EPA Region III Interim Guidelines for the Validation of Data Generated Using Method 1668 PCB Congener Data

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EPA Region III Interim Guidance for the Validation of Data Generated Using Method 1668 Toxic, Dioxin-like PCB Data

The Quality Assurance Team developed interim procedures to be applied when validating PCB data generated using Method 1668, Revision A. The procedures specified in this document are to be used to assess the quality of PCB congeners in a variety of matrices. The following documents were used to develop these data validation procedures: *Region III Modifications to the National Functional Guidelines for Organic Data Review* (September 1994), *National Functional Guidelines for Organic Data Review* (February 1994), the quality control (QC) requirements of EPA Method 1668A (December 1999), the *EPA Region 10 SOP for the Validation of Method 1668 Toxic, Dioxin-like, PCB Data* (December 1995), and the *Region III Dioxin Data Validation SOP* (March 1999). For a complete explanation of the data qualifiers described in this document refer to *Region III Modifications to the National Functional Guidelines for Organic Data Review* (September 1994).

1 Holding Times and Preservation of Samples

1.1 **Review Items**: Form I (or similar laboratory analytical report form), EPA Sample Traffic Report and/or chain-of-custody, raw data, and the SDG Narrative.

1.2 **Objective**

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to time of extraction. In addition the time of extraction to the time the samples were injected is evaluated.

1.3 **Criteria**

Technical requirements for sample holding times for the measurement of PCBs as Aroclors, have only been established for water matrices. The holding times for soils or other matrix are currently under investigation.

The holding time criteria for water samples, as stated in the current 40 CFR Part 136 (Clean Water Act) is as follows:

> For Aroclors in cooled (@4^{o}C) water samples, the technical holding time is 7 days from sample collection to extraction and 40 days from sample extraction to analysis.

The holding time and preservation requirements of PCB congeners in non-water matrices

have not been promulgated by EPA. Therefore, the data validator should used the holding time specified in the EPA approved site-specific Quality Assurance Project Plan (QAPP).

Method 1668A, December 1999, recommends different preservation and holding times for PCB congeners. Refer to Section 8.0 of Method 1668A for preservation and holding time recommendations.

EPA Region III recommends the water holding times be applied to water samples only and use the holding time and preservation requirements in Method 1668A for the non-aqueous samples (or those specified in the EPA-approved QAPP).

Matrix	Method 1668A Preservation Requirement	Method 1668A Holding Time Requirement
Water	Test for residual chlorine. When chlorine present add 80mg sodium thiosulfate for each 1L. Adjust pH to 2-3 with sulfuric acid. Store samples in dark @ 4^{o}C	1 year
Soil (semi-solid, oily, mixed phase samples)	Store in wide-mouth bottle @ 4^{o}C; once at laboratory store @ < -10^{o}C	1 year
Fish and Tissue	Wrap fish or tissue sample in aluminum foil, cooled to <4^{o}C. Lab store in dark at <-10^{o}C	1 year while frozen; Thawed tissue samples must be extracted within 24 hours.
Extracts		40 days from extraction

1.4 **Action**

If 40CFR Part 136 and the QAPP for the samples do not specify a holding time, then the holding time which is recommended by Method 1668A should be used. Whenever samples or extracts are analyzed after holding time expiration date, the results should be considered to be minimum concentrations and must be qualified "J." Samples which are not properly preserved should be qualified with a "J" flag. Professional judgement can be used to qualify samples that were stored incorrectly (not frozen) or significantly exceeded the recommended holding time.

2.0 GC/MS Performance Check

2.1 **Review Items**: PFK mass spectra and mass listing and Form V (or similar form).

2.2 **Objective**

The gas chromatograph/mass spectrometer (GC/MS) instrument performance checks stated in Method 1668 (Section 10.2) are performed to ensure mass resolution, identification, and calibration. Conformance is determined using standard materials; therefore, these criteria should be met in all circumstances.

2.3 **Criteria**

Refer to Section 10.2 of Method 1668 for specific criteria.

2.4 **Action**

Failure to meet either the resolution or the retention window criteria invalidates all calibration or sample collection during the 12 hour time window and are to be flagged "R" as rejected.

3.0 Initial Calibration

3.1 **Review Items:** Form VI (or similar laboratory report form), quantitation reports, and chromatograms.

3.2 **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for PCBs. Initial calibration demonstrates that the instrument is capable of producing a linear calibration curve.

3.3 **Criteria**

Determine if calibration was completed by Isotope dilution (Section 10.4 of Method 1668) or by internal standard method (Section 10.5 of Method 1668). Follow the criteria provided in these sections of the method unless otherwise specified in the QAPP.

3.4 **Action**

If any of the criterion for either calibration method were not met then the result is to be flagged "J" as estimated. If the RSD exceeds 20% for those analytes analyzed by isotope dilution or 35% for those analytes analyzed by the internal standard method, qualify

positive results “J” as estimated and non-detected analytes using professional judgement.

4.0 Calibration Verification Measurements

4.1 **Review Items:** Form VII (or similar form), quantitation reports, and chromatograms

4.2 **Objective**

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument remains capable of producing acceptable qualitative and quantitative data each day that the samples are measured.

4.3 **Criteria**

Refer to Section 15.3 of Method 1668A for specific criteria.

4.4 **Action**

The reviewer should use professional judgement to determine if it is necessary to qualify the data. The following are guidelines:

> If the %D for an analyte is outside the acceptance window, flag positive results “J” and non-detected results “UJ” for that analyte. If the ion abundance criteria are not met results are flagged. “R” as rejected.

5.0 System Performance

5.1 **Review Items:** Quantitation reports and chromatograms

5.2 **Objective**

The performance of the method by the laboratory is examined by determination of the laboratory's ability to perform the method (Initial Precision and Recovery (IPR) Study) and to demonstrate the laboratory's continuing ability to perform the analysis. Refer to Section 15.5 of Method 1668A for ongoing QC requirements.

5.3 **Criteria**

IPR - All cleanup steps used in processing samples shall be included in the IPR study. All analytes shall be within the IPR limits and those listed in Method 1668A. There will be one ongoing precision and recovery aliquot (OPR) sample for each sample set analyzed (batch). The recovery of labeled spiked isomers in samples shall be within the QC limits specified in Table 6 of Method 1668A.
QC limits such as required relative retention times of labeled and native isomers,

theoretical ion abundance rations, recovery limits for OPR and VER standards, and recovery limits for spiked labeled target compounds must be within control limits of Method 1668A.

5.4 **Action**

Results for analytes which do not meet either IPR or OPR requirements should be qualified with either "J" or "UJ." If an analyte is not recovered for an OPR sample, results must be flagged "R" as unusable for that analyte. Failure to meet QC limits of the method may result in measurement values which are flagged "J" or "UJ." In specific cases where major QC limits are exceeded, the data validator may determin that the measurement system is out of control, which would require that all measurement results for a sample be flagged "J" , "UJ" or "R."

6.0 Compound Identification

6.1 **Review Items:** Quantitation reports, Form Is (or similar form), and chromatograms

6.2 **Objective**

The qualitative criteria for target compound identification are provided in EPA Method 1668A to minimize the number of erroneous identifications. An erroneous identification can be either a false-positive (reporting a target compound when it is not present in the sample), or false-negative (not reporting a compound that is present in the sample). Interferences can occur with this method (chlorinated substances such as other PCB congeners, polychlorinated dioxins and furans (PCDDs/PCDFs), methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides that might be found at concentrations several orders of magnitude higher than the analytes of interest. Therefore, Method 1668A established criteria for establishing the present of an analyte are described.

6.3 **Criteria**

The qualitative identification criteria specified in Method 1668 (Section 16.0) must be met for a GC peak to be identified as a PCB congener.

A. The signals for the two exact m/z's in Table 7 must be present and must maximize within the same two scans (Section 16.1)

2. The signal-to-noise ration (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for PCB congener detected in a sample extract, and greater than or equal to 10 for all congeners in the calibration and verification standards (Section 16.2)

3. The ratio of the integrated areas of the two exact m/z's specified in Table 7 must be within the limit in Table 8, or within ± 15 percent of the ratio in the midpoint (CS-3) calibration or calibration verification (VER), whichever is most recent (Section 16.3).

4. The relative retention time of the peak for a congener must be within the RRT QC limits specified in Table 2, or if an alternate column or column system is employed, within its respective RRT QC limits for the alternate column or column system (Section 16.4)

6.4 **Action**

If all of the criteria for identification in Method 1668A Sections 16.1-16.5 are not met, the congener has not been identified and the result for that congener is not to be reported by the laboratory or on the data summary form (validation report). Professional judgement is to be used for determining if congener overlaps (interferences) have occurred. When this occurs all of the identification criteria (Sections 16.1-16.4) may not be met. There may be loss of one or more chlorines from a highly chlorinated congener causing inflated or false concentration for a less-chlorinated congener that elutes at the same retention time. If ion abundance criterion for a detected analyte is outside " 15% theoretical ion abundance ratio but within Region 3 expanded " 25% (note: This expanded criterion is based on the Region III Dioxin/Furan Data Validation Guidance, March 1999.), report positive result as the congener and qualify "J" on the DSF. If ion abundance ratio is outside the " 25%, confirm the value is reported as EMPC by the laboratory.

If internal standard ion abundance ratio is outside " 15% ratio, notify Region 3 WAM for action. When the standards are not positively identified by a laboratory, then the stability of mass spectra is in question. Qualify reported results as "N" and reject (R) the non-detects.

7.0 Method Blanks

7.1 **Review Items:** Form Is (or similar form), extraction log(s), quantitation reports, and chromatograms

7.1 **Objective**

The purpose of laboratory (or field) blank analysis is to determine the existence and magnitude of contamination problems resulting from laboratory (or field) activities. The criteria for evaluation of laboratory blanks apply to any blank associated with the samples (e.g., method blanks, instrument blanks, field generated blanks, and cleanup blanks). If problems with any blank exist, all associated data must be carefully evaluated

to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

7.2 **Criteria**

1. No contaminants should be present in the blanks.

2. The criteria for the frequency of extraction and analysis of method blanks as stated in Section 9.5.2 of Method 1668A shall be followed and demonstrated in the documented data. The maximum amount of PCB congener contamination in method blanks is stated in Table 2 of Method 1668A.

3. A method blank must be extracted with each sample batch as stated in Section 15.6 of Method 1668A.

Verify if the laboratory performed blank correction according to Section 17.6.1.4.4 of Method 1668A. Where possible the un-corrected results should be used for the data validation report.

7.3 **Action**

If a method blank is not analyzed or the frequency of measuring method blanks is not met by the laboratory with the data submitted then the results of all samples shall be qualified "R" as unusable. Any measurement of PCB congeners in a sample that is also measured in any associated blank (lab or field), and the sample concentration is less than 5 times the blank concentration, the result in the sample is qualified "B" due to blank contamination.

If field blanks are not included in the data set, the data validation narrative needs to include a caution to the user that field blanks were not available for review and any contamination due to field conditions or cross contamination could not be assessed.

8.0 Recovery of Spiked C-13 labeled PCB Congeners

8.1 **Review Items:** Form Is (or similar form), quatitation reports, and chromatograms

8.1 **Objective**

Labeled PCB Congeners are added to each sample and method blank prior to extraction. The role of these C-13 labeled spiked compounds is to be an internal standard for the quantitation of native PCB isomers and to serve as surrogates for the assessment of method performance in the sample matrix.

8.2 **Criteria**

The recovery of each C-13 labeled PCB isomer (Section 7.12 of Method must be within

recovery limits as specified in Table 6.

8.3 **Action**

If any of the labeled percent recoveries are outside of the limits provided in Table 6, the individual isomer for that sample is to be qualified "J" as estimated value. For non-detected PCB congeners whose percent recoveries are outside the specified limits, the reporting limit for these cogeners are to be qualified "UJ" as estimated reporting limit.

9.0 Project and Regional Quality Assurance Samples (if applicable)

9.1 **Review Items:** Form Is (or similar), quantitation reports, and chromatograms, QAPP and PE audit results.

9.0 **Objective**

All samples which are identified as a field duplicate, transfer blank, blind spike, blind blank, or performance evaluation (PE) sample need to be reviewed.

9.2 **Criteria**

The applicable QAPP should be referred to regarding any QC requirement for the types of samples listed above. Results should be evaluated to determine the laboratory's ability to adequately measure and document results to meet the PARCC requirements of the QAPP.

9.3 **Evaluation**

4. Ensure that PE samples have been evaluated against true values (contact EPA staff for evaluation).

5. Evaluate results from the QC samples listed above to determine if any result indicates poor performance or out-of-control analytical system.

9.4 **Action**

1. Use professional judgement to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

10.0 Overall Assessment of Data Quality

10.1 **Review Items:** Entire data package, data review results, DAS request, and, if available, the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

10.2 **Objective**

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality, and, if possible, the usability of the data.

10.3 **Criteria**

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

10.4 **Evaluation**

1) Evaluate any technical problems which have not been previously addressed.

2) Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

3) If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP, SAP, and communication with the data user that concerns the intended use and desired quality of the data.

10.5 **Action**

1. Use professional judgement to determine if there is any need to qualify data which were not qualified based on the QC criteria previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his/her assessment of the usability of the data within the given context. Reference the Region III Data Validation Reports Requirements, found in Appendix B of the *Region III Modifications to National Functional Guidelines for Organic Data Review* (September 1994).