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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