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-28.0**

Title: Extraction of Soil/House Dust 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 Soil/House Dust Samples for GC/MS Analysis of Pesticides and PAH

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes procedures for extracting and preparing a dust or soil sample for GC/MS analysis of pesticides and PAH.

2.0 Definitions

2.1 Surrogate Recovery Standards (Surrogate or SRS): The compounds that are used for QA/QC purposes to assess the extraction and recovery efficiency obtained for individual samples. A known amount of these compounds are spiked into the collected sample (dust and soil) prior to extraction. The "surrogate" is quantified at the time of analysis and its recovery indicates 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 Standards (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, detector efficiency, and final extract volume.

3.0 References

3.1 Roinestad, K.S., Louis, J.B., and 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, and 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., and 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. and 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. and 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., Callahan, P.J., Menton, R.G., Gordon, S.M., Lewis, R.G., and Wilson, N.K., "Monitoring Methods for Polycyclic Aromatic Hydrocarbons and Their Distribution in House Dust and Track-in Soil," Environ. Sci. Technol. **29**, 494-500 (1995).

4.0 Discussion

4.1 This procedure involves spiking the dust/soil sample with a surrogate recovery standard, sonication extraction in 10 mL of 10% ethyl ether in hexane, followed by solid phase extraction (SPE) cleanup with a Florisil cartridge, and detection and quantification of the pesticides and PAH by GC/MS analysis. SOP BCO-L-30.0 covers the GC/MS analysis and quantification of the extract for PAH.

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, suggesting that it is not likely to be encountered in samples as a native analyte. $^{13}C_{12}$-DDT, $^{13}C_{12}$-DDE, and chrysene-d12 are perdeuterated chemicals that are not present naturally in the environment. These structurally similar surrogate recovery standards provide essential QA/QC data on extraction efficiency and recovery for each sample. The use of structurally similar IS for GC/MS quantification correct for minor run-to-run variations in injection, chromatography, and ionization.

5.0 Responsibilities

5.1 The sample extractions will be performed by analysts in Battelle's pesticide/PAH extraction laboratory, who are completely familiar with the methods and procedures listed here. The analysts will be responsible for obtaining samples from the Sample Coordinator and ensuring the chain-of-custody forms are properly documented, entering relevant information in the extraction/preparation log books, and sending final extracts for analyses.

5.2 After receipt of the analysis results, the Project Laboratory Director in the pesticide/PAH extraction laboratory will review the data. Once verified, the analysts will be responsible for filing analyte concentration values with the Data Coordinator.

5.3 The analysts will be responsible for following this SOP, for reporting deviations and changes to the supervisory scientist, for making sure that the materials and reagents used are of sufficient purity (as indicated by manufacturer's labels), and for ensuring that the holding times for solutions used have not expired.

6.0 Materials and Equipment

6.1 Materials

6.1.1 Clean quartz fiber filters.

6.1.2 10 mL graduated volumetric pipettes.

6.1.3 Balance with 4-place accuracy (x.xxxx g).

6.1.4 Balance with 2-place accuracy (x.xx g).

6.1.5 Large Kim-Wipes (15 in. x 15 in.).

6.1.6 Latex gloves.

6.1.7 Tweezers and spatulas.

6.1.8 Ultrasonic water bath (Bransonic 52, or equivalent).

6.1.9 1.8 mL glass vials with Teflon-lined screw-caps, muffled and vacuum silylated.

6.1.10 Kuderna-Danish concentrators (small 19/22 3-ball Snyder condenser and 25 mL tube).

6.1.11 Disposable glass pipettes.

6.1.12 Florisil SPE cartridges (Baker, 1g, 6mL).

6.1.13 Multi-port SPE manifold (Supelco or Baker).

6.1.14 2 dram glass vials with Teflon-lined screw caps; muffled and vacuum silylated.

6.1.15 Glass funnels.

6.1.16 Heated water bath.

6.1.17 Analytical syringes.

6.1.18 Glass sample vials (muffled).

6.2 Reagents

6.2.1 Boiling chips (Hengar crystals).

6.2.2 High purity hexane.

6.2.3 Surrogate recovery standard spiking solution (see SOP BCO-L-26.0).

6.2.4 Internal standard spiking solution (see SOP BCO-L-26.0).

6.2.5 Ethyl ether (high purity).

6.2.6 Dichloromethane (distilled-in-glass).

7.0 Procedures

7.1 Extraction of House Dust Samples

7.1.1 Retrieve up to 10 dust samples for simultaneous processing from the Sample Custodian, and sign and date the chain-of-custody forms.

7.1.2 Put on latex gloves.

7.1.3 Weigh out approximately 0.5 g of each dust sample into a prelabeled 20 mL glass vial using a 2-place balance and record the weights in the project pesticide/PAH extraction laboratory notebook. If 0.5 g of dust is not available, then weigh out the amount that is available.

7.1.4 Spike 10 µL of the Surrogate Recovery Standard spiking solution (fenchlorphos, $^{13}C_{12}$-DDT, $^{13}C_{12}$-DDE, and chrysene-d12) onto the dust

and allow the solvent to disperse before addition of the solvent (~ 15 min).

7.1.5 Add 10 mL of 10% ethyl ether in hexane to the dust, put on the cap and swirl to wet. Place the 10 sample vials in an ultrasonic bath and sonicate for 15 min.

7.1.6 Transfer the sample vials to a counter and let them stand for 15 min to allow the particles to settle down. Carefully remove as much of the extract as possible from the sample vial to a Kuderna-Danish (K-D) concentrator through a funnel with a clean quartz fiber filter.

7.1.7 Repeat steps 7.1.5 and 7.1.6. Place the extract from the second extraction in the same sample vial.

7.1.8 Add 3-5 boiling chips to each K-D concentrator, and place the condenser column on top of the K-D concentrator.

7.1.9 Concentrate the extract in a heated (70 to 80°C) water bath to 0.6-0.8 mL.

7.1.10 Remove the KD tube from the water bath and stand it upright in the hood to cool for ~ 5 min.

7.1.11 Remove the condenser and rinse down the sides of the tube with hexane to bring the volume to 1 mL. Vortex for 3 s to mix.

7.1.12 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.

7.1.13 Using a clean Pasteur pipette, transfer a sample extract to an SPE cartridge.

7.1.14 Elute the cartridge into a clean vial with 12 mL of 15% ethyl ether in hexane.

7.1.15 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.

7.1.16 Spike the extract with 10 μL of the Internal Standard spiking solution (pesticides and PAH), and vortex for 3 s to mix.

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

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

7.2 Extraction of Soil Samples

7.2.1 The following procedure is used to select the smallest soil particles for extraction, because the soil sample cannot be dried and sieved without loss of pesticides.

7.2.1.1 Hold the Zip-lock bag containing the soil at a 45°-angle and gently shake the bag up and down for about 20 seconds. Check that the larger soil particles rise to the top and the smaller particles sink to the bottom.

7.2.1.2 While holding the bag in one hand, use the thumb and forefinger of the other hand to grasp the tip of the bag and clamp off ~2 cc of soil below the fingers. Squeeze the fingers together to separate the soil in the bag.

7.2.1.3 Tilt the bag an additional 45° until the soil above the fingers rolls to the side. Open the bag and scoop some soil from that 2 cc amount of soil left in the corner of the bag.

7.2.2 Carry out the extraction of soil in a manner identical to that described above (Steps 7.1.1 through 7.1.18).

7.3 Calculations

None.

7.4 Quality Control

7.4.1 For every 20 homes where dust and soil are sampled, one home will be designated as the site for field duplicates. Because it is impossible to have two identical sites, especially for house dust collection, the field duplicates will consist of split aliquots of bulk dust and split soil collected from this home. The duplicate aliquots of dust and soil will be extracted and

analyzed; the overall precision of the sample preparation and GC/MS analyses should be <30% deviation from the mean.

7.4.2 For every twenty homes, one additional QA/QC sample will be analyzed, consisting of either a laboratory blank or a reference dust (if available). The laboratory blank will be analyzed to determine laboratory contamination, if any, and the reference dust sample will be analyzed as a measure of accuracy.

7.4.3 These analyses will provide 5% QA as field duplicates and 10% overall QA.

7.3.4 Surrogate recovery values of 70-130% in 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 must be re-prepared.

8.0 Records

8.1 The record of the extraction of samples will be maintained in a project laboratory notebook that is retained in the pesticide/PAH extraction laboratory. This notebook will contain the field sample ID, the assigned laboratory analysis number (a unique number that combines the 5 digit lab book number-2 digit page number- 2 digit line number), the date of extraction, and the lot number of acetone used for extraction. Check-off columns will be included for addition of the surrogate and IS, and removal of an aliquot for PAH ELISA. After completion of the analysis, the sample analysis form will be filed with the Data Coordinator. This form will record not only the analyte values (μg/g) but also the recovery of the surrogate recovery standard.

8.2 Records of the laboratory blank levels and reference dust analyte levels 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 analyses. These samples will be identified in the laboratory notebook by the same laboratory analysis coding used for field samples, including the date of extraction, the lot number of acetone used for extraction, and the surrogate recovery value. This notebook will be transferred to the Battelle co-PIs office at the conclusion of the program.