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.