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Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

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Standard Operating Procedure **SOP-BCO-L-12.1**

Title: Extraction of Pesticides from Dermal Wipe Samples

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Extraction of Pesticides from Dermal Wipe Samples

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes procedures for extracting and preparing a dermal wipe sample for GC/MS analysis of pesticides.

2.0 Definitions

2.1 Surrogate Recovery Standard (Surrogate or SRS): The compound that is used for QA/QC purposes to assess the extraction and recovery efficiency obtained for individual samples. A known amount of this compound is spiked into the collected sample (dust, soil, dermal wipe, PUF, etc.) 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 standard is chosen to be as similar as possible to the native analytes of interest. It must not, however, interfere in the analysis.

2.2 Internal Standard (IS): The compound that is added to sample extracts just prior to GC/MS analysis. The ratio of the detection signal of the native analyte to the detection signal of the 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, ionization efficiency, and final volume.

3.0 References

3.1 D. Camann, "Comparison of Dislodgeable Residue and Handwipe Methods for Pesticide Transfer from Floors," Presented at NHEXAS Dust and Dermal Workshop, Research Triangle Park, NC, January, 1994.

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

3.3 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).

3.4 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).

3.5 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).

3.6 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).

4.0 Discussion

4.1 This procedure involves spiking the gauze wipes with a surrogate recovery standards (SRSs), Soxhlet extraction in 10% diethyl ether/hexane, Florisil solid phase extraction cleanup, addition of the internal standard, and analysis. The extract is analyzed using GC/MS for detection and quantification of the pesticides. SOP UA-F-9.1 covers preparation of the dermal wipe media and collection of the dermal wipe samples; BCO-L-15.1 covers the GC/MS analysis and quantification of the extract.

4.2 The procedure outlined here provides for the addition of one structurally similar SRS (fenchlorphos) for diazinon, chlorpyrifos, and malathion; one SRS ($^{13}C_{12}$-DDT) specifically for DDT; and one SRS ($^{13}C_{12}$-DDE) for other organochlorine pesticides. These structurally similar SRSs 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 variation in injection, chromatography, and ionization.

5.0 Responsibilities

5.1 The sample extractions will be performed by analysts of the Battelle pesticide extraction laboratory who are completely familiar with the methods and procedures listed here. The analyst 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 analysis.

5.2 After receipt of the analysis results, the Project Laboratory Director in the pesticide extraction laboratory will review the data. Once verified, the analyst

will be responsible for filing analyte concentration values with the Data Coordinator.

5.3 The analyst will be responsible for following this SOP, for reporting deviations and changes to the Project Laboratory Director, 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 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 mantle for 250 mL round bottom flask.

6.1.3 Variac controller.

6.1.4 Analytical syringes.

6.1.5 Latex gloves.

6.1.6 Tweezers and tongs.

6.1.7 1 dram glass vials with Teflon-lined screw cap; muffled and vacuum silylated.

6.1.8 1.8 mL glass GC vials with Teflon-lined screw-caps; muffled and vacuum silylated..

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

6.1.10 Small 19/22 3-ball Snyder condensers.

6.1.11 Disposable glass pipettes (muffled and stored in clean glass jar).

6.1.12 Vortex mixer (American Scientific Products).

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

6.1.14 60 mL SPE reservoirs (Supelco).

6.1.15 Multi-port SPE manifold (Supelco).

6.1.16 Glass funnels (muffled).

6.1.17 Analytical syringes.

6.1.18 Heated water bath.

6.1.19 Nitrogen evaporator (N-Evap).

6.2 Reagents

6.2.1 Boiling chips (Hengar crystals).

6.2.2 Hexane (high purity).

6.2.3 Diethyl ether (high purity).

6.2.4 Surrogate Recovery Standard (Pesticide) Spiking Solution (see SOP BCO-L-21.1).

6.2.5 Internal Standard (Pesticide and PAH) Spiking Solution (see SOP BCO-L-26.0).

7.0 Procedure

7.1 Extraction Procedure

7.1.1 To the extent possible, retrieve at least 10 samples for simultaneous processing from the Sample Custodian, and sign and date the chain-of-custody form. For the pre-shipment materials suitability test, obtain two wipes from a batch that has been cleaned per SOP UA-F-9.1.

7.1.2 Assemble the Soxhlet extractor in a hood, add 100 mL of 10% diethyl ether in hexane to the flask with 3 boiling chips. (see SOP BCO-L-2.0 for details).

7.1.3 Put on clean latex gloves.

7.1.4 Spike 10 µL of the Pesticide Surrogate Recovery Standard spiking solution onto one wipe using a 10 µL syringe.

7.1.5 Using clean tweezers, place the two wipes into the Soxhlet body, and place the condenser over the Sohxlet body. Turn on the water flow through the condenser.

7.1.6 Adjust the temperature of the flask with the Variac so that the solvent boils smoothly and drips at a constant rate from the condenser into the Soxhlet body. Solvent should fill the extractor body and dump into the flask in approximately 15-20 min. Continue extraction overnight (14h).

7.1.7 Turn off the Variac and remove the heating mantle. Allow the Soxhlet apparatus to cool for 15 min, then remove the condenser.

7.1.8 Tilt the Soxhlet body to pour the remaining solvent from the extractor body into the round-bottom flask.

7.1.9 Using a wide-neck funnel, 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 10% diethyl ether in hexane and add to the KD flask.

7.1.10 Add 3-5 boiling chips to the KD tube/flask. Add the large Snyder condenser to the flask.

7.1.11 Concentrate the extract in a heated (75°C) water bath to ~3 mL. Remove the KD from the water bath and let it stand in the hood to cool.

7.1.12 Rinse down the insides of the flask and tube with hexane to bring the volume to 1 mL. Remove the flask from the tube.

7.1.13 Vortex the tube 2-3 s to mix.

7.1.14 Place SPE cartridges on the SPE manifold, and condition each cartridge in sequence with 6 mL of 50% diethyl ether in hexane, followed by 6 mL of 100% hexane. Close the stem valve on the SPE manifold between solvents so that the cartridge does not go dry.

7.1.15 Using a Pasteur pipette, transfer a sample extract to the SPE cartridge.

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

7.1.17 Use KD concentration to concentrate the extract to 0.6 – 0.8 mL. Rinse down the sides and bring to 1 mL.

7.1.18 Spike the extract with 10 µL of the Internal Standard spiking solution (DBB at 10 µg/mL), 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 required for GC/MS analysis.

7.2 Calculations

None.

7.3 Quality Control

7.3.1 As discussed in SOP UA-F-9.1, the pre-shipment materials suitability test will include extraction and analysis of 2 wipes, with no moistening solution added. This analysis will be carried out for each batch of wipes that are cleaned.

7.3.2 A field blank or field spike sample consists of two moistened wipes that will be extracted together as if an actual sample. 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 the retention of analytes through shipping and handling procedures.

7.3.3 If field blank levels exceed 0.05 µg/sample, the data from the corresponding 20 homes will be flagged and inspected for possible blank correction. Additional sampling media (wipes) 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 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 home/residence that contain these analytes and to refrain from using these materials while a member 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.

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 protocols to verify that the 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 Each group of 20 samples will include a field blank and a field spike. Both sample types will include the moistening solution. A laboratory method blank will not be prepared unless significant pesticide levels (>0.050 μg) are found in the field blank. In that case, the source of contamination must be identified, and 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 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

unique number that combines the 5 digit lab book number-2 digit page number- 2 digit line number), the date of extraction, the lot number of acetone used for extraction, the batch number of the dermal wipes, and surrogate recovery value. This notebook will be transferred to the Battelle co-PIs 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 retained in the pesticide extraction laboratory. This notebook will contain the field sample ID, the assigned laboratory analysis number (see above), the date of extraction, the lot number of acetone used for extraction. Check-off columns will be included for addition of the surrogate and IS, and this will be used to verify that these critical solutions were added.