

Microwave Digestion

To perform an atomic absorption or atomic emission measurement the sample must be dissolved prior to analysis. It is often the case that the sample is not easily dissolved. In such situations fusion or acid digestion may be used, microwave digestion is a form of acid digestion.

Microwave ovens began to find widespread use in chemical laboratories in the late 1980's. The use of laboratory microwave units has become increasingly popular because of the significant improvement in chemical reaction rates that are possible using microwave radiation. A typical microwave acid digestion can be completed in a matter of minutes, whereas the same conventional hot plate digestion can take hours. Microwave digestion usually involves placing a sample in an acid solution and heating to high temperatures and pressures. These extreme conditions will dissolve most materials, but is potentially quite dangerous. The microwave oven has many safety features, all of which must be paid attention to when in use. The conditions for any microwave digestion to be performed will have already been determined for you. It is imperative that safety rules be followed when performing a microwave digestion.

Both HDPE and soil can be digested in concentrated HNO_3 . The HDPE will be completely dissolved, but the soil will not. SiO_2 in the soil cannot be digested in HNO_3 , HF is also required. HF is extremely harmful to touch or breathe so you will not be using HF in your digestions. The metals which are extracted by HNO_3 are the only ones biologically available anyway. *If you are performing a soil analysis by AA you must separate the undissolved solid from the solution after digestion! Any particulate matter can clog the nebulizer in the AA, so filter the particulates prior to analysis!*

The following instructions for use of the microwave must be followed very carefully. Do not perform any steps until you are absolutely sure that step is understood. Without pictures on this document (yet), some instructions will not be entirely clear. Ask the instructor to show you when you are unsure prior to proceeding.

The Microwave Accelerated Reaction System (MARS) 5 is located in room 304.

- When the instrument is initially turned on (switch on right side of unit near the back) two choices appear: 1) Edit/Create Method and 2) Load Method. An appropriate method should already be programmed into the unit for your sample. DO NOT Edit/Create your own method. The (+) and (-) touchpad keys on the front of the unit will allow you to highlight Load Method. Press Select. Next screen gives the choice of CEM or User Directory. Highly User Directory and Select. Highlight the appropriate method and select.
Load Method (Select) --> User Directory (Select) --> Appropriate Method (Select)

For Cr/HDPE select Polyethylene 6

For Pb/Soil select EPA3051X 1-4 or EPA3051X 5-6 depending on the number of samples you are digesting.

Now you must prepare your sample(s) for digestion. Prior to giving instructions, here are important safety guideline for using the MARS5.

Safety Guidelines

Microwave sample preparation imposes a unique set of safety considerations beyond the basics of good laboratory practice.

1. All vessel components must be dry and free of particulate matter. Drops of liquid or particles will absorb microwave energy, causing localized heating which may char and damage vessel components, leading to possible vessel failure.
2. Ensure that the vessels are completely vented of built-up reaction gases and completely depressurized before removing liner and internal components from the polypropylene support module. Failure to do so could potentially result in ejection of acid and injury to the operator.
3. Never install more than 1 safety membrane in the XP-1500 Plus.
4. NEVER attempt to digest samples larger than the recommended maximum 0.40 grams if the organic content and composition of the sample is unknown. Unknown samples should always be predigested for

a minimum of 15 minutes in an unsealed vessel without any heating prior to attempting closed vessel microwave digestion.

5. DO NOT heat concentrated base or salt solutions inside the vessel. Microwave heating of such solutions causes precipitation of salts and formation of crystal deposits which absorb microwave energy and may char into the vessel or electrically arc, leading to possible vessel failure.

6. DO NOT heat high boiling point acids (concentrated sulfuric or phosphoric) inside the vessels without using temperature control limited to 200°C.

7. The vessels have a maximum recommended hold time of 30 minutes at 240°C. Hold times longer than 30 minutes at the maximum temperature or higher may result in softening of the bottom of the support module and may damage the vessel.

8. For digestions using high concentrations of HF in an acid mixture, use the HF-Master Thermowell. The thermowell is made of an HF-resistant industrial gem material. A Teflon-coated thermowell may be used; however, the lifetime may decrease as HF concentration increases.

You can digest up to six samples at a time, but no more than 0.40 grams per vessel. *If you digest too much sample in one vessel excessive pressure can result in an explosion!* Thus you can digest a maximum of 2.4 g of sample at a time. You may want to know the exact mass of sample which you are digesting (why?), so don't forget to record the mass of sample using a 4-place balance. There are two types of digestion vessels; 5 standard vessels and 1 control vessel. The control vessel has connections for temperature and pressure measurements which the system monitors during the course of the digestion. If you are digesting more than 1 sample, it is safest to digest the maximum amount of sample in the control vessel. Our vessels are capable of withstanding 800 psi and 240°C.

Standard Vessel Assembly Procedure

The vessels and assembly tools are located in drawers 40 and 41 in room 304.

1. Obtain a safety membrane for each vessel in which you plan to perform a digestion (up to 6). These are clear plastic circles in a small snap-top black plastic box that says XP-1500 Plus Safety Membranes. The safety membranes are manipulated using the safety membrane installation tool which looks like a pen. Connect a suction cup tool to the end of the pen and touch a safety membrane. Press the button on the side of the pen and a vacuum is formed which allows you to pick up the safety membrane. Place the membrane inside the threaded end of a greenish teflon vent fitting. Press the black button on the pen to release the membrane. ALWAYS use the safety membrane. Ensure that the membrane is lying flat on the bottom of the teflon vent fitting. Failure to seat the membrane in a vessel will result in leakage. This is crucial for the control vessel as a faulty pressure reading can result. Never install more than 1 safety membrane.
2. Weigh the sample and place it into the teflon vessel liner (tall, thin white teflon "beaker"). The sample must be placed in the bottom of the liner so that it will be completely covered by acid. The side walls of the liner must not have sample deposits on them.
3. Add 10 mL of concentrated HNO_3 (for HDPE or soil analyses) to the vessel liner, immersing the sample. Visually look for a reaction. If a reaction occurs, allow the reaction to subside completely before capping the vessel.

CAUTION

A predigestion step must be performed on samples of unknown composition or those suspected of containing easily oxidized and highly reactive compounds such as alcohols, ketones and glycols. Predigestion is performed without microwave heating for a minimum of 15 minutes in an open, unsealed vessel.

4. Place the white, teflon vessel cover with threaded side arm on top of the vessel liner. It should be a fairly snug fit. On top of the vessel cover place a round brown, plastic load disk. The load disk is smooth on 1 side and has a circular depression on the other. Do not use a load disk with a hole through the top as this is for the control vessel. Place the side with the circular

- depression facing up.
5. Take a clean dry sleeve of woven looking material and place the liner into it. The fit should be snug. Install the completed standard vessel assembly into a standard vessel support module. These modules do not have a hole in the screw cap on the top. These support modules are greenish, imposing looking devices with a round, white teflon heat shield on the bottom. On the front in red and blue it says XP-1500 plus, Contents Under Pressure. The vessel assembly should sit on top of the heat shield and the load disk should barely squeeze underneath the screw top.
 6. Screw the teflon vent fitting with the properly seated safety membrane inside onto the threaded stem of the white teflon vessel cover finger tight. Rotate the vessel so that the vent fitting is positioned toward the front of the support module (end with the red and white label). With the standard vessel support module screw at the top centered in the recess area of the brown support disk, tighten the support screw finger tight. Using the torque wrench (it's a fancy ratchet wrench), tighten the screw an additional half turn until you hear/feel a click. It is then tightened to the correct setting of 5 ft. lbs. Do not tighten any further as this can damage the vessel.
 7. Repeat steps 1-6 for the remaining standard vessels.

Control Vessel Assembly Procedure

The white teflon liner, woven sleeve, vent fitting and safety membrane are identical for the standard and control vessels. The brown load disk has a hole drilled through the center, the vessel cover should have a thin sapphire tube sticking out of the bottom, a threaded T where for the pressure sensor, and a hole in the white teflon screw cap top for the temperature sensor. The control vessel support module is slightly taller than the standard vessel support modules, and the green hexagonal screw on the top has a hole drilled through it for the temperature sensor.

1. Install a safety membrane in the Teflon vent fitting as outlined in

step 1 of the standard vessel instructions.

2. Weigh and place the sample into the vessel liner, ensuring that the acid covers the sample. The amount of sample in the control vessel should be no less than the amount of sample in any of the standard vessels.

3. Place the vessel cover on top of the vessel liner. Place the Teflon spacer containing the brown load disk on the control cover with the side of the spacer with the circular depression facing upward. The spacer and the load disk should both have holes in the center and should be aligned.

4. Screw the teflon vent fitting with the properly seated safety membrane inside onto the threaded stem of the white teflon vessel cover finger tight. Tighten the fitting that connects tubing to the pressure transducer. The pressure transducer has light blue tubing, a teflon fitting on one end and a 6-pin electrical connection (3 male + 3 female) on the other. Rotate the vessel so that the vent fitting is positioned toward the front of the support module (end with the red and white label). With the standard vessel support module screw at the top centered in the recess area of the brown support disk, tighten the support screw finger tight. Using the torque wrench (it's a fancy ratchet wrench) tighten the screw an additional half turn until you hear/feel a click. It is then tightened to the correct setting of 5 ft. lbs. Do not tighten any further as this can damage the vessel.

5. The support module screw has a small hole in the center for the temperature probe. It is a thin black wire with a teflon fitting on one end and the probe on the other. It is delicate so handle it with care. Slide the teflon probe holder 6.5 inches from the end of the wire. Insert the thin end of the probe through the hole in the module screw and thread it down until the probe holder is in contact with the module screw and gently press it into the hole in the center of the module screw.

Now that all of the reaction vessels have been assembled, it is time to place them in the turntable and place them in the microwave for digestion. There is a white teflon turntable that holds the vessels and fits into the microwave. There is a

circular raised section in the middle with the numbers 2-12 where vessels are symmetrically arranged. The number 1 slot is for the control vessel and is marked as such.

1. Place each vessel into the turntable by inserting the bullet-shaped locking tab of the support module (on the back) into a slot in the raised center of the turntable. Arrange the vessels symmetrically.
2. Place the control vessel in the turntable in the position labeled “control vessel”. Install the vessel retaining ring on the vessels with the notch of the retaining ring resting on the control vessel. It is a round, white plastic ring of the correct circumference such that it fits around the turntable. If you are only digesting 2 samples, one standard vessel and one control vessel, the vessel retaining ring will not be steady. You should use all of the support modules and place them in the turntable simply to provide stability to the vessel retaining ring.
3. Install the turntable into the microwave instrument, aligning the straight line on the label in the center of the turntable with the flat edge of the turntable lug. On the front panel of the microwave press the button with a picture of a circular arrow to rotate the turntable. Stop when the arrows on the turntable are pointing directly forward towards you. This should position the control vessel in the back left hand corner of the instrument cavity.
4. Connect the pressure transducer to the connector on the right side of the cavity (facing instrument) near the front. This is done by rotating the transducer while gently pressing until the pins slip into the correct position. Now connect the tubing leading from the vessel to the transducer to the clip on the top of the microwave cavity. Now connect the temperature probe into the top of the microwave cavity. Make sure that the lines for the pressure and temperature transducers are not crossed. Permit the table to rotate a few times to ensure that the pressure sensing tubing and the temperature probe do not become entangled.
5. Press START on the front keypad and the digestion will begin. Current temperatures and pressures will be displayed as the digestion proceeds. The P/T button on the front panel toggles the current pressure

and temperature on the instrument screen with a pressure, temperature versus time curve for the entire digestion.

After the digestion is complete

WARNING

There is a 15 minute cool down time programmed into the methods. Be sure that the vessels have cooled sufficiently such that the pressure is less than 200 psi and temperature less than 100°C prior to handling.

WARNING

Always wear gloves, a lab coat and eye protection when handling/venting the vessels.

1. Disconnect the temperature probe from the top of the microwave cavity. DO pull from the white, solid housing at the end of the probe with the numbers on it to disconnect it. DO NOT pull the wire from further back as this will damage the temperature probe.
2. Disconnect the pressure probe from the right hand side of the instrument by simply pulling the black connector away from the wall of the instrument where it is connectd.
3. Remove the vessels and the turntable from the microwave cavity. **PLACE THE VESSELS IN THE HOOD.**
4. Vent standard vessels by grasping the support module with one hand and loosening the Teflon vent fitting by slowly turning it in a counterclockwise direction. A series of slow, partial turns of the fitting will permit decomposition gases and acid vapor to escape through the vent fitting. Do not rapidly loosen the vent fitting by multiple turns. This will permit gases to exit down the threads of the fitting. Upon venting you will see brown gas rush from the fitting. These are NO_x decomposition products of HNO₃. This is a big reason why you should be wearing gloves.

WARNING

Always ensure that the vessel is completely vented and depressurized prior to removing the liner and internal components from the polypropylene support module. Failure to do so could result in ejection of acid and injury.

5. Vent the control vessel in the same way as the standard vessels. Remove the temperature probe and the pressure probe from the control vessel.

WARNING

Avoid tipping the vessel sideways to avoid spilling the contents of the vessel.

6. Disassemble the apparatus.
7. Quantitatively transfer your solutions to an appropriate vessel for analysis.

Cleaning

Immediately after digestion and sample transfer rinse the liners, covers and any other components which may have come into contact with acid with deionized water. Soak these components in a detergent solution, wash then rinse 2X with deionized water. Dry all parts thoroughly and replace all of the components in the appropriate drawers.