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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