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Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
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Standard Operating Procedure **SOP-BCO-L-26.0**

Title: Preparation of Calibration and Surrogate Recovery Solutions for GC/MS Analysis of PAH

Source: The University of Arizona

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

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Preparation of Calibration and Surrogate Recovery Solutions for GC/MS Analysis of PAH

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes procedures for preparing calibration curve solutions for GC/MS analysis of PAH. It also covers preparation of the surrogate recovery standard (SRS) spiking solution, the internal standard (IS) spiking solution, and the field spiking solution.

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. Known amounts of these compounds are spiked into the collected sample (dust, soil, XAD-2, etc.) prior to extraction. The "surrogates" (perdeuterated PAH) are quantified at the time of analysis and their recovery indicates the probable extraction and recovery efficiency for native PAH that are structurally similar. The surrogate recovery standards are chosen to be as similar as possible to the native PAH and do not interfere with the native PAH 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.

2.3 Calibration Curve Solutions: The solutions used to calibrate the detector response and quantify analytes in sample extracts. Five solutions are prepared; each solution contains native analytes, surrogate recovery standards and internal standards. The concentrations of the native analytes and the surrogate vary in these solutions; the concentration of the IS remains fixed.

2.4 Field Spike Solution: The solution of native analytes that is prepared in the laboratory and sent to the field for use. In the field, a small aliquot of this solution is spiked with a syringe onto blank air sampling media (XAD-2). These spiked samples are returned for analysis with the field samples and blanks. The measurement of analyte recovery in these samples is used to assess the effects of sample handling and shipping on the recovery of analytes.

3.0 References

3.1 Chuang, J.C., Hannan, S.W., and Wilson, N.K., "Field Comparison Study of Polyurethane Foam and XAD-2 Resin for Air Sampling of Polynuclear Aromatic Hydrocarbons," Environ. Sci. Technol. **21**, 798-804 (1987).

3.2 Chuang, J.C., Hannan, S.W., Kuhlman, M.R., and Bridges, C., "Evaluation of Sampling and Analytical Methods for Nicotine and Polynuclear Aromatic Hydrocarbon in Indoor Air," Report EPA/600/4-87/031, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1987.

3.3 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 The calibration solutions described here provide: (1) surrogate recovery compounds (perdeuterated PAH) that are structurally similar to native PAH, (2) internal standards (phenanthrene-d10 and benzo[e]pyrene-d12 for PAH analysis; dibromobiphenyl for pesticides analysis) that are structurally similar to the target PAH and pesticides, respectively, and (3) a calibration range that encompasses typical air, soil, and dust concentrations, as determined from previous related studies (cf., Refs. 3.1 and 3.3).

4.2 The calibration curve standards cover the concentration range of 0.001-0.5 μg/mL for PAH. The actual concentration ranges for PAH may vary depending upon the sample matrices.

5.0 Responsibilities

5.1 An analyst in Battelle's pesticide/PAH extraction laboratory will be responsible for preparing the solutions defined here. The analyst will be responsible for ensuring that this SOP is followed, and that deviations and changes are reported to the pesticides/PAH extraction supervisory scientist as quickly as possible and recorded in the laboratory notebook.

5.2 The analyst will be responsible for maintaining accurate and complete records of all solutions prepared, and for preparing new solutions at the appropriate intervals.

6.0 Materials and Reagents

6.1 Materials

6.1.1 Balance with 4 place accuracy (x.xxxx g).

6.1.2 Volumetric flasks of various sizes.

6.1.3 Syringes of various sizes.

6.1.4 Assorted sizes of muffled/silanized glass vials with Teflon-lined screw caps.

6.1.5 1.5 mL V-Vials with Mininert caps (Wheaton and Supelco)

6.1.6 Ziploc bags.

6.2 Reagents

6.2.1 Naphthalene (stock solution Supelco)

6.2.2 Acenaphthalene (stock solution Supelco)

6.2.3 Fluorene (stock solution Supelco)

6.2.4 Phenanthrene (stock solution Supelco)

6.2.5 Anthracene (stock solution Supelco)

6.2.6 Retene (stock solution Supelco)

6.2.7 Pyrene (stock solution Supelco)

6.2.8 Fluoranthene (stock solution Supelco)

6.2.9 Benz[a]anthracene (stock solution Supelco)

6.2.10 Chrysene (stock solution Supelco)

6.2.11 Benzo[k]fluoranthene (stock solution Supelco)

6.2.12 Benzo[e]pyrene (stock solution ChemService)

6.2.13 Benzo[a]pyrene (stock solution Supelco)

6.2.14 Indeno[1,2,3-c,d]pyrene (stock solution Supelco)

6.2.15 Benzo[g,h,I]preylene (stock solution Supelco)

6.2.16 Dibenz[a,h]anthracene (stock solution Supelco)

6.2.17 Coronene (stock solution ChemService)

6.2.18 Quinoline (stock solution Supelco)

6.2.19 Dibromobiphenyl (stock solution ChemService)

6.2.20 Phenanthrene-d10 (neat Merck)

6.2.21 Benzo[e]pyrene-d12 (neat Merck)

6.2.22 Chrysene-d12 (neat Merck)

6.2.23 Benzo[k]fluoranthene-d12 (neat Merck)

6.2.24 Dichloromethane (distilled-in-glass)

7.0 Procedure

7.1 Prepare Stock Solutions

7.1.1 Prepare a stock solution at 1 mg/mL for those PAH that cannot be purchased as stock solutions. Using a 4-place balance, weigh directly into a clean 20 mL vial approximately 0.0100 g (e.g. 9.8 mg) of the analyte. Record the weight in the project laboratory notebook.

7.1.2. Calculate the volume of solvent needed to produce a 1 mg/mL solution, using the equation:

$$\text{solvent vol, mL} = x \text{ mg of analyte} / 1 \text{ mg mL}^{-1}.$$

7.1.3 Add this volume of dichloromethane (DCM) using a 10 mL analytical syringe calibrated in 0.1 mL increments. Replace the cap on the vial and shake gently to mix. Label with the laboratory notebook number (9 digit

unique code: 5 digit lab notebook number-2 digit page number-2 digit line number on which entered), analyte, concentration, solvent used, preparer's initials, and date of preparation. Mark the volume with a felt-tip pen on the outside of the vial. Enter this same data in the laboratory notebook on the page where the preparation is described, together with the lot number and manufacturer of the standard.

7.1.4. Store the solutions at 0°C or below.

7.2. Prepare Internal Standard Solutions and Surrogate Recovery Standards

7.2.1 Prepare the internal standard solution in DCM containing phenanthrene-d10 (50 µg/mL) and benzo[e]pyrene-d12 (5 µg/mL) for PAH analysis, and dibromobiphenyl (10 µg/mL) for pesticides analysis. For each sample extract and calibration standard solution, 10 µL of this internal standard solution spiked into each 1 mL extract will give final concentrations of 0.5 µg/mL of phenanthrene-d10, 0.1 µg/mL of dibromobiphenyl, and 0.05 µg/mL of benzo[e]pyrene-d12. Remove 500 µL of phenanthrene-d10 (1 mg/mL), 100 µL of dibromobiphenyl (1 mg/mL), and 50 µL of benzo[e]-pyrene-d12 (1 mg/mL) and inject into a 10 mL volumetric flask. Add DCM to the 10 mL mark. Mix well and transfer the solution to a clean glass vial.

7.2.2 Label with the laboratory notebook number (9 digit unique code: 5 digit lab notebook number-2 digit page number-2 digit line number on which entered), analyte, concentration, solvent used, preparer's initials and date of preparation. Mark the volume with a felt-tip pen on the outside of the vial. Enter this same data in the laboratory notebook on the page where the preparation is described.

7.2.3 Prepare the SRS spiking solution containing chrysene-d12 at 10 µg/mL in DCM, (10 µL of 10 µg/mL spiked into each matrix for 0.1 µg/mL final concentration). Remove 100 µL of chrysene-d12 (1 mg/mL) and inject into a 10 mL volumetric flask. Dilute with DCM to the 10 mL mark. Mix well and transfer the solution to a clean glass vial.

7.2.4 Repeat step 7.2.2.

7.2.5 Prepare the field spiking solution containing benzo[k]fluoranthene-d12 at 10 µg/mL in DCM, using the same procedure as in step 7.2.3.

7.2.6 Repeat step 7.2.2.

7.2.7 Aliquot ~1 mL volumes of the Field Spiking solution into 6 pre-labeled V-Vials with Mininert caps. Wrap these vials in a Ziploc bag and ship them to UA on dry ice.

7.2.8 Store the remainder of the Field Spiking solution at Battelle in a -20°C freezer.

7.3. Prepare PAH Calibration Standards

7.3.1 Prepare a mixed solution of the target analytes at 5 μg/mL in DCM. Add 50 μL of each 1 mg/mL stock to a 10 mL volumetric flask and dilute to volume.

7.3.2 Pour this solution into a muffled/silanized screw-cap vial, cap, and invert several times to mix.

7.3.3 Label with the laboratory notebook number (9 digit unique code: 5 digit lab notebook number-2 digit page number-2 digit line number on which entered), analyte, concentration, solvent used, preparer's initials and date of preparation. Mark the volume with a felt-tip pen on the outside of the vial. Enter this same data in the laboratory notebook on the page where the preparation is described.

7.3.4 Prepare individual solutions at 5 μg/mL each in DCM for the IS and the SRS. For this, add 50 μL of the 1 mg/mL stock to a 10 mL volumetric flask and dilute to volume.

7.3.5 Repeat steps 7.3.2 and 7.3.3.

7.3.6 Prepare 5 solutions to be used for GC/MS calibration curves, according to the matrix in Table 1, with each solution prepared and diluted in a 10 mL volumetric flask with DCM. The concentration ranges may vary as the sample matrices change.

7.3.7 Dilute each solution to volume with DCM. Pour into a muffled/silanized vial, and label as per step 7.3.3.

7.3.8 Aliquot ~1 mL volumes of these solutions with a clean Pasteur pipette into individual 1.8 mL screw-cap vials that are also so labeled. Label and store as per step 7.3.3.

Table 1. GC/MS PAH Calibration Standards.

Concentration, μg/mL analyte/SRS/IS	μL of 5 μg/mL analyte mix	μL of 10 μg/mL SRS solution	μL of IS solution
0/0/0.5,0.1,0.05	0	0	100
0.005/0.005/0.5,0.1,0.05	10	5	100
0.01/0.01/0.5,0.1,0.05	20	10	100
0.05/0.05/0.5,0.1,0.05	100	50	100
0.10/0.10/0.5,0.1,0.05	200	100	100

7.3.9 Store the vials in a tray in rows according to concentration.

7.4 Calculations

None. The use of these calibration solutions for quantification is discussed in SOP BCO-L-30.0.

7.5 Quality Control

7.5.1 The 0 μg/mL solution will serve as the QA/QC standard for these calibration solutions. The presence of native analytes or a surrogate in these solutions will indicate either carryover from the previous GC/MS run or contamination in the laboratory; either condition requires appropriate handling. For carryover, indicated by proportionately equivalent amounts of all analytes from the previous run, the time that the split valve is closed during injection can be lengthened. For laboratory contamination, indicated by random amounts of analytes in the "zero" standard, the standards must be re-prepared, with greater caution used in cleaning syringes and glassware.

8.0 Records

8.1 The preparation of all standards and solutions will be recorded in the project laboratory notebook. Each solution will be labeled with a unique 9 digit laboratory record book number (5 digit book number-2 digit page number-2 digit line number, e.g., 46680-45-12) corresponding to the record of its preparation.

8.2 All entries will be made in ink, and will be signed and dated in the notebook.

8.3 This notebook will be retained in the laboratory where it is used, and will be transferred to the office of the Battelle co-PI at the conclusion of the program.