United States Environmental Protection Agency

Office of Research and Development

The Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP) Study

Extracting and Preparing Dust and Soil Samples For Analysis of Polar Persistent Organic Pollutants

Battelle
Columbus, OH 43201
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Standard Operating Procedure **CTEPP-SOP-5.15**

Title: Extracting and Preparing Dust and Soil Samples For Analysis of Polar Persistent Organic Pollutants

Source: Battelle

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Exposure Measurements & Analysis Branch

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STANDARD OPERATING PROCEDURE (SOP) FOR EXTRACTING AND PREPARING DUST AND SOIL SAMPLES FOR ANALYSIS OF POLAR PERSISTENT ORGANIC POLLUTANTS

Prepared by: _____ Date: _____

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1.0 Scope and Applicability

This standard operating procedure (SOP) describes the method for extracting and preparing dust and soil samples for analysis of polar persistent organic pollutants.

2.0 Summary of Method

The method for extracting and preparing a dust or soil sample for analysis of polar persistent organic pollutants is summarized in this SOP. It covers the extraction, concentration, and derivatization of samples that are to be analyzed by gas chromatography/mass spectrometry (GC/MS).

3.0 Definition

3.1 Surrogate Recovery Standard (SRS): The compounds that are used for QA/QC purposes to assess the extraction and recovery efficiency obtained for individual samples. Known amounts of these compounds are spiked into the dust or soil prior to extraction. The SRSs are quantified at the time of analysis and their recoveries indicate the probable extraction and recovery efficiency for native analytes that are structurally similar. The SRSs are chosen to be as similar as possible to the native analytes of interest, but they must not interfere in the analysis.

3.2 Internal Standard (IS): The compounds that are added to sample extracts just prior to GC/MS analysis. The ratio of the detector signal of the native analyte to the detector signal of the corresponding IS is compared to ratios obtained for calibration curve solutions where the IS level remains fixed and the native analyte levels vary. The IS is used to correct for minor run-to-run differences in GC injection, chromatographic behavior, and MS ionization efficiency.

4.0 Cautions

Standard laboratory protective clothing, gloves, and eye covering is required.

5.0 Responsibilities

5.1 The project staff who perform the sample extractions will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation laboratory record books, and sending final extracts for analyses.

5.2 The CTEPP Laboratory Team Leader (LTL), the QA Officer or designee, and Task Order Leader (TOL) will oversee the sample extraction operation and ensure that SOPs are followed by all project staff.

6.0 Apparatus and Materials

6.1 Materials

6.1.1 Dionex model 200 Accelerated Solvent Extractor (ASE)

6.1.2 Stainless steel spatulas

6.1.3 Stainless steel plunger

6.1.4 Clean glass wool

6.1.5 Analytical syringes

6.1.6 Silylated wide-neck glass funnels (muffled)

6.1.7 Large Kim-wipes (15" x 15")

6.1.8 Latex gloves

6.1.9 Silylated 4 dram glass vials with Teflon-lined screw caps; muffled

6.1.10 Silylated 1.8 mL glass GC vials with Teflon-lined screw caps; muffled

6.1.11 Kuderna-Danish concentrators (large 24/40 3-ball Snyder condenser, 125 mL reservoir flask and 25 mL tube); (Kontes 570000)

6.1.12 Silylated small 19/22 3-ball Snyder condensers

6.1.13 Disposable Pasteur glass pipettes (muffled and stored in clean glass jar)

6.1.14 Vortex mixer (American Scientific Products)

6.1.15 Graduated cylinders

6.1.16 Heated water bath

6.1.17 Ultrasonic bath

6.1.18 Nitrogen evaporator (N-Evap)

6.1.19 Solid Phase Extraction (SPE) cartridge (Supelco)

6.1.20 Quartz fiber filters

6.1.21 11 mm stainless steel extraction cell

6.1.22 Filter (Dionex-grade D28)

6.1.23 Collection vial, 40 mL (VWR)

6.1.24 Collection vial septa, Teflon/silicone (I-Chem)

6.2 Reagents

6.2.1 Dichloromethane (DCM); distilled-in-glass

6.2.2 n-Hexane (distilled-in-glass)

6.2.3 Boiling chips (Hengar crystals)

6.2.4 Surrogate Recovery Standard Spiking Solution

6.2.5 Internal Standard Spiking Solution

6.2.6 Distilled, deionized water (DI water)

6.2.7 Acetonitrile (distilled-in-glass)

6.2.8 Methanol (distilled-in-glass)

6.2.9 Sodium sulfate anhydride

6.2.10 Sand (reagent grade)

6.2.11 Ethyl ether (distilled-in-glass)

6.2.12 Carbitol (analytical grade)

6.2.13 Diazald (analytical grade)

6.2.14 40% KOH aqueous solution

6.2.15 N-(tert-butylmethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA)

7.0 Procedure

7.1 Packing the ASE cell.

7.1.1 To the extent possible, retrieve 10 to 12 samples from the same materials batch from the freezer and place each sample container on the laboratory bench for approximately ten minutes to come to room temperature. Extract and analyze these samples as a batch.

7.1.2 Put on clean gloves.

7.1.3 Weigh out approximately 0.5 g of dust or 5 g of soil sample into a clean sample vial or weighing dish using a 2-place balance and record the exact weight in the laboratory record book. If 0.5 g of dust is not available, then weigh out the amount that is available.

7.1.4 Weigh out 10 g of sand (for dust sample) or 5 g of sand and 5 g of sodium sulfate anhydride or 2 g of Extrulet (for soil sample); transfer to the same sample vial; mix well. These weights can be approximate and actual weights added will be recorded.

7.1.5 Screw one end cap of the steel cell onto the extraction chamber and place one filter onto the top of the end cap. The filter should cover the frit on the end cap. Place a small amount of sand on top of the filter.

7.1.6 Pack the cell by transferring approximately half of the mixture from 7.1.4. Spike 100 µL of the surrogate recovery standard spiking solution onto the mixture in the cell. *Note that the spiked levels may be changed and the exact spiked amounts will be recorded in the laboratory record book (LRB).* Continue packing the remaining mixture from 7.1.4 to the cell. Place a small amount of sand on top of the packed mixture to reach the top of the cell. Clean off the threads and screw on the other end cap.

7.2 Extraction

7.2.1 Place the cells and the collection vials on the ASE unit

7.2.2 Method for ASE:

Pressure:	2000 psi
Solvent:	acetone
Temperature:	120ºC
Static:	10 minutes
Flush:	100%

Purge: 60 seconds
Cycles:3

7.2.3 After extraction is complete, remove cells and collection vials. Store the sample extracts in a $\leq$-10°C freezer overnight if the extracts are not processed immediately for next step.

7.3 Concentration and derivatization

7.3.1 Using a wide-neck funnel with a clean quartz fiber filter, pour the extract from the round-bottom flask into a Kuderna-Danish concentrator (KD) which has a 125 mL reservoir flask. Rinse the round-bottom flask twice with ~2 mL acetone and add the rinsate to the KD flask.

7.3.2 Add 3-5 boiling chips to the KD tube/flask. Attach the micro Snyder condenser to the flask.

7.3.3 Concentrate the extract in a heated (~80˚C) water bath to 0.6-0.8 mL. Remove the KD assembly from the water bath and let it stand in the hood to cool.

7.3.4 Rinse down the insides of the flask and tube with acetone, to bring the volume to 2 mL, and use KD concentration to reduce volume to 2 mL. Vortex for 3 seconds to mix.

7.3.5 Spike the extract with 10 L of the Internal Standard spiking solution, and vortex for 3 seconds to mix. Split the sample extract into two portions (I and II).

7.3.6 Add 50 µL of methanol to the portion I of the sample extract and methylate it with etheral diazomethane generated in situ from Diazald, carbitol, and 40% aqueous KOH.

7.3.7 Solvent exchange the methylated portion of dust extract into isooctane for SPE cleanup. Most soil sample extracts do not require SPE cleanup steps.

7.3.8 Place SPE cartridges on the SPE manifold and condition each cartridge in sequence with 6 mL of 50% ethyl ether in hexane, followed by 100% of hexane. Close the valve stem on the manifold to prevent the cartridge from going dry between solvents.

7.3.9 Using a clean Pasteur pipette, transfer the isooctane extract to an SPE cartridge.

7.3.10 Elute the cartridge into a clean vial with 12 mL of 15% ethyl ether in hexane, followed by 6 mL of 100% DCM.

7.3.11 K-D concentrate the extract to 0.6 to 0.8 mL and rinse down the sides of the tube with hexane to bring the volume to 1 mL.

7.3.12 Transfer the extract, using a muffled disposable glass Pasteur pipette, to a clean 1.8 mL GC vial for GC/MS analysis. Label the sample vial with its respective sample ID. The target analytes for the portion I sample extract are dicamba, 2,4-D, pentachlorophenol, and 2,4,5-T.

7.3.13 Spike 100 µL of MTBSTFA using a 100 µL syringe into portion II of the sample extract. Vortex for ~3 s to mix.

7.3.14 Transfer the sample extract to a silylated GC vial using a Pasteur pipette. Label the sample vial with its respective sample ID. The target analyte for the portion II sample extract from North Carolina field study is 3,5,6-trichloro-2-pyridinol (3,5,6-TCP). The target analytes for the portion II sample extract from Ohio field study are 3,5,6-TCP and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMP).

7.3.15 Seal the vial with a Teflon septum and placed in one well of the tube-heater sand bath or a convection oven at ~70°C. Record the exact temperature and starting time in the laboratory record book.

7.3.16 Remove the GC vial from the heater after one hour. Record the exact temperature and ending time.

7.4 Store the extract in a $\leq$10˚C freezer until GC/MS analysis.

8.0 Records

8.1 Records of the preparation of field samples, blanks, and matrix spikes will be retained in a LRB that is kept in the extraction laboratory. This LRB will record all sample preparation activities. These samples will be recorded in the LRB by field sample ID and the laboratory generated QA/QC sample will be assigned with a laboratory sample number (a unique number that combines the 5 digit LRB number-2 digit page number-2 digit line number). The date of extraction, the lot number of solvents used for extraction, and the spike level of the surrogate recovery standards and internal standards will be recorded in the LRB.

8.2 The LRB will be retained in the laboratory where these operations are performed until the conclusion of the study and will be archived in a secure room for three years after completion of the study.

9.0 Quality Control and Quality Assurance

9.1 A field blank, laboratory method blank, laboratory fortified blank that will be extracted together with the field samples. The field blank analyses are performed to verify that minimal contamination occurs through sample handling during shipping and field operations.

The laboratory method blank analyses are performed to verify that minimal contamination occurs through sample preparation. The laboratory fortified blank analyses are performed to verify the recoveries of analyte preparation procedures.

9.2 Field crews will be reminded to wear clean clothing, to remove all pesticide products from their residences that may contain the target analytes, and to refrain from using these materials during the field study. Field crews will also be reminded to obtain clean clothing after visiting a home where they know or suspect that these pesticides have been applied within the previous week. Cigarette smoking is not permitted during the field sampling. Field crews should store the samples in a clean environment away from any known combustion sources.

9.3 Surrogate recovery values of 50-150% in blanks, and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 50% or greater than 150%, the data will be flagged. For recoveries greater than 130%, the concentration of the surrogate spiking solution will be checked against a calibration curve to determine whether inadvertent solvent loss has resulted in higher spike levels. If this has occurred, the surrogate spiking solution will be re-prepared and analyzed.

9.4 One laboratory method blank that is analyzed as a sample concurrently with a field sample set will be analyzed for typically every 50 samples processed. If significant target analyte levels (>0.1 μg) are found in the field blanks or laboratory blanks, the source of contamination must be identified and more laboratory blanks, together with additional field blanks, trip blanks, and storage blanks, will be analyzed.

10.0 Reference

10.1 J. C. Chuang, C. Lyu, Y-L Chou, P. J. Callahan, M. Nishioka, K. Andrews, M. A. Pollard, L. Brackney, C. Hines, D. B. Davis, and R. Menton, "Evaluation and Application of Methods for Estimating Children's Exposure to Persistent Organic Pollutants in Multiple Media." EPA/600/R-98/164a, EPA/600/R-98/164b, and EPA/600/R-98/164c (Volume I, II, and III), 1999.