PROCEDURE FOR METALS DATA REVIEW AND AUTHORIZATION

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1. SCOPE AND APPLICATION

This method details the procedures for reviewing and authorizing data produced by analyses of trace metals and minerals in waters, soils, wastes, and other environmental samples. This procedure applies to data produced using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) (DEP SOP MT-061) and Inductively Coupled Plasma Mass Spectroscopy (ICPMS) (DEP SOP MT-074).

2. SUMMARY OF THE METHOD

The analyst exports the data to the Quality Control Manager (QCM). The data is calculated, reviewed, and the sample data is uploaded to the DEP Laboratory Information Management System (LIMS). The reviewer reviews the data for accuracy, completeness, and proper qualification of results based on the quality control (QC) samples. The reviewer uploads the quality control results and authorizes the test/component. The job authorizer reviews the data at the job level and authorizes the job.

3. APPARATUS AND EQUIPMENT

3.1. Computer with operational and stable network connection.

3.2. Chemistry LIMS Account.

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4. DATA WRITE-UP/CALCULATION PROCEDURE

4.1. Login to LIMS and load the QCM software (LIMS menu path: Laboratory/QC/QC Manager).

4.2. Import Instrument Data into QCM Database – An instrument analysis file is imported into the QCM database by using the QCM converter specific to that instrument. The data for a run is linked by a run ID with a .RAW extension. See the SOP for the instrument of interest for details.

4.3. Load QCM Data – Upon successful conversion of an instrument file, the resulting run data is automatically loaded. If the run data is to be loaded at a later time, select the Open command from the File Menu and choose the appropriate run ID with the .RAW extension.

4.4. Sample Name – Ensure that the sample and QC IDs in the *Sample* column are all correct. To edit a sample name, highlight the appropriate sample row(s), left click on the *Sample* column header label and edit. Supplementary information such as dilution factors, replicates, matrix spikes, and worksheet ID may be entered into the sample ID field after the Sample ID itself (must be separated by a space). See appropriate SOP for details.

Note: Field duplicates should be labeled as DUP in QCM (example: ###### DUP) and monitored for precision (RPD < 20 % for results above the PQL).

4.5. Type – The *Type* is automatically assigned upon conversion for all Metals Group instruments. Ensure that the assignments are consistent with Table 1. The Type may be edited by highlighting the appropriate sample row(s), left click on the column header label and edit.

Table 1.

TYPE	DESCRIPTION OF SAMPLES
NONE	Designates samples that should not have calculations performed on them. These might include rinse solutions, samples with known systematic errors, and/or samples where the autosampler probe missed the tube.
CCV	Continuous calibration verification standards.
LFB	Laboratory fortified blanks.
MBLK	Method blank - See section 5.
MDL	Quality control blanks - digested and filtered sample batch blanks and continuing calibration blank checks.
REPL	Replicates – multiple analyses of the same sample upon which precision calculations should be made. Each separate set of replicates should have a replicate ID assigned to each replicate in the set that is unique to that set. In cases where the replicate sample has more than one test ID (e.g., W-ICP and W-HARD), each replicate of each test ID should have separate, unique replicate IDs.

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TYPE	DESCRIPTION OF SAMPLES
SAMP	All normal samples for which concentration information is desired.
SPK	Matrix spikes - all fortified samples should have this designation.
SRM	Standard reference material – used for QC solutions with known and consistent concentrations for which recovery information is required. Examples include interference check solutions, practical quantitation limit (PQL) check solutions, and external reference check solutions.
SUR	Surrogate – not used in metals analyses.

4.6. Prep Batch and Analysis Batch – The prep batch ID refers to the batch of samples prepared together. The analysis batch ID is the group of samples, or batches, run on the same calibration curve with the same set of instrument QC. For each prepared batch of samples, enter the prep batch ID that was assigned during the preparation of the samples using the LIMS prep worksheet manager module. Assign a unique analysis batch ID to every sample in the data set, even if multiple batches. If there is a rerun and it is to be reported with QC run with a previous batch, assign the previous prep batch ID (but a new analysis batch ID) to the batch or samples that were rerun. If the sample was rerun after a redigestion, then it should have a prep batch ID different from the first digestion and analysis. Assign one unique prep batch ID to all instrument QC and all other samples not part of a batch. For samples logged in for the W-HARD test, assign the same prep batch ID that was assigned to the W-ICP test ID of the same sample.

4.7. Spike Code and Spike Factor – Assign the spike code(s) and spike factor(s) to the laboratory fortified blanks (LFBs) and fortified samples (matrix spikes) according to the preparation documentation. For samples with the W-HARD test ID, assign the same spike code and spike factor as the W-ICP test ID of the same sample. Spike factors are divided by any dilution performed on the spikes. For example, if a matrix spike originally had a spike factor of 1.0 but was diluted by two before analysis the spike factor in QCM should be 0.5.

4.8. Test ID – Assign the correct LIMS Test ID to each sample. Assign batch QC samples the same Test ID as the samples they are associated with (i.e. if the QC sample is only scheduled for W-ICPMS but other samples in the batch are for W-ICP the QC sample must be given a W-ICP test assignment when run on an atomic emission instrument). Assign all instrument QC the Test ID corresponding to the filtered water test for that instrument (i.e. W-ICP-F for samples run by ICP-AES, W-ICPMS-F for samples run by ICP-MS, and W-SI-ICP-F for silica samples.). The W-HARD test ID is automatically assigned upon converting the instrument data into raw data in QCM. Do not overwrite the automatically assigned W-HARD test IDs (unless the sample is the QC sample; see the Note in 4.19).

4.9. Matrix – Assign the correct matrix for every sample according to Table 2.

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Table 2.

MATRIX	DESCRIPTION OF SAMPLES MATRIX IS ASSIGNED TO
FILTERED	Undigested water samples.
FILTERED-R	Undigested water samples analyzed by SW-846 methods.
FILT-LFB	LFBs associated with FILTERED batches.
WATER	Digested water samples (including those that were filtered and then prepared due to the presence of a precipitate).
WATER-SLT	Digested water samples with high conductivity (>10,000 µmhos/cm).
WATER-LFB	LFBs associated with WATER batches.
WATER-R	Digested water samples analyzed by SW-846 methods.
WATERLFB-R	LFBs associated with WATER-R batches.
SEDBLOCK	Soils and sediments digested using the hot block for a total recoverable test.
SEDBLK-LFB	LFBs associated with SEDBLOCK batches.
TISSUE	Tissues of every sort.
TISSUE-LFB	LFBs associated with TISSUE batches.
WASBLOCK	Waste samples digested using the hot block for a total recoverable test.
WASBLK-LFB	LFBs associated with WASBLOCK batches.
SPLP	SPLP extracts, regardless of the original sample matrix or digestion method.
SPLP-LFB	LFBs associated with SPLP batches.
TCLP1	TCLP extracts extracted using extraction fluid #1, regardless of the original sample matrix or digestion method.
TCLP1-LFB	LFBs associated with TCLP1 batches.
TCLP2	TCLP extracts, extracted using extraction fluid #2, regardless of the original sample matrix or digestion method.
TCLP2-LFB	LFBs associated with TCLP2 batches.
SED-TOTAL	Sediment samples digested using the total metals method.
SED-TOTLFB	LFBs associated with total metals batches.

4.10. Dilution X – For any samples that were diluted, assign the appropriate dilution factor in this column. The dilution factor is the inverse of the change in concentration. For example, if the sample was diluted by 1/5, the dilution factor is 5. This information is found on the preparation documentation if diluted during preparation, or for filtered samples, should be indicated in the Sample ID field.

4.11. Apply Dil? – Change the value in this column to “Y” for any sample whose dilution factor is not one; otherwise the dilution will NOT be factored into the LIMS result.

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4.12. Weight (g) – For solid/waste/tissue samples, assign the sample weight used for the preparation in this field. For SOLID tests, use the "dry weight" where "*dry weight" = wet weight × percent solid*; for WASTE and TISSUE tests, use the "wet weight". This information is found on the preparation documentation.

4.13. Prep Volume (L) – This field is only used in the calculation of solid samples (e.g., soil, sediment, waste, tissue). The default for this value is 0.050 L. If for some reason a different final volume is used in the preparation of solid samples, make the appropriate changes.

4.14. Comment – This field is used to report important information to the client that is relevant to the interpretation of the data for a particular test and will appear on the final report. A drop-down list in QCM provides a list of common comments.

4.15. Analyst – Ensure that the correct analyst (person who operated the instrument) is listed in this field.

4.16. Date and Time – Ensure that the date and time of analysis are correct. The time format is military time.

Note: When editing the date and/or time fields the appropriate radio buttons must be selected in QCM, otherwise the changes made to the date and/or time will not be saved (e.g., if the date field is selected the date and time can be changed in the menu that pops up but only if the "both" radio button is selected, otherwise the change to the time will not be saved, only the change to the date).

4.17. Notes – Use this field to note any observations made that are important to interpreting the data. This field is also used to automatically document manual edits to a LIMS result. Notes cannot be edited, but only appended to. Sample notes will not appear on the final report that is delivered to the customer therefore, information that is not essential to the customer's interpretation of the data but will allow the laboratory to interpret and reference the data correctly in the future may be entered here.

4.18. Save – Save the data (which will become linked by a run ID with the extension .REV) using the *Save* option from the *Files* menu before proceeding.

4.19. Calculate QC – Select the *Calculate* option from the *Tools* menu to open the Calculation Dialog Box. Select options A (All Rows), 1 (CCV/SRM Recoveries), 2 (Mean + Precision for Replicates), 3 (Spike Recoveries and Precision), and all three sub-options under option 3 (Dilution Factor, Spike Code, and Spike Factor), 4 (LIMS Result), and the sub-option "Automatically Calculate Sig Figs." Click OK.

NOTE: If changes are made to the sample table in QCM after calculation, such as changing the 'type', the QCM line that was edited must be re-calculated before uploading the data.

4.19.1. Hardness – After converting the instrument data into raw data in QCM, new data rows will appear for samples logged in for the W-HARD test. QCM calculates the water hardness result according to SM 2340B, (see below). Verify that the Ca and Mg results come from the same analysis

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cup and are not over calibration. Make sure the applicable QC for Ca and Mg is passing and then toggle the upload column to 'Y'.

Hardness, mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

Note: If the QC sample is logged in for the W-HARD test, after clicking calculate a text box will pop up asking the analyst to select the correct spike background. Choose the appropriate background sample for the matrix spike according to the test ID. Only one spike RPD (SPRPD) is calculated and QCM automatically assigns the test ID for the SPRPD according to the line above, which is W-HARD. This test ID will need to be manually changed to W-ICP by highlighting the row and clicking the 'Test ID' column header.

4.20. Save – If the calculations complete without error, save the data again as in 4.18.

4.21. Prepare Cover Page Form – Form MT-ICPDV is the cover page for analyses conducted with ICP-AES instrumentation and form MT-ICPMS is the cover page for analyses conducted with ICP-MS instrumentation. Controlled versions of forms are located on the Division of Environmental Assessment and Restoration (DEAR) intranet site. An Excel copy of MT-ICPDV can be found on the Chemistry Program's computer network, \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV. The Excel copy for MT-ICPMS is located at \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP or \ICP-MS-iCAP-RQ. Always make sure the most up-to-date form is used by verifying the version number on the Excel form is the same as the version number on the DEAR intranet site. See Appendix A for an example of a cover page.

4.21.1. Generate a list of ALL samples analyzed on the run, including confirmations, using the Component Backlog function of the LIMS.

4.21.1.1. Choose 'Laboratory', 'Technical', and 'Component Backlog'.

4.21.1.2. Select 'P', 'V', and 'W' Status for Tests and select 'V' status for Components.

4.21.1.3. Select 'Standard' Report Type and Show 'Abbreviated Component Names'.

4.21.1.4. Select appropriate Analysis Group(s), Test ID(s), and Sample IDs.

4.21.1.5. Select 'Generate' (Ctrl-G) from the File menu, and then 'Save as Tab Delimited File' (Ctrl-S) and save in your OneDrive folder.

4.21.1.6. Open the file saved in 4.21.1.5. in Microsoft Excel. A Text Import Wizard will appear. Select 'Delimited' and click 'Next'. On the next window, select the delimiters 'Tab' and 'Comma' and click 'Next' again. In the next window, the column data format should be 'General' and click 'Finish.' This generates an Excel file with the Analysis ID, Sample ID, priority, status, and Component List for each sample that was selected. This Excel file is then used to help create the cover page form (see example

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in Appendix A). The cover page form template found in the appropriate instrument folder located on the network location below should be used to make the cover page. Save the completed Excel cover page form in the appropriate instrument folder located on the network: \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals.

Note: All notes written on cover page forms must be in pen, NOT pencil. Also, post-it notes should not be used for anything related to data. Notes on cover page forms related to data must be permanent.

4.21.2. In addition to the sample information on the cover page form, add the instrument name and serial number, analysis date, SOP reference, analysis batch ID, list of related electronic files, analyst's name and date, and the reviewer's name and date in the format given in Appendix A.

4.21.3. List cross references to previous runs, qualifications for data uploaded, and any other observations as directed in the format given in Appendix A.

4.22. Prepare Instrument Solution Log Form – List all calibration solutions, QC solutions, and spike solutions used in the analysis, but not included in the preparation documentation including the ID used in the analysis, serial #, and the expiration date. Use the solution log form template found in the appropriate instrument folder located on the network: \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals. Form MT-STD-LOG is the form used for analyses conducted with ICP-AES and ICP-MS instrumentation. Verify that the solution log form template has the same version number as the solution log form posted on the DEAR intranet site. Ensure that reagents and standards used in the analysis have not expired.

Note: If another instrument's standard is used for some reason (e.g., ICPAES silver standard used on the ICPMS instrument) it must be indicated on the solution log form. The solution log form should also be saved in the same network folder as the analytical run: \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals, then select the appropriate instrument folder.

4.23. Attach the printed instrument solution log form to the printed cover page form. Verify that calibration and check solutions have not expired.

4.23.1. Review sample preparation sheets and verify that the correct preparation method was used and all the preparation information is correct (spikes, spike factors, digestion numbers, dilution, prep volume, etc.). Verify the reagents and standards used during preparation are not expired.

4.23.2. Verify that appropriate blanks, PQLs, LFBs, and matrix spikes were used for each batch of 20 or fewer samples.

4.23.3. Note any observations made by the sample preparation technician (equipment blanks, field duplicates, dilutions, characteristics of the sample and/or digestate, etc.).

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4.23.4. Carefully check the sample IDs, digestion batches, listed components, tests, etc. on the digestion cover page and the digestion sheets for errors. Notify the supervisor if any problems are suspected.

4.24. Cross-reference any previous runs of the samples listed on the cover page form. Be sure to denote if the sample was redigested (how many times if more than once) and rerun (list all data sets). Preparation documentation and the status on the cover page form indicate how many times each sample has been digested.

4.25. Examine Instrument QC Parameters:

Note: ICP emission QC acceptance criteria used are those found in EPA method 200.7 for water samples and EPA method 6010 for solid and waste samples. ICPMS QC acceptance criteria used are those found in EPA method 200.8 for water samples and EPA method 6020 for solid and waste samples. Water samples may be submitted to the lab for the Resource Conservation and Recovery Act (RCRA). In this case, QC acceptance criteria used are those found in EPA method 6010 for ICPAES and 6020 for ICPMS.

4.25.1. External Standard Calibration Check (Tolerance is ± 5 % (AES) and ± 10 % (ICPMS)) – Each instrument runs a NIST traceable standard(s) from a source (vendor) different from that of the calibration solution(s) to verify that the calibration solutions were made correctly. This quality control sample also verifies the calibration curve, serving as the initial calibration verification, and instrument performance. Verify that the recovery for each analyte is within the control limits. If an analyte is NOT within the control limits for this check, no results for that analyte may be reported from the run without appropriate qualification. The laboratory's SOP for data qualification is LB-027. In most cases any samples requiring the affected analyte(s) must be rerun after corrective action has been taken.

4.25.2. Interference Check Solution (ICS) (Tolerance is ± 15 %) – Each instrument runs an interference check solution. Verify that the recovery for each analyte is within the control limits specified above. If an analyte is NOT within the control limits for this check, no results for that analyte may be reported from the run without appropriate qualification. In most cases, any samples requiring the affected analytes must be rerun after corrective action has been taken.

4.25.3. Mixed Element Spectral Interference Check Standard (ICS6010D) – The ICS6010D is used daily to check that the instrument is free from interference from elements typically observed in high concentrations and to check that interference corrections applied are still valid. The concentration measured for any target analytes must be less than +/- the PQL.

4.25.4. Continuing Calibration Verification (CCV) (Tolerance is ± 10 %) – Each instrument is required to run CCVs after at least every tenth analysis tube. Verify that CCVs are run at the required frequency and that the recoveries are within the control limits specified in the appropriate SOP. A result

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must be bracketed by passing CCVs. If a sample is not bracketed by CCVs of the specified frequency or is bracketed by one or two failing CCVs, it may not be reported without qualification. The ICP emission methods also require that before analyzing samples a CCV is analyzed using tighter control limits (denoted as CCVC with a tolerance ± 5 %). If an analyte is NOT within the control limits for this check, no results for that analyte may be reported from the run without appropriate qualification. In most cases, any sample requiring the affected analytes must be rerun after corrective action has been taken.

4.25.5. Continuing Calibration Blank (CCB) – Each instrument must run a CCB initially and after each CCV to verify instrument sensitivity and ensure no contamination is present or that no drift has occurred. Verify that the results acquired for a CCB are below the appropriate instrument's MDL for each analyte. Current instrument MDLs can be found at \\floridadep\data\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals_Mercury. Samples affected by CCBs outside the control limit(s) must either be rerun or qualified according to DEP SOP LB-027.

4.25.6. Instrument Practical Quantitation Limit Check (CPQL) – Each instrument must run an initial CPQL to verify the accuracy of the instrument at or near the PQL level. Verify that recoveries for each analyte are within the 70 – 130 % control limits for a PQL check standard. If the recovery is below 70 % (failure), all results below the MDL and between the MDL and 10X the failure (absolute value) must be 'J' flagged and commented or rerun. If the recovery is above 130 % (failure), all results between the MDL and 10X the failure must be 'J' flagged and commented or rerun. The J qualifier is defined in LB-027.

4.25.7. High Conductivity Standard Reference Material (Tolerance is ± 20 %) – The ICPMS analyzes a purchased, high conductivity water reference material for trace metals when analyzing samples with high conductivity (> 10,000 µmhos/cm) to verify the accuracy of their recovery in this type of matrix. For example, SLEW-3 or NASS-7 purchased from the National Research Institute of Canada. The SRM may be spiked with additional metals to ensure concentrations are above the PQL. It should be run before any high conductivity samples are run. If the recovery is above 120 % (failure), all results below the MDL can be reported without qualification. All other results must be rerun or appropriately qualified. If the recovery is below 80 %, all samples with a conductivity > 10,000 µmhos/cm should be qualified or reanalyzed on a calibration with a passing high conductivity SRM.

4.25.8. Measurement of the Relative Error (%RE) for ICPMS: The ICPMS calibration is evaluated by calculating the % Relative Error for calibration standards ICAP STD 1 and ICAP STD 4. The percent relative error for ICAP STD 1 must be within 70 – 130 %. The percent relative error for ICAP STD 4 is 90 – 110 %. The percent relative error is calculated with the following equation:

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$$\% \text{ Relative Error} = [(x'_i - x_i] / x_i)] \times 100$$

x_i = True value for the calibration standard

x'_i = Measured concentration of the calibration standard

4.26. Internal Standard Acceptance Criteria – Review the internal standard intensities according to the following criteria.

4.26.1. ICP-AES – The intensity of the internal standard must remain within 20 % of its initial value for the run (the initial value is the first QC sample run (usually an instrument blank)). If the internal standard intensity falls outside the acceptance range for any sample, an inspection of the instrumentation must be made to ensure that the failure is not due to instrument performance. If instrument performance is the problem, it must be corrected and the samples rerun. OTHERWISE, for each sample whose internal standard intensity is shown to be consistently outside the acceptance range, that sample must either be 1) analyzed or reprocessed in a run that does not use internal standard correction, 2) analyzed or reprocessed in a run that uses a different internal standard, 3) diluted and rerun, or 4) report with appropriate qualification according to DEP SOP LB-027. For option 3 if the reported result is U or I qualified the comment "The MDL/PQL for X analytes was elevated due to necessary sample dilution." is required. Salt samples (conductivity >10k umhos/cm) are exempt from this comment because their dilutions are standard.

If it appears that the sample may contain the internal standard used, the sample may be analyzed using the method of standard additions, which compensates for the bias introduced by the additional amount of internal standard present in the sample or analyzed using a different instrument that uses a different internal standard.

4.26.2. ICPMS – The internal standard acceptance criteria for natural water samples is 60 – 125 % of the internal standard's initial intensity for the analytical run as per EPA Method 200.8. The internal standard acceptance criteria for solid, waste, and water-RCRA samples is 70 – 130 % of the internal standard's initial intensity for the analytical run as per EPA Method 6020. If one of the internal standard intensities falls outside the acceptance range for any sample where the analytes associated with that internal standard are requested, an inspection of the instrumentation must be made to ensure that the failure is not due to instrument performance. If instrument performance is the problem, it must be corrected and the samples rerun. OTHERWISE, if an internal standard intensity is shown to be consistently outside the acceptance range for a sample and the analytes associated with that internal standard are needed, then that sample must either be 1) rerun or reprocessed with a different internal standard 2) diluted and rerun, 3) run by an alternative method, or 4) report with appropriate qualification according to DEP SOP LB-027. For option 2 if

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the reported result is U or I qualified the comment "The MDL/PQL for (X analyte(s)) was elevated due to necessary sample dilution." is required. Salt samples (conductivity >10k umhos/cm) are exempt from this comment because their dilutions are standard.

If it appears that the sample may contain the internal standard used, the sample may be analyzed using the method of standard additions, which compensates for the bias introduced by the additional amount of internal standard present in the sample or analyzed using a different instrument that uses a different internal standard.

4.27. Examine Batch QC Parameters – Verify that each batch contains 20 samples or less and review the following parameters:

4.27.1. Batch Blank – Verify that there is a method blank (i.e., instrument blank or digestion blank) associated with each batch and that it is assigned the same test as the associated samples and ensure all the results are selected for upload. Verify that each of the analytes required in a batch are below the MDLs for that instrument and preparation method. Current MDLs can be found in \\floridadep\data\DEAR\Labs\Lab5\Chemistry\Common\MDLs_Control_Limits\Metals_Mercury.

Samples affected by contaminated batch blanks must be rerun, reprepared, or qualified and commented according to DEP SOP LB-027.

4.27.2. Batch PQL – Verify that each batch of samples contains a PQL check sample and that the recoveries are within the 70 – 130 % control limits. Samples affected by recoveries outside the control limits must be rerun, reprepared, or qualified as follows:

- If the failure is due to a mis-spike or digestion tube contamination, any sample between the MDL and 10X the contamination should be 'J' flagged and commented or redigested. If the failure is due to a mis-spike and is below 70 %, any sample below the MDL must also be 'J' flagged and commented or redigested.
- If the problem is instrument quantitation or low sensitivity, all samples with results between the MDL and 10X the contamination must be rerun or qualified and commented. If the recovery is below 70 %, all sample results below the MDL must also be 'J' flagged and commented or rerun.

4.27.3. LFB – Verify that each batch contains one LFB for each matrix spike set on the batch and that the recoveries are within the control limits specified in the method. Analytes associated with LFB values outside the control limits must either be rerun, reprepared, or qualified with a "J" qualifier code and have a comment referring to the QC Report on all samples affected. The 'J' qualifier code and comment are generated automatically after the calculations are performed in Data Review/Authorize. If consistent deviations from QC limits, deemed to be caused by systematic

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errors of the procedure, are observed in LFB recoveries/precision, the analyst must locate and correct the source of the problem. Then, the analyst shall repeat the test for all parameters that failed to meet criteria. Repeated failures indicate a systematic problem with the measurement system. If the problem cannot be solved, as a last resort, a new Initial Demonstration of Capability (see DEP SOP LB-007) must be completed and new QC limits must be established within the acceptance criteria provided by the method.

4.27.4. Matrix Spikes – Verify that each batch contains matrix spikes at a frequency of 10 % for EPA methods 200.7 and 200.8 and a frequency of 5 % for EPA methods 6010 and 6020. If there are 10 or less samples in a preparation batch, only one sample requires matrix spikes. If there are more than 10 samples in the preparation batch, two different samples require matrix spike(s) for EPA methods 200.7 and 200.8. Duplicate matrix spikes are required on at least one sample in each preparation batch. Ensure that the recoveries for the required analytes are within the appropriate control limits: 70 - 130 % for high conductivity (> 10,000 µmhos/cm) water samples and 80 - 120 % for low conductivity (< 10,000 µmhos/cm) water matrices (EPA 200.7 and 200.8), and 75 - 125 % for samples analyzed by EPA methods 6010 or 6020. Select the recoveries for the required analytes for upload. Analytes associated with matrix recoveries outside the control limits must either be rerun, reprepared, or qualified with a 'J' qualifier code and have a comment referring to the QC Report (on the QC sample only). The 'J' qualifier code and comment are generated automatically after the calculations are performed in Data Review/Authorize.

Examine the spike relative percent difference (SPRPD) from the duplicate matrix spikes. Ensure that the SPRPD for each required analyte is less than 20 % and that the raw results are within the calibration limits.

The SPRPD is calculated as follows:

$$SPRPD = \frac{S1-S2}{(S1+S2)/2} \times 100\%$$

Analytes associated with SPRPDs outside the control limits must either be rerun, reprepared, or qualified with a 'J' qualifier code and have a comment referring to the QC Report (on the QC sample only). The 'J' qualifier code and comment are generated automatically after the calculations are performed in Data Review/Authorize.

If an analyte background is greater than the added spike concentration, no spike recoveries should be uploaded, but the SPRPD is still uploaded (ensure the spike concentration is within calibration). Any samples on the batch that require the analyte with buried matrix spikes should be commented.

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Accuracy is expressed as % recovery and is calculated as follows:

$$\%\ Recovery = \frac{Spike\ Sample\ Conc. - Original\ Sample\ Conc.}{Actual\ Spike\ Concentration} \times 100\%$$

4.28. Verify that all reported results and QC are within the calibration range. Sample results or batch QC outside the calibration range must be diluted and rerun. If samples are rerun diluted, it is not necessary to rerun the associated QC unless the diluted results are not consistent with the previous run, assuming they were run with the QC initially.

4.29. Verify that the concentration of silver in water samples is less than 100 ug/L. Verify that the concentration of silver in solid samples is less than 500 µg/L. For the analysis of water samples or solid samples containing higher concentrations of silver, smaller volumes or weights from the well mixed sample must be prepared until the concentration of silver falls to an acceptable amount. Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex.

4.30. Verify that all equipment, trip, and field blanks are clean (no detects above the MDL) with respect to all requested analytes. If a requested analyte is detected in the blank, the value must be confirmed and a comment reported to that effect.

4.30.1. If the sample is digested, the presence of the analyte can be confirmed by analyzing the undigested sample. The RPD between the digested result and undigested result must be below 20 % for confirmation. However, if the analyte is not present in the undigested sample it must be redigested for confirmation of the detect.

4.30.2. If the sample is not digested, the presence of the analyte is confirmed by analyzing the sample in duplicate. The RPD between the two analyses of the sample must be below 20 % for confirmation.

4.30.3. If the result for the blank is confirmed a comment is required, “The result for (analyte) was confirmed in the undigested/redigested sample on (date of confirmation)” should be used. If the detection of the analyte in a digested sample is verified by analysis of an undigested sample but the value is not (RPD $\geq$ 20 %) “The presence of (analyte) was confirmed on (date of confirmation)” should be used.

4.30.4. If the detection or the value is not confirmed the data should be analyzed for signs of contamination, mis-labeling, mis-pouring, etc.

4.31. Compare data with any previous runs for consistency. If data from two or more runs are not consistent with each other, the problem must be resolved and documented before reporting. If all batch and instrument QC is within acceptable

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control limits, when a sample has been analyzed three times and two are consistent (RPD < 20%), but one appears to be an outlier, it can be assumed to be an outlier and the two consistent results considered confirmation. If a sample is analyzed three times and no two results have an RPD less than 20%, then the RSD is calculated to check if it is below 15%. If it is not, then the result is J qualified.

4.32. Document corrective action on the cover page form for all required analytes, even if they are not uploaded from the dataset. Any QC failures for analytes requested by the sample should be acknowledged by the analyst and documented on the cover page form. Any sample results that were qualified due to QC failures should be documented on the cover page form. Any samples rerun or redigested should have an explanation as to why they were rerun or redigested on the cover page form.

4.33. Select components for upload (change upload status to "Y") and highlight components to be uploaded in yellow on cover page form (components not uploaded should be highlighted in orange if they need to be rerun).

4.34. Qualify data to be uploaded that has failed QC parameters.

4.35. SAVE the data! It is strongly recommended that the data be saved frequently while reviewing. If the connection is lost or the computer locks up, everything that has not been saved will be lost.

4.36. Upload the sample data – Select *Upload,* then *By Upload Flag* from the *Tools* menu. In the *Result & QC Upload* window, select *Data→Options* and ensure there is a checkmark next to *Upload Samples* only. Click the *Upload Data* icon. The reviewer will upload the QC.

4.37. All calculations including precision, accuracy, standard deviation, and data reduction can be found in section 5.9 of the Quality Manual.

5. DATA REVIEW PROCEDURE

5.1. Review dataset according to the criteria outlined in Section 4 and verify that no errors were made. If any significant errors are found, return the dataset to the analyst for correction. A checklist is provided in Appendix C for convenience.

5.2 Verify that all Excel spreadsheets used during preparation and analysis that contain formula cells are write-protected to minimize inadvertent changes to the formula. Excel spreadsheets that contain formula cells are drafted by the Metals Group supervisor or designee. The drafted Excel sheet is submitted to the QA Officer to be implemented as a controlled form. A pdf version of the form is posted to the Laboratory's website with a control number. The Metals Group supervisor then locks the formula cells and saves a locked Excel copy on the Laboratory's computer network that is used by Metals Group analysts.

5.2.1 List of controlled forms with formula cells

- MT-105C-PS
- MT-60C-PS

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- MT-ICPDV
- MT-MSA
- MT-MULTIPHASE
- MT-SEDWT
- MT-TCLP-SPLP-EXT
- MT-TD
- MT-TURB

5.3. Verify that the percent solid data has been reviewed and saved as a pdf. If the percent solid data has not been reviewed (no pdf), notify the supervisor. Percent solid results are located on the network at \\floridadep\data\LABS\Lab5\Chemistry\InorganicPrep\METALS\% SOLID LOG BOOK\. If an error is found and the percent solid result for a sample is corrected, notify all chemistry groups the sample is logged in for.

5.4. Upload the QC data – Select *Upload,* then *By Upload Flag* from the *Tools* menu (or Ctrl-U). In the *Result & QC Upload* window, select *Data→Options* and ensure there is a checkmark next to *Upload QC* only. Ensure that method blanks for each batch are uploaded with the type MBLK. Review Error Log for any upload errors. Select Ctrl-U to complete the upload to LIMS.

5.4.1 Statistical QC: For the annual detection limit calculation, upload all method blanks for all analytes one time as long as the result is valid. Also upload each batch PQL for all analytes one time as long as the result is valid. Upload one CCB from each analysis for all analytes with the M-BLK type as long as the result is valid. Examples of invalid data include analyzing for a component, but not calibrating for it or gross contamination in the calibration blank resulting in low batch PQL recoveries.

5.5. Sign and date the cover page form where indicated in Appendix A after reviewing and uploading is complete.

5.6. Return the hard copy to the supervisor to keep on his/her desk. Quarterly, the hard copy should be filed in the appropriate metals data filing cabinet until it is boxed and sent to the State Archives.

6. REVIEW AND AUTHORIZATION OF METALS JOBS IN LIMS

This responsibility is primarily that of the group supervisor or designee.

6.1. Monitor jobs as they are logged in throughout each day. Check the tests, analyte lists, matrices, etc. are appropriate. If any discrepancies are found the relevant personnel (e.g., receiving room staff, customer) must be contacted to resolve the problem.

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6.2. Verify that the prep date/time precedes the analysis date/time for all components, samples, and tests.

6.3. Verify that the correct prep date, time, and person are used for each reported component, sample, and test. This is particularly important if certain samples in a job have been redigested.

6.4. If appropriate, verify that the field conductivity agrees with the calculated conductivity (RPD < 20 %) and that the charge balance agrees with the nutrient results (< 20 %). If the agreement is not adequate, the results should be investigated and an appropriate corrective action should be performed (e.g., check nutrient results, confirm with undigested sample, redigest). Check the sample for particulate matter if the results are high.

6.5. Verify that all field duplicates agree with an RPD < 20 % and that sample blanks (equipment, field and trip blanks) are below the detection limit for each requested component. If the field duplicates do not agree, check the samples for particulate matter and, if necessary, rerun and/or redigest. Include an appropriate comment in the report. If the sample blank is digested, the presence of an analyte can be confirmed by analyzing the undigested sample. The RPD between the digested result and the undigested result must be below 20 % for confirmation when results are above the PQL. If the result confirms, add the comment, 'The (analyte) result was confirmed in the undigested sample on (date mm/dd/yyyy)'. If the analyte is not present in the undigested sample, it must be redigested for confirmation of the detect. If the detection of an analyte in a digested sample blank is confirmed by analysis of an undigested sample but the value is not (RPD > 20 %), the comment, 'The presence of (analyte) was confirmed on (date)' should be used. If the sample blank is not digested, the presence of the analyte is confirmed by analyzing the sample in duplicate. The RPD between the two analyses of the sample must be below 20 % for confirmation.

6.6. Verify that passing QC (precision value, matrix spike recoveries, and LFB recoveries) is available for all components, tests, and batches. If the QC does not pass or is unavailable, appropriate qualification codes and comments must be present in both the LIMS and QCM. Before reporting the results, check to see if the QC sample has particulates or is heterogeneous (visually); verify that the correct spike level was used and that it is an adequate spike level to use.

6.7. Verify that unnecessary or duplicate QC is not present. If extra QC is present, select the proper batch ID in Data Review/Authorize, toggle the upload status to "X" for the QC to be omitted and insert an appropriate comment.

6.8. Check the results for a given component across all samples in a given job for consistency (e.g., 25 U vs. 30 U, rounding errors, significant figures, or dilution factors).

6.9. Compare the results from multiple digestions for consistency. If the results are not consistent between digestions, check the sample for particulates or heterogeneity. Include appropriate comments in the LIMS and QCM.

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6.10. Verify, if necessary, that the method of standard additions was used to confirm TCLP results. See DEP SOP MT-068, Section 7.3.

6.11. Verify that the sample results are below violation limits (surface water, RCRA, etc.) if appropriate to the job. Confirm any violation levels that may be suspect or challenged.

6.12. Check for matrix effects and spectral interferences or isobaric polyatomic ion interference when appropriate (failing recoveries, very high analyte levels, internal standard intensities outside of the limit, etc.).

6.13. Check dilution factors where appropriate.

6.14. Verify that suitable qualifying codes and comments are employed for all qualifications.

6.15. After the data associated with a job is thoroughly reviewed and any problems are addressed, authorize the job in LIMS.

7. REFERENCES

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

7.2. DEP SOP MT-068, The Toxicity Characteristic Leaching Procedure (EPA Method 1311) and the Synthetic Precipitation Leaching Procedure (EPA Method 1312)

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

7.4. DEP SOP LB-003, Estimation of Measurement Uncertainty.

7.5. DEP SOP LB-007, Procedure and Policy for Demonstration of Capability for Methods, Instruments, and Laboratory Staff.

7.6. DEP SOP LB-026, Job Level Authorization Checklist.

7.7. DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data and Correcting Quality Control Problems.

7.8. Quality Manual, located on the intranet.

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Appendix A – Example Cover Page Form Labeled for Clarification (fabricated for illustration)

Effective Date: 10/14/2015
Revision Date: 10/13/2015
Revision Author(s): M. Thompson

MT-ICPDV-1.0

AXIAL		80	120	RADIAL	Al, Ca, Fe, Mg,K,Na, Sr, Si	80	120
Scandium	3,892,301	3,113,841	4,670,761	Scandium	395,238	316,190	474,285

Analyst:	**Betina Topolski**	**SOP:**	*MT-061*
Instrument:	Perkin Elmer Optima 7300DV S/N 077C0042701	**Analysis Batch:**	A81850
Data File:	20180205-7300		
Date Analyzed:	February 5, 2018	***Data Reviewed By:***	

Analysis ID	Sample ID	Tray #	Prep Batch ID	Priority	Status						
W-ICP	1963430	200.2_7441	P339217	1	V1				Na		
W-ICP	1963471	200.2_7441	P339217	4	V1	Ca	Mg	K	Na	Hardness	
W-ICP	1963472	200.2_7441	P339217	4	V1	Ca	Mg	K	Na	Hardness	
W-ICP	1963473	200.2_7441	P339217	4	V1	Ca	Mg	K	Na	Hardness	
W-ICP	1963474	200.2_7441	P339217	4	V1	Ca	Mg	K	Na	Hardness	
Batch Notes:											
Previous Analyses:	First analysis										
S-ICP	1961816	3050-SED_109	P339132	5	V1	Sb	Ca		Na	Ag	
Batch notes:	SDPQLDV1 failed for Ca (135%) - sample not affected, the Ca result is greater than 10x the PQL failure.										
	Matrix spikes failed for Sb (~67%) - low recoveries are often observed for Sb using prep method 3050b.										
	The sodium result for 1961816 is below the PQL - redigest with more mass for better quantitation.										
Previous Analyses:	20180202-7300: Batch re-analyzed to verify Ca DPQL failure and Ag LFBSED failure.										
	Ag LFBSED failure confirmed - redigest.										

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Appendix B – Example Instrument Solution Log Form

Analyst: Betina Topolski

Instrument File Name: 20210104-7300

Standard Name	LIMS Serial Number	Expiration Date	Comments
ICPMIN	115121	10/31/21	Al, Fe, Ca, Mg, K, Na calibration standard
ICPMINC	109505	1/30/21	Al, Fe, Ca, Mg, K, Na second source check standard
ICPMINCCV	115122	10/31/21	Al, Fe, Ca, Mg, K, Na calibration verification
ICS2007A	113809	8/11/21	Interelement correction check standard
Internal Standard	117452	12/31/21	Internal standard to monitor instrument response
CPQLDV13	113411	10/31/21	Check standard at instrument PQL level
AG-SIO2	113813	9/1/21	Silver and silica calibration standard
AG-SIO2CCVC/CCV	113811	9/1/21	Silver and silica calibration verification
AG-SIO2C	109469	1/30/21	Silver and silica second source check standard
CPQLSI	115955	4/30/21	Check standard at instrument PQL level for silica
1000 PPM SILICA	106141	3/27/21	Silica filter sample spike for LFB and matrix spikes preparation
ICPMINA	114380	8/31/21	Minerals filter sample spike for LFB and matrix spikes
ICPMET-B	113412	10/31/21	Trace metal calibration standard
ICPMETCCVCB	113413	10/31/21	Trace metal calibration verification
ICPMETCB	115957	1/30/21	Trace metal second source check standard
HW6A	110154	1/30/21	Trace metals filter sample spike for LFB and matrix spikes
HW6B	109042	1/30/21	Trace metals filter sample spike for LFB and matrix spikes
ICS6010D	112852	1/30/21	Interelement correction check standard for 6010D method

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Appendix C - Review Checklist

1. Convert to .RAW data
2. Review or assign Sample Name, Type, Batch ID, Spike Code, Spike Factor, Test ID, Matrix, Dilution Factor, Apply Dilution, Weight Factor, Prep. Volume, Analyst, Date and Time.
3. Save Data.
4. Calculate QC and Save.
5. Cover Page Form
6. Instrument Solution Log Form and Preparation Documentation
7. Percent solid documentation for sediment/soil samples
8. Cross Reference Previous Run
9. Instrument QC – External Standard Check, ICS, CCVs, CCBs, CPQL
10. Internal Standards
11. Batch QC – I-BLK, D-BLK, PQL, LFB, RPD, Spikes, and Spike RPD.
12. Within Calibration
13. Customer Blanks – EB, FB, TB
14. Compare w/ Previous Data
15. Document Corrective Action
16. Select for Upload
17. Deselect Upload for Internal Standards and Errors.
18. Qualify Data with appropriate codes and comment.
19. Save the Data
20. Review
21. Upload
22. Reviewer Sign and Date

Appendix D – Appendix of Significant Changes

1. Section 4.23 edited for clarification and added detail.
2. Section 6 added to specify job review and authorization
3. DEP SOP IG-002 will be archived as a result of incorporating its content in this SOP.
4. Updated Example Cover Page and Instrument Solution Log (Appendix A & B)
5. 6/10/09: Sections 4.26.1 and 4.29 edited to include more detail regarding commenting.
6. 12/14/2009: Added reference to the Chemistry Quality Manual where calculations for data reduction can be found.
7. Sections 4.25.2. and 4.27.2 were edited for clarification.
8. 03/20/2019: Section 4.25.7 created for % Relative Error calibration requirements. Section 5.4.1 created for guidance for uploading statistical QC data. Edited section 4.31 for clarity.
9. Section 4.25.3 was added to include Mixed Element Spectral Interference Check Standard (ICS6010D) requirements.
10. Updated Appendix B (Example Instrument Solution Log Form)
11. Updated network directory. Updated a comment and added clarification.

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