Applying for a Distillation Variance

Commonwealth of Pennsylvania
Department of Environmental Protection
Laboratory Accreditation Program

Table of Contents

1.0 Introduction

All non-potable water testing for compliance with the Environmental Laboratory Accreditation Regulations, 25 Pa Code, Chapter 252 ("Chapter 252"), the National Pollutant Discharge Elimination System ("NPDES") Program, or the Clean Water Act ("CWA") must be performed using a method that is approved by the United States Environmental Protection Agency ("USEPA"), if the USEPA has approved a test procedure for analysis of the specific pollutant (§ 252.307.b and 40 CFR 136.1). Therefore, if a USEPA approved method exists for a given analyte, and a laboratory is testing for that analyte in a sample that is for compliance purposes, the laboratory must follow one of the methods approved by the USEPA. The list of approved methodology for such testing is listed in Title 40 of the Code of Federal Regulations ("CFR"), Part 136.3. Exceptions to the list of approved methodology at 40 CFR 136.3, include methods approved through the USEPA Alternate Test Procedure ("ATP") Program (40 CFR 136.4, 136.5), or methods established as equivalent pursuant to the USEPA's regulations regarding "Method Modification and Analytical Requirements" (40 CFR 136.6).

When testing for certain analytes, the listing of approved methodology requires that manual distillation be performed prior to sample analysis, unless comparability data for representative effluent samples are on file to demonstrate that preliminary distillation is not necessary. However, manual distillation is required to resolve any controversies arising over the results of sample analyses performed without preliminary distillation (40 CFR 136.3, Table 1B, Footnote 6).

When laboratories wish to eliminate the preliminary distillation step from testing performed for Chapter 252, NPDES or CWA compliance, prior approval from the PA Department of Environmental Protection, Laboratory Accreditation Program ("Department") must be obtained. This document describes the procedure for requesting a distillation variance from the Department.

2.0 Who May Apply

2.1 Waste Stream/ Analyte/ Method Combinations

A waste stream is defined as the effluent or product of a ***single*** treatment processing system. The waste stream begins at the entry point for materials into the treatment system, and the waste stream ends at the discharge point for materials from the treatment system. Therefore, each effluent from a wastewater treatment facility, industrial pretreatment process, landfill leachate collection system, point source, outfall or discharge point subject to modified or alternate treatment processes, etc., is considered a separate waste stream. Sometimes separate waste streams may be identified by the issuance of a different NPDES or other discharge permit for each waste stream. Other times, different waste streams may fall subject to the same NPDES permit. For example, in a Wastewater Treatment Facility solid material is separated from the water and treated through a different process. Both the solids and the water are governed by the same NPDES permit. However, the solids and the water represent two different waste streams since they are separated and treated by different processes.

For testing purposes, each waste stream is considered a separate matrix, regardless of the traditional matrix categories defined in Chapter 252 and by the USEPA. For example, if a facility discharges water at two different discharge points, and the effluent from each point has been carried through different treatment processes, each effluent is considered a separate waste stream, and therefore, a separate matrix. Even though, traditionally, these two effluents are considered part of the non-potable water matrix.

Distillation variances are issued for a specific waste stream. Therefore, each waste stream requires a separate distillation variance application and is subject to separate study and evaluation. The

distillation variances are also unique to the analyte tested and the method used to test for that analyte. If a facility requests to eliminate the distillation step from ammonia analysis by Ion Selective Electrode ("ISE"), following *Standard Methods*, SM 4500-NH3 D, then the distillation variance will only apply to ammonia analysis by SM 4500-NH3 D. If the facility wishes to change the analytical method used to analyze ammonia samples from ISE to nesslerization, a separate distillation application must be submitted for the new method. Similarly, if the facility wishes to obtain a distillation variance for another anlayte, such as fluoride, a separate distillation application must be submitted for the new analyte.

2.2 Facility vs. Laboratory

Distillation variances are granted to the facility that generates the waste stream, even if the facility does not operate the laboratory that performs the analytical testing on the waste stream. Distillation variances will not be granted to any subcontracted laboratories that perform analytical testing only. Therefore, applications must be submitted by the facility that generates the waste stream, regardless of where the testing is performed. Any facility may apply for a distillation variance for use by their in-house laboratory or for a subcontracted laboratory that performs the testing. However, the facility that applies for the distillation variance must submit the application and supporting materials to the Department and maintain the appropriate records, in accordance with Section 4.0 of this document.

2.3 Drinking Water Testing

Distillation variances are not applicable to testing of the drinking water matrix. Variance applications for any testing performed under the National Primary Drinking Water Regulations ("NPDWR") (40 CFR 141) or the Safe Drinking Water Act ("SDWA") (35 P.S. §§ 721.1-721.17) will be denied. If testing for compliance with NPDWR or SDWA requires the distillation of samples prior to analysis, the distillation step must be performed, and the facility may not receive a distillation variance.

3.0 Comparability Study

In general, labs must perform a comparability study on each waste stream by analyzing duplicate samples with and without the preliminary distillation step. The results are statistically evaluated to determine whether the data are comparable. Facilities are permitted to employ a contracted laboratory to perform the comparability study. However, the contracted laboratory must be accredited by the Department for the Field(s) of Accreditation ("FOA") for which the variance application is submitted. For example, if a facility applies to eliminate the distillation step from the nesslerization method found in *Standard Methods*, SM 4500-NH3 C (18th ed.), and the facility subcontracts a laboratory to perform the comparability study, the subcontracted lab must be accredited by the Department for ammonia by SM 4500-NH3 C, for non-potable water. The data from the comparability study are submitted to the Department, along with the *Application for a Distillation Variance* form (Section 5.0). The Department will evaluate the results of the comparability study and approve or deny the facility's application.

3.1 Number of Samples & Sampling Location

Seven (7) ***non-***consecutive, representative effluent samples must be collected and analyzed for the comparability study. The sampling should occur over several months, collecting one sample every week or every other week for the study. The facility must develop its sampling plan so that the samples chosen for the comparability study give a representative evaluation of the facility's effluent. If a facility does not choose representative effluent samples for the comparability study, the Department may revoke the facility's distillation variance (Section 6.2). Refer to the definition of *Non-consecutive sample* in Appendix A of this document to ensure that sampling is appropriate for the comparability study.

The seven samples used in the comparability study must be collected from the sampling location required by the facility's discharge permit for the finished and final effluent. If a sampling location is not specified in the facility's discharge permit for the finished and final effluent, then the sample must be

collected from the sampling location routinely used to collect compliance samples for the facility. Under certain circumstances, such as non-detectible analyte concentrations in the final effluent, facilities are permitted to sample from alternate locations. See Section 3.3.3, for additional information regarding permissible alternatives to analyzing the final effluent for the comparability study.

3.2 Sample Collection, Preservation & Holding Time

All samples for use in the comparability study must be collected in accordance with the facility's permit or the required containers, preservation techniques and holding times specified in the Code of Federal Regulations (40 CFR 136.3.e, Table II). For example, 40 CFR 136.3.e, Table II, requires that samples for ammonia analysis be collected in polyethylene, fluoropolymer or glass containers; preserved by refrigeration at ≤6ºC and adjustment to pH<2 with H_2SO_4; and held prior to analysis for no more than 28 days from collection. If ammonia samples are analyzed within 24 hours of collection, the chemical preservation to pH<2 may be omitted. If the facility's permit gives specific container, preservation and holding time requirements that contradict those given in 40 CFR 136.3.e, Table II, the permit supercedes the Federal requirements for the life of the permit.

Samples must also be collected in accordance with the facility's discharge permit for the analyte for which the variance application is submitted. For instance, if the facility's permit requires that 24-hour composite samples are used for compliance monitoring of ammonia, and the facility applies for a distillation variance for ammonia, then 24-hour composite samples must be used in the comparability study.

Composite samples collected with automated samplers and split into separate aliquots for preservation and analysis must be refrigerated during collection, and the aliquots must be preserved within 15 minutes of collection. For these samples, the collection time is the time at which the final aliquot of the composite sample has been collected, and the holding time begins at the collection time (40 CFR 136.3, Table II, Footnotes 2 & 3).

Facilities must consult the individual reference methods for any additional sample treatment required at the time of collection. For example, *Standard Methods* (20th ed.) requires that samples for ammonia analysis that are likely to contain residual chlorine be dechlorinated with sodium thiosulfate immediately upon collection, since chlorine reacts with ammonia (SM 4500-NH_3 A).

Documentation demonstrating that all sample container, preservation and holding time requirements were satisfied for the samples used in the comparability study must be retained by the facility to which the distillation variance is issued. These records must be retained for the life of the variance (Sections 4.0 & 6.1). If the facility that is issued the variance has subcontracted a laboratory to perform the comparability study, the facility must obtain such documentation from the laboratory. Usually, this information is available on the Chain of Custody form.

3.3 Sample Analysis

3.3.1 Methodology

The laboratory performing the comparability study must split the seven effluent samples into two duplicate aliquots. One aliquot must be analyzed according to the reference method used, including the required preliminary distillation protocol. The duplicate aliquot must be analyzed according to the same method, omitting the preliminary distillation procedure. The method used for the comparability study must be approved for use by the USEPA for analysis of the specific analyte (40 CFR 136.3). See Section 1.0, for additional information regarding approved methodology.

Laboratories must perform the comparability study using both sample aliquots following the same reference method, with and without distillation, and using the same determinative technique. For example, a laboratory cannot analyze one set of aliquots using manual distillation with titration as the

determinative step. Then, analyze the duplicate aliquots without distillation using an Ion Selective Electrode ("ISE") as the determinative step. The duplicate aliquots used in the comparability study must be analyzed under the exact same conditions, with the only difference being the presence or absence of the distillation step.

In addition, the comparability study must be performed using the same reference method and determinative technique as that used to analyze routine samples and using the same method indicated on the distillation variance application. For example, if a laboratory analyzes ammonia samples using a nesslerization technique and applies for a distillation variance, the comparability study may not be performed using ISE, since ISE is a different determinative technique than nesslerization. If a laboratory wishes to obtain a variance for a different determinative technique than that used for routine sample analysis, the new technique must be used henceforth for the analysis of routine samples. This must be indicated on the facility's distillation variance application (*Application for a Distillation Variance*, Part B, Item 7).

The samples used in the comparability study must be analyzed in accordance with all applicable sections of Chapter 252 and the reference method used. Sample analysis must include the appropriate initial and continuing instrument calibrations and all appropriate Quality Control ("QC") measures. Chapter 252 requires at least a method blank, laboratory control sample ("LCS") and a duplicate sample be analyzed with each batch of samples (§ 252.402). Additional QC measures, such as matrix spikes, may be required by the reference method used. Refer to the individual reference methods for additional QC requirements.

3.3.2 Reporting Results

The final sample results must be reported in accordance with Chapter 252 and the facility's discharge permit. Sample results must be reported in the proper units, as required by testing program, permit, order, agreement or reference method used. The final sample report must also contain any data qualifiers associated with the data, if applicable.

3.3.3 "Non-Detects"

Data qualified as "non-detect", any sample result that is less than the Quantitation Limit ("QL") for the method, may not be used in the comparability study. Results above the established QL are required for use in the statistical calculations used to compare data submitted for a distillation variance. If a non-detect, less than value, or other result that is less than the QL for the method is obtained for one or more of the seven sample results, the facility must collect and analyze additional samples to yield a total of seven detectible results. If a facility cannot obtain detectible sample results from their finished effluent, the facility may collect samples back through their treatment process to obtain a sample with detectible analyte concentrations. Alternatively, facilities are permitted to "spike" the effluent samples with a known amount of the target analyte to obtain detectible analyte concentrations. However, the effluent sample must be spiked. No Laboratory Control Samples ("LCS") will be accepted as part of the comparability study. Laboratories must indicate that the effluent samples were spiked on the final sample report.

4.0 Recordkeeping

When the comparability study is performed by the facility's in-house laboratory, the facility must retain all raw data records necessary to reconstruct the laboratory activities associated with the analysis of the samples and generation of the final results used in the comparability study, including appropriate initial and continuing instrument calibrations, results of appropriate QC measures, standard and reagent preparation log books, etc. These records must be maintained in accordance with Chapter 252 (§252.706), retained for the life of the variance (Section 6.0), and must be available to Department

personnel during the facility's on-site assessment and upon request. Each facility must also retain a copy of the letter granting the distillation variance for the life of the variance.

When the comparability study is performed by a subcontracted laboratory, the facility issued the variance must retain a copy of the samples' Chain of Custody forms, the final sample testing reports from the laboratory, and the letter granting the distillation variance. These materials must be maintained in accordance with Chapter 252 (§ 252.706), retained for the life of the variance, and must be available to the Department upon request. In addition, the subcontracted laboratory must retain all raw data records necessary to reconstruct the laboratory activities associated with the analysis of the samples and generation of the final results used in the comparability study, including appropriate initial and continuing instrument calibrations, results of appropriate QC measures, standard and reagent preparation log books, etc. These records must be maintained in accordance with Chapter 252 (§252.706), retained for the life of the variance (Section 6.0), and must be available to Department personnel during the laboratory's on-site assessment and upon request.

5.0 Assembling the Application Package

To apply for a distillation variance, submit the following materials to the Department:

1. Submit a completed "*Application for a Distillation Variance*" form. Application forms are available from the Laboratory Accreditation Program web page. Visit www.depweb.state.pa.us/labs, and select "Laboratory Accreditation Program" from the menu bar at the left-hand side of the screen. The "*Application for a Distillation Variance*" form is located under the heading "Forms and Applications". Applications may also be requested by contacting the Department via email at eplabaccredit@state.pa.us or by phone at (717) 346-7200.

2. Submit copies of the final results for the seven samples used in the comparability study. Only the final sample results should be included with your application. *Do not submit raw data necessary to reconstruct the analysis.* Raw data records must be retained in accordance with Section 4.0. If a facility has employed a contracted laboratory to perform the comparability study, copies of the original final sample report provided by the contracted laboratory must accompany the facility's variance application.

Send all application materials to:

US Postal Service:

PA Department of Environmental Protection
Bureau of Laboratories
Attn: Laboratory Accreditation Program
PO Box 1467
Harrisburg, PA 17105-1467

All other modes of delivery (UPS, FedEx, etc.):

PA Department of Environmental Protection
Bureau of Laboratories
Attn: Laboratory Accreditation Program
2575 Interstate Drive
Harrisburg, PA 17110-9332

6.0 What to Expect Next

The Department will statistically evaluate the facility's comparability study and approve or deny the facility's application based upon the data submitted and the facility's discharge requirements. The facility will be notified in writing of the Department's determination.

6.1 Scope & Use of Variance Approval

Facilities will be notified in writing upon approval of the distillation variance application. Variance approvals may only be used for the analyte and waste stream combination indicated in the approval letter. Any waste stream or analyte other than that specified in the approval letter must be analyzed using the required preliminary distillation procedures, if applicable. A separate variance application must be submitted for each additional waste stream/analyte combination.

The variance approvals are also specific to the analytical method used in the comparability study. If the analytical method used for testing compliance samples is changed to a method other than that used in the comparability study, then the facility must submit another distillation variance application for the new method. The facility must ensure that compliance samples are processed using the required preliminary distillation procedures until a variance is issued for the new method. In addition, if a facility with a distillation variance that routinely processes samples without preliminary distillation suspects that interferences are affecting the quality of the analytical data produced, the facility must re-evaluate the need for distillation by performing another comparability study and submitting the results to the Department for review. Manual distillation is required to resolve all controversies arising over the sample results generated without preliminary distillation, even if a distillation variance for the waste stream and analyte has been granted (40 CFR 136.3, Table 1B, Footnote 6).

*All distillation variances will **expire** 5 years from the date of issue.* Therefore, facilities must reapply for a variance every 5 years, or begin processing compliance samples using the required preliminary distillation procedures once the current variance expires. See Section 6.4, for information on distillation variance renewal.

6.2 Revocation of Variance

The Department may revoke a facility's distillation variance for any of the reasons listed in Section 6.3, regarding Denial of Variance Application. The Department may also revoke a facility's distillation variance if the facility is unable to retrieve the raw data and records necessary to reconstruct the comparability study (Section 4.0), or if the facility has knowingly used samples in the comparability study that are not representative of the waste stream. Upon revocation of a facility's distillation variance, the facility must immediately begin processing all compliance samples using the required preliminary distillation procedures.

6.3 Denial of Variance Application

If the Department denies a facility's distillation variance application, the facility will be notified in writing. The Department may deny a facility's application for one or more of the following reasons:

1. Data from the comparability study was evaluated and failed the statistical criteria established by the Department and the USEPA.
2. The facility or laboratory demonstrates an inability or lack of intention to perform the comparability study in accordance with Section 3.0.
3. Falsifying the comparability study.
4. Making misrepresentations to the Department.
5. Failure to submit a complete distillation variance application.
6. Violation of a statute, Chapter 252 or a permit, order or agreement administered by the Department.
7. Engaging in or suspected of engaging in unethical or fraudulent practices.

The above list is not exhaustive, but it is intended to provide examples of reasons the Department may deny a facility's distillation variance application.

If denied a distillation variance, a facility may reapply for the variance by repeating the procedure outlined in this document. The facility must wait at least 6 months from the date of the denial to submit another distillation variance application to the Department.

6.4 Variance Renewal

All issued variances will expire 5 years from the date of issue. Therefore, facilities must submit a renewal variance application every 5 years. The renewal variance applications must be submitted to the Department *at least 60 days prior* to the expiration of the current distillation variance. To obtain a renewal variance, follow the procedure for submitting the initial variance application, as outlined in this document. Renewal applications must be submitted in accordance with Section 5.0. The facility must indicate on the application form ("*Application for a Distillation Variance*") that the application is for renewal, by selecting "Renewal" in Part B, Item 1.

A comparability study must be conducted for the renewal application in accordance with Section 3.0, with the following exceptions:

1. The data used in the comparability study must be from samples collected within one year prior to submittal of the renewal variance application.

2. The samples used in the comparability study must be collected in the next quarter following the quarter in which the previous set of study samples were collected. The quarters are defined as follows:
   1) January 1 – March 31
   2) April 1 – June 30
   3) July 1 – September 30
   4) October 1 – December 31

   The quarter in which the study samples were collected must be indicated on the renewal application form ("*Application for a Distillation Variance*") in Part B, Item 2. Refer to the definition of *Non-consecutive Sample* in Appendix A of this document.

   When a facility has a decreased monitoring requirement for the analyte requested on the distillation variance application, the facility may increase their sampling frequency to collect samples for the comparability study. For example, Happytown Wastewater Treatment Plant is required to collect and analyze samples for ammonia once per quarter. Therefore, collecting seven samples would take more than one year to complete. Happytown Wastewater Treatment Plant may collect one sample per week to obtain the seven samples required for the comparability study. Happytown's discharge permit requires that all sample results be reported to the Department on the monthly DMR form. Therefore, the ammonia results from the extra samples must be included on the DMR form for the appropriate months.

6.5 Variances Issued Prior to 9/1/2007

If a facility had been issued a variance by the Department prior to 9/1/2007, the facility must reapply for a variance in accordance with the procedure outlined in this document by 9/1/2012. Failure to reapply for the previously issued variance by 9/1/2012 will result in revocation of the facility's variance. See Section 6.2 above. Facilities reapplying for a variance that was issued prior to 9/1/2007 should follow the instructions in Section 6.4, regarding Variance Renewal. For renewals of these variances, the information regarding sampling quarter may be omitted from the application.

Appendix A: Definitions

Analyte: The component, compound, element, or isotope to be identified or quantified using a test or analysis.

Batch: 1-20 environmental samples of the same matrix prepared and analyzed together using the same procedures, personnel, and lots of reagents and standards, with a 24-hour maximum allowable time between the start of processing the first sample and the start of processing the last sample.

Drinking Water: Any aqueous sample that has been collected for the purposes of demonstrating compliance with the Pennsylvania Safe Drinking Water Act (35 P.S. §§ 721.1 – 721.17) or from a potable or potentially potable water source.

Duplicate Sample: Two identical sample aliquots analyzed separately using identical procedures. Analysis of duplicate samples gives a measure of the precision associated with laboratory procedures.

Facility: Any entity (sole proprietor, partnership, corporation, association, institution, cooperative enterprise, municipal authority, political subdivision, Federal government or agency, State institution or agency, or other legal entity), which is recognized by law as the subject of rights and duties or is issued a discharge permit that is administered by the Department.

Field of Accreditation (FOA): A combination of matrix, method or technology, or both, and analyte or analyte group for which a laboratory may be accredited.

Holding Time: The maximum amount of time allowed by regulation to elapse between sample collection and initiation of testing or analysis.

Laboratory Control Sample (LCS): A blank matrix, free from the analyte(s) of interest, spiked with a verified, known amount of method analyte(s). Also known as a Laboratory Fortified Blank (LFB) or spike blank.

Matrix: The media of a sample that contains the analyte(s) of interest. Examples are drinking water, non-potable water and solid and chemical materials.

Non-consecutive Sample: Samples not taken in immediate succession. Grab samples with greater than 24 hours between sample collection times are considered non-consecutive samples. Composite samples with greater than 48 hours between sample collection times are considered non-consecutive samples.

Non-potable Water: Any aqueous sample excluded from the definition of drinking water matrix. The term includes wastewater, ambient water, surface water, groundwater, effluents, water treatment chemicals, and toxicity characteristic leaching procedure or other extracts.

Quantitation Limit: The minimum concentration or activity of analyte that can be reported as a final result with a specified degree of confidence. The Quantitation Limit must be equal to or greater than the lowest calibration standard analyzed.

Reference method: The published scientific method or technique used to perform testing or analysis.

Waste Stream: The effluent or product of a single treatment process. The waste stream begins at the point where material to be processed enters a treatment facility or system, and the waste stream ends at the point where the material is discharged from that treatment facility or system. Each waste stream is considered a separate matrix.