Status: Final

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Microwave Assisted Digestion

1. SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes the microwave-assisted acid digestion of aqueous and solid samples, with guidelines from EPA method 3015A for aqueous samples and EPA method 3051A for sediments, soils, sludges, and oils. This SOP describes the procedure to prepare samples for digestion in a laboratory grade microwave oven, using nitric acid (HNO_3) or alternatively nitric acid, hydrochloric acid (HCl), and peroxide (H_2O_2). It is intended as an alternative to EPA methods 3010 for water samples and 3050 for digestion purposes and provides options for addition of hydrochloric acid to improve performance of certain analytes, such as aluminum, iron, antimony, and silver.

As with method 3050, this method does not ensure total decomposition or dissolution of the sample matrices with which it is used, thus the extracted analyte concentrations found may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution of sediments, sludges, and soils for the elements listed in EPA methods 6010 & 6020.

This procedure is recommended for use by laboratory technicians working directly under chemists experienced in sample preparation for inorganic analysis or for use by chemists trained in sample preparation.

2. DEFINITIONS

Accuracy: The closeness of agreement between an observed value and an accepted reference value.

Batch: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will be handled as a separate batch.

Bias: The deviation due to matrix effects of the measured value from a known spiked amount.

Dissolved Metals: The concentration of metals determined in an aqueous sample after the sample is filtered through a 0.45 µm filter.

Field Duplicate (FD): Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently – used to document the precision of the sampling process.

Laboratory Control Sample (LCS): A known matrix spiked with compound(s) representative of the target analytes – used to document laboratory performance

Matrix: The component or substrate (e.g., surface water, soil, solid waste) which contains the analyte of interest.

Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analyte(s), which are added prior to the sample preparation and analysis – used to document the bias of the method in a given sample matrix.

Matrix Spike Duplicate (MSD): A split sample which is spiked with a concentration of target analyte(s) which are identical to those in the matrix spike and added prior to the sample preparation and analysis – used to document the precision and bias of the method in a given sample matrix.

Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing of the method in a given sample matrix - used to document contamination resulting from the analytical process.

Precision: The agreement among a set of replicate measurements without assumption of knowledge of the true value, estimated by means of duplicate/replicate analyses.

Reagent Grade: Equivalent to Analytical Reagent (AR) Grade and ACS Reagent Grade, terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

Reagent Water: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

Reference Material: A material containing known quantities of target analytes in solution or in a homogeneous matrix – used to document the bias of the analytical process.

Split Samples: Aliquots of sample taken from the same container and analyzed independently – used to document inter- or intra-laboratory precision.

Suspended Metals: The concentration of metals determined in the portion of an aqueous sample that is retained by a 0.45 µm filter.

Total acid soluble/recoverable metals: The concentration of metals determined in an unfiltered sample following digestion using hot mineral acid by this method.

3. PRINCIPLE

A representative sub-sample of solid sample or measured volume of aqueous sample is digested with concentrated nitric acid or alternatively a mixture of concentrated nitric, hydrochloric acids

and peroxide at high temperature and pressure in a contained vessel as a means of effectively extracting metals from the sample.

The sample and the acid(s) are placed in a PTFE (Teflon®) vessel and heated in a lab grade microwave for a specified period of time. After the samples have cooled to ambient temperature and pressure, they are transferred to appropriate graduated dilution vials or volumetric flasks and diluted to a known volume. The samples are then analyzed by appropriate metal measurement methods, e.g., EPA 6010C, 6020A, or the 7000 series methods.

4. INTERFERENCES

- The vessels used to contain the samples must be thoroughly cleaned between uses. Artifacts from unclean vessels can produce false readings in the final results.

- Purity of the reagents (e.g. acids) used should be checked by running appropriate blanks.

5. PRESERVATION AND HOLDING TIMES

Samples should be digested within the hold time for analysis (6 months). Samples need to be kept cold (2-6° C) during storage prior to analysis. Plastic bags and aluminum foils are both suitable for storage of flame retardant samples. Flame retardant samples may be stored at room temperature upon receipt. Flame retardant samples must be digested within 6 months of the sampling date and digestates of samples must be stored in a fume food and analyzed within 6 months of the sampling date.

6. EQUIPMENT AND SETUP

(1) Microwave Oven, Laboratory Grade, CEM MARS5, Model 907501, 1200-1500 watts or Milestone ULTRAWAVE with appropriate vessels

(2) Balance, analytical, to ±0.0001 g, Mettler/Toledo Model AE200 or equivalent

(3) Balance, high capacity (2 kg minimum), to ±0.01 g, Mettler/Toledo Model ML4002E or equivalent

(4) Weighing papers, boats, tongue depressors, tweezers, etc.

(5) Pipettors, adjustable, 0.1-1.0 mL and 1-10 mL, calibrated, accuracy to ±0.01 mL

(6) Volumetric flasks (optional)

(7) Dilution vials, 50 mL, graduated, Greiner Bio-one #210-261 or equivalent

(8) Funnels, disposable

(9) Filter paper, Whatman 541 or equivalent

(10) Syringes, disposable with Luer tip, 10 cc

(11) Syringe filters, acid resistant, Pall #4497T Acrodisc or equivalent

(12) Carbon steel blade, Miltex 4-111 No. 11 or equivalent

7. STANDARDS AND REAGENTS USED

(1) Hydrochloric Acid, trace metal grade, BDH Aristar+® or equivalent

(2) Nitric Acid, trace metal grade, EMD Omnitrace® grade or equivalent

(3) Reagent Water (DI Water)

(4) Hydrogen Peroxide, 30%

(5) Mixed metal standards – the "Spike 500" and "LLQC" from "Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectroscopy", DCN: 03.6010.00

(6) "P & Sb Spike 500" from "Standard Operating Procedure for Determination of Phosphorus in Flame Retardant Samples by ICP/AES, DCN: 03.6010.01

(7) "Hg 2.5ppm" and "Hg 250ppb" from "Standard Operating Procedure for Mercury Analysis by Flow Injection Mercury System (FIMS 400) in Solid and Semisolid Wastes by Cold Vapor Technique", DCN: 03.7470.00

(8) Nitric Acid, ACS Reagent grade, for cleaning microwave vessels.

8. METHOD PROCEDURE

8.1. Batch QC Requirements

A batch typically consists of 12-15 samples and must consist of the following QC samples:

- Method Blank (MB): this consists of reagent water of the same amount as the sample size and shall be run with each analytical batch.
- Laboratory Control Sample (LCS): one LCS shall be run with each analytical batch. If there is room, a duplicate (LCSD) should also be run.
- Low Level Quality Control Sample (LLQC): one LLQC shall be run with each analytical batch.
- Matrix Spike (MS): at least one MS shall be run with each analytical batch. If there is room in the carousel, a Matrix Spike Duplicate (MSD) should also be run.

- Sample duplicate (DUP): at least one DUP shall be run with each analytical batch.

Due to size constraints, the minimum QC must consist of 1 MB, 1 LCS, 1 MS, and 1 DUP or MSD, which is sometimes limited due to available sample. These QC standards must meet criteria specified in the appropriate analytical methods when analyzed by either ICP-AES or ICP/MS.

8.2. Instrument QC requirements

The CEM modules need to be weighed before and after digestion to check for losses. A weight loss of >1% of both sample and reagents deems the run suspect and indicates that vessels may have vented during the digestion. The control module is used to monitor temperature and pressure of a single sample. Normally, the sample suspected to have the highest reactivity is placed in the vessel containing the control modules. The Milestone ULTRAWAVE does not require weighing of the vessels, as it is one unified chamber.

Power checks on the microwave and validation of the accuracy of the temperature and pressure gauges should be performed periodically. This check is normally done during the preventive maintenance of the instrument.

8.3. Sample Analysis or Preparation

8.3.1. Pre-Digest Sample Handling – Solid Samples

- Obtain sample(s) from sample receiving area, which is typically in the refrigerator in 161, and check out the sample(s) from the sample custody book.

- Gather digestion vessels.

- Fill in log book (Figure 1) accordingly with date, name, authorization, carousel # (for CEM unit) and vessel #, sample names, etc.

  Note: The vessel # should be filled in randomly.

- Use a weighing boat or equivalent to weigh sample. Weighing to 0.0001 g is highly recommended since the sample size is usually 0.5 g or less. Record weight on log book.

  Note: The sample size for these digestions is normally 0.5 g, however, for highly reactive samples, use 0.25 g or less. The sample size should not exceed 0.5 gram (±5%).

  Note: For flame retardant samples, cut each sample into a minimum of 225 mg, not to exceed 240 mg, using carbon steel blade or equivalent. Record the weight on log book. Weigh a minimum of 225 mg, not to exceed 240 mg, of each chosen sample for duplicate or triplicate and MS/MSD. Some flame retardant samples may require different mass depending on their densities. Use less than 225 mg of

samples if the samples fill up more than half of the digestion vessel and write the notes in the comments section of the log sheet.

- For the vessels designated for MB and LCS/LCSD, add an equivalent amount of reagent water for sample amount used (i.e. 0.5 mL for 0.5 g); vessels for MS/MSD should contain an equivalent amount of sample.

- Pipet standard spike(s) into the vessels for LLQC, LCS/LCSD and MS/MSD. Record type of spike and lot number onto log sheet, please refer to Table 1 for appropriate amounts and concentrations of standard spike.

  Note: The decision to use nitric acid only or a mixture of nitric and hydrochloric acids and peroxide will depend on the nature of the sample and the analytes desired. Check with the analyst for clarification.

- Fill any empty vessel positions with "dummy" placeholders and fill with the same reagents used in the other vessels.

8.3.2. Sample Digestion

- Load the samples into the microwave, ensure the appropriate connections have been made (if necessary), and start the appropriate digestion program.

- Obtain appropriate number of 50 mL graduated dilution vials (equipment section, no. 7) and label each vial with the following information:

  Batch number (from log book)
  ECL sample number
  Date of digestion

- Transfer the sample digestates quantitatively from the vessel to corresponding dilution vial. Rinse vessel with reagent water into vial 2-3 times.

  Note: The digestates for the MB, LCS, and LCSD need to undergo the same steps as any sample. For the "dummy" vessels, discard the nitric acid into the waste bottle in the hood.

- Rinse vessel carefully into the vial with DI water thru the syringe; discard syringe and filter to solid lab waste bags in the hood. Cap the vial with its supplied screw cap.

- Dilute each vial to desired volume with DI water and mix. The usual final volumes with the 50 mL graduated dilution vials are 25 mL for solid samples and 50 mL for liquid samples. Samples are now ready for analysis.

  NOTE: Continued gassing may occur; mix contents carefully and check for gassing often while bringing to volume.

- Transfer carousel with vessel assemblies and torque wrench to cleaning area, proceed to Appendix A, Vessel Cleaning.

8.4. Data Reporting

- All the applicable items need to be filled out on bound notebook pages or appropriate log sheets. A copy of the data page(s) along with the SAR package is then submitted to the analyst for metals analysis.

9. MAINTENANCE AND TROUBLE SHOOTING

- Vessels should be cleaned immediately following sample digestion and prior to storage. Procedures for cleaning and storage are described in the Appendices, Section 12.
- Preventive maintenance on the microwave is to be performed as needed by the manufacturer.

Please refer to the Microwave Oven Operating Manual (Ref 10.2).

10. FIGURES

Microwave Acid Digestion

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Batch #: _____ Digestion Method
Date Digested: _____ □ EPA 3051A □ EPA 3052 Lab Notebook #: _____
Digested by: _____ Microwave: _____ Authorization #s: _____

Carosel #	Vessel #	Sample #	Weight of Sample (g)	Final Volume (mL)	Filtered? (y/n)	Comments

Pipettors used: _____

_____ mL of spike was added to LCS/LCSD
_____ mL of spike was added to MS/MSD _____ (sample #)

Reagent ID & Lot #	Initials

Ramp _____ to _____ °C
Digestion _____ @ _____ °C
Cooldown _____ minutes

(Lot # _____)
(Lot # _____)

Balance used: _____

o Filtered using

	Time	Initials
concentrated HNO3 added		
concentrated HCl added		
Digestion begun at		
Digestion ended at		
Ready for Analysis		

Digestion Chemist / Date

Reviewed by / Date

Figure 1. Microwave Digestion Logbook

11. TABLES

Type of sample	**Sample amount**	**Final volume**	**Spike volume and spike type**	**Acidic mix**
Solid wastes/soil	0.2-0.25 g	25 mL	0.313 mL (Spike 500 and LLQC)	UltraWAVE: HNO_3: HCl (4.5mL: 2.5 mL) or 5mL HNO_3 CEM: HNO_3: HCl (9 mL: 3 mL) or 10 mL HNO_3
Solid wastes/soil	0.2-0.25 g	25 mL	0.1 mL (Hg 2.5ppm and Hg 250ppb)	5mL HNO_3
Flame retardant chemicals	0.225 g	37.5 mL	0.375 mL (P & Sb Spike 500)	HNO_3: HCl: 30% H_2O_2 (4 mL: 0.5 mL: 0.5 mL)
Glass (silicates)	0.2-0.25 g	< 20mL	0.313 mL (Spike 500 and LLQC)	HNO_3: HCl (4.5mL: 2.5 mL) or 5mL HNO_3
Liquid wastes (TCLP leachates)	5 mL	25 mL	0.313 mL (Spike 500 and LLQC)	HNO_3: HCl (4.5mL: 2.5 mL) or 5mL HNO_3
Liquid wastes (TCLP leachates)	5 mL	25 mL	0.1 mL (Hg 2.5ppm and Hg 250ppb)	5mL HNO_3

Table 1: Typical matrix specific parameters

12. REFERENCES

12.1. SW-846, US EPA, HW Test Methods:

(1) 3010, Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis

(2) 3015, Microwave Assisted Acid Digestion of Aqueous Samples and Extracts

(3) 3050, Acid Digestion of Sediments, Sludges, and Soils for Total Metals Analysis

(4) 3051, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

(5) 6010, Analysis of Metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy

12.2. UltraWAVE Operator Manual MA149, Milestone

12.3. Microwave Oven Operating Manual, CEM Corp.

12.4. "Acid Digestion of Aqueous Samples and Extracts for Total Metals", State of California, Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3010.00

12.5. "Acid Digestion of Sediments, Sludges, Soils, and Metallic Samples", State of California, Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3050.00

12.6. "Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectroscopy", State of California, Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.6010.00

12.7. "Determination of Phosphorus in Flame Retardant Samples by ICP/AES", State of California Department of Toxic Substance Control, Environmental Chemistry Laboratory, DCN: 03.6010.01

12.8. "SOP for Microwave Assisted Digestion Using Milestone UltraWAVE Digestion Unit", State of California, Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3051.01

12.9. "Technical SOP for the Operation of the CEM Microwave Digestion Unit", State of California, Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3051.02

13. APPENDICES

Appendix A. Vessel Cleaning

This appendix describes the steps for cleaning the microwave vessels and should be performed after sample digestion (Section 8.3.4)

Rinse interior of vessel with reagent water and discard rinse in waste bottle until vessel appears relatively clean.

Add 10mL of ACS grade nitric acid into vessel. Repeat for all vessels.

Perform the cleaning digestion by following the steps of Section 8.3.4 "Sample Digestion." Discard the ACS grade nitric acid into waste bottle.

Repeat the cleaning digestion using 10 mL of ultrapure (trace level grade) nitric acid.

Note: Experience has shown that two cleanings with nitric acid, one with ACS and one with trace level grade, are adequate. Occasionally, with stubborn samples or some with very high metal content (e.g., glass with 4% barium), an extra cleaning may be needed. In this case, perform two cleanings with ACS grade and one with ultrapure (Omnitrace) nitric acid.

If blank checks are desired, continue with this step, otherwise skip to next step. Transfer contents of each vessel to 50 mL labeled dilution vials, rinse vessel carefully into vial and dilute to 25 mL with reagent water, and cap all vials.

Generously rinse covers and vessels with reagent water. Set aside to dry on clean paper towels or place on drying rack.

Note: An alternative is to store vessels with DI water. Fill CEM vessels to within 5 mm of top with reagent water. Cap vessels, return to support module, tighten hold-down bolt finger-tight, and return to its corresponding spot on carousel. Milestone vials can be stored in a container filled with DI. Store this way until needed for analysis.

14. REVIEW

Signatures	Date
	2/1/2019