NUTRIENTS: QUALITY ASSURANCE AND QUALITY CONTROL

1. SCOPE AND APPLICATION

1.1. The purpose of this Standard Operating Procedure (SOP) is to establish, maintain and document general quality control (QC) for the Nutrients workgroup. The controls used are bias, precision, and detection limit statistics.

1.2. These procedures and calculations are used for all Nutrients analyses. The procedures described in this SOP are general; more specific or stringent requirements are documented in the method and SOP for the relevant test.

2. QUALITY CONTROL

2.1. In general, for every batch of samples (max. 20 samples) digested and/or analyzed, the following quality control samples are analyzed:

- A Laboratory Fortified Blank (LFB)
- Digestion or Method Blank (MBLK)
- One Matrix Spike
- Matrix Spike Duplicate or Sample Duplicate

2.2. Accuracy.

2.2.1. Standardization:

2.2.1.1. Standards are prepared and documented in the Standard Preparation Tracker module of the Laboratory Information Management System (LIMS) program. Guidelines for the preparation of standards are documented in DEP SOP NU-042. Calibration curves are analyzed at the beginning of each analytical run or at the frequency specified in the method SOP. The correlation coefficient for a standard curve must be 0.995 or greater. For all calibrations evaluated using correlation coefficient, the % recovery or % error for each calibrant must be assessed. The control limits are as specified below, or as described in the method SOP.

Calibration range	control limits
Above PQL	% recovery 90 – 110%
PQL	% recovery 70 – 130%
Between MDL and PQL	% recovery 50 – 150% and above MDL
Zero-concentration calibrant	-MDL < result < MDL

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These recoveries verify the working calibration range with every calibration. The curves are also checked against an initial calibration verification standard (ICV). This is a certified standard or other independently prepared (from a stock of a different lot or manufacturer) standard analyzed during each analytical run. The continuing validity of the calibration is verified throughout the run by analyzing check standards (may also be called "continuous calibration verification" standards) at least every 20 samples. Refer to the applicable test SOPs for acceptance limits of the secondary source standards and CCVs. Along with check standards, blanks are analyzed to monitor for contamination, carry over, or baseline problems.

2.2.1.2 All analytical equipment must be calibrated on a regular basis (e.g. calibrate pipettes on a monthly basis). Guidelines for the calibration of auto-pipettes and dispensers are given in DEP SOP CM-032. The calibrations must be documented. All appliances used for storage or analysis (e.g. ovens, refrigerators, digestion blocks, and autoclave) must be monitored every day of use and documentation must be maintained using associated logbooks or the appropriate network drive. The nutrients refrigerators are monitored following the instructions in the Refrigerator Temperature Logging Guide. Please see form NU-REFTEMPGUIDE-1.0. See the supervisor for instructions on equipment calibration and monitoring. All glassware used to measure volumes for analytical purposes must be class A.

2.2.2. Spike Recoveries:

2.2.2.1. A representative sample is spiked with known quantities (preferably approximately 2 to 10 times the PQL) of the analyte before processing. Percent recoveries are calculated for the added analyte. Matrix spike recoveries are indicators of sample matrix interference and contamination. The confidence range is set at 85 - 115 % for water matrices and 80 - 120 % recovery for soil matrices unless the method prescribes more stringent limits.

2.2.2.2. A blank is spiked with known quantities of the analyte (usually at the same concentration as a matrix spike) before processing. Percent recoveries are calculated for the added analyte. LFB recoveries are indicators of method failure and contamination. The confidence range is set at 85 - 115 % for water matrices and 80 - 120 % recovery for soil matrices unless the method requires more stringent limits.

2.2.3. Blanks:

2.2.3.1. Blank results are used to control contamination and to set minimum detection limits (MDL). In general, there are two types

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of blanks associated with an analytical run: method blanks (MBLK) and check blanks (CCB).

2.2.3.2. Method blanks are a part of the batch QC and processed together with the samples through all preparation steps. They are used to monitor the preparation process for possible contamination. One MBLK is prepared for each batch. MBLKs are also used for ongoing method detection limit (MDL) verification. MDLs are set such that the risk of reporting a false positive is less than 1% (Please see ref. 6.6. and 6.7 for MDL verification procedures).

2.2.3.3. A check blank is analyzed at the beginning, at least every 20 samples, and at the end of each run. Use deionized water for blanks and adjust the water to match the sample matrix (i.e. acidify, basify or add salt). Check blanks are used to monitor contamination and carry over that may occur on the instrument during the analytical run.

2.2.4. Practical Quantitation Limit (PQL):

2.2.4.1. The PQL is the concentration above which the analyte can be quantified with the method-required accuracy and precision. Above PQL results are reported unqualified (if all QC measures meet acceptance criteria). Method control limits are not applicable to results below PQL; these results are flagged with an "I" qualifier. The PQL is set during the method validation and verified yearly according to the procedures delineated in Ref. 6.6 and 6.7.

2.2.4.2. PQL level spikes are used for two purposes: a) for ongoing MDL and PQL verification and b) for evaluating instrument performance at the low concentration range. Digested PQL standards are required with each tray of digested samples. For un-digested chemistries, at least one PQL level standard is analyzed with every analytical run. The acceptance range for a PQL recovery is 70 - 130 % recovery. For analytical runs that continue for 24 hours or more, at least one PQL standard should be analyzed every 24 hours.

2.2.4.3. Ongoing MDL and PQL verification require analysis of a spike at the same concentration level as was used during the initial method validation study. Typically, this concentration is the same as the PQL. In these cases, the PQL standard is utilized for ongoing MDL verification. There may be cases where PQL and MDL verification spike are at different concentration levels. In such cases the MDL verification spike (MDLSPK) may be used instead of a PQL level spike with the same acceptance limits.

2.2.4.4 To satisfy the requirements for the ongoing PQL verification, all PQL or MDLSPK failures should be followed with a documented corrective action. Typically, troubleshooting and/or maintenance

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are performed and documented in the instrument logbook. The logbook entry must provide sufficient description of both the technically valid reason for the PQL/MDLSPK failure and the steps taken to correct the problem. If the problem persists, it is reported to the supervisor and addressed following the TNI and EPA guidelines (ref. 6.6 and 6.7).

2.2.5. Other bias assessments:

2.2.5.1. To evaluate any bias possibly introduced during sample preparation, batch QC samples should undergo the same processing steps as samples.

2.2.5.2. If some of the samples are filtered prior to analysis, positive and negative bias checks are required. This can be achieved by filtering the MBLK and an LFB or a check standard. In such cases, samples and QC samples filtered are identified by adding a suffix "_F" to their name.

2.3. Precision.

2.3.1. Any time an instrument takes a replicate reading on a sample or if the sample is analyzed more than one time, the precision needs to be checked.

2.3.2. The relative percent difference (RPD) for batch duplicates must be within 20 %, for values above the PQL, or meet the limit given by the applicable method SOP.

2.3.3. The RPD for field duplicates should be within 20 %.

2.3.4. The acceptance limit for repeat sample analysis and dilutions is 10 % RPD. This limit is applied if a sample is digested/analyzed or diluted into the calibration range multiple times with the same or a different dilution factor for confirmation. All results must be associated with acceptable batch and run QC. If the dilutions were made to mitigate matrix interference this limit does not apply.

3. QUALITY ASSURANCE

3.1. All data and quality control data are reviewed by a supervisor or designate before being accepted as final. See DEP SOP NU-043.

3.2. All maintenance or analytical problems are reported to a supervisor. Document all instrument maintenance in the logbook assigned to the instrument. Also, document equipment calibrations (pipettes, balances etc.) in the assigned notebooks or computer files. See the supervisor for instructions on how to document the instrument maintenance and equipment calibration.

3.2.1 Pipette calibrations are performed on a monthly basis using the Check & Track pipette calibration software as described in SOP CM-032. Pipettes must be calibrated before the date due. Any pipette that is not calibrated prior to the calibration due date should be removed from the laboratory.

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3.3. Field sampling problems such as contamination, labeling, and holding times are reported to a supervisor and noted with the results using the NCR module of the LIMS program.

3.4. Results that are suspect for any reason are qualified and/or noted in the 'Ref. Method and Comment' line of the final report.

3.5. For methods that do not have electronic documentation of the time of analysis the start and end time of the analytical run should be documented by the analyst on the raw data. The end time of the run should be used as the time of analysis in the QC Manager. If samples are close to expiration the individual time of analysis should be noted and used for those samples.

3.6. Quality control results are documented electronically through the QC Manager module of the LIMS program and documented in the report folders as part of the LIMS uploadable sheet. Analysts should be recording % recoveries of the QC samples on their bench sheets, if they are monitoring the analytical run actively at the bench during the run.

4. 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, the cause of the failure evaluated and resolved, and the instrument recalibrated. For further information see DEP SOP NU-043.

5. REMARK CODES (SEE ALSO DEP SOP LB-027)

5.1. Sample results are reported with a remark code (qualifier) when:

5.1.1. They are below the MDL. The result is reported as the MDL followed by the **U** qualifier.

5.1.2. They are below the PQL but at or above the MDL. The results are reported with an **I** qualifier.

5.1.3. They are poured out and analyzed in duplicate, QC manager will calculate the average and append the **A** qualifier.

5.1.4. They are analyzed after expiration. The results are reported with the **Q** qualifier.

5.1.5. They are associated with failing batch or run QC. The results are reported with a **J** qualifier. This includes, but may not be limited to:

- All results in a batch with associated LFB failure.
- The result for the batch QC sample if the matrix spike/s fail.
- The result for the batch QC sample if the associated RPD fails.

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- All sample results associated with a failing bracketing continuing calibration verification standard (CCV). This applies to samples up and down the analytical run until the next passing CCV.
- Samples associated with a contaminated continuing calibration blank (CCB) which must be qualified (result less than 10 times the contamination level; not non-detect).
- All sample results associated with a failing calibration.
- All sample results associated with a failing PQL or SRM (standard reference material/second source standard).

5.1.6 They are obtained from bottles that were damaged and the sample integrity may be compromised. The results are reported with a **J** qualifier. This applies when the damage caused a leakage of sample.

5.1.7. They are incorrectly preserved. The results are reported with a **Y** qualifier. Make sure an appropriate NCR record is created if the preservation issue was not detected at login but during analysis. Check with your supervisor before authorizing associated results.

5.2 The QC Manager module of the LIMS program will assign most of these codes automatically (i.e. I, U, A). The Q qualifier and J qualifier for failed spike recoveries, RPDs, LFBs or CCVs are assigned automatically in the Data Review/Authorize module of the LIMS program.

5.3 All J, Q, and Y qualified samples must be accompanied by a comment. Appropriate comments for Q qualified data and non-automatically assigned J qualified data should be added in the QC Manager. There are default comments for the most common reasons for qualifying data. Please consult your supervisor for the appropriate comment.

6. REFERENCES

6.1. Quality Manual, Bureau of Laboratories, FDEP.

6.2. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines.

6.3. DEP SOP NU-042, Standard Preparation Procedure.

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

6.5. DEP SOP CM-032, Calibration of Auto-Pipettes and Dispensers using the Check & Track software.

6.6. 2016 TNI Standard, EL-V1-2016-Rev.2.1.

6.7. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.0, 40 CFR Part 136, Appendix B.

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Appendix of Significant Changes

12/10/2018 Section 2 was modified for clarity and to include new MDL and PQL verification requirements. References 6.6 and 6.7 were added.

02/07/2020 Added requirements for assessing % recovery of calibrants at and below PQL level. Added policy on addressing PQL/MDLSPK standards failure. Added policy on pipet calibrations.

12/17/2021 Clarified the assessment of precision in section 2.3.2. Amended section 5.1.5 to address qualification of samples associated with a contaminated CCB.

08/14/2023 Added 10 % RPD limit for sample re-analysis and dilutions in section 2.3. Removed the requirement for a specific order of qualifiers if more than one is assigned. Revised section 5 for clarity.

09/24/2024 Added guidance in section 2 for the refrigerator monitoring protocol.

09/15/2025 Clarifications added in sections 2 and 3.

10/19/2026 Clarifications added to section 2.2.

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