

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

## **Extracting and Preparing Air Samples for Analysis of Polar Persistent Organic Pollutants**

Battelle  
Columbus, OH 43201  
Contract No. 68-D-99-011

**Standard Operating Procedure**

**CTEPP-SOP-5.13**

**Title:** Extracting and Preparing Air 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 AIR SAMPLES  
FOR ANALYSIS OF POLAR PERSISTENT ORGANIC POLLUTANTS

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## **1.0 Scope and Applicability**

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

## **2.0 Summary of Method**

The method for extracting and preparing an air sample consisting of a quartz fiber filter (Pallflex) and an XAD-2 cartridge for analysis of polar persistent organic pollutants is summarized in this SOP. It covers the preparation 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 XAD-2 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 Silylated small Soxhlet extraction apparatus consisting of condenser, extractor (31 mm id x 135 mm length), and 100 mL round bottom flasks
- 6.1.2 Heating mantles for 100 mL round-bottom flasks
- 6.1.3 Variac controllers
- 6.1.4 Silylated 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 1 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 Silylated Kuderna-Danish concentrators (large 24/40 3-ball Snyder condenser, 125 mL reservoir flask and 25 mL tubes 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 Muffled 25 mL volumetric flasks
- 6.1.18 Nitrogen evaporator (N-Evap)

## 6.2 Reagents

6.2.1 Acetonitrile (ACN); 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 Diazald

6.2.8 Methanol (distilled-in-glass)

6.2.9 Ethyl ether (distilled-in-glass)

6.2.10 Carbitol (analytical grade)

6.2.11 N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA), Pierce Chemical company

6.2.12 37% KOH aqueous solution

## 7.0 Procedure

7.1 Extraction, Concentration, Methylation, and Silylation.

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

7.1.2 Put on clean gloves.

7.1.3 Place ~2 g of glass wool on the bottom of the Soxhlet extractor body.

7.1.4 Transfer the XAD-2 to the Soxhlet extractor and spike with 100 L of the surrogate recovery standard spiking solution, using a 100 L syringe. Note that the spiked levels

may be changed and the exact spiked amounts will be recorded in the laboratory record book.

- 7.1.5 Using acetone-rinsed tongs and tweezers, place the filter on top of the spiked XAD-2.
- 7.1.6 Assemble the Soxhlet extractor, add ~80 mL of acetonitrile (ACN) to the flask with a few boiling chips.
- 7.1.7 Place the round-bottom flask in a heating mantle and set the Variac at position ~90 so that the ACN boils smoothly and drips at a constant rate from the condenser into the Soxhlet body. The Variac setting may vary slightly depending on the heating mantle used in the extraction. The solvent should fill the extractor body and dump into the flask in approximately 15-20 min. Continue the extraction overnight (~14 h).
- 7.1.8 Turn off the Variac and remove the heating mantle. Allow the Soxhlet apparatus to cool for 15 min, then remove the condenser.
- 7.1.9 Tilt the Soxhlet body to dump the remaining solvent from the extractor body into the round-bottom flask.
- 7.1.10 Using a wide-neck funnel with a clean, ACN wetted, 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 ACN and add the rinsate to the KD flask.
- 7.1.11 Add 3-5 boiling chips to the KD tube/flask. Attach the large Snyder condenser to the flask. Concentrate the extract in a heated (~95°C) water bath to ~10 mL.
- 7.1.12 Change to small Snyder condenser and concentrate the extract to 0.6-0.8 mL. Remove the KD assembly from the water bath and let it stand in the hood to cool.
- 7.1.13 Rinse down the insides of the flask and tube with ACN, to bring the volume to 2 mL, and use KD concentration to reduce volume to 2 mL. Vortex for ~3 s to mix.
- 7.1.14 Spike the extract with 10  $\mu$ L of the Internal Standard spiking solution, and vortex for ~3 s to mix. Split the sample extract into two portions (I and II).
- 7.1.15 Add 50  $\mu$ L of methanol to the portion I of the sample extract and methylate it with ethereal diazomethane generated in situ from Diazald, carbitol, and 37% aqueous KOH.
- 7.1.16 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 (PCP), and 2,4,5-T. Note that when the silylated PCP data have interferences, the methylated PCP data are used since PCP can be determined by either the methylated extract (portion I) or the silylated extract (portion II).

- 7.1.17 Spike 100  $\mu$ L of MTBSTFA using a 100  $\mu$ L syringe into portion II of the sample extract. Vortex for ~3 s to mix.
- 7.1.18 Transfer the sample extract to a silylated GC vial using a Pasteur pipette. Label the sample vial with its respective sample ID. The target analytes for the portion II sample extract from North Carolina field study are 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) and PCP. The target analytes for the portion II sample extract from Ohio field study are 3,5,6-TCP, PCP, and 2-isopropyl-4-methyl-6-hydroxypyrimidine (IMP).
- 7.1.19 Seal the vial with a Teflon septum and placed in one well of the tube-heater sand bath or oven at ~70°C. Record the exact temperature and starting time in the laboratory record book.
- 7.1.20 Remove the GC vial from the heater after one hour. Record the exact temperature and ending time.
- 7.2 Store the extract in a freezer ( $\leq -10^{\circ}\text{C}$ ) 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, consists of a filter/XAD-2 module 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 analytes through sample preparation procedures.
- 9.2 Field crews will be reminded to wear clean clothing and shoes, 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 of a filter/XAD-2 module (that is analyzed as a sample concurrently with a field sample set) will be analyzed typically for typically every 50 samples processed. If significant target analyte levels ( $>0.1 \mu\text{g}$ ) 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.