Analysis of Dissolved Trace Elements in Aqueous Solutions by ICP-MS

1 INTRODUCTION
This procedure is used to analyze aqueous samples for dissolved trace elements in aqueous solution using inductively coupled plasma mass spectrometer (ICP-MS).

2 SCOPE AND APPLICATION

2.1 OVERVIEW
2.1.1 Available elements are measured with minimal intervention by the analyst, though certain samples may require dilution or filtration. No digestion is required prior to analysis of dissolved elements (for samples requiring digestion, see protocol 19_01_02). Standards are prepared using 0.5% nitric acid, and elemental standards for desired analytes. Specific ratios and volumes are not given in this method and must be determined on a case-by-case basis in order to maximize performance.

2.2 METHOD DETECTION LIMIT
2.2.1 New MDLs should be derived for every run to account for variations in the method. A table which includes the most recent MDLs can be found in Section 10 of this document.

2.3 ACCEPTABLE RANGES
2.3.1 The acceptable range for this method is 0 to 500 µg/L.

2.4 TRAINING TIME
2.4.1 The training time required for this method is 2-3 days.

2.5 SAMPLE PRESERVATION
2.5.1 For metal analysis, samples should be acidified (HCl). No preservation is required for anion samples. All samples should be stored in the refrigerator until analysis can be performed.

3 REQUIRED TRAINING
3.1.1 Basic lab and instrument training as detailed in the Standardized Laboratory Training Plan (07_01_09.001).

4 EQUIPMENT AND MATERIALS

4.1 APPARATUS AND MATERIALS
4.1.1 50 mL centrifuge tubes (Fisherbrand, 06-443-20).
4.1.2 Syringe filter, 25mm with 0.45 µm polyethersulfone membrane (VWR 28145-503 or equivalent).
4.1.3 Disposable syringe with polypropylene plunger, 20 mL (Fisher).
4.1.4 Adjustable micropipettes with reference tips (Eppendorf, Thermo Scientific).
4.1.5 Santoprene tubing (Spectron Inc., SIT-SANSD-049-3).
4.1.6 Peristaltic pump tubing, 0.508mm (Thermo, 1320050).
4.1.7 Sample cone, 4450 (Thermo, 3600812).
4.1.8 Ni skimmer cone 0.5, insert version (Thermo, 1311870).
4.1.9 Skimmer cone insert, 3.5 (Thermo, 1318480).
4.1.10 Sample cone gasket (Thermo, 1310900).
4.1.11 Teflon tube, 5.0M (Thermo, 1041071).
4.1.12 Teflon tube, 1/16 O.D .02ID, 10 feet (Thermo, 1600061).
4.1.13 iCap Q quartz torch (Thermo, 1230790).
4.1.14 Quartz injector, 2.5mm ID (Thermo, 1305600).
4.1.15 Sampling cone gasket (Thermo, 1310900).
4.1.16 Skimmer cone insert, 3.5 (Thermo, 1318480).
4.1.17 Skimmer iCap Q/Qnova Ni for insert, 0.5mm orifice (Thermo, 1311870).
4.1.18 Cyclonic quartz spray chamber iCap Q (Thermo, 1317080).
4.1.19 MicroMist nebulizer, 0.4 mL/min (Thermo, BRE0009386).
4.1.20 Torch socket iCap Q/Qnova (Thermo, 1231000).
4.1.21 iCap Q/Qnova Quartz Torch (Thermo, 1230790).
4.1.22 Quartz injector, 2.0mm ID iCap Q/Qnova (Thermo, 1305640).

4.2 REAGENTS AND STANDARDS
4.2.1 Tube B working solution (Thermo, THERMO-4AREV).
4.2.2 Working setup solution (Thermo, THERMO-5A).
4.2.3 Nitric acid, trace metal grade (Fisher, A509-P212).
4.2.4 Hydrochloric acid, trace metal grade (Fisher, A508-P212).
4.2.5 Distilled deionized water (DDW).
4.2.6 Barium standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLBA2-2Y).
4.2.7 Copper standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, CLCU2-2Y).
4.2.8 Manganese standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLMN2-2Y).
4.2.9 Strontium standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLSR2-2Y).
4.2.10 Arsenic standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, CLAS2-2Y).
4.2.11 Yttrium standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLY2-2Y).
4.2.12 Uranium standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLU2-2Y).
4.2.13 Iron standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, PLFE2-2Y).
4.2.14 Selenium standard solution, 1000 µg/mL, 125 mL (SPEX Certiprep™, CLSE2-2Y).

5 SAFETY PRECAUTIONS

5.1 SAFETY PRECAUTIONS

5.1.1 Always wear a lab coat and gloves while handling acids.
5.1.2 All solvents and chemicals should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Material Safety Data Sheets (MSDS) are available for all materials used in this procedure, and should be referred to regarding specific handling procedures and toxicity.

5.2 WASTE DISPOSAL

5.2.1 ALL acidic solutions must be neutralized with sodium bicarbonate before disposal into the sanitary sewer. Do not allow any un-neutralized acids or acidic solutions to drain into any sink in the building.
5.2.2 Check the Sewer Disposal List in Room 203 for the list of substances that can be disposed of down the sanitary sewer.

6 SOLUTIONS AND REAGENTS

6.1 0.5% NITRIC ACID SOLUTION

| Nitric Acid (HNO₃) | 63.01 g/mol | 40 mL |
| Distilled Deionized Water | 18.015 g/mol |

Protocol: There is a container on the work bench of the ICP-MS Lab (Room 204A) designated for the creation and storage of 0.5% Nitric Acid for the ICP-MS. When this container is empty, fill it halfway with distilled deionized water. Then, simply add 40 mL of concentrated nitric acid to the container, and fill the container to the established line using more distilled deionized water from the dispenser on the wall. Remember to add the water first, and then add the acid. All mixing and use of concentrated acids should occur in the corrosion control lab (Room 205) to reduce corrosion inside of the instrument.
Storage: Excess solution can be stored in the designated plastic containers in the ICP-MS lab.
Disposal: Acids should be neutralized using sodium bicarbonate before disposal in any of the lab drains.

7 STANDARD SOLUTIONS

For metal analysis, all blanks and calibration standards will be prepared with 0.5% nitric acid (v/v) in distilled deionized water. For some other samples, distilled deionized water is used instead. Refer to training for unique situations (including anions).

7.1 BLANKS

7.1.1 Two types of blanks are required for analysis. The calibration blank is used in establishing the calibration curve. The rinse blank is used to flush the system between samples and standards.

7.1.1.1 The calibration blank ought to consist of the same stock of 0.5% nitric acid used to prepare the final dilutions of the calibration standard solutions. This 50 mL centrifuge tube should be kept full throughout standard preparation to ensure the process is as uniform as possible.

7.1.1.2 The rinse blank is 0.5% nitric acid should always be kept full in Standard Rack Spot 1. Add new 0.5% nitric acid from carboy in Room 204A as needed.

7.2 ICP STOCK STANDARD (10,000 NG/ML)

7.2.1 Single element solutions can be found in the Acids and Corrosives Storage in Room 204A. Standards are generally 10^6 ng/mL concentration, (refer to the ICP-MS Standards Inventory on Box).

7.2.2 To prepare a mixed analyte, pipette each of the desired single element stock solutions into a centrifuge tube depending on concentration. See example calculations below.

10^5 ng/mL solution: Pipette 1 mL single element stock

7.2.2.1 10^6 ng/mL solution: Pipette 100 µL single element stock

7.2.3 Bring to a final volume of 10 mL using a pipette.

7.2.4 Stock standards may be stored for up to 6 months in the refrigerator. Keep all stock standards together in the fridge for ease of use.

7.3 CALIBRATION STANDARDS (0.1, 0.5, 1, 5, 10, 50, 100 NG/ML)

7.3.1 Prepare the calibration standards (0.1, 0.5, 1, 5, 10, 50, 100) using the following equations:

7.3.1.1 100 ng/mL: 500 µL of 10,000 ng/mL Stock Standard + 49.5 mL 0.5% HNO3

7.3.1.2 50 ng/mL: 200 µL of 10,000 ng/mL Stock Standard + 39.8 mL 0.5% HNO3
7.3.1.3 10 ng/mL: 4 mL of 100 ng/mL Standard + 36 mL 0.5% HNO3
5 ng/mL: 4 mL of 50 ng/mL Standard + 36 mL 0.5% HNO3
7.3.1.4 1 ng/mL: 4 mL of 10 ng/mL Standard + 36 mL 0.5% HNO3
7.3.1.5 0.5 ng/mL: 4 mL of 5 ng/mL Standard + 36 mL 0.5% HNO3
7.3.1.6 0.1 ng/mL: 4 mL of 1 ng/mL Standard + 36 mL 0.5% HNO3
7.3.1.7 0 ng/mL: 40 mL 0.5% HNO3

7.3.2 Calibration standards may be re-used for multiple runs if there is sufficient volume. Ensure at least 20 mL solution in each calibration standard tube before each run.

7.3.3 Fresh dilute calibration standards should be prepared every two weeks, or as needed.

8 PROTOCOL

8.1 SAMPLE PREPARATION

8.1.1 Samples which are absent of particulate matter can be transferred directly into autosampler tubes for analysis. There should be approximately an inch of sample in each tube to ensure flow into the autosampler probe.

8.1.2 If particulate matter is present in the sample solutions, they must be filtered to avoid clogging the ICP-MS tubes and nebulizer. If necessary, utilize a polyethersulfone filter. Filter samples through filter paper into ICP-MS autosampler tubes before analysis.

8.2 SAMPLE RE-ANALYSIS

8.2.1 Dilute and re-analyze samples that are more concentrated than the linear range for a particular analyte.

8.2.2 This should be indicated in Qtgra under Evaluation Results → Concentrations, where samples outside the linear range will be highlighted in red.

8.3 ICP-MS START-UP GUIDE

8.3.1 Note: Always wear gloves when handling any part of the instrument including pumps, tubing, and any samples/standards. The computer/desk area and the chiller are no glove areas.

8.3.2 Close all open programs on the computer, and perform a daily re-start. This helps to eliminate any communication errors before starting the instrument.

8.3.3 Once the computer has restarted, open the three programs needed to run the ICP-MS. These are Qtgra, Instrument Control (IC), and Camera. Maximize the Qtgra window.

8.3.4 Turn on the chiller by pushing the power button (no glove area).

8.3.4.1 Check water level on the front of the chiller – add DI water from carboy under desk if necessary.
8.3.5 Check levels of spent waste and 0.5% HNO3 containers located on the desk to the right of the auto sampler.

8.3.5.1 Fill HNO3 if necessary from the 0.5% HNO3 container located next to the DDI water dispenser.

8.3.5.2 Empty waste container in the Acids lab sink.

8.3.6 The peristaltic (peri) pump is located on the right side of the iCAP RQ.

8.3.6.1 There are 2 tubes: yellow (outlet) and clear (inlet). Both tubes should be replaced daily or after 8 hours of continuous use. When in doubt, change the tubing!!

8.3.6.2 Attach the outlet tube on the last groove at the back of the peristaltic pump, first securing one side and then the other in the plastic grooves underneath the pump. Attach the inlet tube on the second to last groove at the back of the peristaltic pump. The peristaltic pump will spin in a clockwise direction. It is a common error to place the tubes in the opposite direction to the flow path. Avoid this by referencing the arrow above the peristaltic pump, and tracing the intended flow path of the tubes to ensure they are going through the pump in the correct direction. Close the plastic flaps. Lock tubes into place with the notches.

8.3.6.3 When locking tubes into place with the notches, avoid touching the screws on top. Loosening or tightening these screws can change the uptake time of the instrument.

8.3.7 Ensure that there is a centrifuge tube filled with a blank solution of 0.5% nitric acid in the Standard rack, Vial 1. Make sure that the cap of the centrifuge tube is off.

8.3.8 Warm-Up

8.3.8.1 From Qtega -> ‘Get Ready’ button -> Select ‘Warm Up’ for 15 minutes - > OK

8.3.8.1.1 Do not select ‘Perform Validation Tests’ – this will be done later.

8.3.8.2 Watch the camera to ensure that plasma is ignited and monitor Log View Tab for any errors until you see the “Operate” message.

8.3.8.3 Allow warm-up to finish, software will notify when it is ready. During the warm-up, monitor the flow into and out of the peristaltic pump. Cancel the warm-up only if you do not see consistent flow both to and from the peristaltic pump. The flow will be checked more thoroughly in the next step.

8.3.9 Checking Plumbing and Performance

8.3.9.1 Check pump flow.

8.3.9.2 Intake flow should appear to be a steady, unbroken stream of solution. This can be checked by introducing an air gap into the autosampler. This can be done by lifting the sampling probe from the blank solution for a few seconds to introduce an air bubble. Lower probe back into solution.

8.3.9.2.1 Confirm that the air bubbles moves steadily through the inflow tube.
8.3.9.2.2 If air bubble is not present, or if it is not moving steadily, there is an issue with the tubing/pumping. **Do not proceed. Call for help.**

8.3.9.3 Output flow should be a broken stream of solution because the tube is slightly larger in diameter. However, the flow should still be steady and fast.

8.3.9.3.1 Check to ensure that there are very small consistent bubbles in the tube coming out of the bottom of the spray chamber.

8.3.9.3.2 Check for any liquid build-up at the elbow of the spray chamber. If you see any drops of liquid inside the chamber, turn off the instrument following the proper procedure and call for help.

8.3.10 Performance Report (PR) – **If your performance report fails for any reason, get assistance from a trained member of staff. Performance Verification failure should only be diagnosed UNDER SUPERVISION.**

8.3.10.1 In IC, use ASX-560 tab to command probe to Tune solution (generally located in Standard Row, Vial 10). Make sure the solution is filled to 50 mL.

8.3.10.1.1 Allow the pump to take up tuning solution for 120 seconds by clicking the High mode of peri pump, one can monitor the flow by clicking Run (in ‘Control’ tab) in IC located at Top Left Corner. After the tuning solution has reached plasma a rise in peak will be seen, after that click Normal mode in peri pump and allow to stabilize the speed for ~40 seconds before running PR. **NOTE:** Not allowing pump to stabilize generally will lead to Mass Calibration errors.

8.3.10.1.2 Alternatively, you can allow the tuning solution to be taken up using the Normal mode of the peri pump, but this will take roughly 240 seconds. Occasionally, turning the peri pump from Normal to High using IC has caused communication errors.

8.3.10.2 Begin by running a Performance Report (PR) in STD mode.

8.3.10.2.1 From IC -> Performance Report (in ‘Wizards’ tab)

8.3.10.2.1.1 To run a report in STD: ‘Run an Existing Report’ -> STD -> Next -> Next

8.3.10.2.2 If the PV passes, continue on to subsequent steps.

8.3.10.2.3 If the only PV failure is sensitivity, allow the instrument to run for a few minutes and retry the PR – the machine often just needs time to settle itself. If the PR continues to fail, continue on to subsequent steps.

8.3.10.3 Run a Performance Report (PR) for STD Biweekly.

8.3.10.3.1 From IC -> Performance Report (in ‘Wizards’ tab)

8.3.10.3.1.1 To run a report in STD Biweekly: ‘Run an Existing Report’ -> STD Biweekly -> Next -> Next

8.3.10.3.2 If the PV passes, continue on to subsequent steps.

8.3.10.3.3 If the PV fails, careful attention should be given to the parameters which are failing. For additional instructions based on which parameters are failing, please see section ______.
8.3.10.4 Run a Performance Reports (PR) in KED mode.

8.3.10.4.1.1 To run a report in KED:
- Change measurement mode to KED (from 'Measurement mode' tab in IC)
- ‘Run a Report in the Active Measurement Mode’ -> Next -> Next

8.3.10.4.1.2 If the PV passes, Performance Verification is completed. You may now proceed on to creating a lab book and running samples. For instructions on this, please refer to section 8.3.12.

8.3.10.4.1.3 If the PV fails in KED mode, run Autotune KED line 1, and then run the PR in KED mode again.

8.3.10.5 Diagnosing Reasons for STD PV Failure (For advanced troubleshooting, please refer to the Instrument Manual)

8.3.10.5.1 Mass
- Run Mass Calibration using Setup Solution, then re-run STD Biweekly Performance Verification step.

8.3.10.5.2 Doubly Charged
- If the value is < 4.5%, decrease the Extraction Voltage. Make sure Lithium does not drop below 40,000 counts, then repeat a Performance Report for STD Biweekly.
- If the value is ≥ 4.5%, run AutoTune High Matrix ++, then repeat a Performance Report for STD Biweekly.

8.3.10.5.3 Oxide
- If the value is < 3.5%, decrease the Nebulizer Gas flow by 0.005 and observe for 1 minute. Repeat this until the value drops below 3%, then repeat a Performance Report for STD Biweekly.
- If the value is ≥ 3.5%, run STD AutoTune, then repeat a Performance Report for STD Biweekly.

8.3.10.5.4 Intensity
- If the change in intensity is major (~10x), clean the cones. Once you have done that, run STD AutoTune and observe. Compare the values to the 'Limit' column values found in the screenshot at the end of this SOP. If you feel the values will pass, repeat a Performance Report in STD Biweekly. If you feel they will fail, run CaliTune STDS, then CaliTune 100 volt, then STD Autotune again. Once all that is complete, repeat a Performance Report in STD Biweekly.

8.3.10.5.5 Only Background 4.5
- From the Experiment Configuration tab, change to iCap RQ mode. On the left panel, click on Mass Calibration and change the value in the CCT RF Amplitude offset. The value should be the knee where Li intensity drops in CCT Mass to DAC offset in
Calitune STDS autotune report. For more details, go through the file named '4.5Bkg Performance Report Failure in STD or STDS mode in Qtegra for ICP-MS' in 'Troubleshoot info' folder.

8.3.10.6 AutoTune
8.3.10.6.1 From IC -> AutoTune (in ‘Wizards’ tab) -> Autotune Wizard
8.3.10.6.2 Ensure probe is in TuneB solution (generally located in Standard Row, Vial 10).
8.3.10.6.3 ‘Run an existing Autotune sequence’ -> Next -> Select the autotune sequence from the list
8.3.10.6.4 Pay attention to which AutoTune adjustments affect which sensitivity parameters. For example, you might notice that adjustments to the extract lens affect one parameter, while adjustments to the nebulizer gas affect another. Know which adjustments affect the parameters that caused the PR failure.

8.3.10.7 If the Performance Report fails, another option is to reference old tune settings from successful runs to manually adjust the instrument.
8.3.10.7.1 From IC -> Tune Settings (in ‘Measurement Mode’ tab) -> History
8.3.10.7.2 CTRL + Click on two AutoTune reports, your most recent (failed) run and a previous (successful) run
8.3.10.7.3 Click “Compare” to see which instrument tune settings are different. Use this information to make minor adjustments to instrument settings before running the PR again.

8.3.10.8 A Troubleshooting AutoTune can also be run if PR fails after tuning.
8.3.10.8.1 From IC -> AutoTune Wizard in AutoTune dropdown menu (in ‘Wizards’ tab)
8.3.10.8.2 Select High Matrix AutoTune Troubleshoot

8.3.11 Wash all tuning solution from the probe.
8.3.11.1 From IC ASX-560 tab, command the probe to a Rinse solution containing 0.5% HNO₃.
8.3.11.2 ‘Run’ while viewing the analyte levels; the levels will be high at first (due to presence of tuning solution) but will eventually decrease to near zero. ICP-MS is verified for any measurement of choice, like dissolved elements, total digested elements or speciation (all have separate SOP).

8.3.12 Creating a LabBook.
8.3.12.1 In Qtegra -> LabBooks (in left side bar)
8.3.12.2 Create a LabBook using an existing Template or LabBook or from a blank Template.
8.3.12.3 Analytes
8.3.12.3.1 Select desired element analytes, taking care to select the isotopes with the least amount of interference.
8.3.12.4 Acquisition parameters
8.3.12.4.1 Dwell time should always be set to ~0.1s for all analytes.
8.3.12.5 Standards
 Include an entry for each standard you will be including in your calibration.

When creating a new entry, select ‘Create from Analyte List’ to ensure that all the analytes you are testing are accounted for in your standards.

Manual Sample Control

Turn off manual sample control.

Sample List

Adjust so that the only columns shown are “Label” “Status” “Evaluate” “Sample Type” “Standard” “Main Runs” “Rack” and “Vial” This can be done by right clicking the top row of the sample list and then selecting appropriate columns.

Enter each blank, standard, and sample you will run.

Input 3 main runs for each sample/standard.

Between the standards (which have high concentration) and the samples (which require detection of low concentrations), run the blank a couple of times to ensure minimal contamination.

For this purpose, do not select “BLK” as the sample type as this will include these runs as part of the calibration. Choose “unknown” instead.

Select all boxes to automatically export all data. (Note: If Bold in Qtegra, there are unsaved changes.)

8.3.13 Samples

Samples in the Standard rack must have a volume of at least 20 mL or more in order for the probe to be able to detect them.

8.3.14 Scheduling LabBooks and Running Samples

To schedule a LabBook, click ‘Schedule’ on the toolbar of the LabBook. The icon looks like a green play button. This adds the LabBook to the Scheduler.

In the Scheduler, select the LabBook and click ‘Run’ to start the measurement. The icon also looks like a green play button. Continue to monitor the instrument throughout the course of the run.

Once the LabBook completes, the autosampler will return to its ‘Home’ position. This will place the probe above the rinse reservoir, meaning it is not drawing up any liquid. This could cause the plasma could run dry, potentially melting the torch. To prevent this, be ready to shut down the instrument as soon as the LabBook completes. Another option is to add an automatic shutdown to the sequence. For instructions on how to do this, please reference the ICP-MS Shutdown Guide below.

8.4 ICP-MS SHUTDOWN GUIDE

Qtegra → ‘Get Ready’ button → Shutdown

Remove tubing from the peristaltic pump to maintain their flexibility.

Before turning off chiller:
8.4.3.1 Ensure that IC → Advanced (in side bar) → Sampling Depth is equal to 15.

8.4.3.2 Log View should show log message ‘Standby’.

8.4.4 Turn off chiller.

8.4.5. You can **add automatic shutdown** to a sequence by clicking the ‘option’ button to the right hand side of the scheduler at the bottom (where you click ‘run’ for the second time) and then select the ‘closedown on an empty queue’ under System Options, for auto shutdown after the sequence is complete (if you are doing it for the first time, double check in person, if the auto-shutdown command worked).

9 DATA REDUCTION AND STATISTICS

9.1.1 Qtegra software generates the calibration curves and performs the quantitation

10 QUALITY ASSURANCE

10.1 MDLs

10.1.1 New MDLs should be calculated for every run to account for variations in method. Some example MDLs are listed below.

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<th>Replicate no.</th>
<th>Elemental Standard (ng/mL)</th>
<th>Calculated Concentration (ng Ba/mL)</th>
<th>Calculated Concentration (ng Sr/mL)</th>
<th>Calculated Concentration (ng Zn/mL)</th>
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**STATISTICS**

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<th>Calculated Concentration (ng U/mL)</th>
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**STATISTICS**

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<td>Standard deviation</td>
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<td>% RSD</td>
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**REFERENCES**

11.1.1 EPA Method 6020 – Inductively Coupled Plasma Mass Spectrometry

**ADDITIONAL READING**
11.2.1 Water Sciences Laboratory Analytical SOP, Title: ICP-MS Start Up Guide, Staff, March 2, 2018 – Present, University of Nebraska, Lincoln, NE.

11.3 ATTACHMENTS

This section should be used to reference any outside documents, such as excel sheets, which are associated with this method. Any files referenced in this section should be placed on Box under Lab Manual – Part 5 Supporting Files.

12 PREVIOUS ISSUES AND CHANGES

<table>
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<th>Issue</th>
<th>Issue Effective Dates</th>
<th>Author</th>
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<td>001</td>
<td>March 14th, 2018 – December 12th, 2018</td>
<td>Suzanne Polzkill and Tania</td>
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12.1 ISSUE CHANGES

12.1.1 Issue 001:
- Original Issue

12.1.2 Issue 002:
- Updated information on equipment and materials
- Updated information on data reduction and statistics
- Fixed formatting issues

13 DIAGRAMS, FIGURES, AND PHOTOGRAPHS
## Sensitivity

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**Figure 1**: Screenshot of Performance Verification with STD Biweekly values