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# CCP-TP-183

Revision 0

# CCP
# Microwave Assisted Digestion of Homogeneous Solids and Soil/Gravel

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# 1. ABSTRACT

Closed vessel microwave digestion is used to prepare homogeneous solids and soil/gravel samples for total metals characterization. This Central Characterization Project (CCP) procedure, which is based on EPA SW-846 Method 3051, uses a mixture of nitric and hydrochloric acids to improve recoveries of several troublesome analytes, including silver and antimony. A MARS microwave sample preparation system is used to perform this procedure.

# 2. APPLICABILITY

This method is applicable for microwave-assisted digestion of homogeneous solids and soil/gravel samples for total metals characterization per the requirements of the Waste Isolation Pilot Plant (WIPP) Waste Analysis Plan (WAP). Digestates from this method may be used for ICP-AES determination of WAP-required metals. WAP metals include antimony, arsenic, barium, beryllium, cadmium, chromium, lead, nickel, selenium, silver, thallium, vanadium, and zinc. Mercury cannot be determined reliably in digestates prepared from this method.

This procedure functions as an Idaho Cleanup Project (ICP) Use Type 2 document for performing operations in the Analytical Laboratories Department (ALD) facilities.

Personnel performing this procedure will be trained and qualified in accordance with CCP-QP-002, *CCP Training and Qualification Plan*, prior to performing this procedure.

# 3. DISCUSSION

## 3.1 Microwave Digestion

Closed vessel microwave acid digestion is a widely accepted technique to prepare samples for metals analysis. Microwave heating accelerates digestion as the microwave energy heats the sample and matrix uniformly through absorption of radiation rather than heat conduction. The use of sealed Teflon digestion vessels allows both elevated pressures and temperatures. Considerably less time is required for digestion than similar procedures carried out at atmospheric pressure that are limited by the boiling point of the acid. The time required to achieve a desired temperature or pressure is a function of several parameters including the mineral acid matrix used in the digestion, the volume of digestion matrix, and the available power in the microwave cavity.

Control of the temperature and pressure during closed vessel digestions is critical to both the reproducibility and safety of the method. Current microwave technology includes systems to monitor the pressure and temperature within a “control vessel.” The temperature and pressure in the control vessel represents the temperature and pressure within other vessels in same microwave system. Control

of the digestion temperature/pressure stabilizes the reaction conditions and allows for improved reproducibility. Temperature/pressure control also minimizes equipment damage from weakened and/or overpressurized vessels.

This method provides instructions for the use of the CEM MARS Microwave Accelerated Reaction System (MARS). A single stage procedure using concentrated nitric and hydrochloric acids is used to digest homogeneous solids and soil/gravel samples. The digestion is controlled at an operational temperature limit of 150 °C. The system maintains the control parameter for five minutes. The digestion provides satisfactory recoveries for all analytes even though the 175 °C temperature limit of SW-846 Method 3051 is not attained with this mixture of acids.

### 3.2 MARS System

The MARS consists of a laboratory microwave oven with built-in pressure controller, a fiber optic temperature probe, and lined digestion vessels. The microwave system allows operator selectable output of up to 1200 watts at a frequency of 2450 MHz. The standard pressure control system for the MARS is the ESP-1500 Plus (Electronic Sensor-Pressure). The ESP-1500 Plus consists of two parts: the control electronics and connector, and the ESP sensor. The control electronics and connector are located within the instrument. The ESP sensor consists of a pressure sensing load-cell mechanism and a cavity connector. The ESP sensor connects the reference vessel to the ESP-1500 Plus connector located in the microwave cavity. The standard temperature control system for the MARS is the RTP-300 Plus. The microwave transparent temperature probe is inserted into a thermowell that extends into the control vessel and the probe connects to a snap-in port within the microwave cavity. The temperature probe emits a feedback signal to the system magnetron regulating the power output.

The MARS delivers 1200 watts of microwave energy when operated at full power. To allow finer control, the operator is allowed to select one of three power levels and one of five operating control types. The power level is selected based on the number of vessels to be used in the digestion. The operating control types include standard control, ramp to temperature, ramp to pressure, power/time control, and microvap. In this method the ramp-to-temperature mode is used as the control type. The instrument controls the power output, up to the maximum selected, to ensure the temperature inside the control vessel achieves the programmed level within the specified time. The MARS has capacity for 14 digestion vessels.

The HP-500 Plus is the digestion vessel used with the MARS. The HP-500 Plus consists of a 100-mL, chemically resistant liner and cover to contain and isolate the sample. An advanced composite sleeve reinforces the vessel liner and the assembly is sealed using a polypropylene support module. The HP-500 Plus is

designed for a maximum operating temperature of 210 ºC and a maximum operating pressure of 350 psig. All vessel components are transparent to microwave energy so the sample and the matrix liquid can absorb the maximum amount of incident microwave energy.

EPA SW-846 Method 3051 requires calibration of the microwave power at least every six months unless the microwave system uses temperature feedback control capable of replicating the performance specifications of the method. The MARS system is always used with temperature control, and microwave power calibration therefore is not required with this system.

# 4. SAFETY PRECAUTIONS

## 4.1 Chemical Hazards

4.1.1 Handle all chemicals per MCP-3635, "Chemical Hygiene Plan."

4.1.2 Wear the following standard laboratory PPE in the lab:

A. Lab coat

B. Safety glasses with side shields

C. Substantial footwear

D. Appropriate gloves.

4.1.3 Change gloves immediately upon chemical contact.

4.1.4 Handle corrosives per ACLP-0.27, "Routine Handling of Corrosives."

4.1.5 Handle all spills per ACLP-0.24, "Laboratory Spill Cleanup."

## 4.2 Radiological Hazards

4.2.1 Perform all work under an applicable RWP per MCP-7, "Radiological Work Permit."

4.2.2 Handle nonroutine samples per ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples."

4.2.3 If overpressurizing or venting of vessels occurs, request RCT survey work area before continuing work.

4.2.4 Obtain RCT support when transferring radiological samples in open containers.

4.2.5 Handle all samples in a glovebox until acid has been added in order to minimize potential spread of alpha contamination.

4.2.6 Keep hood sash closed while samples are digesting in the microwave.

**4.3 Microwave Hazards**

4.3.1 Be cautious of high pressure and temperatures attained due to heating acid solutions in sealed, lined digestion vessels.

4.3.2 Vent exhaust from the microwave blower into the hood exhaust system.

**WARNING**

**Failure to decrease the microwave power level for smaller sample loadings may cause the lined vessels to overpressurize and result in catastrophic vessel failure.**

4.3.3 Ensure that the microwave power level is set to the value appropriate for the number of samples being digested.

4.3.4 Allow the vessels to cool for at least 10 minutes in the microwave cavity with the magnetrons power off before opening the microwave system door.

4.3.5 Allow the vessels to cool until the pressure inside the control vessel drops below 50 psig and 100 °C prior to venting.

4.3.6 Manually vent the vessel into the microwave cavity or a fume hood before opening vessels or vessel connections.

**WARNING**

**Failure to use safety membranes appropriately may result in venting of toxic gases and/or sample and may result in vessel failure.**

4.3.7 Do not install more than one safety membrane in a lined digestion vessel.

4.3.8 Use a new safety membrane for each sample run.

4.3.9 Do not exceed the sample loading of 0.55 g for each sample.

4.3.10 Ensure the sample loading and the reactivity of the sample in each vessel is nearly the same in order to minimize the possibility of overpressurizing vessels.

4.3.11 Do not allow digestion temperatures to exceed 300 $^{o}$C as fluoropolymer materials may soften.

**WARNING**

**Use of vessels with cracks or fissures in the body or cap may result in unsafe operating conditions.**

**NOTE:** *The repeated cycles of elevated temperatures and pressures during this procedure cause a reduction in the mechanical strength of vessel components. At present it is not possible to predict the lifetime of these vessels.*

4.3.12 Inspect the digestion vessels per Section 7.1 and discard components showing signs of degradation.

### 4.4 Waste Disposition and Pollution Prevention

4.4.1 Manage all waste generated per ACLP-0.40, "Analytical Laboratories Waste Management."

## 5. APPARATUS AND REAGENTS

### 5.1 Apparatus

5.1.1 General Equipment

5.1.1.1 Plastic funnels, Nalgene 4250-0055, or equivalent

5.1.1.2 Analytical balance, 100-g minimum capacity and 1-mg sensitivity

5.1.1.3 Bottles, wide mouth, Nalgene 2104-0002, I-CHEM N311-0060, or equivalent

5.1.1.4 Disposable syringes, 60-mL, or equivalent

5.1.1.5 Membrane removal tool, CEM Part No. 301640, or equivalent

5.1.1.6 Mechanical pipetors, 0.500- and 1.00-mL, Eppendorf, or equivalent, whose calibration has been verified per ACLP-2.06, "Mechanical Pipetor Calibration Verification Procedure for Spectrochemistry."

5.1.1.7 Pipetor tips, 1–200 µL, Fisherbrand p/n 21-197-8E, or equivalent

5.1.1.8 Pipetor tips, 201–1000 µL, Fisherbrand p/n 21-197-8A, or equivalent

5.1.1.9 Printer

5.1.1.10 Repipet dispensers, 10-mL, or equivalent

5.1.1.11 Spatula, Fisher Scoopula, or equivalent

5.1.1.12 Syringe filters, 0.45-µm, 25-mm diameter, surfactant-free cellulose acetate (SCFA), Nalgene 191-2045, or equivalent

5.1.1.13 Tweezers, 4-inch, or equivalent

5.1.1.14 Vessel liner transport rack, custom, fabricated from HDPE

5.1.1.15 Vessel liner drying rack, custom, fabricated from HDPE

5.1.1.16 Volumetric flasks, 50-mL, Class A glass or Class B polymethylpentene

5.1.1.17 Weighing boats, quartz, approximately 5-mL

5.1.1.18 Tweezers, 8-inch, or equivalent

5.1.2 Microwave Accelerated Reaction System, Model MARS (with pressure control and temperature control)

5.1.2.1 HP-500 Plus Standard Vessel Assembly, 100-mL, CEM p/n 431690, or equivalent

5.1.2.1.1 Sleeve, composite, CEM p/n 431740, or equivalent

5.1.2.1.2 Liner, CEM p/n 431110, or equivalent

5.1.2.1.3 Cap, HP-500 Plus Standard, CEM p/n 431250, or equivalent

5.1.2.1.4 Load disc, CEM p/n 430500, or equivalent

5.1.2.1.5 Vent nut, CEM p/n 431313, or equivalent

5.1.2.1.6 Support module with label, CEM p/n 431636 and 431795, or equivalent

5.1.2.1.7 Nut, 19 mm, CEM p/n 430507, or equivalent

5.1.2.2 HP-500 Plus Control Vessel Assembly, 100-mL, CEM p/n 431797, or equivalent

5.1.2.2.1 Sleeve, composite, CEM p/n 431740, or equivalent

5.1.2.2.2 Liner, CEM p/n 431110, or equivalent

5.1.2.2.3 Cover, control, CEM p/n 431255, or equivalent

5.1.2.2.4 Nut, thermowell, CEM p/n 325028, or equivalent

5.1.2.2.5 Load disc, CEM p/n 430501, or equivalent

5.1.2.2.6 Spacer, CEM p/n 325210, or equivalent

5.1.2.2.7 Vent nut, CEM p/n 431313, or equivalent

5.1.2.2.8 Control support module with label, CEM p/n 431775 and 431795, or equivalent

5.1.2.2.9 Screw, 19-mm, CEM p/n 430508, or equivalent

5.1.2.2.10 Plug, probe, CEM p/n 325215, or equivalent

5.1.2.2.11 Ferrule nut, CEM p/n 431311, or equivalent

5.1.2.3 Safety membrane, CEM p/n 431300, or equivalent

5.1.2.4 Fiber optic temperature gauge, RTP-300 PLUS, or equivalent

5.1.2.5 ESP-1500 Plus Pressure Control System, or equivalent

5.1.2.6 Sample turntable, 14-position, CEM p/n 431355, or equivalent

5.1.2.7 Safety membrane installation tool, or equivalent

5.1.2.8 Torquing tool or preset torque wrench set at 5 ft·lb, or equivalent

5.1.2.9 Thermowell, CEM p/n 326280, or equivalent

## 5.2 Reagents

Use Analytical Reagent Grade chemicals and ASTM Type II conductivity or better water for preparation of all reagents, standards, and samples, unless otherwise specified.

5.2.1 Nitric acid ($HNO_3$), concentrated (70%), Trace Metal Grade

5.2.2 Hydrochloric acid (HCl), concentrated (37%), Trace Metal Grade

5.2.3 Spike stock solution(s) (SpSt). One or more standard solutions provided by the Quality Control Laboratory per ACLP-1.01, "Preparation of Quality Control Reagents and Standards," and tracked and used per ACLP-2.05, "Control, Distribution and Use of Spectrochemical Standards." The solutions are used to prepare matrix spike (MS) and matrix spike duplicate (MSD) samples. Typically an SpSt concentration is 100 times the desired matrix spike added concentration for each analyte. Typical SpSt composition follows:

Spike Stock Part A (SpStA)

| Component | Concentration |
|---|---|
| Antimony (Sb) | 100 µg/mL |
| Arsenic (As) | 100 µg/mL |
| Barium (Ba) | 100 µg/mL |
| Beryllium (Be) | 100 µg/mL |
| Cadmium (Cd) | 20 µg/mL |
| Chromium (Cr) | 100 µg/mL |
| Nitric acid | 2% minimum |
| Hydrochloric acid | As needed |

Spike Stock Part B (SpStB)

| Component | Concentration |
|---|---|
| Lead (Pb) | 100 µg/mL |
| Nickel (Ni) | 100 µg/mL |
| Selenium (Se) | 20 µg/mL |
| Silver (Ag) | 100 µg/mL |
| Thallium (Tl) | 100 µg/mL |
| Vanadium (V) | 100 µg/mL |
| Zinc (Zn) | 100 µg/mL |
| Nitric acid | 2% minimum |

5.2.4 Laboratory Control Sample (LCS). Use Environmental Resource Associates (ERA) CLP soil standard or equivalent, which contains all target analytes at quantifiable concentrations. This material has established statistical control limits. Use the solid LCS within the manufacturer-specified shelf life or within 5 years of receipt if the manufacturer does not specify a shelf life.

## 6. SAMPLE HANDLING

6.1 Store samples at 4 °C before digestion.

**NOTE:** *SW-846 allows a range of ±2 °C around the specified storage temperature.*

6.2 Store digestates at room temperature until analysis.

6.3 Digest samples within 180 days of sample collection.

6.4 Analyze samples in analytical batches. An analytical batch is defined as a suite of samples that is processed as a unit, using the same analytical method, and within a specific time period. An analytical batch can be up to 20 samples (excluding laboratory QC samples), all of which are received by the laboratory within 14 days of the validated time of the sample receipt (VTSR) of the first sample in the batch.

# 7. PROCEDURES

## 7.1 Vessel Inspection

7.1.1 IF vessel liners need cleaning,
THEN clean the liners per Section 7.8.

7.1.2 Use the Teflon inner vessels and support modules together as sets instead of arbitrarily mixing them.

**NOTE:** *This minimizes the possibility that one or more vessels will seal incompletely after they have been through a series of digestion cycles.*

7.1.3 Visually inspect the lined digestion vessels for distortion or mechanical damage, dark yellow staining, cracking, pitting, grooving, or other signs of use-related stress.

7.1.4 Inspect support modules for signs of acid degradation (deep yellow coloring).

**NOTE:** *A damaged support module is brittle and low in strength.*

7.1.5 Replace any items showing damage or signs of excessive wear.

## 7.2 Preparing Samples and QC Samples for Microwave Digestion

**NOTE:** *The terms "vessel liner" and "digestion vessel" are used generically in this section and refer to the HP-500 Plus vessel.*

7.2.1 Prepare the LB.

7.2.1.1 Place an empty, clean quartz weighing boat in a vessel liner.

7.2.1.2 Record the unique identifier of the LB in the digestion record as "LB-LLL-pp," where "LLL" is the ALD logbook number and "pp" is the page number.

7.2.2 Aliquot the LCS.

7.2.2.1 Mix the solid LCS material.

7.2.2.2 Weigh 0.5 ± 0.05 g of the LCS into a quartz weighing boat.

7.2.2.3 Place the quartz boat containing the LCS into a vessel liner.

7.2.2.4 Record the unique identifier of the LCS in the digestion record as "LCS-LLL-pp," where "LLL" is the ALD logbook number and "pp" is the page number.

7.2.3 Aliquot each sample in the analytical batch.

**NOTE 1:** *When possible, the largest and/or most reactive sample should be placed in the vessel outfitted with the pressure/temperature control cover.*

**NOTE 2:** *The total variation in sample weights should be less than 0.025 g or 5%. The maximum sample size to be used is 0.55 g. All the samples in a batch to be digested should be nearly the same in quantity and type, when possible.*

**NOTE 3***:* *At least one matrix spike (S) and one matrix spike duplicate (SD) are required for each analytical batch.*

7.2.3.1 Mix the sample.

7.2.3.2 Weigh 0.5 ± 0.05 g of sample into a quartz weighing boat.

7.2.3.3 Place the quartz weighing boat into a vessel liner.

7.2.3.4 IF the sample is selected for spike (S) and spike duplicate (SD) preparation,
THEN weigh two additional 0.5 ± 0.05-g sample aliquots into separate quartz weighing boats.

7.2.3.4.1 Place the quartz weighing boats into vessel liners.

7.2.3.4.2 Record the identifiers for the spike and spike duplicate as the lab sample ID plus the suffix "S" for the spike and "SD" for the spike duplicate.

7.2.4 Slowly add 6 mL of concentrated Trace Metal Grade $HNO_3$ to each digestion vessel.

7.2.5 Add 5 mL of concentrated Trace Metal Grade HCl to each digestion vessel.

7.2.6 Pipet 0.5 mL of spiking solution part A (SpStA) and 0.5 mL of spiking solution part B (SpStB) directly into both the matrix spike (S) and matrix spike duplicate (SD) vessels, and record the volume and identity of the solutions added.

7.2.7 Set the samples aside in the fume hood for at least 20 minutes to allow time for the most reactive components to react and evolve gases without pressure buildup inside the vessels.

**7.3 Assembling HP-500 Plus Vessels and Connecting the HP-500 Plus Control Vessel**

7.3.1 IF the turntable is NOT in place in the microwave cavity, THEN place the turntable into the instrument cavity with the straight line on the label in the center of the turntable aligned with the flat edge of the turntable lug.

7.3.2 Assemble the HP-500 Plus standard vessels.

**CAUTION**

**Installing more than one safety membrane can cause the vessel to rupture if it overpressurizes.**

**NOTE:** *When assembling vessels for cleaning, it is not necessary to install a new safety membrane into the vent fitting as long as the safety membrane from the analytical run is in place.*

7.3.2.1 Install a single safety membrane into the vent fitting.

7.3.2.1.1 Use the safety membrane installation tool to remove a safety membrane from the storage case.

7.3.2.1.2 Place the membrane into the fitting and press firmly to release it into the vent fitting.

**CAUTION**

**Failure to properly seat the membrane in the vent fitting of a standard vessel will result in leakage.**

7.3.2.1.3 Ensure that the membrane is laying flat on the bottom of the vent fitting.

7.3.2.2 Place the vessel cover on top of the vessel liner.

7.3.2.3 Place the brown load disk on the cover, ensuring that the circular depression on the disk is facing upward.

**CAUTION**

**Using a HP-500 Plus vessel without a heat shield in the bottom of the support module and a sleeve between the liner and support module can cause the support module to soften, resulting in vessel failure.**

7.3.2.4 Insert the liner into a clean, dry sleeve.

7.3.2.5 Ensure a heat shield is placed in the bottom of the support module.

7.3.2.6 Install the completed vessel assembly into the support module with the vent stem oriented towards the right side of the support module.

7.3.2.7 Screw the vent fitting onto the vent stem of the cover.

7.3.2.8 Rotate the vessel so the vent fitting is positioned toward the front of the support module (end with label).

**NOTE:** *The front of the support module is the end with the label.*

7.3.2.9 Center the support module screw in the recessed area in the control cover and tighten the screw finger tight.

7.3.2.10 Tighten the screw with the torque wrench until the torque wrench clicks (approximately one-half turn).

7.3.2.11 Place the vessel into the turntable by inserting the bullet-shaped locking tab of the support module into a slot in the raised center of the turntable.

7.3.2.11.1 Press the turntable key to rotate the turntable when needed.

7.3.2.11.2 Space the vessels as evenly as possible around the turntable so the load will be properly balanced.

7.3.3 Assemble and connect the HP-500 Plus control vessel.

**CAUTION**

**Installation of the thermowell ferrule nut in the cover assembly prior to installation of the thermowell will distort the opening in the cover. Installation of the thermowell will be difficult or impossible and leakage can occur.**

7.3.3.1 IF the thermowell is NOT installed in the HP-500 Plus control vessel cover,
THEN perform the following steps:

7.3.3.1.1 Insert the open end of the thermowell into the locking ferrule nut and slide it through the temperature port cover.

7.3.3.1.2 Tighten the locking ferrule nut finger tight.

7.3.3.1.3 Verify that the thermowell is locked securely by holding the cover and slightly pulling on the thermowell; the thermowell should not feel loose.

7.3.3.2 Install a single safety membrane into the vent fitting.

**CAUTION**

**Installing more than one safety membrane can cause the vessel to rupture if it overpressurizes.**

7.3.3.2.1 Use the safety membrane installation tool to remove a safety membrane from the storage case.

7.3.3.2.2 Place the membrane into the fitting and press firmly to release the membrane into the vent fitting.

**CAUTION**

**Failure to properly seat the membrane in a control vessel will result in leakage and an incorrect pressure reading.**

7.3.3.2.3 Ensure that the membrane is laying flat on the bottom of the vent fitting.

7.3.3.3 Place the vessel cover on top of the vessel liner.

7.3.3.4 Place the Teflon spacer on the control cover.

7.3.3.5 Place the brown load disk on the control cover, ensuring the circular depression on the disk is facing upward.

**CAUTION**

**Using an HP-500 Plus control vessel without a heat shield in the bottom of the support module and a sleeve between the liner and support module can cause the support module to fail, resulting in vessel failure.**

7.3.3.6 Thread the Teflon vent fitting onto the vent stem of the vessel cover.

7.3.3.7 Insert the liner into a clean, dry sleeve.

7.3.3.8 Ensure a heat shield is in place in the bottom of the support module.

7.3.3.9 Install the completed control vessel assembly into the support module, placing the vessel assembly in the support module with the vent stem oriented towards the right side of the support module.

7.3.3.10 Lock the vessel assembly in place by rotating the locking tab.

7.3.3.11 Tighten the pressure tubing leading from the ESP-1500 Plus to the pressure port on the control cover.

7.3.3.12 Rotate the vessel so the vent fitting is positioned toward the front of the support module (end with label).

7.3.3.13 Center the support module screw in the recessed area in the control cover and tighten the screw finger tight.

7.3.3.14 Use the torque wrench to tighten the screw until the wrench clicks (approximately one-half turn).

7.3.3.15 IF the RTP-300 Plus is NOT positioned in the probe holder, THEN slide the probe holder onto and ~6–7 inches up the RTP-300 Plus probe.

7.3.3.16 Insert the RTP-300 Plus through the module screw.

7.3.3.17 Slide the probe holder down the RTP-300 Plus and gently press it into the hole in the center of the module screw.

7.3.3.18 IF the MARS is off,
THEN position the power switch in the On position.

**NOTE:** *Following a series of screens, the **Main Menu** screen will appear.*

7.3.3.19 Place the control vessel in the turntable in the position labeled Control Vessel.

7.3.3.20 Install the vessel-retaining ring on the vessels with the notch of the retaining ring resting on the control vessel.

7.3.3.21 Press the turntable key to rotate the turntable and position the control vessel in the back left-hand corner of the instrument cavity (facing instrument).

**CAUTION**

**Loosening the pressure line nut during installation of the ESP-1500 Plus can cause leakage and corrosion of the connections on the sensor and bulkhead fitting.**

7.3.3.22 Connect the ESP-1500 Plus pressure controller to the connector on the right side of the instrument cavity (facing instrument).

7.3.3.22.1 Rotate the ESP-1500 Plus while gently pushing it into the correct position to align it with the connector port.

7.3.3.22.2 Push the ESP-1500 Plus into the connector port until the polypropylene guard is fully seated against the connector port.

7.3.3.23 Snap the RTP-300 Plus into the connector in the top of the cavity, ensuring it does not cross the ESP-1500 Plus cable.

7.3.3.24 Position the pressure tubing in the guide ring mounted on the roof of the cavity.

7.3.3.25 Permit the turntable to rotate 2 or 3 times to ensure the pressure sensing tubing and the temperature probe do not become entangled.

7.3.3.25.1 IF problems are observed,
THEN rotate the turntable until the control vessel is in the far left-hand corner and correct the problem.

7.3.3.25.2 Permit the turntable to rotate 2 or 3 times to ensure the pressure sensing tubing and the temperature probe do not become entangled.

7.3.3.25.3 Repeat Steps 7.3.3.25.1 and 7.3.3.25.2 as needed to ensure the pressure sensing tubing and temperature probe are not entangled.

7.3.3.26 Close the door to the MARS.

### 7.4 MARS Setup and Operation

**NOTE:** *The operating program for the digestion is stored in the microcomputer in the **User Menu** under the name **Mod 3051 MARS** (Table 1, Operating Program Parameters for MOD 3051 MARS, provides the operating parameters). Mod 3051 MARS is edited with each analytical run to ensure the appropriate power level is used to accommodate the number of vessels in the microwave. A single heating stage is used in this method. When loaded and started, the procedure will run automatically to heat the samples until an operational temperature limit of 150 °C is attained and holds at this value for 5 minutes. The instrument microcomputer will vary the microwave power output to ensure the programmed temperature is achieved. Following the digestion, a ten-minute cool-down period is activated. During this period the instrument fans continue to operate and the door remains locked to prevent handling of the vessels at higher temperatures and pressures.*

7.4.1 Use the arrow keys to highlight **Edit/Create Method** and press the Select key to display the **Directory Menu** screen.

7.4.2 Use the arrow keys to highlight **User Directory** and press the Select key to display the **User Directory** screen.

7.4.3 Use the arrow keys to highlight **Mod 3051 MARS** method.

7.4.4 Press the Select key to review the parameters of the method and display the **Select Vessel Type** screen.

7.4.5 Ensure the HP-500 vessel type is highlighted and press the Next key to move to the **Select Control Type** screen.

7.4.6 Use the arrow keys to highlight **Ramp To Temperature** from the **Select Control Type** screen and press the Select key to display the **Enter Methods Parameters** screen.

7.4.7 IF the power level displayed on the screen is NOT appropriate for the sample loading per the guidelines in the following table,
THEN highlight the wattage to be edited using the arrow keys and select the appropriate power for the number of vessels to be microwaved.

General guidelines for 100% power

| Number of Vessels | Power Level |
|---|---|
| 1–2 | 300 watts |
| 3–5 | 600 watts |
| 6 or more vessels | 1200 watts |

7.4.8 Review all other method parameters displayed on the **Enter Methods Parameters** screen to ensure agreement with the following table:

Table 1. Operating Program Parameters for MOD 3051 MARS.

| Stage | Power | | Ramp | PSI | °C | S | Hold |
|---|---|---|---|---|---|---|---|
| | Max | % | | | Control | | |
| 1 | 1200 W | 100 | 15:00 | 250 | 150 | No | 5:00 |

7.4.8.1 IF the displayed method parameters do NOT agree with Table 1,
THEN change the displayed method parameter to agree with the parameters outlined in Table 1.

7.4.9 Press the Next key twice to display the **Method Information** screen.

7.4.10 IF the number-of-vessels parameter does NOT agree with the current sample loading,
THEN use the arrow key to highlight the parameter and change it using the number pad.

7.4.11 IF any other parameters on the **Method Information** screen need to be updated,
THEN highlight the parameter using the arrow keys and correct the information.

7.4.12 Press the Next key to save the method and return to the **Main Menu**.

7.4.13 IF the method to be performed is NOT showing on the screen as the current method,
THEN use the arrow keys to highlight **Load Method** and press the Select key.

7.4.13.1 Use the arrow keys to highlight **User Directory**.

7.4.13.2 Press the Select key to display the **User Directory** screen.

7.4.13.3 Use the arrow keys to highlight **Mod 3051 MARS**.

7.4.13.4 Press the "1" key to review the method program.

7.4.13.5 IF modification to the method is required,
THEN edit the method parameters per Steps 7.4.4 through 7.4.12.

7.4.14 Print the method.

7.4.15 Date and initial or sign the method printout and retain it for inclusion with the sample raw data.

7.4.16 Press the Home key to return to the main menu.

7.4.17 Press the Start key.

7.4.18 IF the ESP-1500 Plus measures a pressure reading greater than 50 psig AND a warning screen appears,
THEN press the "2" key to zero the pressure sensor and allow the run to continue.

7.4.19 Digest the samples.

7.4.19.1 IF problem(s) are detected,
THEN halt the system temporarily with the Stop key, correct the problem(s), and resume the stage with the Start key.

7.4.19.2 IF the digestion is stopped by the operator
OR by the Reacti-Guard Cavity Sensing System due to vessel overpressurization,
GO TO Section 7.5 for overpressurization recovery.

7.4.20 IF the minimum operational temperature of 150 °C was NOT attained, THEN perform the following steps:

7.4.20.1 IF the digestion has been performed twice, GO TO Section 7.6 to vent and open the vessel.

7.4.20.2 Remove the vessel from the microwave cavity and vent the vessel per Steps 7.6.1 through 7.6.8.4.

7.4.20.3 Remove the safety membrane.

7.4.20.4 Install a new safety membrane per Step 7.3.2.1.

7.4.20.5 Screw the blue vent fitting onto the threaded stem of the cover.

7.4.20.6 IF the vessel is a standard vessel, THEN reinstall the completed vessel assembly in the turntable.

7.4.20.7 IF the vessel is a control vessel, THEN connect the control vessel to the microwave.

7.4.20.8 GO TO Step 7.3.3.15 and redigest the samples.

## 7.5 Overpressurization Recovery

**CAUTION**

**Damage to the vessel liner and cover often occurs when a vessel overpressurizes and vents.**

**NOTE:** *The Reacti-Guard Cavity Sensing System is a vibration sensor that responds to unusual motion (usually the result of a vessel overpressurization) within the microwave cavity. When an event is detected, the microwave heating program is paused and an error message is displayed on the screen. The purpose of the Reacti-Guard Cavity Sensing System is to protect against instrument damage due to an undetected vessel event and continued heating of released liquids/vapors inside the cavity.*

7.5.1 IF the digestion is stopped by the operator
OR by the Reacti-Guard Cavity Sensing System due to vessel overpressurization,
THEN allow the vessels to cool and request a radiological evaluation of the work area by an RCT.

7.5.1.1 IF radiological survey results are within the applicable RWP guidelines for hood work,
GO TO Step 7.5.2.

7.5.1.2 IF radiological survey results exceed the guidelines for hood work but do NOT exceed the limiting conditions for hoods that void the RWP,
THEN decontaminate the work area.

7.5.1.3 IF radiological survey results exceed the levels of the limiting conditions that void the RWP,
THEN stop work and contact both ALD management and RadCon management for direction.

7.5.2 Remove the overpressurized vessel(s) from the sample turntable.

7.5.3 Contact the Spectrochemistry technical lead to determine if the overpressurized sample(s) should be discarded.

**NOTE:** *When sufficient sample exists, the content from the overpressurized vessel(s) is normally discarded and the affected samples redigested.*

7.5.4 Reload the program that was operating when overpressurization occurred.

7.5.5 Edit the power level as necessary to correspond to the reduced sample loading (see Step 7.4.7).

7.5.6 Continue digestion of the samples by restarting the program and running to completion per Step 7.4.20.

## 7.6 HP-500 Plus Venting and Opening Procedures

7.6.1 Allow the vessels to cool in the microwave cavity for ten minutes with the turntable rotating.

**NOTE:** *The pressure and/or temperature vs. time profile prints automatically.*

7.6.2 Date and initial or sign the pressure and/or temperature vs. time profile printout, and retain it for inclusion with the sample raw data.

7.6.3 Open the oven door and allow the turntable to rotate until the control vessel is located in the right front corner.

7.6.4 Wait until the pressure in the control vessel is less than 50 psig and the temperature in the control vessel is less than 100 ºC.

7.6.5 Disconnect the RPT-300 Plus temperature probe from the microwave cavity.

7.6.6 Disconnect the ESP-1500 Plus pressure controller from the connector port on the right side of the instrument cavity.

7.6.7 Remove the vessel-retaining ring.

7.6.8 Perform the following steps for each digestion vessel:

7.6.8.1 Remove a vessel assembly from the turntable.

7.6.8.2 IF the vessel assembly includes the control vessel, THEN remove the RPT-300 temperature probe from the vessel by loosening the probe holder at the top of the module screw and gently pulling the probe from the thermowell and through the module screw.

7.6.8.3 Ensure that the vessel is in an operating fume hood and that the vent stem is directed into the hood.

**WARNING**

**Improper positioning of the vessel during venting can result in the spread of chemical or radiological contamination.**

7.6.8.4 Slowly relieve the pressure on the vessel.

7.6.8.4.1 Grasp the support module with one hand.

7.6.8.4.2 Loosen the Teflon vent fitting by slowly turning in a counter-clockwise direction.

7.6.8.4.3 IF the vent fitting cannot be loosened due to the position of the vent fitting against the support frame,
THEN crack the module screw and rotate the vessel assembly towards the center and repeat Step 7.6.8.4.2.

7.6.8.4.4 Use a series of slow, partial turns to loosen the fitting to ensure the decomposition gases release through the fitting.

7.6.8.5 IF the vessel assembly includes the control vessel,
THEN loosen the module screw and rotate the assembly to center the vent fitting.

7.6.8.5.1 Remove the ESP-1500 Plus pressure controller by loosening the fitting that connects the pressure tubing to the pressure port on the control cover.

**WARNING**

**Failure to vent and depressurize prior to removing the liner and internal components from the polypropylene support module can result in ejection of acid and injury to the operator.**

7.6.8.6 Remove the vessel from the support frame.

7.6.8.7 Remove the vent fitting from the vent stem.

7.6.8.8 Carefully remove the vessel from the sleeve.

7.6.8.9 Remove the vessel cover and rinse the inside of the cover and walls of the vessel with a small stream of water from a fine-tipped wash bottle, using as little water as possible.

7.6.8.9.1 IF the vessel being rinsed is the control vessel,
THEN rinse the outside of the thermowell and rinse the inside cover.

7.6.8.10 Transfer the contents of the vessel to a 50-mL volumetric flask.

**NOTE:** *Quantitative transfer of the undissolved solids to the volumetric flasks is not required or desirable.*

7.6.8.10.1 Use a plastic funnel and water rinses to transfer the digestate from the vessel liner to the volumetric flask.

7.6.8.10.2 Rinse the vessel walls and undissolved solids thoroughly.

7.6.8.10.3 Transfer the quartz boat to the plastic funnel and rinse thoroughly with water, collecting the rinsate in the 50-mL volumetric flask.

**NOTE:** *It is acceptable to continue rinsing the vessel liner following transfer of the quartz boat as long as the volume of rinsate does not exceed the volume of the flask.*

7.6.8.11 Dilute the sample in the volumetric flask to volume with water and mix thoroughly.

## 7.7 Digestate Filtering

7.7.1 Allow the digestates to sit until the undissolved solids are settled.

7.7.2 Filter each digestate.

7.7.2.1 Attach a 0.45-µm syringe filter to a disposable syringe.

7.7.2.2 Remove the syringe plunger and decant as much of the digestate as possible into the syringe, minimizing transfer of the undissolved solids.

7.7.2.3 Replace the plunger and filter the digestate through the 0.45-µm syringe filter into a clean polyethylene bottle.

### 7.8 Cleaning HP-500 Plus Vessels and Quartz Boats

**NOTE 1:** *Cleaning of the digestion vessels may be repeated as necessary to ensure contaminates are removed from the equipment.*

**NOTE 2:** *Cleaning of the control vessel and standard vessels may be performed in any order, either simultaneously or sequentially.*

7.8.1 Rinse the vessel liner with water to remove any undissolved sample residues from the vessel liner and discard to the appropriate waste stream.

7.8.2 IF quartz boats are to be cleaned,
THEN place a quartz boat in vessel liner.

7.8.3 Add 20 mL of concentrated nitric acid to each vessel.

7.8.4 Assemble standard vessels per Steps 7.3.1 and 7.3.2.

7.8.5 Assemble the control vessel per Step 7.3.3.

7.8.6 Ensure the MARS power switch is on.

7.8.7 Use the arrow keys to highlight **Load Method**.

7.8.8 Press the Select key.

7.8.9 Use the arrow keys to highlight **User Directory**.

7.8.10 Press the Select key to display the **User Directory** screen.

7.8.11 Use the arrow keys to highlight **Clean**.

7.8.12 Press the Select key.

7.8.13 Press the “1” key to review the method program.

**NOTE:** *The program for **Clean** should show a run time of 15 minutes at 100% power and a time of 5 minutes at the programmed pressure limit of 100 psig.*

7.8.14 Ensure the MARS vents into an operating fume hood.

7.8.15 Press the Home key to return to the main menu.

7.8.16 Close the door to the MARS.

7.8.17 Press the Start key.

7.8.18 IF the ESP-1500 Plus measures a pressure reading greater than 50 psig AND a warning screen appears,
THEN press the "2" key to zero the pressure sensor and allow the run to continue.

7.8.19 Allow the cleaning program to run to completion.

7.8.20 Open the oven door and allow the turntable to rotate until the control vessel is located in the right-front corner.

7.8.21 Disconnect the RTP-300 temperature probe from the microwave cavity.

7.8.22 Disconnect the ESP-1500 Plus pressure controller from the connector port on the right side of the instrument cavity.

7.8.23 Remove the retaining ring.

7.8.24 Remove a vessel assembly from the turntable.

7.8.25 IF the vessel assembly includes the control vessel,
THEN remove the RPT-300 temperature probe from the vessel by loosening the probe holder at the top of the module screw and gently pulling the probe from the thermowell and through the module screw.

7.8.26 Slowly relieve the pressure on the vessel.

7.8.26.1 Ensure the vent fitting is facing into the fume hood.

7.8.26.2 Grasp the support module with one hand.

7.8.26.3 Loosen the Teflon vent fitting by slowly turning in a counter-clockwise direction.

7.8.27 Use a series of slow, partial turns to loosen the fitting to ensure the decomposition gases release through the fitting.

7.8.28 Remove the safety membrane from the vent fitting and discard it.

7.8.29 IF the vent fittings require cleaning,
THEN perform the following steps:

7.8.29.1 Rinse the vent fittings with water.

7.8.29.2 Allow the vent fittings to dry completely before use.

**NOTE:** *Incomplete drying of vent fittings can cause leakage when under pressure.*

7.8.30 Loosen the retaining nut and rotate the vessel, as necessary, to remove the ESP-1500 Plus pressure controller by loosening the fitting that connects the pressure tubing to the pressure port on the control cover.

7.8.31 Remove the vessel from the support frame.

7.8.32 IF the support module requires cleaning,
THEN perform the following steps:

7.8.32.1 Rinse the support module with water.

7.8.32.2 Allow the support module to dry completely before use.

7.8.33 Carefully remove the sleeve.

7.8.34 Remove the brown load disk.

7.8.35 Rinse the brown load disks thoroughly with water.

7.8.36 Remove the vessel cover.

7.8.37 Rinse the vessel liner, vessel cover, and quartz boats thoroughly with water, and allow them to air dry in a clean location.

## 7.9 Microwave System Maintenance

**NOTE:** *Individual tasks in this section may be performed at any time and in any order, as needed.*

7.9.1 Complete the following maintenance monthly:

7.9.1.1 Examine the door, seals, and door interlocks to verify they are clean and working properly.

7.9.1.2 Ensure that no loosening of, or damage to, the door hinges or latch has occurred.

7.9.1.3 Ensure that the door closes securely.

7.9.1.4 Wipe the microwave cavity, including the exhaust screen at the back of the cavity, with a damp Teri towel.

7.9.1.5 Do not use abrasive cleaners to clean the microwave cavity because they may scratch the fluoropolymer cavity coating, degrading its ability to resist corrosive vapors.

7.9.1.6 Clean the exhaust outlet by removing the exhaust hose and wiping the space inside the exhaust outlet with a paper towel or a Teri towel.

7.9.2 Perform equipment maintenance, troubleshooting, and repair per manufacturer instructions.

## 8. QUALITY CONTROL REQUIREMENTS

8.1 Process a minimum of one laboratory (reagent) blank (LB) per sample batch to determine if contamination from the analytical process or any memory effects are occurring. This blank consists of all the reagents in the same amounts as are added to the samples and includes a quartz weighing boat in the blank vessel. Rotate the inner vessels and covers used for the LB so all are monitored for contamination at a routine frequency.

8.2 Process at least one matrix spike (MS) and one matrix spike duplicate (MSD) in each analytical batch. The MS and MSD are used to determine the accuracy of the method for a specific matrix. The matrix spike duplicate is also used to determine the precision of the method for a specific matrix.

8.3 Process at least one LCS in each analytical batch. The LCS is used to determine method accuracy.

8.4 If an analytical batch is split into groups of samples for processing in different microwave loadings, process a minimum of one LB and one LCS with each group of samples. Additional matrix spikes and matrix spike duplicates are not required.

8.5 Before analyzing any samples, prepare and digest seven replicate aliquots of solid reference material containing all target analytes. The LCS may be used for this purpose. See CCP-TP-182, *CCP Determination of Metals by ICP-AES for TRU Waste Characterization* for acceptance criteria for these method performance samples.

8.6 On a semiannual basis, repeat the method performance demonstration in Section 8.5 using at least four replicate standards.

## 9. CALCULATIONS

None (see determinative method, CCP-TP-182)

## 10. RECORDS

Records generated during the performance of this procedure are maintained as QA records in accordance with CCP-QP-008, *CCP Records Management*, and will be compiled in the Supporting Data Package, in accordance with CCP-TP-188, *CCP Analytical Data Recording, Review and Reporting.*

QA/Nonpermanent

- Copy of applicable pages of Digestion Record
- Pressure and/or Temperature vs. Time Profile Printout
- Method Printout

## 11. REFERENCES

11.1 ACLP-0.21, "Work Control Procedure for the Analysis of Nonroutine Samples"

11.2 ACLP-0.24, "Laboratory Spill Cleanup"

11.3 ACLP-0.27, "Routine Handling of Corrosives"

11.4 ACLP-0.40, "Analytical Laboratories Waste Management"

11.5 ACLP-1.01, "Preparation of Quality Control Reagents and Standards"

11.6 ACLP-2.05, "Control, Distribution and Use of Spectrochemical Standards"

11.7 ACLP-2.06, "Mechanical Pipetor Calibration Verification Procedure for Spectrochemistry"

11.8 CCP-QP-002, *CCP Training and Qualification Plan*

11.9 CCP-QP-008, *CCP Records Management*

11.10 CCP-TP-182, *CCP Determination of Metals by ICP-AES for TRU Waste Characterization*

11.11 ACMM-8909-JSA, "Microwave Assisted Digestion of Homogeneous Solids and Soil/Gravel"

11.12 MCP-7, "Radiological Work Permit"

11.13 MCP-3635, "Chemical Hygiene Plan"

11.14 EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Third Edition, Method 3051, "Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils," U.S. Environmental Protection Agency, 1986

11.15 HP-500 Plus, XP-1500 Plus and OMNI Vessel Accessory Sets and Autovent Options, Revision 6, CEM Corp, Matthews, NC, 2001

11.16 New Mexico Environment Department, "Hazardous Waste Facility Permit Issued to Waste Isolation Pilot Plant," EPA No. NM4890139088, current revision (WIPP WAP) 1999

11.17 CEM Corporation, *Operations Manual, MARS 5, Microwave Accelerated Reaction System*, Revision 0, 2001