National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 821560

Standard Operating Procedure **SOP-BCO-L-27.0**

Title: Extraction of Air Samples for GC/MS Analysis of Pesticides and PAH

Source: The University of Arizona

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

Notice: *The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and collaborated in the research described here. This protocol is part of the Quality Systems Implementation Plan (QSIP) that was reviewed by the EPA and approved for use in this demonstration/scoping study. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.*

Extraction of Air Samples for GC/MS Analysis of Pesticides and PAH

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes methods for extracting and preparing an air sample consisting of a quartz fiber filter (Pallflex) and an XAD-2 cartridge for analysis of pesticides and PAH. It covers the preparation of samples that are to be analyzed by GC/MS.

2.0 Definitions

2.1 Surrogate Recovery Standard (Surrogate or 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 "surrogates" 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 surrogate recovery standards are chosen to be as similar as possible to the native analytes of interest, but they must not interfere in the analysis.

2.2 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.

3.0 References

3.1 Roinestad, K.S.; Louis, J.B.; Rosen, J.D., "Determination of Pesticides in Indoor Air and Dust," J. AOAC Intl. **76**, 1121-1126 (1993).

3.2 Bogus, E.R., Watschke, T.L, Mumma, R.A., "Utilization of Solid-Phase Extraction and Reversed-Phase and Ion-Pair Chromatography in the Analysis of Seven Agrochemicals in Water," J. Agric. Food Chem. **38**, 142-144 (1990).

3.3 Bagnati, R., Benfenati, E., Davoli, E., Fanelli, R., "Screening of 21 Pesticides in Water by Single Extraction with C18 Silica Bonded Phase Columns and HRGC-MS," Chemosphere **17**, 59-65 (1988).

3.4 Loconto, P.R., Gaind, A.K., "Isolation and Recovery of Organophosphorous Pesticides from Water by Solid-Phase Extraction with Dual Wide-Bore Capillary Gas Chromatography," J. Chromatogr. Sci. **27**, 569-573 (1989).

3.5 Sherma, J., Bretschneider, W., "Determination of Organophosphorous Insecticides in Water by C18 Solid Phase Extraction and Quantitative TLC," J. Liquid Chromatogr. **13**, 1983-1989 (1990).

3.6 Chuang, J.C., Mack, G.A., Kuhlman, M.R., Wilson, N.K., "Polycyclic Aromatic Hydrocarbons and Their Derivatives in Indoor and Outdoor Air in an Eight-Home Study," Atmos. Environ. **25B**, 369-380 (1991).

4.0 Discussion

4.1 This procedure involves spiking the XAD-2 with a surrogate recovery standard solution, Soxhlet extraction of the filter and XAD-2 together with 150 mL of dichloromethane (DCM) for 14 h, Kuderna-Danish evaporation to 1 mL and solvent exchange into hexane (for SPE cleanup), addition of an internal standard solution, then analysis using GC/MS for detection and quantification of the pesticides and PAH. SOP BCO-L-15.1 covers the GC/MS analysis and quantification of the extract for pesticides; PAH analysis is addressed in SOP BCO-L-30.0.

4.2 The procedure outlined here provides for the addition of structurally similar surrogate recovery standards (fenchlorphos, $^{13}C_{12}$-DDT, $^{13}C_{12}$-DDE, and chrysene-d12). Fenchlorphos is not used in residential applications and is rarely used in agricultural applications, and $^{13}C_{12}$-DDT, $^{13}C_{12}$-DDE, and chrysene-d12 are perdeuterated chemicals (that are unlikely to be encountered in samples as native analytes). These structurally similar surrogate recovery standards provide essential QA/QC data on extraction efficiency and recovery for each sample. The use of a structurally similar IS for GC/MS quantification corrects for minor run-to-run variations in injection, chromatography, and ionization.

5.0 Responsibilities

5.1 The sample extractions will be performed by staff members of the Atmospheric Sciences and Applied Technology Department at Battelle.

5.2 These staff members will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/preparation log books, sending final extracts for analyses, and filing analyte concentration values with the database coordinator.

6.0 Materials and Reagents

6.1 Materials

6.1.1 Small Soxhlet extraction apparatus consisting of condenser, extractor (31 mm id x 135 mm length), and flask (250 mL round bottom); (Kontes 585000-0021).

6.1.2 Heating mantles for 250 mL round-bottom flasks

6.1.3 Variac controllers

6.1.4 Silanized glass wool

6.1.5 Analytical syringes

6.1.6 Wide-neck glass funnels (muffled)

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

6.1.8 Latex gloves

6.1.9 1 dram glass vials with Teflon-lined screw caps; muffled and vacuum silanized.

6.1.10 1.8 mL glass GC vials with Teflon-lined screw caps; muffled and vacuum silanized.

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 Small 19/22 3-ball Snyder condensers.

6.1.13 Disposable 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 Dichloromethane (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 (see SOPs BCO-L-21.1 and BCO-L-26.0).

6.2.5 Internal Standard Spiking Solution (see SOPs BCO-L-21.1 and BCO-L-26.0).

6.2.6 Distilled, deionized water (DI water)

7.0 Procedure

7.1 Extraction and Concentration

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 the middle of the XAD-2 with 10 µL of the surrogate recovery standard spiking solution (pesticides and PAH), using a 10 µL syringe.

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 150 mL of high purity DCM to the flask with a few boiling chips.

7.1.17 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.

7.1.18 Spike the extract with 10 μL of the Internal Standard spiking solution (phenanthrene-d10, dibromobiphenyl, and benzo[e]pyrene-d12 at 50, 10, and 5 μg/mL, respectively), and vortex for 3 s to mix.

7.1.19 Transfer the extract, using a muffled disposable glass Pasteur pipette, to a clean prelabeled 1.8 mL GC vial for GC/MS analysis. Mark the volume on the side of the vial and label the sample with the laboratory notebook number and field sample ID.

7.1.20 Store the extract in a -20°C freezer until GC/MS analysis.

7.2 Calculations

None.

7.3 Quality Control

7.3.1 As discussed in SOP BCO-L-29.0, the pre-shipment verification for residue levels of pesticides and PAH in filter and XAD-2 batches is performed individually on a filter and XAD-2 from a single filter/XAD-2 module. This is done to pinpoint the specific media that may be contaminated, before use.

7.3.2 A field blank or field spike sample consists of a filter/XAD-2 module that will be extracted together. The field blank analyses are performed to verify that minimal contamination occurs through sample handling during shipping and field operations. The field spike analyses are performed to verify retention of analytes through shipping and handling procedures.

7.3.3 If field blank levels exceed 0.1 μg/sample, the data from the corresponding 20 homes will be flagged and inspected for possible blank correction. Additional sampling media (filter and XAD-2) will be sent to the field within 3 days for additional field blank measurements. The field team responsible for the flagged data will be requested to process these field blanks under field conditions as quickly as possible; their analyses at Battelle will be carried out as soon as these samples are received.

7.3.4 Field crews will be reminded to wear clean laboratory coats and shoes, to remove all pesticide products from their residences that may contain these

analytes, and to refrain from using these materials while part of the field crew. Field crews will also be reminded to obtain a clean laboratory coat 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.

7.3.5 Field spike recovery values of 70-130% of the true value will be acceptable. Recoveries of less than 70% will require a review of field and analytical protocol to verify that procedures are being correctly implemented, especially those having to do with storage at Blue Ice/ freezer temperatures after field collection. For recoveries greater than 130%, the preparation date of the field spiking solution will be checked, and recoveries in a second field spike sample (any matrix) prepared by the same field crew will be checked. If the expiration date on the spike is imminent, and/or another field spike has a high recovery, a new field spiking solution will be prepared and shipped immediately.

7.3.6 Surrogate recovery values of 70-130% in blanks, field spikes, and actual samples will be deemed acceptable, and no correction to the data will be made. For recoveries less than 70%, the data will be flagged, and the analyte concentrations will be corrected (divided) by the percent recovery of the surrogate. 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 is re-prepared.

7.3.7 One laboratory blank of a filter/XAD-2 module (that is analyzed as a sample concurrently with a field sample set) will be analyzed for every 50 samples processed. If significant pesticide or PAH levels (>0.1 μg) are found in the field 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.

8.0 Records

8.1 Records of the field blank levels and field spike recovery values will be retained in a project laboratory notebook that is kept in the pesticide/ PAH extraction laboratory. This notebook will serve as a continuing file for reference on expected performance of the methods and likely contaminant levels that will arise as a result of field handling. These samples will be identified in the laboratory notebook by field sample ID and the assigned laboratory analysis number (a

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unique number that combines the 5 digit laboratory book number-2 digit page number-2 digit line number), the date of extraction, the lot number of DCM used for extraction, the batch number of the XAD-2 and filter, and surrogate recovery values. This notebook will be transferred to the Battelle co-PI's office at the conclusion of the program.

8.2 The record of the extraction of samples will be maintained in a project laboratory notebook that is kept in the pesticide/PAH extraction laboratory. This notebook will contain the field sample ID, the assigned laboratory analysis number (see above), the date of extraction, and the lot number of acetone used for extraction.