Point Source Discharger Sampling Workshop for the DRBC Stage 2 PCB TMDL

PCB Analysis by EPA Method 1668A

January 11 & 20, 2005

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EPA Method 1668A

Method Background

- EPA began method development in 1995
- HRGC/HRMS used for selectivity and sensitivity
- Initially focused on the 12 CB congeners designated as toxic by the World Health Organization (WHO)
  - the “WHO list” congeners
- Method was validated in 1995 by one lab
  - Pacific Analytical, Inc.

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EPA Method 1668A

Method Background

- Method published in March 1997 (EPA-821-R-97-001)
- In mid-1997, EPA began expanding the method for analysis of the 209 CB congeners (Method 1668A)
- Method validated by one lab (Axys Analytical Services)
- Method validation study published in March 2000
- Study was peer reviewed and comments incorporated into method revision
- Method 1668A published in December 1999
  - EPA-821-R-00-002

EPA Method 1668A

Method Background

- EPA initiated an Interlaboratory Method Validation Study in the Fall of 2003
  - Includes analysis of wastewater, biosolids and fish tissue
- EPA reported delays in obtaining the study data
- Interlaboratory Method Validation Report reportedly to be issued in early 2005

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EPA Method 1668A

Method Summary

- Isotope dilution quantitation technique is used for the 12 toxic WHO list congeners and the earliest and latest eluting congener at each level of chlorination (homolog group)
- $^{13}C_{12}$- labeled analogs of the CBs. Added to the sample pre-extraction
- All other congeners are quantitated using the internal standard quantitation technique
  - Using a labeled compound that is not an exact analog

EPA Method 1668A

Method Summary (aqueous samples)

- Extraction
  - Aqueous – 1-L sample size extracted with methylene chloride using SPE, Separatory Funnel or CLLE
- Cleanups
  - Back-extraction with sulfuric acid and/or base, and GPC, silica gel, or Florisil
- Extract Concentration
  - Solvent reduced to 20 ul
- Analysis
  - HRGC/HRMS with quantitation by isotope dilution or internal standard technique

Project Analytical QC Requirements

Objective

- Ensure that comparable data is generated amongst the various stakeholders and laboratories to meet DRBC DQOs

Resources

- DRBC website has summary of sampling and analytical requirements
- http://www.state.nj.us/drbc/PCB_info.htm
- EPA Method 1668A Project QC Requirements posted on the DRBC website

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Project Analytical QC Requirements

- Analyze samples according to the project-specific modifications to EPA Method 1668A
- Questions or concerns with the QC requirements should be discussed with the DRBC prior to implementing any changes

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Project Analytical QC Requirements

Target Analyte List

- Analyze samples for 209 congeners

Sample Collection, Storage and Holding Times

- 2-L aqueous sample size
  - COLLECT replicate volume in the event of breakage or reanalysis
- In some instances, collection of precisely a 2-liter volume may not be possible. If the sample size falls below 2-liters, the Estimated Detection Limits (EDLs) will become elevated above project objectives. If the volume exceeds 2-liters, the additional volume poses difficulties in extracting the sample properly. The sample size collected can acceptably range from 1.8-liters to 2.1-liters, but should be as close as possible to 2-liters.

Project Analytical QC Requirements

Sample Collection, Storage and Holding Times

- Lab must document container cleanliness and traceability
- 2-L amber glass container supplied by lab

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Project Analytical QC Requirements

Sample Collection, Storage and Holding Times

- Lab must supply reagent grade water for field blanks

Extraction and Cleanup

- Entire contents of the sample volume must be extracted
- Do NOT separate solids if greater than 1% as described in Section 11.5 of Method 1668A

Project Analytical QC Requirements

Extraction and Cleanup

- All pre-extraction spike additions must be added to the 2-L bottle containing the sample prior to extraction
- Lab may extract using equipment to accommodate the 2-L volume
- Alternatively – serially or simultaneously extract two 1-L portions.
- Combine solvent prior to cleanups
- Concentrate samples to a final volume of 20 ul

Project Analytical QC Requirements

Extraction and Cleanup

- Process all method blanks, OPR samples, field blanks or other QC samples IDENTICALLY to the samples including same extract cleanups

Column/Retention Time Calibration

- Project requires the use of the SPB-octyl column

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Project Analytical QC Requirements

Initial Calibration

- Minimum of 5 levels for each of the toxic/level of chlorination (LOC) congeners
- Low calibration standard for the project must be 0.5 ng/ml

Project Analytical QC Requirements

Method Blanks

- Method blanks must meet the decision rules or replicate sample(s) must be reextracted and reanalyzed
  - An individual congener cannot exceed 20 pg/L
  - If a congener exceeds 20 pg/L and the associated sample concentration exceeds 10× the amount in the blank, then no action is required
  - If a congener exceeds 20 pg/L and the congener is not found in the associated field sample, then no action is required
  - The total PCB concentration cannot exceed 300 pg/L

Project Analytical QC Requirements

Rinsate Blanks

- Rinsate blanks must meet the decision rules or samples may need to be recollected and reanalyzed (decisions rules are an interim goal)
  - An individual congener cannot exceed 40 pg/L
  - If a congener exceeds 40 pg/L and the associated sample concentration exceeds 3× the amount in the blank, then no action is required
  - If a congener exceeds 40 pg/L and the congener is not found in the associated field sample, then no action is required
  - The total PCB concentration cannot exceed 600 pg/L

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Project Analytical QC Requirements

Qualitative/Quantitative Issues

- Data Reporting
  - Report results for all 209 CB congeners
  - Report data using project Qualifier Codes
    - Provides mechanism for reporting co-eluting congeners
  - Report results according to hardcopy data package deliverable and DRBC EDD specification

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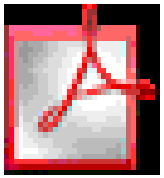

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Qualifier Codes

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Co-Eluting Congeners

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Project Analytical QC Requirements

- Data Reporting
  - Report data to the sample specific Estimated Detection Limit (EDL)
  - “J” flag for values less than the concentration equivalent to the low calibration standard but greater than the EDL

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Thank You

Setting the Standards for Innovative Environmental Solutions

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