STANDARD OPERATING PROCEDURE FOR THE PREPARATION OF SPIKED SORBENT SAMPLES USING FLASH EVAPORATION SPIKING ONTO XAD-2®

1.0 PURPOSE

The purpose of this document is to provide a detailed Standard Operating Procedure (SOP) for preparing spiked sorbent by spiking selected Title III semivolatile organic compounds (SVOCs) onto clean, dry XAD-2® using a flash evaporation spiking technique.

2.0 SCOPE AND APPLICABILITY

2.1 Scope

This SOP covers the preparation of the standard solution and sorbent media (XAD-2®) and the procedure for the preparation and storage of the spiked sorbent samples.

2.2 Applicability

This SOP is applicable to the spiking of selected SVOCs, surrogates, and internal standards. Recoveries >60% have been demonstrated in laboratory studies for the following compounds:

Analytes:

Toluene
n-Octane
Chlorobenzene
o-Xylene
Cumene
Bromobenzene
3-Chlorotoluene
Dichloroethyl ether
1,4-Dichlorobenzene
3',4'-Difluoroacetophenone
p-Cresol
Acetophenone
Nitrobenzene
Hexachloroethane
Isophorone
1,2,4-Trichlorobenzene
Naphthalene
Quinoline
2-Methylnaphthalene

Biphenyl
4-Nitrophenol
Dibenzofuran
Fluorene
Hexachlorobenzene
Lindane

Internal Standards:

1,4-Dichlorobenzene-d_4
Naphthalene-d_8
Phenanthrene-d_{10}
Acenaphthene-d_{10}
Chrysene-d_{12}
Perylene-d_{12}

Surrogates:

2-Fluorophenol
Phenol-d_5
2,4,6-Tribromophenol
Nitrobenzene-d_5
2-Fluorobiphenyl
p-Terphenyl-d_{14}

The recommended range for spiking these analytes is 200 μg to 1000 μg of each analyte in methylene chloride solution. the lower part of the range was selected because, assuming 100% recovery, an extracted amount of 200 μg/5 mL final extract volume will yield an amount injected on column (1 μL injection) of 40 ng. An injection of 40 ng should be within a factor of two or three of the analytical detection limit. If 100% recovery is not achieved, a recovery of 60% at the 200 μg spiking level should still yield approximately 24 ng on column, a value near but slightly above the analytical detection limit. If 1000 μg of an analyte is spiked with 100% recovery, the value for the extract of 1000 μg/5 mL will yield an injection of 200 ng on column. This injected amount is at or slightly above the top of the typical calibration range for semivolatile analysis.

3.0 METHOD SUMMARY

This method describes a procedure for the preparation of spiked sorbent samples by spiking selected SVOCs that have been volatilized onto a bed of XAD-2®. The analytes are vaporized by injecting a liquid solution into a heated injection port and are transferred by a flowing inert gas (helium of clean nitrogen) onto the sorbent. This method of spiking is referred to as flash evaporation.

4.0 INTERFERENCES

Any component used during the preparation of the spiked sorbent may act as a source of analytical interferents. Organic solvents may contain keepers or radical scavengers (for example, cyclohexene in methylene chloride) which may act as analytical interferents. Styrene, oxygenates, acids, esters, aldehydes and phenolic compounds may be interferents present on XAD-2®. Exposure of the filters to organic solvent vapors (such as in a laboratory atmosphere) may cause sorption of these compounds onto the XAD-2®. Interferences may be minimized by using only solvents of known purity and using only precleaned XAD-2®.

5.0 SAFETY

The preparation of spiked sorbents may expose the analyst to some chemical and physical hazards. Material safety data sheets (MSDSs) must be obtained, and listed guidelines should be followed for each analyte and solvent used. Any preparation of standard solutions should be performed in a hood. Personal protective equipment such as chemical resistant gloves, laboratory coats and laboratory safety glasses must be used while handling organic solvents or the chemicals listed above. The heated injection port used during the spiking procedure is a potential burn hazard. Therefore, it is recommended that the analyst use heat resistant gloves while attaching or removing the XAD-2® glass sampling module to or from the injection or port fittings. Gloves must also be abrasion resistant for protection against broken glassware. Spiking operations should be performed in a hood or well-ventilated area.

6.0 MATERIALS AND APPARATUS

XAD-2® glass sampling modules (40-g size) as shown in Figure 1. Pre-extracted glass wool (i.e., Soxhlet® extracted with methylene chloride).
Standard syringes with stainless steel® needles (10-500μL).
Thermocouples attached to temperature readout device.
Gas bubble flow meter.
Injection port with silicone rubber septum and silanized glass liner.
Analytical balance (4-place minimum).
Volumetric flasks.

7.0 CHEMICALS AND REAGENTS

Methylene chloride - Spectrometric or equivalent grade.
SVOC analyte standards - highest purity available.
Method 8270 internal standards (available commercially in a mixture).
Method 8270 surrogates (available commercially in a mixture).
Helium - Ultrapure, compressed gas (99.9999%).
Nitrogen may also be used.

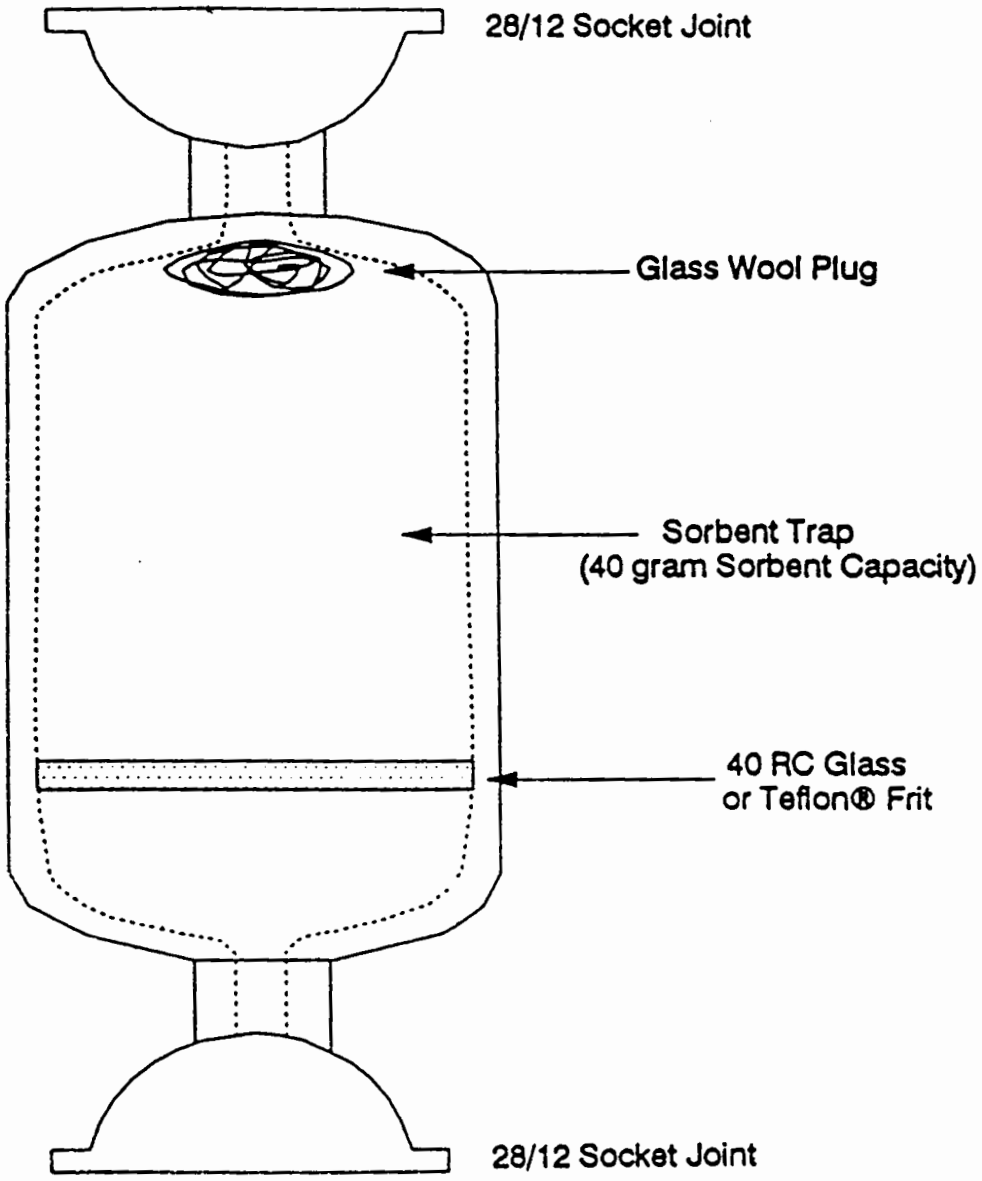

Figure 1. XAD-2® Glass Sampling Module

8.0 PROCEDURE

8.1 Selection of Compounds

Compounds were selected from the semivolatile organic compounds listed in Title III of the Clean Air Act Amendments of 1990. Compounds were selected on the basis of the following criteria:

1. They were expected to show acceptable to excellent recoveries from sorbent and acceptable to good chromatography.
2. The corresponding isotopically-labeled surrogates, fluorinated analogs, or homologs had to be commercially available. These isotopically-labeled or analogous compounds could be used in the preparation of spiking mixtures for either dynamic spiking at a field site or spiking onto sorbents which might contain the native materials upon returning from field testing.

8.2 Preparation of Spiking Solution

One or more compounds selected for spiking may be chosen from the analyte list given in Section 2.2. A stock solution containing the analytes in methylene chloride at a concentration of 7500 μg/mL may be prepared by weighing the individual compounds on an analytical balance, adding the compounds to a volumetric flask, and diluting to volume with methylene chloride. The stock solution should be mixed well using sonication if necessary. Analytical calibration standards may be prepared from this stock solution by diluting aliquots of the stock solution with methylene chloride. Surrogate standards should be prepared according to SW-846 Method 3500 (if SW-846 Method 8270 will be used as the analytical method). The stock solution should be stored in the refrigerator at 4°C with no headspace, and should be replaced after one year.

8.3 Preparation of XAD-2® for Spiking

XAD-2® sorbent should be cleaned as described in SW-846 Method 0010. Analysis to demonstrate cleanliness may be performed by GC/MS.

8.4 Preparation of Apparatus for Spiking

The injection port containing an inert gas purge system may be assembled wherein the inert gas flow (30mL/min) is passed through a stainless steel® tee fitted with a septum injector. The XAD-2® sampling module is connected downstream of the tee using appropriate Swagelok® fittings as shown in Figure 2. The injection port must be heated to 300°C. With a list of applicable analytes that includes semivolatile organic compounds boiling over a wide range of temperatures, temperature of the injector is a critical parameter to ensure that the liquid spike volatilizes completely and is quantitatively transferred to the sorbent resin. Complete wrapping with heating tape may be necessary to ensure that there are no cold spots

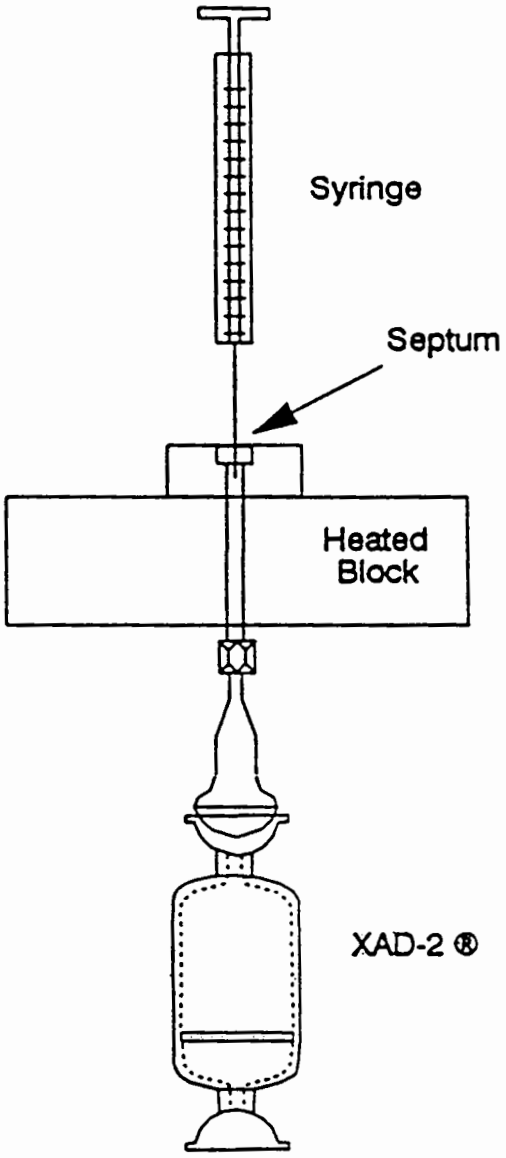

Figure 2. Flash Evaporation Spiking Apparatus

in the spiking apparatus. If a heating tape wrap is used for heating, care must be taken to ensure that no XAD-2® sorbent resin inside the sampling module is scorched.

In addition, the connection between the XAD-2® sampling module and the gaseous spiking apparatus (usually a ball joint) must be gas-tight in order to prevent release of volatilized spiking compounds. A buildup of XAD-2® particles inside the ball joint will prevent an effective seal. Both parts of the ball joint must be scrupulously clean for an effective seal.

The bottom ball joint closure must be removed from the XAD-2® sampling module prior to introducing gas flow from the injection system to prevent pressure buildup within the sampling module.

Verify that the flow of inert gas through the spiking apparatus is adequate before spiking is initiated.

8.5 Preparation of Syringes for Spiking

New syringes must be used, if possible. The syringes must be rinsed a minimum of five times with methylene chloride prior to use of the syringe with the spiking solution in order to minimize contamination and to prevent carryover between samples.

8.6 Spiking Procedure

The spiking procedure may be carried out as follows:

1. The XAD-2® glass sampling modules must be prepared by adding 40 g of clean, dry XAD-2® to each sampling module. The caps on the end of the trap should then be removed.
2. The sampling module must be attached in a vertical position to an injector port heated to 300°C.
3. The inert gas flow (30 mL/min) through the port must be turned on.
4. The desired volume of the 7500 μg/mL spiking solution (Section 10.0) should be injected through the injector port. It is recommended that the total spiking volume not exceed 100μL and that only 10 to 20 μL aliquots are injected at a time. The solution should be injected slowly.

NOTE: If high spiking levels are used (> 1000 μg) a syringe pump should be used, if possible. A syringe pump will allow large volumes to be introduced into the XAD-2® sampling module slowly and consistently. In using a syringe pump, there must be no leaks in the connecting tubing from the syringe pump to the injector port. Use of a syringe pump requires approximately 50 μL of additional spiking solution in the syringe to allow for the occurrence of evaporation of the spiking solution.

5. The XAD-2® sampling module should be allowed to remain attached to the injector port after spiking for 10 minutes with the inert gas flowing.

6. The glass XAD-2® sampling module should be removed from the heated injector and a piece of pre-extracted glass wool placed on top of the XAD-2® in the trap. Note addition of glass wool after spiking. The caps should be replaced on the end of the trap and the caps should be wrapped with Teflon® tape. The helium flow should be turned off at this point prior to removal of the sampling module.

8.7 Spiked Sample Preservation

After spiking has been completed, the XAD-2® may be extracted and analyzed immediately or stored for up to two weeks in a 4°C (±2°C) refrigerator that is free of organic solvents. Prior to refrigerating, the glass sampling modules must be sealed tightly at both ends, and wrapped securely. Teflon® tape may be used to aid in sealing the ends.

8.8 Analytical Procedure

The spiked XAD-2® may be extracted using Soxhlet® extraction as described in the SW-846 Method 3540. The extracts may be applicable to analysis by gas chromatographic and mass spectrometric methods such as the SW-846 Method 8270.

9.0 SHORT HAND PROCEDURE

1. Analytes must be selected from the list of applicable compounds.
2. The analyte and surrogate stock solutions must be prepared.
3. The XAD-2® must be prepared for spiking (SW-846 Method 0010).
4. The injection port must be prepared for flash evaporation spiking.
5. The syringes must be prepared for injection of the spiking standard.
6. Spiking must be performed in the heated injection port with helium gas purge.
7. Spiked XAD-2® must be either immediately analyzed or preserved at 4°C (±2°C).

10.0 CALCULATIONS

Calculation of the volume of stock solution to be spiked:

$$V_s = (C_a \times V_e)/C_s$$

where:

V_s = Volume of the stock solution to be spiked (μL)
C_a = Total analyte (surrogate) concentration to be spiked onto the XAD-2® (ng/μL)
V_e = Final extract volume (μL)
C_s = Concentration of the stock solution (ng/μL)

11.0 QUALITY CONTROL

A minimum of three XAD-2® sampling modules must be spiked at a time to allow for statistical evaluation of reproducibility. The analyst must prepare and analyze a method blank (with each set of samples extracted) spiked only with internal standards in order to monitor laboratory and instrument contamination. The analyst must ensure that all reagents, solvents and gases used are of the highest purity available (spectrometric grade or equivalent for solvents), and that all glassware, syringes, equipment and sorbent used are clean. Further, spiking and preservation must be conducted in areas that are as free of organic vapor as possible.

12.0 DOCUMENTATION

Laboratory notebooks must be used to record all procedures. The notebooks should be signed and reviewed by the analyst and a supervisor or designated personnel. Chain of custody forms must be used to track all spiked samples once they are generated.

13.0 PUBLISHED REFERENCES

EPA SW-846 Method 0010
EPA SW-846 Method 3500
EPA SW-846 Method 3540
EPA SW-846 Method 8270

TECHNICAL REPORT DATA

1. REPORT NO.	2.	3
EPA/600/A-96/125		

4. TITLE AND SUBTITLE	5. REPORT DATE
Standard Operating Procedure for the Preparation of Spiked Sorbent Samples Using Flash Evaporation Spiking Onto XAD-2	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. F. McGaughey, Eastern Research Group J. T. Bursey, Eastern Research Group C. M. Morris, U.S. EPA	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Eastern Research Group P.O. Box 2010 Morrisville, NC 27560	11. CONTRACT/GRANT NO. 68-D4-0022

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S.Environmental Protection Agency NERL, AMRD, QAD Research Triangle Park, NC 27711	Standard Operating Procedure
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This Standard Operating Procedure is a method developed to spike semi-volatile organic compounds on solid adsorbents by flash evaporation for use as quality assurance and performance evaluation standards.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI
Semi-volatile organic compounds, flash evaporation, solid adsorbent		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	20. SECURITY CLASS *(This Page)*	22. PRICE