Distillation Variance Procedure

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Commonwealth of Pennsylvania
Department of Environmental Protection
Laboratory Accreditation Program

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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).

Footnote 6 of Table 1B in 40 CFR 136.3 states, "Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation."

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 Applicability

2.1 Methodology

2.1.1 Ion Chromatography ("IC")

Laboratories performing analysis of samples using IC are not required to perform comparability studies or submit an application for approval of a distillation variance. The nature of IC removes potential interference and laboratories are permitted to analyze compliance samples without the preliminary distillation step when analyzing samples with IC.

2.1.2 Ion Selective Electrode ("ISE")

Laboratories performing analysis of samples using ISE are required to perform an abbreviated comparability study. This abbreviated study and evaluation of the data is described in Section 3.1.1 of this procedure.

2.1.3 Titration or Spectrophotometer

Laboratories performing analysis of samples using titration or a spectrophotometer are required to perform comparability studies and submit an application for approval of a distillation variance. The Department will review the application and determine if a variance can be granted before the laboratory may choose to analyze compliance samples without the preliminary distillation step. The comparability study and application submission requirements are described in Sections 3.1.2 and 5.0 of this procedure.

2.2 Waste Stream/ Analyte/ Method Combinations

The Department requires that each waste stream be evaluated for potential interference before allowing the elimination of the distillation step. 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 for a particular methodology. Therefore, each waste stream requires a separate comparability study. 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-NH_3 D, then the distillation variance will only apply to ammonia analysis by SM 4500-NH_3 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 analyte, such as fluoride, a separate distillation application must be submitted for the new analyte.

2.3 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.

2.4 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

The Department's application of the 40 CFR 136.3, Table 1B, Footnote 6 explanation of the distillation variance procedure is as follows:

- Labs must perform a comparability study on each waste stream by analyzing either one or seven samples per waste stream depending on the analytical methodology performed.
- 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 method and analyte (for example Ammonia by Ion Selective Electrode) for which the variance sought.

3.1 Number of Samples & Sample Analysis

The 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.

3.1.1 Ion Selective Electrode

One (1) effluent sample must be collected and analyzed for the comparability study.

The laboratory is not required to distill the samples for this study. The accredited laboratory must analyze the un-spiked sample, a matrix spike, and matrix spike duplicate of this sample for a total of three (3) analyses of the same sample. The concentration of the MS and MSD must be the same and must be analyzed within the same analytical batch.

The % Recovery of the un-spiked sample as compared to each MS and MSD must be between 90-110% and the RPD of the MS and MSD must be < 20%. If these criteria are met, the laboratory may assume "comparability" and a distillation variance application is not required. Refer to Section 4.0 for Recordkeeping requirements and Appendix A for calculations. Analysis of subsequent compliance samples from the same waste stream may occur without the preliminary distillation step.

If the % Recovery is not within 90-110% or the RPD is > 20%, analysis of compliance samples from the waste stream will require a preliminary distillation step.

3.1.2 Titration or Spectrophotometer

Seven (7) ***non-***consecutive, representative effluent samples must be collected and analyzed for the comparability study. 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.

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 deny or revoke the facility's distillation variance (Section 6.2).

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.

The samples results used in the variance application must contain a measureable amount of the target analyte. Samples resulting in concentrations below the lowest calibration standard cannot be included in the seven samples used to determine if a variance can be granted. The measured concentration of the samples must be at least three times ("3X") the concentration of the lowest calibration standard used to establish the initial calibration. A facility that has historically low or non-detect concentrations of the target analyte must spike both of the duplicate aliquots, prior to distillation, with an appropriate amount of the analyte to obtain a concentration of at least 3X the lowest calibration standard.

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). Refer to the individual reference methods for additional QC requirements.

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 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.

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.

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 Application Package

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

1. Submit a completed "*Distillation Variance Application*" 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 right-hand side of the screen. The "*Distillation Variance Application*" form is located under the heading "Forms and Applications". Applications may also be requested by contacting the Department via email at eplabaccredit@pa.gov 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 Evaluation of the Variance Application

6.1 Approval of a Variance Application & 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).

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.

6.2 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 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.

6.2 Revocation of Variance

The Department may revoke a facility's distillation variance for any of the reasons listed in Section 6.2, 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.

Appendix A: Calculations

A.1 Percent Recovery of Matrix Spike Sample

$$\%Rec = \frac{(C_m - C_b)}{C_k} * 100$$

Where,
%Rec = the percent recovery of the analyte of interest (%)
C_k = the true value of the spike added to the sample (mg/L)
C_m = the measured concentration of the MS or MSD (mg/L)
C_b = the measured concentration of the un-spiked sample (mg/L)

A.2 RPD of the Matrix Spike and Matrix Spike Duplicates

$$RPD = \frac{|(C_1 - C_2)|}{((C_1 + C_2) / 2)} * 100$$

Where:
RPD = the relative percent difference between the two measurements (%)
C_1 = the measured concentration of the MS (mg/L)
C_2 = the measured concentration of the MSD (mg/L)