NUTRIENTS GROUP QUALITY ASSURANCE AND DATA AUTHORIZATION GUIDELINES

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1. SCOPE AND APPLICATION

This document is a general guideline for supervisors and analysts describing QC protocols, the applicable procedures to follow in case of QC failures, and when approving results from the raw analytical data. **Refer to the relevant standard operating procedure (SOP) for quality control (QC) requirements that are specific to a given analysis** (see also Table 5.1 of the DEP Quality Manual). Also see DEP SOP LB-027 (Standard Operating Procedure for Reporting Qualified Data) for specific directions on how to qualify data when quality control results are outside established control limits.

2. QUALITY CONTROL PROCEDURES FOR SAMPLE ANALYSES

2.1. Batch Definition - Many of the QC samples will be associated with sample batches. Batches are groups of 20 or less samples that are prepared and/or analyzed concurrently. All samples in the batch as well as batch QC are subjected to the same prep/analysis procedure, by the same personnel and using reagent(s) with the same reagent ID(s). Samples are generally divided into batches based on matrix groups (see Appendix A).

2.2. Calibrations

2.2.1. Calibration establishes the relationship between instrument response and concentration of an analyte. Most commonly regression fits are used for this purpose. The minimum number of non-zero calibration point required to ensure that the selected fit preserves at least three degrees of freedom is specified in the table below.

Type of Calibration Curve	Minimum Number of Non-zero Calibration Standards
Linear Fit	5
Quadratic Fit	6
Tertiary Fit	7

Please refer the DEP Quality Manual and TNI 2016 standard for a more comprehensive discussion (6.3 and 6.5).

2.2.2. A calibration should be performed at the start of every analytical run. The lowest calibration standard must be at or below the Practical Quantitation Limit (PQL) and above the Method Detection Limit (MDL). Results are reported to the client using the entire calibration range, starting with the MDL up to the highest calibration level. Results below PQL are reported with the I qualifier, indicating that they are estimates. Results below the MDL are reported as the detection limit with the U qualifier. Concentrations above the calibration range are diluted into the range or reported J qualified.

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2.2.3. Because results below PQL are reported to the client, it is especially important to ensure that sufficient accuracy and precision in the lower concentration range can be achieved. Therefore, in many cases the calibration curves used for the analyses are constructed to be weighted more heavily in the lower concentration range. This can be achieved by applying calibration fits that are 1/x or 1/x2 weighted. If instrument/software does not allow for weighted calibration fit, the number of calibration points in the lower calibration range may be increased, sometimes including calibration points below the PQL. Additionally, the Nutrients group does not use calibrations forced through zero, instead a zero-concentration calibration point (blank) may be included in the curve to account for the bias of the method.

2.2.4. For calibrations that use regression fits, the correlation coefficient must be equal to or greater than 0.995. Assessment criteria for calibration curves that do not fall in the above category are described in the individual method SOPs.

For all calibration curves evaluated using correlation coefficient, the relative error for each calibration point is assessed as well. This is done by evaluating either the % relative error or % recovery. Relative error is defined as

$$\%Relative\ Error = \frac{X_{i-}' X_i}{X_i} \times 100\%$$

and % recovery is

$$\%Recovery = \frac{X_i'}{X_i} \times 100\%$$

where X_i' is measured concentration of the calibration standard and X_i is true value of the calibration standard. The two quantities are directly related: %Relative Error = %Recovery – 100%.

Separate evaluation criteria are applied to the different regions of calibration curves: the region above PQL, the PQL, the region below PQL, and the zero-calibration point.

For the region above the PQL the acceptable range for the % recovery of the calibrants are set to be at least equal to the accuracy targets for the method, typically 90 - 110%, or as specified in the method SOP.

For the PQL, the threshold value between quantifiable range and qualitative range, the % recovery acceptance limits will be set equal to the control limits for the PQL-level check standards (2.3.3). These limits are usually 70 - 130%, or as specified in the method SOP.

For the qualitative range between MDL and PQL, the % recovery acceptance limits of 50 - 150% are applied. If the lower limit allows

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results below MDL, it is adjusted to the MDL level. Any calibration point that does not meet the qualitative identification criteria will be automatically rejected.

The acceptability of zero-concentration calibration standards is treated in the same way as for blanks, requiring that the absolute value of the result is below MDL.

2.2.5. Every calibration should be verified by analyzing an initial calibration verification standard at the beginning of an analytical run (2.3.2) and continuous calibration verification standards throughout the run (2.3.6). Additionally, the quality of data in the low concentration range is assured by daily analysis of PQL-level check standards whenever applicable. Please refer to the individual method SOPs for control limits.

2.3. Analytical Run QC Controls and Limits

2.3.1. Method Blank (MBLK): There must be a method blank for every batch of samples. The digested/undigested method blank result is considered as passing if below the MDL. Method blank data is collected and utilized for the ongoing MDL verification. For details see reference 6.4.

2.3.2. Alternate Quality Control Standards (AltQC): Alternate quality control standards are standards that are prepared from a different source or a different lot number than the one used for preparing calibrants. When available, traceable standards are preferred as AltQCs. They are used as initial calibration verification standards (ICV) and must be analyzed at the start of every analysis. The result must fall within the manufacturer's limits, or 85 – 115 %, or as specified in the SOP. Additionally, for digestive chemistries AltQCs are used to demonstrate the efficiency of the preparation procedures and must be prepared and analyzed with every digestion tray.

2.3.3. Practical Quantitation Limit (PQL) standards: PQL standards should be analyzed at the start of every analytical run. For prepared chemistries there should be one PQL standard per preparation worksheet. For analytical runs that continue for 24 hours or more, at least one PQL standard should be analyzed every 24 hours. The acceptance limits for PQL standards are 70-130 %. In most chemistries PQL standards also serve as MDL spikes (Please see 2.3.7).

2.3.4. Matrix Spikes and Duplicates: Analyze a matrix spike, a matrix spike duplicate and/or a sample duplicate for every batch of samples. The acceptance limits for sample or spike duplicates is a relative percent difference (RPD) of less than 20 % if both results are above the PQL. The sample spike recovery limits are 85-115 % for aqueous matrices and 80-120 % for solid matrices or as specified in the SOP. Duplicate spikes are analyzed to obtain precision data for analytes that are frequently below detection in the samples.

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2.3.5. Laboratory Fortified Blanks (LFBs): An LFB must be analyzed with every batch of samples. Acceptance limits for recoveries should be 85-115 % or as specified in the SOP.

2.3.6. Check Standards and Blanks serve as the continuous calibration verification standards (CCV) and blanks (CCB). Analyze a low to mid-level check standard and an instrument blank for every 20 samples and at the beginning and end of the run or as specified in the SOP. The acceptance limits for blank results are below the MDL and above the negative value of the MDL (-MDL < blank < MDL). The check standards acceptance limits for most nutrient and general chemistry parameters are 90-110% recovery or as specified in the SOP. In a few cases, the acceptance limits are 85-115%. It is preferable that check standards pass within the 93-107% recovery range. If they fall in the ranges of 90-93% or 107-110%, then the analysis still passes but the standards and/or instrument may need to be assessed for problems.

2.3.7. MDL Spikes: An MDL spike is a low-level LFB spiked at the same concentration as was used for the initial method validation. An MDLSPK must be processed through all preparation and analysis steps that are used for samples. MDLSPK data are collected for the purpose of the ongoing MDL and PQL verification. For practical purposes, one MDL spike (MDLSPK) is usually prepared and analyzed with each analytical run. For prepared chemistries, one MDLSPK is usually prepared for each preparation worksheet. MDLSPK results are uploaded to LIMS and are used along with MBLK data for the ongoing MDL and PQL verification. The following minimum requirements should be met for the ongoing MDL and PQL verification (please see ref. 6.4):

- During every quarter in which samples were analyzed, at least two MDLSPKs and at least two MBLKs should be analyzed in separate batches on each instrument;
- A minimum of 7 MDLSPK and MBLK data points must be collected each year.

For analyses that are performed infrequently, it is especially important to monitor the analysis schedule to fulfill the above requirements.

If the MDLSPK level is below the PQL, acceptance limits of 50 – 150 % are applied, unless there are other considerations based on the expected method performance that are discussed in the SOP of the specific analysis. For MDLSPKs at or above PQL general control limits of the method apply. Instances where an MDLSPK is not detected or does not meet qualitative identification criteria may indicate that MDLSPK concentration was set too low. Such instances should be carefully evaluated. If instrument conditions and maintenance are not sufficient to achieve an acceptable evaluation a new initial validation may be necessary.

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Whenever possible, a single standard can be used as both an MDLSPK and a PQL standard.

2.4. Field QC Controls and Limits

2.4.1. The acceptance limit for the precision for field duplicates is less than 20 % RPD.

2.4.2. The acceptance limit for results for equipment, field and trip blanks is a result below the MDL.

3. DATA REVIEW

3.1. Check to see that the analytical run meets the requirements for calibration and QC controls given in Section 2. Refer to Section 4 for protocols for handling QC control failures.

3.2. Check the peak shapes on the charts (where applicable) for anomalous results (poor peak shape, air spike etc.). In addition to seeing that the run meets the quality control requirements there are some additional potential checks listed below (many of these checks are performed using the calculations function of Data Review in LIMS):

3.2.1. Compare NH3 and TKN results when the ammonia results are greater than the TKN MDL.

3.2.2. Compare PO4 and TP results

3.2.3. Compare TOC and DOC results

3.2.4. Compare NO2NO3 and NO3 and NO2 results

3.2.5. Compare TN and TKN and Nitrate-Nitrite. Compare TN and Ammonia and Nitrate-Nitrite.

3.2.6. Compare results of filtered samples versus unfiltered samples

3.2.7. Check field duplicates

3.2.8. Check blanks (field, trip, equipment)

3.2.9. Ensure that comments are entered when needed (confirmation of blank contamination etc.)

3.2.10. Compare results with field parameters (e.g. a sample with pH of 4 and a high alkalinity needs to be rechecked)

3.2.11. If applicable, check charge balance

3.2.12. Check for any applicable non-conformance reports (NCRs)

3.2.13. Check sample expiration date

3.3 Check that any sample or batch reanalyzed or put back for redigestion is accompanied by a comment on the analytical run stating the reason. Reasons should be based on the failure to meet quality control measures, errors in sample

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handling, other instrument parameter failures, or the failure to meet other applicable protocols or criteria.

4. PROTOCOL IN CASE OF FAILURES OF THE QC LISTED IN SECTION 2

4.1. Calibration Problems

4.1.1. Failing Calibrations: A calibration is considered failing, if:

- The correlation coefficient is lower than 0.995.
- The % Recovery or % Relative Error of any of the calibration standards does not meet the criteria in 2.2.3 or in the specific chemistry SOP.
- The ICV (ALTQC; see 2.3.2.) is not meeting acceptance criteria.

Corrective Action: Stop the run and troubleshoot the problem. Recalibrate and reanalyze the samples. Document the problem and resolution in the instrument logbook. If the problem persists inform a supervisor. Samples must be J qualified if reported from an analysis with failing calibration.

4.1.2. Removal or replacement of calibration levels: It is a strongly enforced practice that the calibration is assessed as promptly as possible. In most cases, a problematic calibration is discarded, the cause of the problem is corrected, and a fresh calibration performed. Under exceptional circumstances, a calibration point removal or replacement may be considered as an alternative, if it complies with the policies outlined in the 2016 TNI standard, Volume 1, Module 4, section 1.7.1.1.

4.1.3. Sample Results that are over calibration: If a sample result is above the highest calibration standard, it needs to be diluted and reanalyzed. The result from the diluted sample can still be reported with the initial batch QC. If the sample cannot be reanalyzed then the result can be reported qualified with a “J” and a comment.

4.2. Analytical QC Problems

4.2.1. Method Blanks: k If a method blank is contaminated then report only samples that are 10 times the level of the method blank result or less than the MDL (i.e. not contaminated). The remainder within the associated batch need to be qualified (see DEP SOP LB-027) or redigested/reanalyzed.

4.2.1.1 When the results cannot be redigested/reanalyzed, they must be qualified using the ‘V’ qualifier code. A comment warning the data user of potential bias should be provided with the qualified data.

4.2.1.2. If a method blank has a negative result and the absolute value of the negative number is greater than the MDL, then proceed

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as follows: A. Assess the cause of the problem. Negative blanks may be random failures, caused by a poor calibration, or a loss of sensitivity during the analytical run. B. If there is no indication of a systematic problem (calibration, loss of sensitivity), reanalyze the batch on the same or a subsequent analytical run. Otherwise recalibrate the instrument and reanalyze the batch. C. In cases where reanalysis is not an option: Multiply the negative number by 2 and use the absolute value of the result as the new MDL. Calculate a new PQL and apply both to the entire batch. Comment I qualified data with the following comment: Result may be biased low due to analytical difficulties.

4.2.2. AltQC: If the AltQC fails then the entire analytical run is in question and results cannot be reported unqualified. Either the calibration standards or the alternate QC standard could be prepared incorrectly and must be checked.

4.2.2.1. Exception 1: If the failure is due to an obvious mechanical error such as an air spike and the run is still in progress then the AltQC may be reanalyzed at a later point in the run.

4.2.2.2. Exception 2: If the run is still in progress and the failure is determined to be due to an improperly prepared AltQC standard then a properly prepared AltQC standard along with the failed AltQC standard can be placed side by side at a later point in the run. If the original AltQC failure is confirmed and the correctly prepared AltQC passes, the calibration is considered valid.

4.2.3. PQL: At least one PQL standard is usually analyzed every time a calibration is performed, preferably at the beginning of the run (for some analyses a PQL is not appropriate). If the PQL fails, the samples should not be reported un-qualified. Investigate the reason for the failure carefully. Perform any troubleshooting and maintenance procedures as needed and reprocess the run or redigest the samples. Also refer to section 2.3.7 for assessment of the PQL failure, if applicable.

4.2.4. Matrix Spikes: Samples that are digested or distilled prior to analysis have a separate set of guidelines than for those that have no preparation prior to analysis.

4.2.4.1. Digested /Distilled Analytes

a.: If one or both spikes fail and the background level is less than the spiked concentration, then the result for the spiked sample must be qualified or the batch must be redigested and reanalyzed. Prior to redigestion the cause of the spike failure needs to be evaluated (error, interference). If interferences are considered unique to a small set of

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samples within the batch, then the original batch may be broken down into sub batches prior to redigestion. Each sub batch must then have a representative duplicate, spike and LFB.

b: If samples are diluted due to matrix interference, then all samples within that batch, other than blanks (field, equipment or trip) must be diluted by at least as much as the spiked sample.

c: If the spike fails due to analytical interference, not digestion, then the original digestates of the samples and spikes can be diluted and reanalyzed.

4.2.4.2. Analytes Needing No Preparation

a: If one or both spikes fail and the background level is less than the spiked concentration, then the results of the spiked sample batch must be qualified, or the samples must be reanalyzed. The cause of the spike failure needs to be evaluated (error, interference). If the analytical run is still in progress, then samples can be respiked on the same run and it may not be necessary to reanalyze every sample in the affected batch. There are numerous causes of spike failures and many different methods of handling them. Some causes and methods are indicated below. Other situations not described below need to be evaluated by the supervisor.

b: If one or both spikes fail and a mechanical error is suspected (e.g. wrong pipet or solution used, air spike) then the sample can be respiked as long as the run is still in progress.

c: If the sample concentration is high enough to cause failure (sample concentration is greater than or equal to the spike concentration) then it is recommended that a sample of lower concentration within the batch be spiked. If this is not possible then the samples in the batch can be reported with the test comment “Batch matrix spike recovery data is unavailable because of high analyte concentration in the QC sample”.

d: Spikes fail due to matrix interference. If the interference appears to be limited to a small number of samples within the batch, then sub batches can be designated. The samples with interferences can be treated separately from the rest of the samples in the original batch. The rest of the samples form a new batch and a sample from the new batch must be duplicated and spiked. The spiking protocol for the

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samples with the interference needs to be decided by the supervisor.

4.2.5. Matrix Replicates: Acceptance limits for precision for laboratory matrix duplicates are less than 20 % RPD or less than 15 % RSD for results that are greater than the PQL. If the precision fails outside these limits, then the result for the sample must be qualified or the batch of samples needs to be redigested/reanalyzed. If interferences are considered unique to a small set of samples within the batch, then the original batch may be broken down into sub batches prior to reanalysis. Each sub batch must then have a representative duplicate, matrix spike and LFB. If samples are diluted, then all samples within that batch must be diluted by at least as much as the duplicate sample. Samples do not have to be redigested prior to reanalysis if the cause of the failure is due to the instrumental analysis rather than the digestion. If a mechanical error causes failure (air spike, poor injection) and the run is still in progress then the sample and duplicate can be placed at a later point in the run.

4.2.6. Check Standards and Blanks: If check standards (CCVs) fall outside the limits specified in the SOP, then the samples that are bordered by the failed standard should be reanalyzed or reported as estimates (J qualified). In addition, the qualified samples must be accompanied by a comment. If a blank result (CCB) is greater than or equal to the MDL, then samples bordered by the failed blank should be reanalyzed unless they are 10 times higher than the blank result (i.e. the contamination is insignificant compared to the sample result) or below the detection limit (i.e. not contaminated). In cases where reanalysis is not an option, the samples are reported J-qualified and the qualified samples must be accompanied by a comment. If a blank has a negative result and the absolute value of the negative number is greater than the MDL, then reanalyze the samples bordered by the failing blank. In cases where reanalysis is not an option: Multiply the number by a factor of 2 and use the absolute value of the result as the new MDL. Calculate a new PQL and apply both to the samples bordered by the failing blank. Comment I qualified data with the following comment: Result may be biased low because of analytical difficulties.

4.3. Field QC Limits

4.3.1. Field Duplicates: If field duplicates do not duplicate within 20 % RPD then there are several steps to be taken. First check to see if samples were logged in correctly. Also check to see if samples appear different (e.g. one might contain more particulate matter than the other). If everything checks out okay, then the samples need to be redigested and/or reanalyzed for confirmation. If the results do not confirm within 20 % of their original results, then refer to Section 4.4 of this document.

4.3.2. Sampling Blanks (Field, Equipment and Trip): If the results for sampling blanks show contamination then the results need to be confirmed unless

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the associated sample results are at least 10 times higher than the blank results. Prior to confirmation check to see if the samples were logged in correctly and if the samples physically appear to be blanks. If everything checks out okay, then the samples need to be redigested /reanalyzed. If the results do not match the original result then refer to Section 4.4 of this document.

4.4. Confirmation of Results: There are a number of situations which call for a sample to be redigested/reanalyzed to confirm a result. If the second analysis confirms the result, then it can be reported. If the second result does not match the initial result within 10 % (for values over the PQL, and acceptable QC for both analyses) then the entire batch of samples associated with the initial result needs to be evaluated. There are a number of reasons why a sample result would vary greater than 10 % between runs e.g. the sample could be difficult to homogenize due to large amounts of particulate matter. In this case the other samples in the batch would not have to be analyzed unless they also contained a lot of particulate matter. Sample IDs could have been labeled incorrectly during the analysis. In this case all of the samples in the batch may need to be reanalyzed. Each situation needs to be evaluated by a supervisor. The 10 % RPD limit for repeat sample analysis is applied if a sample is analyzed or diluted into the calibration range twice with the same or a different dilution factor for confirmation. Both results must have acceptable QC. If the dilutions were made to mitigate matrix interference this limit does not apply.

5. CORRECTIVE ACTIONS

Contact a supervisor and report any non-compliant QC results. There are many different reasons for QC failures. In general, for any failure associated with the initial calibration (failure of independent standard, correlation coefficient out-of-compliance etc.) the run should be aborted and the instrument should be recalibrated.

When the root cause of an LFB or CCV failure is identified and suitable corrective actions taken, create a Non-Conformance Report (NCR) for documentation. For details on NCRs see DEP SOP LB-002. The NCR is linked to specific samples, jobs or events affected by the NCR.

6. DATA ARCHIVAL

6.1. The raw data for analytical runs is archived in paper format. Typically, each report folder should contain the following items - results report(s), bench sheet(s), backlog(s), reagent and standard sheet(s), the calibration report(s), method parameters, and QC assessments uploaded from QC Manager to LIMS at the time of test authorization. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

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6.2. Instrument raw data files and data transfer files for upload to QC manager are copied after each run to an appropriate subfolder of the Nutrients drive under \\floridadep\data\\LABS\Lab3\Chem_data\Inorganic\Nutrients\.

6.3. Copies of all available standards and reagents certificates of analysis are stored in the \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\IC\Certificates of Analysis folder.

6.4. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in

\\floridadep\data\\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations\ .

7. REFERENCES

6.1. DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data.

6.2. Quality Manual, Bureau of Laboratories, Florida DEP

6.3. DEP SOP LB-002, Non-Conformance Reporting System

6.4. EPA Definition and Procedure for the Determination of the Method Detection Limit, Revision 2

6.5. 2016 TNI Standard, Revision 2.1

APPENDIX A - Nutrients Matrix Groups

Group 1 - Surface fresh, ground water, drinking water
Group 2 - Salt water
Group 3 - Effluent, Influent
Group 4 - Solids, Wastes
Group 5 - Not natural matrix (e.g. PT samples, USGS samples)

Appendix of Significant Changes

11/02/2011	Section 4.2: Clarification on the procedure for reporting data associated with low failures for Method Blanks and Check Blanks.
12/14/2017	Section 5 on corrective action was added. Section for was edited to add more detail and clarity.
12/14/2018	Revised Section 2: Added the requirement that a PQL standard is analyzed at least once every 24 hours during a run. Added a paragraph on ongoing MDL and PQL verification (MDLSPK).
12/12/2019	Section 2.1: expanded the batch definition. Section 4.1: added a paragraph on removal or replacement of calibration points.

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02/06/2020	Expanded section 2.2 to add minimum number of calibration points required, assessment of relative error for calibrants, and use of ICV and CCV. Clarified section 2.3.2. Added paragraph 4.1.2. for removal and replacement of calibration points. Added Data Archival section.
12/17/2021	Revised sections 4.2.3 describing corrective action for CCB failures and 4.2.6. describing corrective action for a failing PQL.
08/18/2023	In section 4.4 the acceptance limit for repeat sample digestion/analysis or dilutions for confirmation was changed to 10 % RPD. Paragraph 3.3 was added. It requires comments be added on the analytical run with a reason for reanalysis or redigestion, if needed. In Appendix A a matrix goup was added for samples that are not representative of a natural matrix, like PT-samples and USGS samples.
12/18/2024	File path links were updated.
12/19/2025	Section 6.5 was removed because the links are no longer available.

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