Fortification of Matrix Samples

Chapter 8: **MATRIX SAMPLES**
AHETF-8.E.3.

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1.0 PURPOSE AND SCOPE

1.1 This SOP describes the methods by which agricultural worker exposure monitoring matrices, (*i.e.*, inner dosimeters, hand washes, face/neck wipes, inner socks, outer head patches, inner head patches, and OVS tubes) are to be spiked. This SOP applies to the use of all worker exposure matrices when used for producing field fortification recovery data for the Agricultural Handlers Exposure Task Force (AHETF).

1.2 This SOP was revised to add fortification sample size when only upper and lower inner dosimetry will be used in the study, section 2.1.a. Minor typographical errors were also corrected throughout the text.

2.0 EQUIPMENT/REAGENTS REQUIRED

2.1 The following examples of equipment and solutions are required for each day that field fortifications are to be conducted:

a. Exposure monitoring matrix samples based upon protocol specified monitoring matrices (inner dosimeter material cut according to SOP AHETF-8.A. [upper and lower sections for two section monitoring or upper/lower arms & legs and front/rear torso for six section monitoring], moistened face/neck wipes, OVS tubes, and hand wash solutions, and if required, 50 cm^2 and 100 cm^2 head patches [made of inner dosimeter material], and socks).

b. Appropriate containers for fortified matrix samples (*e.g.*, bags, bottles, jars, *etc.*)

c. Appropriate pipettes (*e.g*. 1.0 mL, non-graduated Pasteur pipettes, *etc.*)

d. Appropriate syringe (*e.g*., 100 µL)

e. Distilled or deionized water

f. Anionic detergent solution (0.01% v/v Aerosol® OT 75). Refer to the SOP AHETF-8.B for solution preparation.

g. Paper towels

h. Disposable gloves

i. Aluminum Foil

j. Rinsing solvent (to be the same as the solvent used to make spiking solutions)

3.0 SPIKING MATERIALS

3.1 Spiking materials may be in the following forms:

a. Active ingredient (ai) in an organic solvent

b. Formulated product in water

c. Formulated product pre-weighed into a container in which a specific amount of water is to be added in the field prior to being spiked onto (into) a matrix material.

d. Pre-spiked OVS tubes.

4.0 SPIKING TECHNIQUES

4.1 There are two (2) basic procedures that may be used for the fortification of worker dermal exposure matrices for the AHETF. They are by pipette and by vial.

4.2 When applying a spiking material to the various matrices, it is important to ensure that the solution/suspension gets well mixed prior to spiking and/or distributed as evenly as possible.

4.3 The spiking material needs to be distributed mechanically, typically with a pipette or vial, over the largest amount of matrix area as possible.

4.4 **Spiking ai in solvent:** A volume, typically 1 mL, of spiking solution will be drawn up into the pipette and then applied appropriately to the matrix of choice.

4.5 **Spiking formulated product in water:** A well-mixed aliquot, typically 1 mL, will be taken from a well-shaken bottle of the formulation suspended in water. The shaking may be done by hand, on a stirring plate, or using a mechanical shaker. Once the suspension looks evenly distributed, an aliquot is taken and applied appropriately to the matrix of choice.

4.6 **Spiking using entire solution vials:** Vials containing a known aliquot of a known concentration of spiking material will be sent to the field along with instructions on how to apply the spike to a matrix. The person doing the spiking will take a given spiking vial, unscrew the cap, and apply the contents to the matrix. The contents may be poured directly from the vial or removed via a Pasteur pipette (or equivalent). Use of a pipette may be desired for smaller matrices where more exact placement of material is necessary. The vial and pipette will sometimes be rinsed several times with the solvent (*e.g.* deionized or distilled water, acetone, acetonitrile, *etc.*) that was used to prepare the solution and applied to the matrix or as directed by the analytical laboratory (see below). The vial shall be retained with the fortified sample. The cap should be discarded and should not be rinsed. Vials should be marked with a label that may be tied to the vial with string or is a self adhesive label, which may be removed easily from the vial and will not interfere with analysis of fortified matrices.

5.0 SPIKING PROCEDURES

5.1 Inner Dosimeters

a. The dosimeters must be placed on a piece of aluminum foil prior to spiking. After spiking and weathering (if applicable), the sample will be wrapped in the same piece of foil it was placed on for spiking and weathering then inserted into the sample container.

b. The spiking material will be added to inner dosimeters; ensure the fortification is added to a dosimeter that has been folded to provide at least 6 layers of cloth. This insures that all the material is absorbed by the cloth.

c. When spiking with solution vials, the person doing the spiking will unscrew the cap and apply the contents to the matrix. The vial will be rinsed several times as directed by the analytical laboratory with the solvent that was used to prepare the solution or suspension. This may be done several times, however; too much solvent will cause the spike to run through the fabric, so judgment is needed. The empty spiking vial will be placed on its aluminum foil with the matrix prior to folding the foil.

d. When pipetting the solution onto the dosimeter, the tip of the pipette may be used to help distribute the spike (typically 1 mL) in lines evenly over the surface of the dosimeter. At no time can there be a bead of spiking material left on the surface. (The spiking liquid may tend to bead up on the surface. Gently pushing the pipette tip over the bead will help to get the liquid into the matrix.)

e. For dosimeters exposed to ambient conditions, the inner dosimeters will be folded over after fortification and covered with a single layer of shirt material during exposure. Effort should be made to ensure that the spiking solution has been completely absorbed by the material prior to covering.

5.2 Hand Washes

a. When spiking from a solution or suspension in the field, the appropriate amount of spiking solution (typically 1 mL) will be added to the hand wash.

b. When spiking with vials, the cap to the solution vial will be unscrewed from the vial and discarded without rinsing. The contents will be added to a 500 mL Aerosol OT (AOT) sample and the vial then dropped into the sample. The sample will then be swirled or the jar inverted to ensure proper mixing of the spiking material with the sample matrix.

5.3 OVS tubes

a. The tubes will be spiked at the laboratory with the proper amount of analytical standard. The tubes will always be spiked with an ai solution using a syringe. The spike will be applied by inserting the needle through the glass fiber filter and approximately one quarter of the way into the front sorbent bed.

b. Depress the syringe plunger slowly to avoid the ai solution from "bleeding out" of the sorbent and adhering to the glass tube. Each tube will be spiked with a minimum of 5μL up to, but not exceeding, 100 μL of solution. The actual amount of spiking solution to use will be determined by the analytical laboratory and documented in the raw data.

c. Tubes fortified in the laboratory will be sent frozen in plastic bags to the field. The bags will be to be taken out of the freezer and allowed to come to ambient temperature before they are used in the field. Just before they are to be put on the personal air sampling pumps, they should be taken out of the bag and allowed to finish equilibrating with the environment. They then will be placed onto the pumps and air pulled through them for the approximate length of time the worker replicates are in the field.

5.4 Face/Neck Wipes

a. Pre-wet two face/neck wipes as described for field samples in SOP AHETF-8.C.

b. When spiking with solution vials, the two gauze pads will first be placed into the sample jar or on clean foil. The contents of the vial will then be transferred onto the gauze pads. The vial will be placed with the sample without being rinsed. The cap will be discarded without rinsing. The sample will be wrapped in foil and placed in a plastic bag, or the jar will be capped and sealed after fortification, as appropriate. In the laboratory, the vial will be rinsed as part of the extraction procedure.

c. When pipetting the solution onto the wipe, the tip of the pipette may be used to help distribute the spike (typically 1 mL) in lines evenly over the surface of the wipe, if necessary.

5.5 Socks

a. The socks must be placed on a piece of aluminum foil prior to spiking. After spiking and weathering, the sample will be wrapped in the same piece of foil it was placed on for spiking and weathering then inserted into the sample container.

b. When adding spiking material to socks, ensure the sock sample consists of 2 socks (1 pair). The actual spiking material will be to be placed on the one sock (2 layers) that is closest to the foil.

c. When spiking with prepared solutions in vials, the person doing the spiking will unscrew the cap and apply the contents to the matrix. The cap will be discarded without rinsing. The vial will be rinsed several times with the solvent that was used to prepare the solution, as directed by the analytical laboratory. Multiple rinses may be done; however, too much solvent will cause the spike to run through the fabric, so judgment is needed. Place the empty spiking vial in its aluminum foil with the matrix.

d. When pipetting the solution onto the dosimeter, the tip of the pipette may be used to help distribute the spike (typically 1 mL) in lines evenly over the surface of the dosimeter. At no time can there be a bead of spiking material left on the surface. (The spiking liquid may tend to bead up on the surface. Gently pushing the pipette tip over the bead will help to get the liquid into the matrix.)

e. For socks exposed to ambient conditions, place two socks together on aluminum foil, pour the spiking solution evenly on the upper sock, then fold the two socks over each other. Outer dosimeter shirt material **should not** be placed over the sock sample.

5.6 Outer Head Patches

a. For field fortification samples, only, an outer head patch will consist of 6 layers of inner dosimeter material, each layer cut to a 50 cm^2 area wrapped in aluminum foil. The foil should be placed underneath the pile of patches and used to wrap the weathered spiked patch sample once the weathering period is completed.

b. The field fortification suspensions will be applied to the topmost layer of patches. The additional layers will be used to ensure that no spiking material leaches out onto the foil that underlies the pile of patches.

c. Outer head patches **will not be** covered during the weathering period.

5.7 Inner Head Patches

a. For field fortification samples, only, an inner head patch will consist of 4 layers of inner dosimeter material, each layer cut to a 100 cm^2 area, wrapped in aluminum foil. The foil should be placed underneath the pile of patches and used to wrap the weathered spiked inner dosimeter patch sample once the weathering period is completed.

b. The field fortification suspension will be applied to the topmost layer of material. The additional layers will be used to ensure that no spiking material leaches out onto the foil that underlies the pile of patches.

c. Inner head patches will be covered with chemical resistant headgear similar to the type worn by the workers during the application period, or other suitable material to simulate the headgear, as approved by the Study Director.

6.0 FORTIFICATION SAMPLE IDENTIFICATION AND HANDLING

6.1 Refer to SOP AHETF-8.F. for the procedures to uniquely identify fortification samples.

6.2 Fortification samples that are exposed under the open sky should have the necessary materials to protect the samples in the event of rain.

6.3 Fortification samples are packaged, stored and transported in the same manner as the test samples for a particular matrix. The fortification samples should not be placed into the same shipping/storage container with control samples or with field samples.