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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