PREPARATION OF WATER SAMPLES FOR METALS ANALYSIS BY ICP-AES AND ICP-MS

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1. SCOPE AND APPLICATION

This standard operating procedure (SOP) details the digestion of water samples for metals analysis and is applicable to surface, ground, drinking, effluent, saline, and waste waters. This method is used to prepare samples with test IDs W-ICP, W-ICP-R, W-ICPMS, and W-ICPMS-R.

Refer to DEP SOP MT-061 for a list of analytes tested by ICP-AES and DEP SOP MT-074 for a list of analytes tested by ICP-MS.

2. SUMMARY OF THE METHOD

This procedure follows EPA method 200.2 (hot plate) modified and validated for use with a block digester. 1 mL of concentrated nitric acid (HNO_3) and 0.5 mL of concentrated hydrochloric acid (HCl) are added to 50 mL of sample in a disposable polypropylene tube and heated at 95° C for 4 hrs. Heating the sample with acid reduces interference caused by organic matter and increases the solubility of metallic species. The sample is then reconstituted to 50 mL with deionized (DI) water.

This method is suitable for the preparation of aqueous samples containing silver concentrations up to 0.1 mg/L. Samples containing higher concentrations of silver must be diluted to a concentration of < 0.1 mg/L silver prior to preparation.

This method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples

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having unknown concentrations of sulfate, analysis should be completed as soon as possible.

3. APPARATUS AND EQUIPMENT

3.1. 50 mL disposable polypropylene digestion cups (used with the Environmental Express Digestion System)

3.2. 15 mL polypropylene centrifuge tube and cap, Corning or equivalent

3.3. Environmental Express Digestion Block

3.4. Plexiglas digestion box or fume hood

3.5. Pipettes:

3.5.1. 200 uL Eppendorf

3.5.2. 1000 uL Eppendorf (100-1000uL)

All pipettes are calibrated using the Check-and-Track software and certificates are saved according to DEP SOP CM-032.

3.6. NIST-traceable thermometer

3.7 NIST-traceable timer

4. REAGENTS AND CHEMICALS

See DEP SOP MT-069 for standard and reagent documentation, labeling requirements, and expiration dates. All bottles of reagents and standards (purchased and prepared) in the laboratory are required to have laboratory information management system (LIMS) labels which includes a serial number.

4.1. Trace metal grade nitric acid (HNO_3) - The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

4.2. Trace metal grade hydrochloric acid (HCl) - The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

4.3. DI water

4.4. Spiking and PQL Solutions (these solutions are purchased or prepared by the metals analysis group. **Inform the supervisor of the Metals Group when the prepared stocks are either within two weeks of expiration, as indicated by the label on the bottle, or within two weeks of running out.)**:

4.4.1. Digestion PQL Solutions (DPQLDV# and DPQLICAP#) - A suffix is added to these abbreviations to indicate the current PQL solution used (e.g. 9, 10, etc.). The DPQLDV# is prepared in two parts: DPQLDV# contains all metals except silver and DPQLDV#_AG contains silver only. The expiration date of these standards will be no longer than the expiration dates of the stock individual metal

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standards provided by the manufacturer. Stored at room temperature.

4.4.2. Mineral Spike Solution (ICPMINA) - Purchased stock solution for preparing the minerals laboratory fortified blank (LFBMIN). Expiration date provided by the manufacturer. Stored at room temperature.

4.4.3. Trace Metal Spike Solution (HW#) - A suffix is added to this abbreviation to indicate the current solution. This trace metal spike solution is prepared in two parts: HW#A contains all metals except silver and HW#B contains silver only. The expiration date of these standards will be no longer than the expiration dates of the stock individual metal standards provided by the manufacturer. Stored at room temperature.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Routinely, water samples are preserved at the time of sampling in the field with HNO_3 to a pH of 2 or less. Sample pH is checked in the receiving room upon arrival. If the sample arrives with a pH > 2, it is acidified in house to an acceptable pH and preparation **cannot** be started for at least 24 hours. Such samples are marked with a red cross on the sample bottle top. The pH is checked again with pH paper by the prep analyst and documented in the comments section of the prep worksheet in Prep Worksheet Manager before preparation. Document the lot number and expiration date of the pH paper used to check the pH of a sample. Samples are stored at room temperature in the metals water sample storage room located in the Receiving Room, C301.

6. SAMPLE PREPARATION PROCEDURE

6.1. Generate a backlog report using the LIMS. A backlog template should be created to include all "W" status water tests in the metals group.

6.2. Using a printout of the backlog report choose a "batch" of water samples for digestion. Batch water samples according to conductivity. Water samples with conductivities below 10,000 µmhos/cm are batched together and water samples with conductivities greater than 10,000 µmhos/cm are batched together. (For more guidance on sample batching, see section 7 of the SOP or contact your supervisor). It is helpful if a batch of water samples contains samples for only one instrument test (W-ICP or W-ICPMS). However, if a sample has two instrument tests scheduled, then its batch will be analyzed on both instruments and needs to contain all appropriate quality control (QC).

6.3. Samples are then placed on a reservation through the LIMS sample reservation program. Reservations for the following day must be made before 2 pm.

6.3.1. From the LIMS menu, select Laboratory> Receiving> Sample Reservations

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6.3.2. Choose option one of six to create a new reservation by selecting the radio button. Continue to next page by selecting the 'Next' button.

6.3.3. Select the name of the person creating the reservation and also select the name of the person the samples are reserved for. Click 'Next'.

6.3.4. Choose the date as well as the start and end time for the reservation. Click 'Next' to continue to the next page.

6.3.5. Select the analysis group and test for the samples to be reserved. Click the arrow button to select the test, then click 'Next'.

6.3.6. Input the first sample ID to be reserved and the last sample ID to be reserved and then click 'Add samples to list'.

6.3.7. Samples can be removed from the reservation by highlighting the sample ID and clicking 'Remove selected samples'. Click 'Next'.

6.3.8. Review the summary of samples reserved and if correct, click 'Finish'.

Note: The technician may also pull samples themselves from the receiving room if a sample custodian is unavailable, or if changes must be made to the samples in the batch prior to prepping.

6.4. Sample Custody and Preparation Worksheet - Metals water samples are stored in room C301 (Receiving Room). Prior to preparation, the technician assigned to the preparation must possess custody, as defined in the Laboratory's Quality Manual, of the sample. A sample cannot be prepared for analysis unless it has been properly "checked out" by the lab technician to perform the digestion. If a sample is currently in the custody of another laboratory staff member, the custody must be transferred to the lab technician that is to prepare the sample BEFORE beginning to work with the sample. Sample custody can be transferred either at a transfer station, several of which are located throughout the laboratory (this can only be done if the transfer involves the same sample ID), or by returning the sample to the Receiving Room (C301) and "checking out" the sample (the latter procedure must be followed if a different sample ID on the same sample is involved). Once custody has been established, create a worksheet using the LIMS Preparation Worksheet Manager. The Preparation ID that should be used is '200.2'.

6.5. Using the spiking tables in section 7.4, determine which QC samples to include with the batch of samples. If necessary, ask a supervisor to review the selection to ensure the correct QC is being included.

6.6. Prepare the block for digestion. Wipe any dust and particles from the interior of the surface of the heating block and the clean box with a lint-free wipe dampened with DI water. Turn on the heating block and set the temperature to a setting that will heat the samples to the acceptable temperature range of 92 – 97° C (this requires setting the block

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temperature at a point between 108 °C and 115 °C for Environmental Express heating blocks).

Note: The temperature of the heating block must be monitored and recorded before digestion on each day of use. Place 1 tube with DI water on the block and insert a thermometer. After the temperature has stabilized and reached the acceptable temperature range of 92 – 97° C, read the temperature of the thermometer inserted into the digestion tube and record it on the prep worksheet in Prep Worksheet Manager in the 'Block Temperature' box along with the well position using the format xx.x C; W. pos. xx. To ensure all positions are reaching an acceptable temperature, the position the technician chooses to record the temperature on should move sequentially each day they prep. For example, if the technician starts with position 1, the next prep batch digestion should be 2, and then the next ones are 3,4,5 and continuing until all positions on the block have been used. Once all position of the block have been used and recorded, the technician will repeat the cycle starting at position 1. The thermometer used in this temperature verification must be calibrated against a NIST traceable thermometer annually or purchased with a NIST-traceable certificate of analysis. Refer to DEP SOP LB-035 for thermometer calibration instructions. The date of calibration, next calibration due date and the serial number must be properly labeled on the thermometer.

6.7. Prepare the digestion tubes by labeling each tube to be used in the digestion with the sample's identification number and/or the QC sample's name. Prepare the necessary labels using the SATO label printer with any spike information, dilution factors, and other pertinent information on them and apply to the tubes. Labels may be handwritten only if printed labels are not available. All metals water sample digestions are prepared in disposable polypropylene tubes designed to fit in the Environmental Express Digestion Blocks.

Note: All digestion tubes and lids must be triple rinsed with DI water. To do this, fill each digestion vessel and lid three times with DI water and discard the rinse down the drain. In addition, replace the DI water frequently and rinse the squeeze bottle tip with DI water prior to use.

6.8. Disposable tubes and caps should be handled with extreme care. A significant source of zinc contamination in water digestions comes from disposable latex gloves. Most gloves are coated with high concentrations of zinc as a result of the vulcanizing process used to make them. **Nitrile gloves are available that do not contain high amounts of zinc and should be used whenever handling metals samples**. Extreme care should be taken not to touch the inner surfaces of the tubes or caps.

6.9. Tighten the sample bottle cap and invert the sample bottle three to four times to ensure a good mixing. When pouring the spikes, invert the sample bottle several times in between each aliquot that is poured. **This is a very important step in the digestion procedure.** Carefully pour 50 mL of each sample into the respectively labeled tube. It is critical for the volume of the sample in each tube to be as accurate as possible. It may be

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necessary to slightly over pour the sample and remove a small amount with a disposable plastic pipette to obtain 50 mL accurately. Depending on the surface tension of each sample it may be difficult to read the meniscus. If a sample cannot be accurately dispensed, contact a supervisor for assistance.

Note: EPA Method 200.2 instructs to transfer 100 mL ± 1 mL of sample to the digestion vessel. The 50 mL disposable polypropylene digestion cups (used with the Environmental Express Digestion System) are certified to contain a volume of 50 mL ± 0.2 mL. Prep technician must check pH of each sample using pH strips to verify that the pH is less than 2. If pH of sample is less than 2, then prep technician will record this information on the digestion prep batch. Information to include besides pH<2 is the lot and expiration of the pH strips. If the pH is greater than 2, the sample should be sent back to receiving with the comment that the sample needs to be preserved with nitric acid to pH<2. Receiving will create an NCR and the prep technician must wait at least 24 hours before checking out the sample and re-checking the pH.

6.10. Prepare the matrix spikes according to the elements to be analyzed. Pipette the appropriate volume (see 7.4) of each spike solution into each sample to be spiked. The pipette is used to deliver an accurate volume of spike; ensure that the pipette is calibrated.

6.11. Make sure the fume hood or pull-down trunks are "ON" and operating properly. If not, notify the staff in charge of safety and your supervisor immediately.

6.12. Add 1.0 mL of HNO_3 and 0.5 mL of concentrated HCl to each sample tube. The serial numbers of the HNO_3 and HCl used are entered on the prep worksheet in Prep Worksheet Manager. Check the expiration dates to ensure expired reagents are not being used. Place the tubes in the heating block.

6.13. Once on the heating block, close the clean box door and heat the samples for a total of 4 hours. The four-hour digestion period is tracked using a NIST traceable timer with expiration date. While the samples are digesting, the QC and reagent information can be documented/verified on the prep worksheet. Also document on the sheet (in the comments section) the presence of any particulate matter present before digestion, after digestion, or any irregularity associated with any sample on the digestion tray. The comment pH<2(Lot#...Exp…) must also be listed in the comment section for each sample.

6.14. After the heating cycle is complete, turn off the power to the heating block and allow the samples to cool (about 30 minutes). The samples will lose significant volume during the digestion. Working with one tube at a time, bring the volume back to 50 mL with DI water using the mark on the tube as a reference line. Samples should be placed on a stable surface when reconstituting the samples back to the 50 mL volume and the volumetric mark should be at eye level when adding the DI water. When viewing the

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tube at an angle (i.e. not at eye level) or if the sample is held freely in a person's hand while filling, it is difficult to accurately fill the tube. This will result in incorrect results and will warrant redigestion.

6.15. Screw a cap on each sample digestion tube and mix the contents thoroughly by inverting the digestion tube several times.

6.16. Sample Blanks (Equipment blanks, Field blanks, etc.) - Include a 15 mL centrifuge tube of undigested blank for each test in a batch. Rinse the centrifuge tube three times with DI water prior to filling with sample.

Note: All dilutions should be made by the ICP and ICPMS *analysts* with 2 % HNO_3 / 1 % HCl in DI water in throughly rinsed 15 mL orange capped centrifuge tubes prior to analysis. If dilutions are made by prep staff by request of supervisory staff, the following instructions should be followed.

6.17. Determine if any of the samples need to have dilutions made (based on conductivity). Make dilutions according to the chart below:

Dilution Factor	Amount of Diluent	Volume of Sample	Final Volume
2	5 mL	5 mL	10 mL
3	6 mL	3 mL	9 mL
4	7.5 mL	2.5 mL	10 mL
5	8 mL	2 mL	10 mL
10	9 mL	1 mL (1000 uL)	10 mL
20	9.5 mL	0.5 mL (500 uL)	10 mL
50	9.8 mL	0.2 mL (200 uL)	10 mL
100	9.9 mL	0.1 mL (100 uL)	10 mL

ICPMS:

Sample conductivities	Dilution factors for samples and matrix spikes
<10,000 umhos/cm	no dilution needed
>10,000 umhos/cm	4 and 10

ICP:

Dilutions for samples requesting mineral analytes:

Sample conductivities	Dilution factors for samples and matrix spikes
1500 – 5000 umhos/cm	5
5000 – 12,000 umhos/cm	10
12,000 – 30,000 umhos/cm	20
30,000-40,000 umhos/cm	50; also a separate 3 if Fe needed.
Over 40,000 umhos/cm	50; also a separate 4 if Fe needed.

Dilutions for samples requesting additional analytes:

Sample conductivities	Dilution factors for samples and matrix spikes

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<10,000 umhos/cm	no dilution needed
10,000-40,000 umhos/cm	3
>40,000 umhos/cm	4

6.18. The samples are now ready for analysis. Write the prep worksheet (e.g. 200.2_####) ID on a label and place the label on the sample rack. Make sure all documentation is completed properly on the prep worksheet including but not limited to the prep person, digestion start and end date, digestion start and end time, reagent serial numbers, spike serial numbers, sample IDs, dilution factors, block ID, block temperature, and sample comments. Be sure to note any and all information in the comments section that might be useful to the analyst and/or reviewer.

Notify the supervisor when all fields of the prep worksheet are complete. The supervisor will verify the completeness and correctness of the prep worksheet and mark the worksheet as reviewed if acceptable. After the tray is finished, the prep technician will then turn the samples from "W" to "V" status by completing the prep worksheet in Prep Worksheet Manager. This must be done BEFORE the tray is sent up to the metals analysis lab.

7. QUALITY CONTROL

Note: A digestion batch is defined as a set of twenty samples or less. Batch water samples according to conductivity. Water samples with conductivities below 10,000 µmhos/cm are batched together and water samples with conductivities above 10,000 µmhos/cm are batched together.

7.1. Digestion Blank - One per digestion batch.

7.2. Digestion PQL - One per digestion batch per analysis test. Digestion PQL Solutions (DPQLDV# and DPQLICAP#) are prepared by the analyis group. A suffix is added to these abbreviations to indicate the current PQL solution used (e.g. 9, 10, etc.). The DPQLDV# is prepared in two parts: DPQLDV# contains all metals except for silver and DPQLDV#_AG contains silver only.

7.3. Laboratory Fortified Blanks (LFB) - The trace metal spike solution (HW#) is prepared by the analysis group in two parts, HW#A (all metals except silver) and HW#B (silver only). A suffix is added to these abbreviations to indicate the current HW solution used (e.g. 4, 5, etc.). The mineral spike solution (ICPMINA) is a purchased solution.

All preparation batches must have at least one laboratory fortified blank (LFB).

7.4. Matrix Spikes - Matrix spikes are prepared by adding a known amount of analyte to a sample. 10 % of samples must be spiked, therefore for a batch of 20 samples, two samples will be chosen to spike.

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Samples that have the test W-ICP and require **sodium, potassium, calcium, magnesium, iron, or aluminum** will have a mineral spike series. The table below lists the spikes needed:

W-ICP		
D-BLK		
DPQLDV#		1000 uL DPQLDV#
LFB MIN		1000 uL ICPMINA
Sample A		
Sample A matrix spike		1000 uL ICPMINA
Sample A matrix spike		1000 uL ICPMINA
Sample C		
Sample C matrix spike		1000 uL ICPMINA

Samples that have the test W-ICP and require more than the mineral analytes will require the following spikes:

W-ICP with minerals/trace metals requested		
D-BLK		
DPQLDV#		1000 uL DPQLDV#
DPQLDV#_AG		1000 uL DPQLDV#_AG
LFB MIN		1000 uL ICPMINA
LFB HW#		1000 uL LFB HW# A 1000 uL LFB HW# B
Sample A		
Sample A matrix spike		1000 uL ICPMINA
Sample A matrix spike		1000 uL LFB HW# A 1000 uL LFB HW# B
Sample A matrix spike		1000 uL LFB HW# A 1000 uL LFB HW# B
Sample C		
Sample C matrix spike		1000 uL ICPMINA
Sample C matrix spike		1000 uL LFB HW# A 1000 uL LFB HW# B

<u>Note</u>: If a batch for ICP-MS is prepared containing high conductivity samples (>10,000 umhos/cm), the HW spiking is doubled from 200 µL to 400 µL (marked with * in tables below)

If a batch contains only samples requiring the W-ICPMS test the following spiking scheme can be used.

W-ICPMS		
D-BLK		

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DPQLICAP#		1000 uL DPQLICAP
LFB LW		200 uL LFB HW# A* 200 uL LFB HW# B*
Sample A		
Sample A matrix spike		200 uL HW# A* 200 uL HW# B*
Sample A matrix spike		200 uL HW# A* 200 uL HW# B*
Sample C		
Sample C matrix spike		200 uL HW# A* 200 uL HW# B*

Samples that have both the W-ICPMS and W-ICP tests will be spiked as follows:

W-ICP / W-ICPMS		
D-BLK		
DPQLDV#		1000 uL DPQLDV#
DPQLICAP#		1000 uL DPQLICAP
LFB MIN		1000 uL ICPMINA
LFB HW#		1000 uL HW# A 1000 uL HW# B
LFB LW#		200 uL LFB HW# A* 200 uL LFB HW# B*
Sample A		
Sample A matrix spike		1000 uL ICPMINA
Sample A matrix spike		1000 uL HW# A 1000 uL HW# B
Sample A matrix spike		1000 uL HW# A 1000 uL HW# B
Sample A matrix spike		200 uL HW# A* 200 uL HW# B*
Sample A matrix spike		200 uL HW# A* 200 uL HW# B*
Sample C		
Sample C matrix spike		1000 uL ICPMINA
Sample C matrix spike		1000 uL HW# A 1000 uL HW# B
Sample C matrix spike		200 uL HW# A* 200 uL HW# B*

8. SAFETY/HAZARDOUS WASTE MANAGEMENT

8.1. Treat all samples as if they are hazardous material by wearing gloves, safety glasses, lab coats, and following other pertinent safety guidelines.

8.2. The heating block should always be used in a fume hood or in a clean box with a pull-down trunk. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides.

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8.3. Make sure the hoods or trunk lines are operating properly. In case of faulty hoods or trunk lines, contact your supervisor and the laboratory safety staff as soon as possible.

9. REFERENCES

9.1. Laboratory Quality Manual, located on the Division of Environmental Assessment and Restoration (DEAR) website.

9.2. EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements.

9.3. Federal Register, Chapter 40, Part 136, Table II, footnote 19 (Preservation and Holding Time).

9.4. DEP SOP MT-061, Analysis of Selected Metals by Dual View Inductively Coupled Plasma-Atomic Emission Spectroscopy, ICP-AES.

9.5. Laboratory Health and Safety Plan, located on the DEAR website.

9.6. DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure.

9.7. DEP SOP LB-035-1.1, Calibration of Lab Thermometers using a Constant Temperature Calibration Bath.

9.8. DEP SOP MT-074, Standard Operating Procedure for the Thermo ICAP Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

9.9. DEP SOP CM-032 Calibration of Auto-Pipettes and Dispensers using the Check & Track Software System

Appendix of Significant Changes

Section 3.4 - edited for change in equipment.

Section 6.1 – 6.17 edited for changes to LFBs and clarity.

Section 7.0 – 7.8 edited for changes to LFBs and spiking factors, clarity, and addition of details.

11/19/2009 Section 2. Changed EPA 600/4-79-020 to EPA method 200.2 as reference method. EPA 200.2 is listed in our QC manual and LIMS view/print analysis report as the prep method in use.

11/19/2009 Section 1. Added list of applicable tests and reference to analytical SOPs.

11/19/2009 Section 5. Included contingency for samples that were preserved incorrectly.

11/19/2009 Section 7.4. Reorganized tables of spiking schemes for clarity.

11/19/2009 Added table of contents as SOP became longer than 10 pages. Added information from EPA method 200.2 to section 2.

11/19/2009 Added reference to Table II of 40CFR that describes preservation and holding times for metals.

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11/02/2010 Section 6.1. Screen shot of backlog template removed because it was out of date.

11/02/2010 Section 6.7. Information about thermometer used for hotblock temperature monitoring is no longer recorded in the hotblock calibration logbook because it is recorded elsewhere.

11/02/2010 Section 6.8. Nitrile gloves, not latex gloves, should always be used when handling samples for metals analysis.

11/02/2010 Section 6.16. Undigested aliquot for sample blanks should be included with tray when it is sent to the analysis lab. This information was separated from dilution information into a new section.

11/02/2010 Section 7.3. Two sets of sample duplicates no longer required.

11/02/2010 Section 7.4. Special spiking situation for W-SURF-SLT and samples with conductivity greater than 10,000 umhos/cm no longer required as the samples are now batched separately.

11/02/2010 Changed EPA 600/4-79-020 to EPA method 200.2 in reference section. EPA 200.2 is listed in our QC manual and LIMS view/print analysis report as the prep method in use. (This was updated in section 2 in 2009, but this reference was not updated).

11/04/2013 Section 5. Documentation of pH verification for samples preserved in the laboratory added. Section 7. Duplicate sample requirement removed.

10/29/2014 Section 6 modified to reflect changes in the block temperature documentation and the new prep worksheet procedures.

05/23/2019 Minor changes: added NIST traceable timer, removed spiking on a balance check, added pipette calibration software reference, added recording well position for temperature probe, added double spiking HW (400 µL) for high conductivity samples scheduled for W-ICPMS.

05/20/2020 Minor changes: added comment about the information that needs to be labeled on the thermometer and added another dilution factor column under section 6.17.

05/18/2021 Section 2. Hydrochloric acid (HCl) was changed from 1 mL 50 % HCl to 0.5 mL concentrated HCl. Section 4.2.1 concerning preparation of 50 % HCl was deleted. Section 6.12 was changed from 1 mL of 50 % HCl to 0.5 mL concentrated HCl.

05/16/2022 Added requirement to check pH of samples immediately prior to digestion procedure. The comment that the pH<2, along with the recording of the lot and expiration of the pH strips, must be recorded for each sample in the digestion batch. This information is included in the Notes section under section 6.9 and re-emphasized in section 6.13.

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