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 Optical Emission Spectroscopy (ICPOES) (DEP SOP MT-061) and Inductively Coupled Plasma Mass Spectrometry (ICPMS) (DEP SOP MT-074).

2. SUMMARY OF THE METHOD

The analyst exports the raw data from the instrument and imports it to the Quality Control Manager (QCM) within the DEP Laboratory Information Management System (LIMS), where the data is calculated, examined for accuracy, and uploaded to the database. The reviewer assesses the data for proper qualification based on the quality control (QC) sample results, uploads the QC, and authorizes the test and/or component(s). The second-level reviewer assesses the completeness of the data with its associated QC and authorizes the job.

3. APPARATUS AND EQUIPMENT

3.1. Computer with operational and stable network connection.

3.2. DEP Chemistry LIMS Account.

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4. DATA CONVERSION & CALCULATION PROCEDURE

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

4.2. Import Instrument Data into QCM – Once the raw data file from the instrument is exported onto the network (See the specific SOP for the instrument of interest for details), import the raw file by following the QCM menu path: File>Convert Instrument File, select the appropriate .CSV data file, and click Open. The file is then converted from .CSV to .RAW.

4.3. Load QCM Data – Upon successful conversion of an instrument file, its run data is immediately loaded. If the data file has previously been converted but not yet reviewed, load the file by following the QCM menu path: File>Open. Select the Raw Data radio button, then choose the appropriate file name with the .RAW extension. If the data file has previously been reviewed and saved but corrections need to be made, load the file as in the steps above, but select the Rev Data radio button, then choose the appropriate file name with the .REV extension. Once the file is loaded, the data will be organized by number in the first column, "Cup", which functions as a row index number.

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

Note: Field duplicates shall 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) and left-clicking on the column header.

Table 1.

TYPE	DESCRIPTION
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	Continuing Calibration Verification standard.
LFB	Laboratory Fortified Blank.
MBLK	Method Blank (See Section 5). These include the first filtered continuing calibration blank of the analytical batch and all digested prep batch blanks.

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TYPE	DESCRIPTION
MDL	Method Detection Limit quality control blank. These are all the subsequent filtered continuing calibration blanks of the analytical batch.
REPL	Replicate. Multiple analyses of the same sample upon which precision calculations shall be made. Each separate set of replicates shall have a unique replicate ID assigned in the *Type* column (example: REPL A), and each individual replicate within the set shall have a unique identifier in the *Sample* column (example: ####### A and ####### B). In cases where the replicate sample has more than one Test ID (e.g., W-ICP and W-HARD), the replicates of each Test ID should have separate, unique replicate IDs (example: REPL A and REPL B).
SAMP	Sample. All normal unknown samples for which concentration data is desired.
SPK	Matrix Spike. All fortified samples.
SRM	Standard Reference Material – 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 prep 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 in the LIMS Prep Worksheet Manager module (Laboratory>Technical>Prep Worksheet Manager). Assign a unique analysis batch ID to every sample in the data set, even if there are multiple prep batches. If a sample is to be rerun and reported with QC from a previous batch, assign the previous prep batch ID but a new analysis batch ID. If the sample was redigested, it will have a new prep batch ID different from the first digestion and analysis. Assign a new, unique prep batch ID to all instrument QC and all other samples not part of a prep batch. For samples requiring the W-HARD Test ID, assign the same prep batch ID as 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 will 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 filtered water Test ID

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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 data in QCM. Do not overwrite the automatically assigned W-HARD Test IDs (unless the sample is the QC sample; see the Note in Section 4.19.).

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

Table 2.

MATRIX	DESCRIPTION
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	Hot Block Digested soils and sediments for total recoverable metals analysis.
SEDBLK-LFB	LFBs associated with SEDBLOCK batches.
TISSUE	Tissues of every sort.
TISSUE-LFB	LFBs associated with TISSUE batches.
WASBLOCK	Hot Block Digested waste samples for total recoverable metals analysis.
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 fromextraction fluid #1, regardless of the original sample matrix or digestion method.
TCLP1-LFB	LFBs associated with TCLP1 batches.
TCLP2	TCLP extracts from extraction fluid #2, regardless of the original sample matrix or digestion method.
TCLP2-LFB	LFBs associated with TCLP2 batches.
SED-TOTAL	Microwave digested sediment samples for total metals(“true total”) analysis.
SED-TOTLFB	LFBs associated with SED-TOTAL 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

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concentration. For example, if the sample was diluted by 1/5, the dilution factor is 5. For digested samples, the preparer will indicate it on the preparation worksheet. For filtered samples, the analyst will indicate it 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.

4.12. Weight (g) – For solid/waste/tissue samples, assign the sample weight in this field. For SOLID tests, enter the "dry weight" where,

$$dry\ weight = wet\ weight \times percent\ solid$$

For WASTE and TISSUE tests, enter 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 for data interpretation. This field is also used to automatically document manual edits to a LIMS result. Notes cannot be edited, 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 relevant to the laboratory for future interpretation and reference may be entered here.

4.18. Save – Save the data (converts a copy of the .RAW file to .REV) using the *Save* option from the *File* 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/SUR Recoveries)", "2 (Mean + Precision for Replicates)", "3 (Spike Recoveries and Precision)" all three sub-options under option 3 ("Dilution Factor", "Spike Code",

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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 .RAW data into .REV data in QCM, new data rows will appear for samples with the W-HARD Test ID. QCM calculates the water hardness result according to SM 2340B, (see below). Verify that the Ca and Mg results come from the same analysis 'Cup' (same Test ID, dilution factor, etc.) and are not over calibration. Make sure the applicable QC for Ca and Mg are passing, then toggle the upload column to 'Y'.

$$Hardness, \frac{mg}{L} as\ CaCO_3 = \left[2.497 \times \left(Ca^{2+}, \frac{mg}{L}\right)\right] + \left[4.118 \times \left(Mg^{2+}, \frac{mg}{L}\right)\right]$$

Note: If the QC sample is associated with both the W-ICP and W-HARD Test IDs, after clicking *Calculate*, a text box will appear, asking the analyst to select the correct spike background. Choose the appropriate background sample for the matrix spike associated with its matching 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. Manually edit this Test ID for the newly calculated SPRPD to W-ICP by highlighting the row and clicking the 'Test ID' column header.

4.20. Save – Once the calculations are complete, save the data again as in Section 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 these forms are located on the Division of Environmental Assessment and Restoration (DEAR) intranet site. An Excel template of MT-ICPDV can be found on the Chemistry Program's computer network, \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals\ICPAESDV. An Excel template for MT-ICPMS is located at \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals\ICP-MS-iCAP-RQ or \ICP-MS-iCAP-MSX-1. Always verify the most up-to-date version is used by comparing the revision number on the Excel form to the revision number on the official form on the DEAR intranet site. See Appendix A for an example of a cover page.

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

4.21.1.1. Choose 'Laboratory'>'Technical'> 'Component Backlog'.

4.21.1.2. Select 'P', 'V', and 'W' Status for Test, and select 'V' Status for Component.

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

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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' (Ctrl-S). Follow the prompts to save in your OneDrive folder.

4.21.1.6. Open the file previously saved in 4.21.1.5. in Microsoft Excel. When prompted to locate the text file, select 'All Files' next to the *File Name* box for it to appear in the list. Select it, then click 'Open'. A Text Import Wizard pop-up will appear. Select 'Delimited', then click 'Next'. Select 'Tab' and 'Comma' as Delimiters, then click 'Next' again. Select 'General' as the Column data format, 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 and will be used to help create the cover page form. Save the completed Excel cover page form in the appropriate data folder for the appropriate instrument located at: \\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 shall 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 at: \\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 revision 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 shall also be saved in the same data folder as the analytical run and cover page form for the appropriate instrument, located at: \\floridadep\data\LABS\Lab3\Chem_Data\Inorganic\Metals.

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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(s), 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 included 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.).

4.23.4. Carefully check the Sample IDs, prep batches, listed components, Test IDs, 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: ICPAES 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 % (ICPAES) and ± 10 % (ICPMS)) – Each instrument runs a NIST traceable standard(s) from a second 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 DEP SOP 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

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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 analyzed on ICPAES before each run to check that the instrument is free from spectral interference from elements typically observed in high concentrations and to check that applied interference corrections 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 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 ICPAES methods also require that before analyzing samples, the first CCV is analyzed using tighter control limits (denoted as CCVC, with a tolerance of ± 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 analyte(s) 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\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics\Annual MDL Calculations. 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 results between the MDL and the absolute value of 10X the failure must be 'J' qualified with a comment or rerun. If the recovery is above 130 % (failure), all results between the MDL and 10X the failure must be 'J' qualified with a comment or rerun. The 'J' qualifier is defined in DEP SOP 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

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Research Institute of Canada. The SRM may be spiked with additional metals to ensure concentrations are above the PQL. It shall 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 shall 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:

$$\%\ Relative\ Error = \frac{[x_i' - x_i]}{x_i} \times 100$$

$$x_i = True\ value\ for\ the\ calibration\ standard$$

$$x_i' = Measured\ concentration\ of\ the\ calibration\ standard$$

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

4.26.1. ICPAES – 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 must be 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) reported with appropriate qualification according to DEP SOP LB-027. For option 3, if the reported result is "U" or "I" qualified, add the required comment, "The [MDL/PQL] for [analyte(s)] was elevated due to necessary sample dilution." Salt samples (conductivity >10,000 µmhos/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.

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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 must be 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 required, 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) reported with appropriate qualification according to DEP SOP LB-027. For option 2, if the reported result is "U" or "I" qualified, add the required comment, "The [MDL/PQL] for [analyte(s)] was elevated due to necessary sample dilution." Salt samples (conductivity >10,000 µmhos/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 ID 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 at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Metals\QC Statistics\Annual MDL Calculations.

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 shall be

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'J' qualified 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' qualified 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' qualified 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 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 by the analyst 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 matrices 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.

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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 (i.e. the spike is "buried"), no spike recoveries shall be uploaded, but the SPRPD is still uploaded (ensure the spike concentration is within calibration). Any samples in the batch that require the analyte with buried matrix spikes shall be commented, "Batch matrix spike recoveries for [analyte(s)] are unavailable [for one of two spiked samples] because of high analyte concentration in the QC sample."

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

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

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 µg/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 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 with a comment reported.

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.

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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 [analyte] result was confirmed in the [undigested/redigested] sample on [date of confirmation]" shall 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 comment, "The presence of [analyte] was confirmed on [date of confirmation]" shall be used.

4.30.4. If the detection or the value is not confirmed, the data shall 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 are within acceptable control limits, and if 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 are 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 shall be acknowledged by the analyst and documented on the cover page form. Any sample results that were qualified due to QC failures shall 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 shall 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.

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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
- 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\DEAR\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 whose test is applicable to that sample.

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 calculations, upload each method blank for all analytes (one time) as long as the results are valid. Also upload each batch PQL for all analytes (one time) as long as the results are valid. Upload the first analysis CCB ('Type' as MBLK) from each analysis batch for all analytes as long as the results are valid.

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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 shall 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. as appropriate. If any discrepancies are found, the relevant personnel (e.g., receiving room staff, customer) must be contacted to resolve the problem.

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 shall be investigated and an appropriate corrective action shall be performed (e.g., check nutrient results, confirm with undigested sample, redigest, etc.). 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]’ shall 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.

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6.6. Verify that passing QC (precision value, matrix spike recoveries, and LFB recoveries) are 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 Data Review/Authorize 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 Data Review/Authorize and QCM.

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 interferences where 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 Data Review/Authorize.

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.

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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. Laboratory Quality Manual, located on the intranet.

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.
12. 09/08/2026 – Expanded Section 4. Grammatical and formatting changes throughout the document. Updated all network file paths.

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