

Extraction of Polyaromatic Hydrocarbons (PAHs) from Soils by Pressurized Solvent Extraction (PSE)

Introduction

Pressurized solvent extraction is a new technique that reduces solvent consumption and sample preparation time. Solvent is pumped into an extraction vessel containing the sample and is heated and pressurized. The pressurized solvent at high temperature accelerates the extraction process by increasing the solubility of the analyte in the solvent and also increasing the kinetic rate of desorption of the analyte from the sample matrix.

Pressurized solvent extraction can be used to replace soxhlet and sonication techniques and is approved for use as EPA Method 3545A. This method is a procedure for extracting water insoluble or slightly water soluble, semi-volatile organic compounds from soils, clays, sediments, sludges, and waste solids. The EPA Method 3545A is applicable to the extraction of semi-volatile organic compounds, organophosphorous pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs.

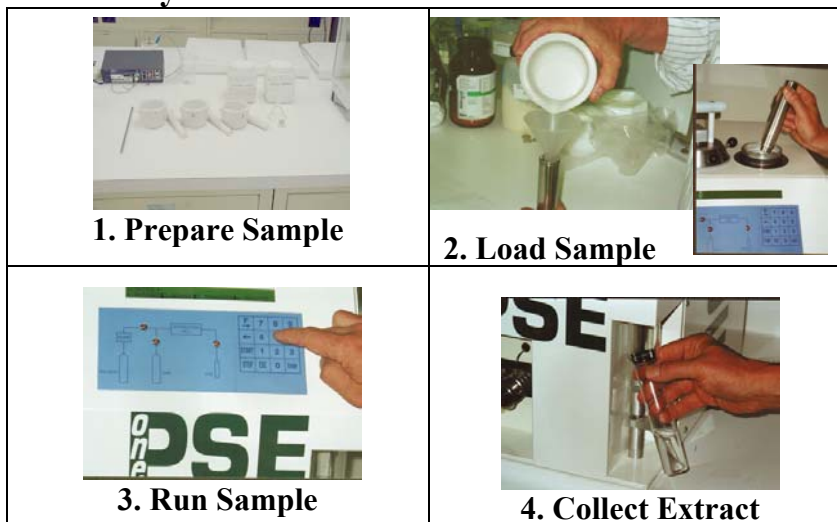
Equipment

- ✓ Applied Separations' *one* PSE Pressurized Solvent Extractor
- ✓ 11 mL Extraction Vessel-Cat.#10625
- ✓ GC or GC/MS
- ✓ Oven – for drying
- ✓ Desiccator
- ✓ Crucibles
- ✓ Grinding Apparatus
- ✓ Analytical Balance

Solvents and Materials

- ✓ Acetone – pesticide grade
- ✓ Methylene Chloride – pesticide grade
- ✓ N₂ - high purity grade
- ✓ Sodium sulfate (anhydrous, granular)
- ✓ S/S Frits (10 micron)- Cat. #10710
- ✓ Cellulose Filter Disk-Cat. #10711
- ✓ Collection Vials (60mL for extract collection)-Cat.#10650
- ✓ *Spe-ed*TM Matrix-Cat.#7950
- ✓ Ottawa Sand–Cat. #10548

Summary of Method



Procedure

Sample Preparation

Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Air-dry the sample at room temperature for 48 hours in a glass tray or on hexane-rinsed aluminum foil. Alternatively, mix the sample with an equal volume of anhydrous sodium sulfate or *Spe-ed* Matrix (pelletized diatomaceous earth) until a free-flowing powder is obtained.

Note: *Dry, finely ground soil/sediment allows the best extraction efficiency for nonvolatile, nonpolar organics. Air-drying may not be appropriate for the analysis of the more volatile organics because of losses during the drying process. The use of sodium sulfate as a drying agent can lead to clogging of the frits in the vessel with recrystallized sodium sulfate.*

Dry sediment and soil samples amenable to grinding. Grind or otherwise reduce the particle size of the sample so that it either passes through a 1-mm sieve or can be extruded through 1-mm hole. Disassemble grinder between samples, according to manufacturer's instructions, and decontaminate with soap and water, followed by acetone and hexane rinses.

Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The analyst may add anhydrous sodium sulfate, *Spe-ed* Matrix (pelletized diatomaceous earth), sand, or other clean, dry reagents to the sample to make it more amenable to grinding.

Grind a sufficient weight of the dried sample to yield the sample weight needed for the determination method (usually 10-30 g). Grind the sample until it passes through a 10-mesh sieve.

Determination of Percent Dry Weight

When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

Warning: *The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.*

Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Dry this aliquot overnight at 105 °C. Allow to dry in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100\%$$

Load the Sample

Prepare the extraction vessel(s) for analysis by placing a cellulose filter disk in the bottom opening followed by a 10µm s/s frit, and secure them in place with the retaining nut. Transfer the ground sample to an extraction vessel of the appropriate size for the aliquot. Generally, an 11 mL vessel will hold about 10 g of material, a 22 mL vessel will hold about 20 g of material, and a 33 mL vessel will hold about 30 g of material. The weight of a specific sample that a vessel will contain depends upon the bulk density of the sample and the amount of drying agent that must be added to the sample in order to make it suitable for extraction. Analysts should ensure that the sample aliquot extracted is large enough to provide the necessary sensitivity and choose the extraction vessel size accordingly. Matrix spikes and surrogate spikes may be added to the appropriate extraction vessels as required.

Add clean Ottawa sand to within 1 cm of the top of the vessel's interior flange (see illustration on page 4-3 of User's Manual).

Place the extraction vessel into the instrument as described in the *one* PSE operator's manual. Place a precleaned collection vial in the instrument for each sample. Ensure that the pump is primed and that the extraction solvent is acetone/methylene chloride (1:1, v/v). Program the instrument using the following parameters:

Extraction Conditions

*Program the following extraction parameters on the one PSE
Program A Mode – 11 mL vessel*

Solvent:	Acetone/Methylene chloride (1:1, v/v)
Temperature:	100 ° C
Pressure:	100 Bar
Cycles:	1
Static:	5 minutes
Pause:	N=0
Flush:	Solvent/gas/repeat flush:20 sec/2min/0

Optimize the conditions as needed. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction vessel is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the samples. Any pressure in the range of 100 BAR should suffice. Once established, the same parameters should be used for all samples extracted for the same analysis type.

Collection

Collect each extract in a clean vial. Allow the extract to cool after the extraction is complete.

The extract is now ready for concentration, cleanup, or analysis, depending on the extent of interferants and the determinative method to be employed. Refer to EPA Method 3600 for guidance on selecting appropriate cleanup methods. Excess water present in extracts may be removed by filtering the extract through a bed of anhydrous sodium sulfate. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or sample analysis.

References

US EPA Method 3545 – Pressurized Fluid Extraction
US EPA Method 3600 – Clean up

Safety

The use of organic solvents, elevated temperatures, and high pressures present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. However, the following sections describe additional steps that should be taken.

Extraction vessels in the *one* PSE oven are hot enough to burn unprotected skin. Allow the vessels to cool before removing them from the oven, or use appropriate protective equipment (e.g. insulated gloves or tongs) as recommended by the manufacturer.

During the gas purge step, some solvent vapors may exit through a vent port in the instrument. Connect this port to a fume hood or other means to prevent release of solvent vapors to the laboratory atmosphere. This precaution also applies to the removal of post extraction solvent from the collected extract.