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 analysis of minerals and trace metals 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 a modified version of EPA method 200.2 (hot plate digestion), validated for use with a block digester. Aliquots of 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 hours. 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 once cooled.

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. Plexiglass digestion box or fume hood

3.5. Pipettes:

3.5.1. 200 µL Eppendorf

3.5.2. 500 µL Eppendorf

3.5.3. 1000 µL Eppendorf

3.5.4. Any mechanical pipette may be used if it is properly recorded on the prep sheet, has a current calibration date, and has a current calibration certificate generated from the Check-and-Track software, indicating its current calibration status. All pipettes are calibrated using the Check-and-Track software and calibration certificates are saved according to DEP SOP CM-032.

3.6. NIST-traceable min/max 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 include 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 - Provided on tap at the laboratory sink and stored in clean wash bottles.

4.4. Spike and Practical Quantitation Limit (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 depletion.**

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4.4.1. Digestion PQL Solutions (DPQLDV# and DPQLICAP#) - A suffix is added to these abbreviations to indicate the current PQL solution (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 dates of these standards will be no later than the soonest expiration date provided by the manufacturer of the single element stock standards from which they were made. 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 later than the soonest expiration date provided by the manufacturer of the single element stock standards from which they were made. Stored at room temperature.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are stored at room temperature in the metals water sample storage room located in the Receiving Room, C301. 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 with HNO_3 to pH < 2, and the time of addition of nitric acid is recorded. Such samples are marked with a red cross on the sample bottle top. Preparation **cannot** begin for **at least 24 hours**. On the day of prep, before preparation, the pH is checked again with pH paper by the prep analyst. The prep analyst shall document the pH as well as the lot number of the pH paper and its expiration date in the 'Sample Comments' column of the prep worksheet in Prep Worksheet Manager in LIMS. If the sample is still not measuring at a pH of 2 or below, include a comment on the prep worksheet that the sample needs to be preserved with nitric acid to a pH < 2, and the receiving team will create a Non-Conformance Report (NCR). Return the sample to the receiving room, where more nitric acid will be added by the receiving team, and the time of addition of nitric acid is once again documented. The prep analyst must wait **another 24 hours** before checking the pH again. Once the pH is less than 2, the prep analyst shall proceed with sample preparation.

6. SAMPLE PREPARATION PROCEDURE

6.1. Generate a Backlog Report - Using LIMS, a backlog template should be created to include all samples requiring water tests in the metals group currently in "W" status, indicating the samples are waiting for preparation.

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6.1.1. From the LIMS menu, select Laboratory> Technical> Backlog Reports.

6.1.2. To open a backlog report from an existing template, click Template> Open. Then, select the appropriate user from the drop-down menu, highlight the appropriate template, and click 'OK'. Click the 'Generate Backlog Report' icon.

6.1.3. To create a new backlog report template suitable for water sample preparation for metals analysis, adhere to the following steps: If an existing template is open, click the 'Close Template' icon. Then, under 'Analyses…', click 'Select'. In the pop-up menu, under 'Main Group:', select 'CHEMISTRY'. Under 'Analysis Group:', select 'Metals-Water'. With 'Show Removed' unchecked, highlight the applicable metals test IDs (see Section 1) and click the 'Add' arrow to move them to the 'Selected…' column. Click 'OK'.

6.1.4. Under 'Test Status…', check 'W'. Set 'Orientation' to 'Landscape', and under 'Include…', check 'Sample Notes' and 'Required Components'.

6.1.5. The options under 'Available Fields' are customizable. Some suggested fields to include on the generated report in the order of the user's preference are: Sample ID, TestID, Priority, Field Conductivity, Salinity, Matrix, Date Required, Date Logged In, Reserved, On Worksheet, Worksheet ID, Lab Location, Reprep Info, Job ID, and Project ID. Highlight the Available Fields of choice and click the 'Add' arrow to move them to the 'Selected Fields/Column Order' box. The order of the fields can be adjusted by highlighting a Selected Field and clicking the 'Move Field Up' or 'Move Field Down' arrows located below the box.

6.1.6. The 'Size' column refers to the column width of the field on the generated report, which can be adjusted to the user's preference by highlighting the Suggested Field and clicking on the 'Size' column header to open a pop-up window. Use the arrows to adjust the Size to the desired number and click 'OK'.

6.1.7. The data displayed on the backlog report may be sorted according to the user's preference. A few Suggested Fields to move to the 'Sort By' box are Date Required, Date Logged In, Priority, and Sample ID. To do so, highlight the Suggested Field and click on the appropriate 'Add' arrow. The order of the fields can be adjusted by highlighting a field in the 'Sort By' box and clicking the 'Move Sort Up' or 'Move Sort Down' arrows located below the box.

6.1.8. To save the template, click the 'Save Template' icon. In the pop-up window, select the appropriate user. To save as a new template, under 'Template…', type a new name in the box and click 'OK'.

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To overwrite an existing template, highlight the template intended to be overwritten and ensure the name box is populated with the same name. Click 'OK'. In the top left corner, click the 'Generate Backlog Report' icon.

6.2. Batch Samples - 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 or contact your supervisor). It would be helpful if a batch of water samples requires only one instrument test (either W-ICP or W-ICPMS). However, if a sample requires both instrument tests, then its batch will be analyzed on both instruments and must contain all appropriate quality control (QC) samples.

6.3. Place a Sample Reservation - Samples are then placed on a reservation through the LIMS sample reservation program. Reservations for the following day must be made before 2:00 p.m.

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

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

6.3.3. Select the name of the person creating the reservation ('By:') and the name of the person the reservation is for ('For:'). Click 'Next'.

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

6.3.5. Select the 'Analysis Group' for the samples to be reserved. In this case, select 'Metals-Water'. Then, highlight the appropriate test(s) from the 'Available Tests' column and click the arrow button to move them to the 'Selected Tests' column. Click 'Next'.

6.3.6. To add sequential sample IDs, input the first sample ID to be reserved and the last sample ID to be reserved, then click 'Add samples to list'; or, to search for samples, click 'Add Samples By Status' and highlight desired samples, then click 'Ok'.

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 the sample reservation, and if correct, click 'Finish'; otherwise, click 'Back' to edit.

6.4. Sample Custody and Preparation Worksheet - Metals water samples are stored in the Receiving Room, C301. Prior to preparation, the technician assigned to the preparation must possess custody of the sample, as defined in the DEP Laboratory Quality Manual. A sample cannot be prepared for analysis unless it has been properly "checked out" by the lab technician to

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perform the digestion. If a sample is currently in custody of another laboratory staff member, custody must be transferred to the lab technician intending 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). Refer to DEP SOP LB-023 for more information on using LIMS to maintain sample custody, check out and check in samples, and transfer custody. Once custody has been established, create a prep worksheet using the LIMS Prep Worksheet Manager, found at Laboratory> Technical> Prep Worksheet Manager. Click the 'Create a prep worksheet' icon. Under 'Preparation ID', select '200.2'. Click the 'Samples Checked Out' icon and follow the prompts to add the samples to the worksheet from the appropriate user with custody. Under 'Assign To…', select the appropriate lab prep technician. Click the 'Create the new worksheet' icon.

6.5. Determine QC - Using the spike 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 included.

6.6. Prepare the Heating 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, such as a Kimwipe, dampened with DI water. Turn on the heating block and set the temperature so that the samples will heat to the acceptable temperature range of 92 – 97° C (this requires setting the block temperature at a point between 108 °C and 115 °C for Environmental Express heating blocks).Place one 50 mL disposable polypropylene digestion tube filled with DI water in a well on the block and insert a NIST-traceable min/max thermometer. Record the serial number of the thermometer used on the prep worksheet under the 'Thermometer ID' field. After the temperature has stabilized and reached the acceptable temperature range of 92 – 97° C, read the temperature of the thermometer and record it on the prep worksheet in the 'Block Temperature (C)' field along with the well position using the format 'xx.x C; W.pos: xx'. To ensure all well positions are consistently reaching the acceptable temperature over time, the well position the technician chooses each day shall move sequentially. For example, if the technician chooses well position 1 on day 1, the next chosen position on day 2 shall be 2, and so on until all positions on the block have been utilized. Once all well positions of the block have been tested and recorded, the technician shall repeat the cycle beginning with position 1.

Note: The temperature of the heating block must be monitored and recorded before digestion on each day of use. The thermometer used 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

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of calibration, next calibration due date, and serial number must be properly labeled on the thermometer.

6.7. Prepare the Labels - All metals water sample digestions are prepared in 50 mL disposable polypropylene tubes designed to fit in the Environmental Express Digestion Blocks. The digestion tubes shall be labeled with the sample ID and/or the QC name. Include any spike information, dilution factors, and other pertinent information. Prepare the necessary labels using LIMS and the SATO label printer. In LIMS, navigate to Laboratory> Receiving> Print Preparation Labels. Click on the 'Metals Prep. Labels' icon. You may populate the label information by typing manually; or by clicking on the 'Load Sample IDs from prep worksheet' icon or clicking on the 'Load sample IDs checked out by operator' icon. Select the appropriate worksheet or user from the pop-up window and click 'OK'. The 'Sample' column should contain the sample ID or QC name. The 'Text1' column should contain the date, and the 'Text2' column should contain the worksheet number. Print the labels with the SATO label printer and apply them to the tubes. Be sure to create an extra label with the worksheet number and date to attach to the sample tray. Labels may be handwritten only if printed labels are not available.

6.8. Prepare the Digestion Tubes - The disposable digestion 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 shall be used whenever handling metals samples. Extreme care shall be taken not to touch the inner surfaces of the tubes or caps.**

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

Note: Each new lot number of digestion tubes shall be tested for volume accuracy prior to use. Four digestion tubes from each lot number are tested using the Check-and-Track software according to DEP SOP CM-032, as is done with pipettes. Record the temperature and relative humidity of the room using a NIST-traceable thermometer. Using the scale, tare the weight of the empty vessel, then record the weight of DI water filled to the 50 mL mark. The software will calculate the volume of water. Store the results in the same location as the pipette calibrations in the appropriate folders for the year and month at: \\floridadep\data\DEAR\Labs\Lab5\Chemistry\Pipette\Inorganic_Metals.

6.9. Checking the Sample pH and Pouring the Samples - Note any particulates in the sample. Tighten the sample bottle cap and invert the sample bottle three to four times to ensure a good mixing. Check the pH of each sample using pH strips to verify that the pH is less than 2. If the pH is less than 2, record this information under the 'Sample Comments' column of the prep

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worksheet along with the lot number and expiration date of the pH strips used as well as the presence of any particulates in the sample. For example, the comment 'pH <2 (LOT:xxxxxx, EXP: xx/xx/xxxx, Particulates)' will suffice. If the pH is greater than 2, follow the instructions in Section 5. Carefully pour 50 mL of each sample into the respectively labeled tube. When pouring the spike samples, invert the sample bottle several times in between each aliquot poured to ensure consistent homogeneity. **This is a very important step in the digestion procedure.** It is critical for the volume of the sample in each tube to be as accurate as possible. It may be necessary to slightly overpour 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. Be sure to place the tube on a level surface and read the meniscus at eye level. If a sample cannot be accurately dispensed, contact a supervisor for assistance.

Note: EPA Method 200.2 instructs the technician 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.

6.10. Prepare the Matrix Spikes - A properly calibrated pipette is used to dispense an accurate volume of spike solution. Ensure that the intended pipette's calibration is current. Pipette the appropriate volume (see Section 7.4) of each applicable spike solution into each QC sample determined from Section 6.5, according to the elements required by the test. Record each spike solution serial number in the appropriate 'Spike #' field on the prep worksheet. Record the amount (µL) of each spike solution pipetted for each applicable sample in the appropriate 'Spike # Amount' column. Record the serial number of each pipette used under the appropriate 'Mechanical Pipette ID #' field.

6.11. Check the Fume Hood - 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 Reagents - Prior to pipetting, check the reagent expiration date. Never use an expired reagent. Add 1.0 mL of HNO_3 and 0.5 mL of HCl into each sample tube. Enter the serial numbers of the HNO_3 and HCl used on the prep worksheet under the 'Reagent 1' and 'Reagent 2' fields, respectively. If it isn't automatically populated, record the amount (µL) of each reagent pipetted for each sample in the appropriate 'Reagent # Amount' column. If different from Section 6.10, record each pipette used under the appropriate 'Mechanical Pipette ID #' field. Place the tubes in the heating block.

6.13. Start the Timer - Once on the heating block, close the clean box door, start the timer, and heat the samples for a total of 4 hours. Record the 'Prep Start Date/Time' on the prep worksheet. The four-hour digestion period is tracked using a NIST-traceable timer with expiration date. Record the

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serial number of the timer under the 'Timer ID' field. While the samples are digesting, all necessary prep worksheet information may be recorded and verified. In particular, record/verify the information in the 'Sample Comments' column, such as the pH, the presence of any particulate matter before digestion or after digestion, or any irregularity associated with any sample in the batch.

6.14. Turn Off the Heating Block and Let Cool - After the heating cycle is complete, read the min and max temperatures on the thermometer and record them on the prep worksheet in the 'Block Temperature (C)' field (after the starting temperature and well position) in the format 'xx.x C; W.pos: xx; Min/Max: xx.x/xx.x C'. The acceptable min/max temperature range is 92 - 97°C. Turn off the power to the heating block, carefully place the samples back into the batch tray, and allow them to cool (about 30 minutes). The samples will have lost significant volume during the digestion.

6.15. Reconstitute the Samples - Working with one tube at a time, reconstitute the samples to 50 mL with DI water, carefully observing the meniscus at the fill line. Samples shall be placed on a stable surface with the meniscus and fill line at eye level while reconstituting. If viewing the 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 will be difficult to accurately fill the tube. This will result in erroneous results and warrant redigestion. 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.

<u>Note</u>: All dilutions shall be made by the ICP and ICPMS analysts (not prep staff) with 2 % HNO_3 / 1 % HCl in DI water in thoroughly rinsed 15 mL orange-capped centrifuge tubes prior to analysis. If dilutions are made by the prep staff by request of the supervisory staff, the following instructions shall be followed.

6.17. Dilutions - Determine if any of the samples need dilutions, 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 µL)	10 mL
20	9.5 mL	0.5 mL (500 µL)	10 mL
50	9.8 mL	0.2 mL (200 µL)	10 mL
100	9.9 mL	0.1 mL (100 µL)	10 mL

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ICPMS:

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

ICP:

Dilutions for samples requesting mineral analytes:

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

Dilutions for samples requesting additional analytes:

Sample conductivities	Dilution factors for samples and matrix spikes
<10,000 µmhos/cm	no dilution needed
10,000 – 40,000 µmhos/cm	3
>40,000 µmhos/cm	4

6.18. Send Prep Worksheet for Review and Samples to Analysis Lab - The samples are now ready for analysis. Make sure the batch label with the worksheet number (e.g. 200.2_#####) and date is attached to the sample tray. Make sure all documentation is completed properly on the prep worksheet, including but not limited to: the prep technician, digestion start and end date, digestion start and end time, reagent serial numbers, spike solution serial numbers, sample IDs, dilution factors, block ID, block temperature, thermometer ID, timer ID, all mechanical pipette IDs, and sample comments. Be sure to record all information in the sample comments column 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 if acceptable, will add their name in the 'Reviewed By' field. Once the prep worksheet has been successfully reviewed and accepted, complete the prep worksheet in Prep Worksheet Manager by clicking on the 'Complete' button at the bottom left of the open prep worksheet window. This will change the samples' status from 'W' to 'V', indicating that sample preparation is complete and that samples are awaiting analysis. This **must** be done BEFORE the tray is sent up to the metals analysis lab. Print a copy of the completed prep worksheet and send it along with the sample tray to the metals analysis lab.

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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 that contains DI water only.

7.2. Digestion PQL - One per digestion batch per analysis test. Digestion PQL Solutions (DPQLDV# and DPQLICAP#) are prepared by the metals analysis group. A suffix is added to these abbreviations to indicate the current PQL solution (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) - All batches must have at least one LFB. The trace metal spike solution (HW#) is prepared by the analysis group in two parts: HW#A contains all metals except silver and HW#B contains silver only. A suffix is added to these abbreviations to indicate the current HW solution (e.g. 4, 5, etc.). The mineral spike solution (ICPMINA) is a purchased solution.

7.4. Matrix Spikes - Matrix spikes are prepared by adding a known amount of analyte to a sample. A minimum of 10 % of samples in a batch must be spiked. Therefore, for a batch of 20 samples, two samples shall be chosen to spike, named A and C. Sample A shall be spiked in duplicate.

Samples with the W-ICP test requesting **sodium, potassium, calcium, magnesium, iron, or aluminum** require a mineral QC series. The table below lists the QC needed:

W-ICP QC with minerals only requested		
D-BLK		
DPQLDV#		1000 µL DPQLDV#
LFBMIN		1000 µL ICPMINA
Sample A		
Sample A matrix spike MIN1		1000 µL ICPMINA
Sample A matrix spike MIN2		1000 µL ICPMINA
Sample C		
Sample C matrix spike MINC		1000 µL ICPMINA

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Samples with the W-ICP test requesting trace metals in addition to the mineral analytes require the following QC:

W-ICP QC with minerals & trace metals requested		
D-BLK		
DPQLDV#		1000 µL DPQLDV# 1000 µL DPQLDV#_AG
LFBMIN		1000 µL ICPMINA
LFBHW#		1000 µL HW#A 1000 µL HW#B
Sample A		
Sample A matrix spike MIN		1000 µL ICPMINA
Sample A matrix spike HW1		1000 µL HW#A 1000 µL HW#B
Sample A matrix spike HW2		1000 µL HW#A 1000 µL HW#B
Sample C		
Sample C matrix spike MINC		1000 µL ICPMINA
Sample C matrix spike HWC		1000 µL HW#A 1000 µL HW#B

<u>Note</u>: If a batch for ICP-MS contains high conductivity samples (>10,000 µmhos/cm), the HW# spike solution amount is doubled from 200 µL to 400 µL (marked with * in the tables below).

For batches containing only samples with the W-ICPMS test, the following QC are required:

W-ICPMS QC		
D-BLK		
DPQLICAP#		1000 µL DPQLICAP#
LFBLW#		200 µL HW#A* 200 µL HW#B*
Sample A		
Sample A matrix spike LW1		200 µL HW#A* 200 µL HW#B*
Sample A matrix spike LW2		200 µL HW#A* 200 µL HW#B*
Sample C		
Sample C matrix spike LWC		200 µL HW#A* 200 µL HW#B*

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Sample batches with both the W-ICPMS and W-ICP tests require the following QC:

W-ICP & W-ICPMS QC		
D-BLK		
DPQLDV#		1000 µL DPQLDV#
DPQLICAP#		1000 µL DPQLICAP#
LFBMIN		1000 µL ICPMINA
LFBHW#		1000 µL HW#A 1000 µL HW#B
LFBLW#		200 µL HW#A* 200 µL HW#B*
Sample A		
Sample A matrix spike MIN		1000 µL ICPMINA
Sample A matrix spike HW1		1000 µL HW#A 1000 µL HW#B
Sample A matrix spike HW2		1000 µL HW#A 1000 µL HW#B
Sample A matrix spike LW1		200 µL HW#A* 200 µL HW#B*
Sample A matrix spike LW2		200 µL HW#A* 200 µL HW#B*
Sample C		
Sample C matrix spike MINC		1000 µL ICPMINA
Sample C matrix spike HWC		1000 µL HW#A 1000 µL HW#B
Sample C matrix spike LWC		200 µL HW#A* 200 µL 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. Refer to the DEP Health and Safety Manual for additional safety measures and procedures.

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.

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

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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. DEP Health and Safety Manual, located on DEAR's intranet site.

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

9.7. DEP SOP LB-035, 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.

9.10. DEP SOP LB-023, Maintaining the Custody and Storage of Environmental Samples in the DEP Laboratory.

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.

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.

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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.

05/31/2023 Added a pagraph on mechanical pipettes in Section 3.5.3.

05/02/2024 Added reference to min/max thermometer in section 3.6. Added clarification for ensuring pH<2 in section 5. Added a couple of statements about reading and documenting min/max temperature on prep sheet.

05/07/2025 Minor formatting, grammatical, and awkward phrasing corrections throughout the document. Section 4. Added source of DI water. Section 5.

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	Added more information and clarification on the procedure for testing the pH of samples from the main laboratory point of view. Section 6.1. Added the procedure for creating a backlog report template and generating a backlog report suitable for the sample preparation. Section 6.3. Added more detail and clarification on the process for sample reservation. Section 6.4. Added more detail on the sample custody procedure and referenced DEP SOP LB-023. Section 6.6. Provided more information and clarification on how to choose a well position for the thermometer and how to record it on the prep worksheet. Section 6.7. Added the procedure for generating and printing labels. Section 6.8. Relocated the note regarding the care and handling of the digestion tubes and caps. Section 6.9. Added more information and clarification on the procedure for testing the pH of samples from the prep technician's point of view as well as how to document the information on the prep worksheet. Incorporated much of the information from the corresponding note into the main section. Section 6.10. Noted how to record matrix spike and pipette information on the prep worksheet. Section 6.12. Noted how to record reagent information on the prep worksheet. Section 6.13. Noted how to record the prep start time and timer information on the prep worksheet. Section 6.14. Noted how to record the min and max temperatures on the prep worksheet. Moved the procedure for reconstituting samples to Section 6.15. Section 6.18. Added information and clarification regarding the process for prep worksheet review and completion. Section 8.1. Referenced the Laboratory Health and Safety Plan. Section 9. Updated the location of the Laboratory Health and Safety Plan. Added DEP SOP LB-023 as a reference.
04/29/2026	Minor formatting and grammatical corrections throughout the entire document. Updated new pipettes in Section 3. Added a note in Section 6 regarding the procedure for checking the volumetric accuracy of the 50 mL digestion tubes and included the network path where results are stored. Updated the proper name of the DEP Health and Safety Manual.

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