Heavy Metal Sample Preparation and Extraction

1. Scope:

This document provides a procedure for the preparation of feed and fertilizer samples for heavy metals analysis. There are two methods available for preparing samples and either is acceptable, however microwave digestion is preferred as it is a closed vessel digestion. Closed vessel digestion is required for mercury analysis.

2. Principle:

Samples are extracted in acid to decompose the matrix and release analytes of interest. Vegetation samples directly submitted to the Pesticide Residue group are received from that group as ground/homogenized.

3. Safety:

- Consult the appropriate Safety Data Sheet (SDS) for information on the safe handling of all the chemicals used in this method.
- Safety precautions should always be taken to avoid skin and eye contact and inhalation during digestion of materials and reagents.
- Gloves, eye protection, and a lab coat shall be worn when handling hazardous materials and reagents.
- Nitric acid and hydrochloric acid are very toxic and extremely corrosive. The acidification of samples containing reactive materials may result in the release of toxic gases and can be exothermic. Any manual sample acidification shall be performed in a fume hood.
- For both the hot block and UltraWave, read the operating manual carefully before using and follow instructions with utmost care.

4. Equipment and Supplies:

4.1. General

- Analytical Balance (Mettler AE 200 or equivalent)
- Polypropylene sample vials with screw top, 50mL
- Filter Mate, PTFE certified filter and plunger
- LCMS water CAS# 7732-18-5 (Fisher Cat# W6-4)
- Nitric acid (65%) CAS# 7697-37-2 (Fisher Cat# A509-P212)
- Hydrochloric acid, ultra-pure trace metals grade CAS# 7647-01-0 (Fisher Cat# A508-P500)

4.2. For UltraWAVE Digestion
- UltraWave Microwave (Milestone MA149-013)
- TFM Vessel 900 mL (Cat# HB00070B)
- TFM Sample rack holder (Cat # MCL0111)
- Weighing adapter (Cat # GRV1807)
- UW- 15 Disposable Glass vessel (Cat# L00079D)
- PTFE vial cap (Cat# DD00134)
- Rock bottom plate with 15 numbered position (Cat# MCL00299)
- Weighing paper/boats

4.3. For Hot Block Digestion
- Hot block
- Polypropylene sample digestion vials, 100mL

5. Sample Preparation

5.1. General

5.1.1. Verify the analytical balance.

5.1.2. For the hot block, label 100mL digestion vessels with the sample number including method blank (MB) and quality control (QC) samples and place them in a sample digestion rack.

5.1.3. For the UltraWAVE, no forms of labelling should be done on the vessels as it could cause spontaneous reactions. The sample rack with numbered positions should be used with the bottom plate to maintain sample traceability.

5.1.4. Mix each sample thoroughly before weighing.

5.1.5. Weigh a portion of homogenized sample (~0.2-1g based on guarantee) into the appropriate vessel. For organic samples being digested using the UltraWAVE, do not weigh more than 0.7g. Record the weight of each sample on the sample digestion sheet.

5.1.6. Either a NIST, AAFCO, or Magruder reference sample is used for the QC and is weighed in the same manner as the samples.

5.1.7. The MB is prepared by weighing ~1g of LCMS water.

5.1.8. Add ~1mL of deionized or LCMS water to each solid sample and soak for ~5 minutes.

5.1.9. For the UltraWAVE: In a fume hood, SLOWLY add 5mL concentrated HNO_3 dropwise to each sample (for mercury analysis, add 4mL HNO_3 and 1mL of HCl). Tap the vial slowly to minimize spraying and foaming. Cap the vessels

and place them inside the 15-position carousel making sure the carousel is evenly balanced. Fill any empty positions with "dummy" placeholders that contain the same reagents used in the other vessels. Allow acid to react with the samples for ~30 minutes. Samples can be left overnight at this step or proceed with the UltraWAVE digestion.

5.1.10. For the hot block: In a fume hood, SLOWLY add 5mL concentrated HNO_3 to each sample. Place a watch glass over each sample vial and allow acid to react with samples for ~30 mintues. Samples can be left overnight at this step or proceed with the hot block digestion.

6. Sample Digestion:

6.1. Sample Digestion using the UltraWAVE

6.1.1. Turn the chiller on.

6.1.2. Turn the nitrogen gas on by turning the valve of the regulator clockwise until it is fully open and verify the outlet pressure is 650-700 psi.

6.1.3. Fill the reaction chamber PTFE liner with the manufacturer's recommended base load (130mL DI water plus 5mL nitric acid). This provides uniform heat transfer to all the samples. The base load must be replaced for every run.

6.1.4. Verify that the O-ring is into the proper groove of the PTFE vessel. If it looks softened and overlaps, replace it with a new one.

6.1.5. Inspect the chamber to verify there is no particulate matter as it could lead to a spontaneous reaction.

6.1.6. Place the PTFE vessel with the base load inside the chamber. To move the vessel in and out, pull out and hold up the locking device attached to the back part of the cover with one hand and turn the complete cover to the left with the other hand. To return the cover to its original position, pull the locking device up and swing the cover ahead.

6.1.7. Load the carousel inside the chamber and align the notch with the temperature probe, making sure carousel is well centered.

6.1.8. Lower the carousel by pressing the "arrow down" button.

6.1.9. Hand tighten the clamp and check if mechanical lock in the center of the clamp is activated.

6.1.10. Press the "start" button to begin the digestion.

6.1.11. Monitor the digestion process in the “run” tab. Sudden peaks on pressure or temperature curves might indicate combustion inside the vessel. The STOP button on the screen will immediately shut down the instrument in case of emergency.

6.1.12. Allow the samples to cool in the digestion vessels, making sure the temperature is 25℃ ± 2℃ and pressure is at 0 bar before opening the microwave (temperature and pressure are displayed on the terminal’s “system” tab).

6.1.13. Verify the lock in the center of the clamp is deactivated then untighten the clamp.

6.1.14. Press the “arrow up” button to pull up the carousel.

6.1.15. Wipe the bottom of the vessels with a paper towel to remove nitric acid solution. Carefully remove the carousel and transfer to a fume hood.

6.1.16. Dry and clean the metallic components of the microwave with ethanol and apply silicon oil using a Kimwipe (this should be done after every run).

6.1.17. Cover the chamber with a plastic lid to keep the dust out.

6.1.18. Quantitatively transfer the vessel contents to a 50mL digestion vial. Rinse vessels and caps at least twice with LCMS grade or DI water and add to the vial. Fill to the 50mL mark with LCMS water and filter using the FilterMate filter and plunger.

6.1.19. Place the caps in a plastic container with 2% nitric acid solution for cleanup. Rinse with DI water and air-dry before use.

6.2. Sample Digestion using Hot Block

6.2.1. Heat the hot block to 90 ± 5°C.

6.2.2. Place prepared samples in a rack, place in the hot block, and reflux for ~60 minutes (without boiling). Monitor samples to avoid drying.

6.2.3. After the samples have refluxed, remove from the hot block using the transfer racks and allow to cool in a fume hood.

6.2.4. Rinse the watch glass with LCMS water, collecting rinseate in the sample vessel and discard the watch glass.

6.2.5. Transfer sample extracts into 50mL sample vessels. Rinse each digestion vessel at least three times with LCMS water and transfer rinseate into the

sample vessel. Fill to the 50mL mark with LCMS water and filter using the FilterMate filter and plunger.

7. References:

7.1. UltraWAVE operator Manual MA149, Milestone

7.2. Hot block system manual

7.3. “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

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