PROCEDURE AND POLICY FOR DEMOSTRATION OF CAPABILITY FOR METHODS, INSTRUMENTS, AND LABORATORY STAFF

1. SCOPE AND APPLICATION (Refer to Section 1.6 of TNI 2009, V1M4, V1M5 and V1M7)

   1.1. This SOP is to be used for the following situations:

   a. validation of an EPA or Department-approved laboratory method not already used in the laboratory;

   b. validation of a new analyte(s) in a specified matrix using an EPA or Department-approved laboratory method;

   c. substantial modification of a Department-approved laboratory method that warrants validation;

   d. validation of a new method for analyte(s) in a specified matrix which is not an EPA or Department-approved laboratory method;

   e. validation of an analytical Method for analyte(s) in a specified matrix where a Department-approved method already exists. This alternative method is one intended to be used in place of an existing Department-approved laboratory method;

   f. validation of a new instrument or a major upgrade of software or hardware for an instrument.

   g. Initial or on-going demonstration of capability for an analytical procedure for which the analyst will be responsible.

   1.2. This SOP is intended to be used only by laboratory managers, supervisors or experienced senior analysts.

2. VALIDATION PROCEDURE

   The validation protocols involve:

   2.1. **New Methods**: For situations listed in section 1.1.a, 1.1.b and 1.1.c, perform the following:

   2.1.1. A method detection limit (MDL) study. Prepare a minimum of seven (7) laboratory fortified blanks (LFB) at one to five times the estimated MDL concentration and process each through the entire analytical method. (Note: For biological methods where an MDL or LFB cannot be prepared e.g., BOD and chlorophyll, substitute with at least 7 replicates of a standard solution.) For uncensored methods, method blanks can be used to determine the MDL. Derive the detection limit using the Student's t value appropriate for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom. If the calculation is based on method blanks a systematic bias can be taken into account. The MDL should be above the average blank level. In cases where the calculated

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

MDL is more than 10 times lower than the concentration level of the LFB's the study may be performed again using a lower spiking level. For details, refer to the FDEP Quality Manual and Chapter 40, Part 136 Appendix B Paragraphs 5 and 6 of the Code of Federal Regulations for "Definition and Procedure for the Determination of the Method Detection Limit".

2.1.2. Initial demonstration of capability (IDOC). Prepare and analyze four (4) laboratory fortified blanks or four (4) aliquots of the analyte(s) diluted in a volume of clean quality system matrix at the concentration specified, or if unspecified, 1 to 4 times the practical quantitation limit (PQL) concentration. Calculate accuracy and precision for each parameter of interest. Refer to 2009 TNI Standard, V1M4, Section 1.6.2.2 for details. The PQL is derived using criteria outlined in the laboratory's Quality Manual.

2.1.3. For Whole Effluent Toxicity (WET) analyses, the Initial Demonstration of Capability consists of conducting five valid standard reference toxicant tests for each method. The IDOC will be performed by at least one current member of the toxicity laboratory work unit or work cell.

2.1.4. Limit of Detection (LOD) Verification (see also CM-026 and TNI (2009) V1M4, 1.5.2.1): The laboratory shall verify the LOD for the method for each target analyte of concern in the quality system matrices whenever a spiking solution is commercially available (unless spiking is inappropriate – one example is pH). All sample-processing steps of the analytical method shall be included in the determination of the LOD. The validity of the LOD shall be confirmed (on each instrument used for the analysis) by qualitative identification of the analyte(s) in a QC sample in each quality system matrix containing the analyte at no more than 3*x* the LOD for single analyte tests and 4*x* the LOD for multiple analyte tests. Refer to TNI (2009) V1M4, 1.5.2.1 for additional requirements and information.

2.1.5. Limit of Quantitation (LOQ) Verification: The test method PQL for each analyte shall also be defined as the LOQ. The LOQ is verified by successful analysis of a QC sample containing the analytes of concern in each quality system matrix at a concentration of 1-2*x* the claimed LOQ. A successful analysis is one in which the recovery of each analyte is within the established test method criteria (where provided at the LOQ) or client data quality objectives for accuracy. Additional information can be found in TNI (2009) Standard, EL-V1M4, *Quality Systems for Chemical Testing.*

2.2. **New or Alternative Methods:** When encountering situations listed in section 1.1.d and 1.1.e, follow the method validation requirements in the "New and Alternative Analytical Laboratory Methods", DEP-QA-001/01, referenced in QA Rule 62.160 of Florida Administrative Code. Check with the QA officer for an up-to-date copy of this document before proceeding with the validation. Below is the summary of the procedure.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

2.2.1. Choose the limited-use method, which is intended to be used only by our laboratory for the testing of an analyte (or analytes) in a sample matrix of interest. A statewide-use method is, in most instances, not applicable to our laboratory's needs.

2.2.2. Conduct MDL, precision and accuracy determinations.

2.2.3. If an alternative method validation is being conducted, an equivalency study will be required. Prepare seven (7) matrix replicates each for the alternative method and the method intended to be replaced. Statistically evaluate the equivalency of the two methods at 95 % confidence interval.

2.2.4. Submit required documentation to Quality Assurance Subsection of the FDEP Water Quality Standards program for review and approval. For certain EPA projects, such as NPDES or drinking water associated projects, validation documentation may need to be further submitted to EPA Region 4 for review and approval. In addition, consult with clients as to whether NELAC certification is required or not. Apply for NELAC certification with the Florida Department of Health in Jacksonville as needed.

2.3. **New Instruments:** When encountering the situation listed in section 1.1.f., first bring instrument and software up to factory specifications.

2.3.1. Sensitivity Study. If required, conduct instrument detection limit (IDL) determination. The IDL should be equal to or lower than the established MDL. The IDL is determined in the same manner as the MDL but without any sample processing steps included.

2.3.2. Stability Study. If required, prepare a continuing calibration verification (CCV) standard and perform 4 to 7 replicate analyses. The % RSD (relative standard deviation, a measure of reproducibility) and chromatographic retention time window (if applicable) must be equal or better than established method requirements.

2.3.3. Perform method calibration procedure. Compare the correlation coefficient and/or % RSD data for each analyte to the method requirements. The new data must meet method requirements.

2.3.4. All major software upgrades must be validated to ensure that method requirements are met. This validation may include performing an initial calibration, CCV, and blank analysis. If the upgrade is limited to software only and the old analytical data files are compatible with the new software, then a validation may be performed by re-processing an old analytical data set using the new software. The resulting files must be equivalent between new and old sets.

2.4. **Continuing Demonstrations of Capability (CDOC):** For situations involving initial or ongoing demonstrations of capability listed in section 1.1 g., several options are available.

2.4.1. Section 1.6.3.2, V1M4 and V1M5 of the 2009 TNI standard allows for a documented process of analyst review to satisfy requirements for a CDOC.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

For routine analyses that are frequently performed by seasoned lab analysts, the lab's normal workflow for reviewing data before it is reported to the customer serves this purpose well.

Lab analysts generate reports after completing an analytical run that are reviewed by their supervisors. The report typically includes raw instrument data including calibration data and is reviewed by the supervisor for QC failures or other deviations from method requirements. Procedures for the review of routine analytical data are documented in DEP SOPs, LB-026, MT-058, NU-043, VO-010, GC-001, SV-011, BB-031 and BB-032.

Laboratory supervisors will review data from all analytical runs using the protocols described above. The supervisor will look for systematic failures of initial calibration verification samples, continuing calibration verification samples, laboratory control samples, method blanks, surrogates, and other quality control checks that might be appropriate. Systemic failures are those quality control failures having more than the allowed number of marginal exceedances defined in the 2009 TNI standards or failures for which there is no obvious explanation (such as missed autosampler injections, etc.). Analysts will repeat analyses for samples associated with systemic failures; if the analyst is unable to correct the problem on subsequent analyses, the analyst will be re-trained and assigned completion of an Initial Demonstration of Capability (IDOC) before further analytical work on client samples can be submitted for approval.

This review of routine QC data by lab supervisors is an active, ongoing process that evaluates the capability of the analyst on a continuing basis. When the supervisor finishes the review, he/she signs off the analyst's bench sheets and lab report and authorizes the data in the LIMS. The sign-off and authorization signify that the analyst has met all QC requirements for that method and has demonstrated the capability to perform the analysis.

Routine QC data from analytical runs including LCS recoveries, matrix spike recoveries, PQL recoveries, sample duplicate precision, blank values, etc. are uploaded to the LIMS as part of the data review and reporting process. This data can be readily retrieved from the LIMS for any analyst and method for verification by an external or internal auditor. Sample duplicate precision may also be used for microbiological testing as a continuing demonstration of capability.

For Wet Effluent Toxicity (WET) tests, the continuing demonstration of capability consists of conducting at least one Standard Reference Toxicant annually by at least one current member of the work unit. Acceptable results for a blind Performance Testing (PT) samples can also serve as a continuing demonstration of capability.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

2.4.2. Alternatively, for analyses that are performed infrequently or analysts that rarely perform the analyses (less than once per quarter), or analyses that do not have available routine QC data, the analyst must perform or satisfy one of the following four options once every 12 months.

2.4.2.1. Analysis of a single blind sample. The blind sample could be prepared by a supervisor or a senior analyst or be purchased from an EPA NELAC-certified chemical standards vendor. The results must fall within our laboratory established accuracy and precision limits for the analytical procedure of the concern if blind sample is prepared in house. Otherwise, the results must pass all acceptable limits provided by the vendor.

2.4.2.2. An initial method demonstration of capability (see section 2.1.)

2.4.2.3. Analysis of at least four consecutive laboratory control samples (LCS) or laboratory fortified blanks for chemical parameters. The results must fall within our laboratory established accuracy and precision limits.

2.4.2.4. Successful analysis of authentic samples with results statistically indistinguishable from those obtained by another trained analyst.

Additional options for Microbiology:

2.4.2.5 Analysis of one sample in duplicate for each target organism and test. The results must meet laboratory precision acceptance criteria.

2.4.2.6 Analysis of one sample or blank spiked with a known quantity of the target organism. The results must meet laboratory accuracy acceptance criteria.

If an analyst fails to demonstrate on-going capability using the criteria listed above, then the analyst must complete a successful initial DOC to demonstrate capability. The analyst will be suspended from reporting data until the successful completion of the initial DOC.

2.5. **Annual LOD Verification**: Refer to DEP SOP LB-031, *Limit of Detection Verification.*

3. ACCEPTANCE CRITERIA

3.1. Method Detection Limit (MDL). The derived detection limits must meet method-prescribed detection levels if they are included. If the derived detection limits cannot achieve the Department's objective, the analyst and supervisor must evaluate and propose options to the Section manager on practical considerations for lowering the detection levels. Modifications may include increasing sample volume, decreasing extract size, adding sample cleanup steps, and improving instrument sensitivity, etc. A Section representative will discuss analytical

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

assessment and limitations and estimated method development cost with clients to determine the extent of analytical modications to be explored.

3.2. Precision and Accuracy. The analyst and supervisor shall ensure that the validated method can achieve the listed acceptance ranges for precision and accuracy in the method, if available. If unavailable, for organic methods, the generally acceptable in-house targets for accuracy should be 60 % to 130 % for all matrices; precision targets shall be 30 % for soil and waste, and 30 % and 25 % for water for chemical and biological analyses, respectively. For inorganic methods, the acceptable targets for accuracy should be 80 % to 120 % for water matrices and 75 % to 125 % for solid matrices and 20 % for precision. If initial testing indicates that these criteria cannot be achieved, break down the procedure into smaller steps to determine where the dominant variations are. Attempt different procedural options to reduce the variance, which in turn will allow a better understanding of the method's limitations. The analyst and supervisor shall present the laboratory findings to the Section manager to determine the acceptable ranges and/or other analytical options. Precision and accuracy criteria for chemical and biological parameters are listed in Tables 5.1 and 5.2 of the Laboratory QA Manual.

4. POST-METHOD-VALIDATION EVALUATION

4.1. Method Detection Limits and Laboratory Background Interferences.

4.1.1. After 20 to 30 analytical runs, evaluate laboratory background interferences against the initial established method detection limits (IEMDL) using available method blanks. If interferences or method blank contamination appear to be clearly higher than the IEMDL, both the analyst and supervisor need to locate the source of interference or contamination and attempt to eliminate or reduce it. If it is deemed not feasible under the current laboratory environment, re-adjust the method detection limit to a level equal to twice the highest detected interferences or contaminant level, excluding outliers. Inform affected clients regarding MDL adjustments.

4.1.2. During on-going practice of a method, if laboratory background interferences, at any time, are observed to be persistently higher than usual, corrective actions need to be taken as in 4.1.1.

4.2. Precision and Accuracy.

4.2.1. After 20 to 30 analytical runs, evaluate precision and accuracy using available laboratory fortified blank data against the initial established acceptable ranges. If statistically significant out of limits are observed, analyst and supervisor need to identify and eliminate/reduce the dominant source of the problem. If it is deemed not possible, the analyst and supervisor will present the case to Section manager to either re-adjust the QC limits, and/or discuss analytical options.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.2.2. If at any time during routine laboratory operations, a method precision and accuracy assessment consistently produces out of control data, corrective actions described in 4.2.1 will be instituted. Re-validation of the method should be considered if corrective actions are not successful.

5. DOCUMENTATION STORAGE

All validation documents must be stored at a designated storage place.

[1] The LOD and demonstrations of capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the the method performance will not be affected by sub-matrix distinctions within these group. Otherwise, LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

Quality System Matrices:

Air and Emissions – including gas and vapor, collected whole or where constituents are concentrated on/in sorbent tubes, impinge solution, filters, polyurethane foam or other air sampling devices or sorbents;

Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;

Biological Tissue – includes all biologically-derived material including plant, animal, fish or shellfish derived material;

Chemical Waste – a product or by-product of an industrial process that results in a material not defined elsewhere; because of unanticipated matrix effects from unknown materials of this nature, it is anticipated that deriving LODs for this sub-matrix category would be pursued upon client request only for specific well-defined projects and materials;

Drinking Water – water from a designated potable source;

Non-aqueous Liquid – an organic liquid with < 15 % solids; because of unanticipated matrix effects from unknown materials of this nature, it is anticipated that deriving LODs for this sub-matrix category would be pursued upon client request only for specific well-defined projects and materials;

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may vary from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

Solids – includes soils, sediments, sludges and other materials with > 15 % settable solids.

6. REFERENCES

6.1. DEP SOP LB-026, *Job Level Authorization Checklist.*

6.2. DEP SOP LB-031, *Limit of Detection Verification*

6.5. DEP SOP MT-058, *Procedure for Metals Data Review and Authorization.*

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

6.5. DEP SOP VO-010, *Data Review/Authorization Procedures for the Volatile Organics and Methyl Mercury Laboratory.*

6.6. DEP SOP GC-001, *Quality Assurance/Quality Control in the GC Pesticides Laboratory.*

6.7. DEP SOP SV-011, *BNA Group Data Review/Authorization Checklist.*

6.8. DEP SOP BB-031, *LIMS QC Manager Data Uploading Instructions for Bench Biology and Microbiology Samples.*

6.9. DEP SOP BB-032, *Test Level Authorization of Uploaded Results for Bench Biology Samples.*

6.10. TNI (2009) Standard, EL-V1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis;*

6.11. FDEP Quality Manual

APPENDIX OF CHANGES

04/01/2010 Added text related to quality system matrices

02/14/2012 Revised the criteria used for on-going or continuing demostrations of capability in section 2.4.

10/05/2012 Revised the criteria used for on-going or continuing demostrations of capability in section 2.4. Added section 6 for references.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.