Standard Operating Procedure for:

Microwave Digestion of Water Samples for the Determination of Total Trace Metal Concentration (Micro Total Trace Metals.doc)

Missouri State University

and

Ozarks Environmental and Water Resources Institute (OEWRI)

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1 Identification of the method

1.1 Operation of the MARS Microwave Digestion System to determine total trace metal concentration of water samples. Total metals include all metals that are organically or inorganically bound and that are within the dissolved and suspended fraction.

1.2 If water samples are drinking water samples that are colorless, odorless, and have a turbidity of <1 NTU, analyze samples directly via Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma Optical Emissions Spectroscopy (ICP-OES). Samples of this nature should be acidified to pH <2 with concentrated trace metal nitric acid immediately after collection and analyzed within the appropriate hold time for the analyte of interest. Undigested samples, like these, should be compared with digested samples to ensure comparable results.

1.3 Turbid surface and ground water samples should be digested using this method.

2 Applicable matrix or matrices

This instrument can be used for natural water samples.

3 Detection limit

The operating ranges for this instrument are: temperature 0º to 300ºC and internal pressure control up to 1500 psig. The detection limit will vary depending on the element of concern. The desired performance criteria for this analyses are:

a. Detection limit: 0.01 mg/L Cu, 0.01 mg/L Pb, 0.02 mg/L Zn
b. Precision: ≤ 20%
c. Accuracy: ≤ 20%
d. Minimum Quantification Interval: 0.01 mg/L

4 Scope of method

These procedures allow Missouri State University (MSU) laboratory personnel to use the MARS Microwave Digestion System which provides rapid multi-elemental acid leach digestion prior to Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) use. The procedures in this method are applicable for the following elements: aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silver, sodium, thallium, vanadium, and zinc. MSU projects generally focus on copper, zinc, and lead, therefore those standards are listed in Section 11 of this SOP. The preparation of additional standards will be necessary if other elements are of interest.

5 Summary of method

The procedures follow Standard Method 3030K and guidelines provided by the manufacturer. Water samples are digested in 5ml of trace metal grade concentrated nitric acid for 20 minutes. The digestion takes place in an inert polymeric microwave vessel that is sealed and heated within the microwave system. The temperature profile of each sample is 160 ± 4°C within 10 minutes and 165 to 170 °C for 10 minutes which

allows specific reactions to occur for digestion. The cooled analyte is allowed to settle, centrifuged, or filtered and diluted if necessary before being analyzed by AAS or ICP-OES.

6 Definitions

6.1 Analytical batch: The set of samples processed at the same time to a maximum of 10 samples.

6.2 Calibration standard: A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

6.3 DDI water – Deionized water further purified by a Barnstead Cartridge Deionization Nanopure II System that pretreats, exchanges ions, and removes organics.

6.4 De-ionized water blank (DIB): This blank should not contain any concentration of analyte and is not processed or digested like the standards, checks, or samples. The de-ionized water blank should be less than the laboratory reagent blank (LRB).

6.5 Field blank (FB): An aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

6.6 Field duplicate (FD): Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

6.7 Laboratory control check (LCC): A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

6.8 Laboratory duplicate (LD): Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. The division of one sample into two samples for separate analysis. A laboratory duplicate is made primarily to assess precision associated with analytical procedures.

6.9 Laboratory matrix spike (LS): An aliquot of a sample to which a known amount of analyte is added before sample preparation. The LFM is used to evaluate analyte recovery in a sample matrix.

6.10 Laboratory reagent blank (LRB): An aliquot of deionized water treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

6.11 Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

a. To calculate the MDL:
b. Prepare a solution with the concentration of the element of interest near the estimated MDL
c. Analyze seven portions of this solution over a period of at least three days
d. Include all sample processing steps in the determination
e. Calculate the standard deviation (*s*).
f. From a table of the one-sided *t* distribution select the value of *t* for 7 – 1 = 6 degrees of freedom at the 99% level. This value is 3.14
g. The product 3.14 times *s* is the desired MDL.

6.12 Relative Percent Difference (RPD): calculated as the difference between a sample and duplicate results, divided by the average of the sample and duplicate results, multiplied by 100%.

6.13 Rinsate blank - Prepared by using analyte-free water in decontaminated equipment or instrumentation, such as filtering apparatus, to determine residual contamination from that equipment or instrumentation.

6.14 Quality control check sample (QCC): A sample containing analytes of interest at known concentrations (true values). The quality control check sample is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

7 Interferences

7.1 The digestion of water samples containing organic materials produces high pressures that can cause the plastic rupture membrane in the blue pressure cap of the vessels to rupture resulting in potential sample loss. Consult with the project manager to determine if the sample size should be reduced to prevent sample loss.

7.2 Some refractory sample matrix compounds, such as silicon dioxide and alumina, may not be completely dissolved during digestion and can sequester target analytes. The resultant elements are considered nonmobile in the environment and are excluded from aqueous pollutant transport mechanisms.

8 Health and safety

8.1 Protect from water borne illness by wearing protective gloves while filtering undigested water samples, avoid touching eyes, nose and mouth and washing hands frequently with soap and water.

8.2 Calibration standards contain high concentrations of metals and concentrated acids so exposure should be as low as reasonably achievable. Wear protective gloves and eye protection and prevent any contact with skin or lungs. These chemicals have the potential to be highly toxic or hazardous: cadmium granules, ammonium hydroxide, sodium hydroxide, phosphoric acid, sulfanilamide, and hydrochloric acid. For details consult the MSDS located in Temple 125.

8.3 Pressure is used to produce high temperatures in specified time periods. Inspect each digestion vessel for flaws that might result in system damage and sample loss before adding sample or reagents. Report flaws or deterioration to the project manager. In addition, insure that only one rupture membrane is inserted into the blue pressure cap so the vessel can vent if pressure or temperature become to high. More than one membrane in the pressure cap can result in vessel damage.

8.4 Consistently fill and seal each digestion vessel to ensure similar conditions for all vessels on the carousel and mirror the exact matrix and conditions for the control vessel.

8.5 Toxic fumes are produced during digestion. All digestion vessels will be vented and opened in a properly operating fume hood and care will be taken when opening the microwave system after the completion of a digestion run.

8.6 Wear appropriate clothing for a chemical laboratory: close toed shoes, limited jewelry, lab coat, hair out face, etc.

9 Personnel qualifications

All laboratory technicians have a working knowledge of laboratory housekeeping, sample handling and labeling, analytical procedures, and health and safety protocols. Missouri State University (MSU) laboratory personnel who have written Standard Operating Procedures for the instrumentation used and who provide consistent oversight of the laboratories have trained all laboratory technicians. All projects involving the use of laboratory instrumentation are under the supervision of a project manager.

10 Equipment and supplies

10.1 MARS Microwave Digestion System unit
10.2 Digestion vessel and caps
10.3 Control vessel and temperature probe
10.4 Cartridges and carousel
10.5 Rupture membranes and suction pen
10.6 Trace metal free bottles with lids
10.7 Trace metal free centrifuge tubes
10.8 Volumetric ware: flasks, graduated cylinders, etc.
10.9 Filtration apparatus and glass fiber filters

10.10 Safety materials: eye goggles, gloves, etc.
10.11 Laboratory Notebook, Pen

11 Reagents and standards

Make standards and controls while sample digestion is taking place. Standards and controls are not digested.

11.1 Concentrated trace metal grade nitric acid

11.2 *Inorganic Ventures* Pre-made Trace Metal Standard: 1.0 mg/L Cu; 1.0 mg/L 1.0 Pb; 2.0 mg/L Zn.

11.3 Double deionized water (DDI)

11.4 Pre-made Trace Metal Standard: The pre-made standard, purchased from Inorganic Ventures, contains the concentrations listed in the table below.

	Cu	Pb	Zn
Pre-made Trace Metal Standard Concentration (mg/L)	1.0	1.0	2.0

11.5 High Standard: Add 10 ml of the Pre-made Trace Metal Standard from 11.2 to a 100 ml volumetric flask. Add 5 ml of *trace metal grade* concentrated nitric acid. Dilute to 100 ml with DDI water and mix well to achieve the resultant concentrations shown in the table below.

	Cu	Pb	Zn
High Standard Resultant Concentration (mg/L)	0.1	0.1	0.2

11.6 Laboratory control check (LCC): Add 5 ml of the Pre-made Trace Metal Standard from 11.2 to a second 100 ml volumetric flask. Add 5 ml of trace metal grade concentrated nitric acid. Dilute to 100 ml with DDI water and mix well to achieve the resultant concentrations shown in the table below.

	Cu	Pb	Zn
Control Standard Resultant Concentration (mg/L)	0.05	0.05	0.1

11.7 Low Standard: Add 1 ml of the Pre-made Trace Metal Standard from 11.2 to a third 100 ml volumetric flask. Add 5 ml of trace metal grade concentrated nitric acid. Dilute to 100 ml with DDI water and mix well to achieve the resultant concentration shown in the table below.

	Cu	Pb	Zn
Low Standard Resultant Concentration (mg/L)	0.01	0.01	0.02

11.8 Quality control check sample (QCC):

11.8a Concentrated trace metal grade nitric acid

11.8b 10 mg/ml (10,000 mg/L) Cu Standard

11.8c 1 mg/ml (1,000 mg/L) Pb Standard

11.8d 10 mg/ml (10,000 mg/L) Zn Standard

11.8e Double deionized water (DDI)

11.8f Combined Trace Metal Standard: Use each metal standard listed from 11.8a to 11.8d to prepare the combined trace metal standard. Combine the varying volumes of each metal standard as shown in the table below to a 100ml volumetric flask and dilute to 100 ml with DDI water. Mix well.

	Cu	Pb	Zn
Combined Trace Metal Standard Volume (ml)	0.1	0.1	0.2
Combined Trace Metal Standard Resultant Concentration (mg/L)	10.0	10.0	20.0

11.8g Add 1 ml of the Combined Trace Metal Standard prepared in 11.8f to a second 100 ml volumetric flask. Add 5 ml of trace metal grade concentrated nitric acid. Dilute to 100 ml with DDI water and mix well to achieve the resultant concentrations shown in the table below.

	Cu	Pb	Zn
QCC Resultant Concentration (mg/L)	0.1	0.1	0.2

11.9 Laboratory Reagent Blank (LRB): Add 5 ml of trace metal grade concentrated nitric acid to a 100 ml volumetric flask. Dilute to 100 ml with DDI water and mix well

12 Sample collection, preservation, shipment and storage

12.1 Water samples are not collected using this procedure, refer to the OEWRI Water Sample Collection SOP for water collection procedures. Samples should be acidified to pH <2 with *trace metal grade* concentrated nitric acid at time of collection.

12.2 Samples are not shipped off of the MSU campus, but are sealed and transferred upstairs to the chemistry laboratories in Temple Hall.

12.3 Samples are stored in a refrigerator in Temple Hall room 125 at 4°C before being transferred upstairs to the chemistry laboratories. The hold time for water samples for metal analyses is 6 months. Samples must be analyzed within 6 months.

12.4 The trace metals only filtering apparatus will be used with all trace metal related projects because it contains a pre-washed plastic or TFE filter support to filter samples without contamination.

12.5 Only glass fiber filters that have been sealed and stored in the trace metals cabinet will be used to filter samples.

13 Quality control

13.1 All standards, replicates, and blanks should be prepared at the same time, covered during nonuse and transport, and used immediately to prevent contamination.

13.2 Only trace metal apparatus will be used during trace metal determinations and will be taken from and stored in the trace metal cabinet only.

13.3 All glassware and bottles used during trace metal determinations will be pre-washed and stored appropriately to prevent contamination.

13.4 All data including quality control data will be maintained and available for reference and inspection by the project manager during and after the analyses.

13.5 A duplicate should be prepared for every tenth sample and processed and analyzed as a true sample. Refer to the OEWRI Standard Operating Procedures for Using the ICP for Trace Metal Determinations in Water Samples.

13.6 Standards should be analyzed after every twentieth sample. Refer to the OEWRI Standard Operating Procedures for Using the ICP for Trace Metal Determinations in Water Samples.

13.7 The control and blank should be analyzed after every fifth sample. Refer to the OEWRI Standard Operating Procedures for Using the ICP for Trace Metal Determinations in Water Samples.

14 Calibration and standardization

Refer to the MARS Microwave Digestion System manual for unit calibration and consult with a project manager for any questions regarding the Microwave Digestion System.

15 Procedure

15.1 Vessel Preparation and Cleaning

a. Unscrew blue pressure cap and insert a clear plastic rupture membrane into the cap using the suction pen. Screw blue pressure cap back onto digestion vessel until finger tight.

b. Use a clean graduated cylinder to transfer 45 ml of doubly-deionized water into each vessel.

c. Add 5 ml of trace metal grade concentrated nitric acid.

d. Close each vessel with clear lid containing blue pressure cap. Place tan disk on top of lid with clamp depression side up.

e. For cleaning purposes fill the control vessel with 5 ml of *trace metal grade* concentrated nitric acid. The lid for the control vessel contains an opening for the temperature probe as well as a lance for the temperature probe.

f. Place vessels in gold pressure jackets and position in the digestion chamber so that the blue pressure cap is accessible. Screw clamp on top of the digestion chamber down into depression on the brown disk. Use wrench to tighten clamp an additional 1/3 turn.

g. Place digestion chambers into carousel. Position the control vessel in slot 1. Fill all slots with filled vessels. If the carousel in not filled with samples, fill remaining vessels with 45 ml of reagent water and 5 ml of trace metal grade or concentrated nitric acid. Different programmed methods with different power, time, and temperature profiles will have to be used for a carousel that is not completely filled. Water sample digestion is a two staged procedure that heats the samples to 160±4ºC (545 W) in 10 minutes and then permits a slow rise to 165 to 170 ºC (344 W) for 10 minutes.

h. Position carousel in microwave on turntable.

i. Insert the temperature probe into the control vessel carefully making sure that the probe is at the bottom of the lance without breaking the probe or the lance.

j. Close microwave door. If the home screen reads "'Start' Current Method: EPA 3015H – HP500" use the "-" button to move the highlighted area over that selection. Press the "SELECT" button to begin the digestion. Take extra care to select this method only. Other methods require different vessels. If the home screen does not read "'Start' Current Method: EPA 3015H – HP500", highlight "Load Method". Press the "SELECT" button. Highlight "CEM Director". Press the "SELECT" button. Use the "-" button to move the highlighted area over "EPA 3015H - HP 500" and press the "SELECT" button. The instrument should automatically go to the home screen. Use the "-" button to move the highlighted area over "'Start' Current Method: EPA 3015H – HP500" and press the "SELECT" button to begin the digestion.

k. At completion of the microwave program, allow vessels to cool for at least 5 min in the microwave before removal. Remove carousel from microwave and allow the vessels to cool to near room temperature.

l. Remove each cartridge from the carousel. Vent each vessel under the fume hood by unscrewing the blue pressure cap. Remove each vessel from the cartridge and remove each lid from the vessels under the fume hood. Transfer acid waste to the acid waste container under the hood for proper disposal by MSU chemistry laboratory technicians.

m. Store vessels in an airtight bag that is labeled and placed in a clean environment.

15.2 Water Sample Digestion

a. Unscrew blue pressure cap and insert a clear plastic rupture membrane into the cap using the suction pen. Screw blue pressure cap back onto digestion vessel until finger tight.

b. Shake grab sample while still in plastic sample collection containers before transferring. (All water samples should have been acidified to pH<2 in the field following collection.)

c. Use a clean graduated cylinder to transfer 45 ml of grab sample into vessel. Rinse graduated cylinder with doubly-deionized water between samples.

d. Add 5ml of <u>trace metal grade</u> concentrated nitric acid.

e. Close each vessel with clear lid containing blue pressure cap. Place tan disk on top of lid with clamp depression side up. Label each vessel with a tie-on tag only.

f. The control vessel will contain one of the samples like the other vessels, but the lid for the control vessel contains an opening for the temperature probe. Carefully insert the temperature probe into the vessel ensuring that the end of the probe is at the bottom of the vessel.

g. Place vessels in gold pressure jackets and position in the digestion chamber so that the blue pressure cap is accessible. Screw clamp on top of the digestion chamber down into depression on the brown disk. Use wrench to tighten clamp an additional 1/3 turn.

h. Place digestion chambers into carousel. Position the control vessel in slot 1. Fill all slots with filled vessels. If the carousel is not filled with samples, fill remaining vessels with the exact matrix used in the sample vessels. Different programmed methods with different power, time, and temperature profiles will have to be used for a carousel that is not completely filled. Water sample digestion is a two staged procedure that heats the samples to 160±4ºC (545 W) in 10 minutes and then permits a slow rise to 165 to 170 ºC (344 W) for 10 minutes.

i. Trip blanks, field blanks, rinsate or equipment blanks, method blanks, duplicates, and replicates should be distributed throughout the carousel and included on various carousels throughout the digestion of all samples.

j. Position carousel in microwave on turntable.

k. Insert the temperature probe into the control vessel carefully making sure that the probe is at the bottom of the vessel without breaking the probe.

l. Close microwave door. If the home screen reads "'Start' Current Method: EPA 3015H – HP500" use the "-" button to move the highlighted area over that selection. Press the "SELECT" button to begin the digestion. Take extra care to select this method only. Other methods require different vessels. If the home screen does not read "'Start' Current Method: EPA 3015H – HP500", highlight "Load Method". Press the "SELECT" button. Highlight "CEM Director". Press the "SELECT" button. Use the "-" button to move the highlighted area over "EPA 3015H - HP 500" and press the "SELECT" button. The instrument should automatically go to the home screen. Use the "-" button to move the highlighted area over "'Start' Current Method: EPA 3015H – HP500" and press the "SELECT" button to begin the digestion.

m. Make standards and controls while samples are digesting as described in section 11 of these Standard Operating Procedures.

n. At completion of the microwave program, allow vessels to cool for at least 5 min in the microwave before removal. Remove carousel from microwave and allow the vessels to cool to near room temperature.

o. Remove each cartridge from the carousel. Vent each vessel under the fume hood by unscrewing the blue pressure cap. Remove each vessel from the cartridge and remove each lid from the vessels under the fume hood.

p. Quantitatively transfer sample from the vessels to trace metal acid-cleaned plastic bottles.

15.3 Filtration

If particulates are present, samples should be filtered or decanted before analysis using ICP-OES. Allow samples to sit over night to allow particulates to settle to the bottom of the bottle. If particulates have settled after that time period, decant the sample by slowly pouring the liquid portion of the sample into a trace metal acid-cleaned plastic bottle. Do not allow any particulate to be transferred to the bottle. Use the Standard Operating Procedures for Inductively Coupled Plasma Optical Emission Spectroscopy for Trace Metal Determination in Water Samples to analyze the decanted samples.

If particulates have not settled to the bottom of the bottle after that time period, transfer samples to acid-washed TFE or high-density plastic tubes and centrifuge. Decant the sample from the tubes by slowly pouring the liquid portion of the sample into a trace metal acid-cleaned plastic bottle. Do not allow any particulate to be transferred to the bottle. Use the Standard Operating Procedures for Inductively Coupled Plasma Optical Emission Spectroscopy for Trace Metal Determination in Water Samples to analyze the decanted samples.

If samples remain cloudy after centrifuging, filter samples through a glass fiber filter. Set up the trace metal free filtration units using a sink aspirator. Start aspiration by turning the water on and draw 50mL of deionized water through the filtering device to decontaminate the device. Place a glass filter inside the plastic filtration unit. Transfer each sample through the filter and collect the filtrate in separate 50ml containers. Rinse the filtration unit with DDI water. Place a glass filter inside the plastic filtration unit. Use the Standard Operating Procedures for Inductively Coupled Plasma Optical Emission Spectroscopy for Trace Metal Determination in Water Samples to analyze the filtrates.

16 Data acquisition, calculations, and reporting

These procedures are not used for data acquisition, calculations, or reporting. Standard resultant concentrations are listed in the tables in section 11 of these standard operating procedures.

17 Computer hardware and software

The MARS Microwave Digestion System is preprogrammed with methods used for MSU laboratory analyses. Refer to the MARS Microwave Digestion System manual for unit hardware and software information and consult with a project manager for any questions regarding the Microwave Digestion System.

18 Method performance

Refer to the instrument manual for precision data. The temperature profile will be within ±5°C of the mean of the temperature profile, but the pressure will vary depending on the acid mixture, digestion products, and insulation properties of the vessels.

19 Pollution prevention

All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU College of Natural and Applied Sciences. Volumes of standards and reagents made should mirror the number of samples being analyzed. Adjustments should be made to reduce waste.

20 Data assessment and acceptable criteria for quality control measures

There is no data acquisition associated with these procedures.

21 Waste management

Entire samples are quantitatively transferred for qualitative analysis therefore no wastes are generated. Acids used for cleaning the vessels and glassware should be transferred to the acid waste container under the hood for proper disposal by MSU chemistry laboratory technicians.

22 References

Standard Methods for the Examination of Water and Wastewater. 1995. 19th Edition. APHA, AWWA, WEF Publishers.

23 Tables, diagrams, flowcharts and validation data

There are no tables, diagrams, flowcharts or validation data for this method