



#617

Extraction of TPH (Total Petroleum Hydrocarbon) from Soils by Pressurized Solvent Extraction (PSE)

Introduction

Underground fuel tanks that develop leaks are a prime source of groundwater and soil contamination. The United States Environmental Protection Agency (EPA) estimates that there are presently 5 – 7 million underground storage tanks in the United States, and about 1.4 million of these are used to store petroleum fuel products. Approximately 1.6 million tanks are currently regulated by the EPA. Soxhlet and sonication techniques have been traditionally used to monitor the petroleum hydrocarbon contamination of soils and sediments caused by underground storage tank leakage. Unfortunately, these conventional extraction methods are labor intensive and require large volumes of solvent.

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.

The *fast* PSE is an automated system which processes six samples simultaneously. The parallel processing technology of the *fast* PSE dramatically increases sample throughput compared to Soxhlet and pressurized solvent extraction systems that employ serial processing. In addition to rapid extraction times, significant reduction in solvent consumption is achieved.

PSE *fast* APPLICATIONS

#617

Pressurized solvent extraction can be used to replace Soxhlet and sonication techniques and is approved for use as EPA Method 3545A. This application describes a procedure for extracting petroleum hydrocarbon contaminants such as diesel and waste oil in soils with significant time-savings and solvent reduction. The method is applicable to the extraction of waste oil organics (WOO), diesel range organics (DRO), and total petroleum hydrocarbons from soils.





Equipment

- ✓ Applied Separations' *fast* PSE Pressurized Solvent Extractor
- ✓ 11 mL Extraction Vessels-Cat.#10625
 - Note: the *fast* PSE can run 6 samples simultaneously
- ✓ Gas chromatograph with flame ionization detector (GC-FID)
- ✓ Analytical Balance
- ✓ Sample concentrator

Solvents and Materials

- ✓ Acetone
- ✓ Methylene chloride
- ✓ *n*-Tricosane (C₂₃) - to act as surrogate
- ✓ Silica gel-100/200 mesh, Davisil grade 634 or equivalent
- ✓ *Spe-ed*TM Matrix- Cat. #7950
- ✓ Collection Vials (60mL for extract collection)-Cat. #10650
- ✓ Cellulose Filter Disk-Cat. #10711
- ✓ S/S Frits (10 micron)- Cat. #10710
- ✓ Ottawa Sand-Cat. #10584
- ✓ 10 x 250 mm chromatographic columns or disposable pipettes
- ✓ 100 mL beaker

Summary of Method

 <p>1. Prepare Sample</p>	 <p>2. Load Sample</p>
 <p>3. Run Sample</p>	 <p>4. Collect Extract</p>

Procedure

Prepare Sample

Discard any foreign objects such as sticks, leaves, and rocks. Mix the sample thoroughly, especially composited samples. Inspect the dry sample. If the sample particle size is too large, grind or otherwise reduce the particle size of the soil so that it passes through a 1mm sieve. Soil samples that are wet should be weighed into a 100-mL beaker and mixed with *Speed Matrix*.

Note: Speed™-Matrix should be purified by heating at 400°C for four hours in a shallow tray or by extraction with methylene chloride. The silica gel should be activated by heating for at least 16 hours at 130°C in a shallow glass tray, loosely covered.

PSE *fast* APPLICATIONS

#617

Load Sample

Prepare the extraction vessels for analysis by placing a cellulose filter disk in the bottom opening followed by a 10 μ m s/s frit, and secure them in place with a retaining nut. Place prepared sample into extraction vessel. Add 1-mL of *n*-tricosane to sample in extraction vessel. Add clean Ottawa sand to within 1 cm of the top of the vessel's interior flange as directed in User's Manual.

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

Extraction Conditions

Program the following extraction parameters on the fast PSE Program A Mode – 11 mL vessels

Solvent:	Methylene chloride/acetone (1:1, v/v)
Temperature:	175 ° C
Pressure:	130 Bar
Static:	5 minutes
Solvent Module:	1*
Cycles:	1
Pause:	N=0
Flushing Program:	Solvent/gas/repeat flush: 1 min/2 min/0

***Note:** *If automatic solvent selection module is used, enter the appropriate position number (i.e. 2, 3, or 4).*

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.

PSE *fast* APPLICATIONS

#617

Collect Extract

Collect each extract in a clean 60 mL vial. Allow the extract to cool after the extraction is complete.

Extract Cleanup

If it is necessary to remove coextracted interferants from the sample use EPA Method 3630. Weigh out 2-10 g of activated silica gel and place in a 10-mm ID glass chromatographic column. Top silica gel with 4 to 5 cm of sodium sulfate. Note that the amount of sodium sulfate will vary according to the moisture content of the sample. Transfer the sample extract onto the column. Rinse the collection vial two or three times and transfer each rinse to the column. Elute the column with sufficient hexane or methylene chloride to ensure recovery of the analytes (see EPA Method 8440 for guidance).

Analysis

After cleanup, the samples are ready for volume adjustment and further analysis. The samples can be analyzed by employing EPA Method 8015 (GC/FID).

References

US EPA Method 3545A – Pressurized Fluid Extraction
US EPA Method 8015- Halogenated Volatiles (GC/FID)

PSE *fast* APPLICATIONS

#617

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 *fast* 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.