GUIDANCE DOCUMENT

Passive PE Sampling in Support of In Situ Remediation of Contaminated Sediments: Standard Operating Procedure for PE Analysis

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14. ABSTRACT

This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in polyethylene devices (PEDs) to sample hydrophobic organic compounds (HOCs) in aquatic and sediment environments.

15. SUBJECT TERMS

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Standard Operating Procedure
for the Extraction and Analysis of Polyethylene (PE) Used
in Polyethylene Devices (PEDs)

1.0 SCOPE AND APPLICATION

1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in polyethylene devices (PEDs) to sample hydrophobic organic compounds (HOCs) in aquatic and sediment environments.

1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.

1.3 This extraction procedure is applicable to PE used in laboratory- or field-exposed PEDs.

2.0 SUMMARY OF METHOD

2.1 Upon recovery from the field exposure, the PE, while still in the PED, should be carefully cleaned (e.g. remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a drop of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted three more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.

2.2 A shaker table or some other suitable mechanical agitation is recommended for the extractions to facilitate PE-solvent contact.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric and surfaces, and so it must be handled using clean techniques.

3.2 While the formation of biofilms and epiphytic growth on PE surfaces does not compromise their behavior in the field during deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via water-wetted Kimwipe® wiping may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be removed by using solvent-saturated wipes (<minute contact times) followed by immediate Surrogate standard addition and solvent extraction.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: amber glass vials (foil-lined lids)

4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent

4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent

4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg.)

4.5 Food-grade aluminum foil

4.6 Stainless steel forceps

4.7 Single-edge razor blades

4.8 Teflon (or similar non-contaminating material) cutting board

4.9 Glass transfer pipettes.

4.10 Kimberly-Clark Kimwipe® or equivalent

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grad or equivalent (other solvent suited to analytes of interest).

5.2 Organic-free reagent water (as defined in SW-846 Chapter One)

5.3 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

6.0 PREPARATION AND HANDLING

6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.

6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.

6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.

6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

7.0 PROCEDURE

7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.

7.1.1 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed by using a clean wipe followed by a rinse with organic-

free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.

7.1.2 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40mL). Vial must be large enough for complete immersion of PE without excessive PE folding.

7.1.3 Known masses of surrogate compounds (Appendix 1) in a methylene chloride-compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.

7.1.4 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.

7.1.5 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.

7.1.6 After the final extract transfer, the PE is allowed to air dry in the extraction vial and weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.

7.2 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).

Typical final extract volumes are:

50-250 μL for water column-exposed PE

1-10 mL for contaminated sediment bed-exposed PE

8.0 QUALITY CONTROL

8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets like PAHs and PCBs that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng / g PE

Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility (±1σ/mean, N=6): <10%
Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%
Surrogate standards should be recovered from PE samples at 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N≥3): <20%.
The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall with suitably narrow bounds.

8.2.5 Detection limits using PE samples: <1 ng / g PE
Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes such as PAHs and PCBs analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

9.0 METHOD PERFORMANCE

9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.

9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009).

10.0 REFERENCES

Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. Environ. Sci. Technol., 43, 8888-8894, 2009.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The lab preparing the PEDs must coordinate PRC choices with the lab doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**	
PRCs	d10-phenanthrene	d10-pyrene	d12-chrysene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**			
PRCs	^{13}C PCB-28	^{13}C PCB-52	^{13}C PCB-101	^{13}C PCB-153	^{13}C PCB-180	
Surrogates	^{13}C PCB-19	d_6 PCB-77	^{13}C PCB-105	^{13}C PCB-167	^{13}C PCB-170	^{13}C PCB-194
Injection Standards	d17-39	d22-104	d34-55	d40-150	d52-188	

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of 13C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C PCB 178
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167