorption correction: Variable alphas
l. Intensity model: Net intensity
m. Minimization target: absolute error, 16 standards
n. Alphas: None
o. Line overlap correction: None
p. Corrected Intensity offset: On, -0.02588 kcps
q. Quadratic Correction: Off
r. Sample measurement time: 80 seconds
s. Background measurement time: NA

Line Selection for Standards

a. Ca: KA1-HR-Min
b. Al: KA1-HS-Min
c. Fe: KA1-HR-Min
d. Mg: KA1-HS-Min
e. Si: KA1-HS-Min
f. K: KA1-HR-Min
g. Na: KA1-HR-Min
h. S: KA1-HS-Min

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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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