

Accelerated Solvent Extraction (ASE) of Hydrocarbon Contaminants (BTEX, Diesel, and TPH) in Soils

INTRODUCTION

Underground storage tanks containing hydrocarbon-based fuels are found worldwide. Many of these underground storage tanks are known to have leaks, allowing gasoline, diesel or other fuels to contaminate the surrounding soil. As of 1992, there were two million underground tanks being monitored for leaks and an additional three million not monitored for leaks within the United States alone. Obviously, the ability to determine the level of hydrocarbon contamination in soils is an important analytical tool.

In the United States, U.S. EPA Methods 3540 (Soxhlet) and 3550 (sonication) are presently used for the extraction of hydrocarbons from soils prior to their analytical determination. Similar methods are used worldwide. Soxhlet extraction is time-consuming (four or more hours) and requires 250–500 mL of solvent for 10 to 30 g samples. Sonication requires 150–500 mL of solvent, and is a labor intensive method requiring multiple extraction and decanting steps for each sample. In addition, both of these methods use CFC-113 (Freon® 113) as the extraction solvent. The use of chlorofluorocarbons is being eliminated in many countries of the world. Clearly, an alternative to standard extraction procedures is needed.

Accelerated Solvent Extraction (ASE®) is an innovative sample preparation technique that combines elevated temperatures and pressures with liquid solvents to achieve fast and efficient removal of analytes of interest from various matrices. With ASE, extractions can be done in very short periods of time and with minimal amounts of solvent as compared to conventional sample extraction techniques such as Soxhlet or sonication. For example, 10 g dry samples can be completely extracted in less than 15 min with less than 15 mL of solvent. ASE has been demonstrated to be equivalent to existing extraction methodologies such as Soxhlet and automated Soxhlet for most RCRA (Resource Conservation and Recovery Act) analytes from solid and semisolid samples. It meets the requirements of U.S. EPA Method 3545, Pressurized Fluid Extraction. The analytes included in Method 3545 are the semivolatiles (BNAs), organochlorine and organophosphorous pesticides (OCPs and OPPs), polychlorinated biphenyls (PCBs), and chlorinated herbicides. This note reports the use of ASE for the extraction of diesel fuel, gasoline (BTEX), and total petroleum hydrocarbons (TPH) from soils.

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EQUIPMENT

ASE 200 Accelerated Solvent Extractor* equipped with 11, 22, or 33 mL extraction cells

Gas Chromatograph with Flame Ionization Detector (GC-FID)

Analytical balance

Infrared spectrophotometer (IR), single wavelength or FTIR

Dionex vials for collection of extracts (40 mL, P/N 49465; 60 mL, P/N 49466)

*ASE 150 and 350 can be used for equivalent results.

SOLVENTS

Pentane

Hexane

Acetone

Methylene chloride

Perchloroethylene (PCE)

All solvents are available from Fisher Scientific.

EXTRACTION CONDITIONS

Extraction Conditions

Dry Samples (less than 40% (wt) water)

Sample Size: 3–20 g

Solvent: Perchloroethylene (IR determination);
Pentane or hexane (GC)

Temperature: 100 °C

Pressure: 1500 psi*

Static Time: 5 min

Flush Volume: 60%

Purge Time: 60 s

Cycles: 1

*Pressure studies show that 1500 psi is the optimum extraction pressure for all ASE applications.

Wet Samples (greater than 40% (wt) water)

Sample Size: 3–20 g, mixed 1:1 with ASE Prep DE (P/N 062819)

Solvent: Perchloroethylene (IR determination);
Hexane/acetone, 1:1 volume (GC)

Temperature: 200 °C

Pressure: 1500 psi

Static Time: 5 min

Flush Volume: 60%

Purge Time: 60 s

Cycles: 1

Note: If the sample has a high clay content, the extraction should be performed twice. The extracts should be combined before analysis.

Quantitation

Analytical determinations of the hydrocarbons in the soil extracts were performed by infrared spectrophotometry (IR) or gas chromatography (GC). Quantitation of the total petroleum hydrocarbon (TPH) content was done using the procedure described in U.S. EPA Method 8440. After collection, the extracts were passed through sodium sulfate and silica gel to remove water and polar constituents. An aliquot of the extract was then placed in the IR analyzer. The TPH value was determined by comparison to a three-point calibration curve constructed from dilutions of a stock solution of a 2:3:3 volume ratio of chloro- benzene, isooctane, and *N*-hexadecane made up in perchloroethylene (PCE).

Quantitation of diesel from dry and wet soils was performed using GC with the following conditions: 30 m × 0.25 mm i.d. Rt_x-5 (Restek) capillary column (1 μm film); FID at 310 °C; split injector at 250 °C; 0.5 μL injection; 50:1 split; temperature programmed from 40 to 265 °C at 20 °C/min after a 4 min hold, with a 10 min hold at final temperature. The peak area was summed from 0.8 to 17.0 min. Hexacosane was added to the sample vials as the internal standard after volume adjustment to 5 mL.

A standard containing volatile compounds representing gasoline range organics (GRO) and the low end of diesel range organics (DRO) was spiked (100 μL of a 1 mg/mL/component solution) onto clean sand to investigate the recovery of these compounds under ASE conditions. The quantitation was done by GC under the following conditions: 30 m × 0.25 mm i.d. Rt_x-5 (Restek) capillary column (1 μm film); FID and splitless injector at 300 °C; 5 μL injection; temperature programmed from 40 to 200 °C at 8 °C/min after a 4 min hold, with a 1 min hold at final temperature. Helium was the carrier gas at 30 cm/s. Acetophenone was added to the vials after collection as an internal standard. The same conditions were used to determine the recovery of pentane spiked on sand.

RESULTS AND DISCUSSION

Extractions of TPH were done using Reference Soil from Environmental Resource Associates (ERA). This is a clay top soil with less than 10% water by weight that has been ground and sieved. The TPH levels varied between 1200 and 2500 mg/kg (ppm) and were certified by ERA. Eighty-five samples in the 4 to 8 g range were extracted using PCE and analyzed by IR as detailed above. The average recovery was 103% of the certified value with 2.7% RSD.

Clean blank samples of the same soils were spiked with No. 2 diesel fuel and extracted using pentane and hexane. GC was used as the analytical method. Pentane was investigated because it is more volatile, and it facilitates sample concentration. The average recovery when using pentane was 99.7% with 0.47% RSD ($n = 3$). The average recovery using hexane was 101% with 2.4% RSD ($n = 3$).

Experiments were performed to investigate the recovery of more volatile compounds by spiking a standard mixture on clean sand in an extraction cell. Methylene chloride was the solvent and the cell temperature was 60 °C, with a 5 min heatup, 5 min static method, and the pressure at 10.3 MPa (1500 psi). Four extractions were performed, and duplicate injections were made (see Table 1 for the results). Good recoveries for all compounds, even the more volatile BTEX compounds (benzene, toluene, ethylbenzene, and xylene) were obtained. Under the same conditions, the recovery of pentane (36 °C bp) was 90.1% with 1.8% RSD.

The conditions used with dry samples did not give complete recovery of the hydrocarbon contaminants when used with wet samples, particularly those having a high clay content. This was presumed to be due to the low miscibility of nonpolar solvents with the water in the samples. As the temperature was increased, the recoveries improved, but the extraction was not complete. When a more polar solvent (acetone) was mixed with the nonpolar solvent (hexane), quantitative recovery was obtained. With the temperature at 200 °C and hexane/acetone (1:1) as the solvent (GC determination), the recovery of the diesel was 97.0% with 2.2% RSD ($n = 3$).

When using IR as the determinative method, it is not possible to add a polar solvent to enhance the miscibility of the solvent with the wet soil due to spectral interferences from the added solvent. In that case, it is necessary to perform two extractions on each clay sample and combine the extracts.

Table 1. Recovery by ASE of Volatile Compounds Spiked on Sand

Compound	Avg. (%), $n = 4$	RSD (%)
Benzene	99.7	2.5
Toluene	99.5	2.7
Ethylbenzene	100.0	3.7
<i>o</i> -Xylene	99.6	1.2
<i>n</i> -Nonane	97.1	2.6
<i>n</i> -Decane	98.1	1.0
<i>n</i> -Undecane	99.5	0.9
Naphthalene	99.9	1.7
2-Methylnaphthalene	99.4	2.3
<i>n</i> -Tetradecane	99.0	2.2
<i>n</i> -Pentadecane	97.2	3.0

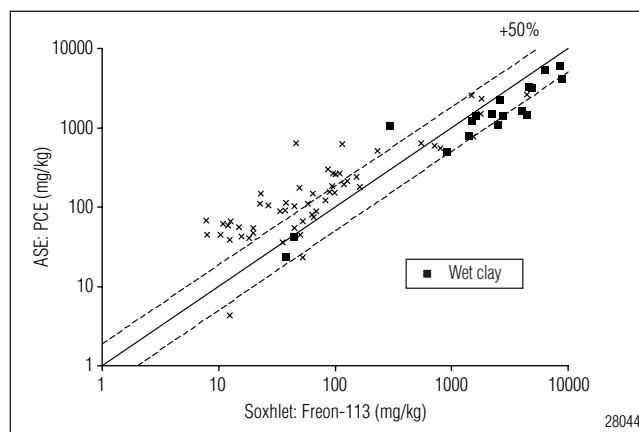


Figure 1. Extraction of total petroleum hydrocarbons: ASE (using PCE) compared against Soxhlet (using Freon-113); analysis by IR. Plotted points represent a variety of soil samples. Wet clay soils are identified by filled boxes.

An environmental laboratory (Quanterra Environmental Services, North Canton, Ohio) also investigated the use of ASE for the extraction of TPH from soils. In this case, real samples from the normal sample flow of the laboratory were used. Portions of each sample were extracted using Soxhlet with Freon-113 (overnight extraction), and portions were extracted using PCE with ASE (single pass at 200 °C). The results are shown in Figure 1 in which the results from the soil samples by ASE are plotted versus those obtained from the same samples by Soxhlet. The solid line represents a complete 1:1 correspondence between the two methods. The dashed line gives the $\pm 50\%$ boundaries for the data.

The data show that the results are usually higher with ASE than with Soxhlet (more data points above the line than below it). The average recovery by ASE as compared to Soxhlet is 120%. This figure also shows that ASE (single extraction) generally gave lower results than those obtained by Soxhlet for wet clay samples. However, if two extractions were performed on the wet clay samples and the extracts combined, the results by ASE were generally equal to or greater than those results obtained by Soxhlet (see Figure 2).

Note: If the sample has a high clay content, the extraction should be performed twice. The extracts should be combined before analysis. When using hexane/acetone with wet samples and the 33 mL cells, it may be necessary to extend the purge time to 300 s to ensure that all of the solvent is removed from the cell prior to being returned to the cell carousel.

CONCLUSION

Accelerated solvent extraction is equivalent to existing extraction methods (Soxhlet, automated Soxhlet, and sonication) for the removal of hydrocarbons from solid matrices, such as soils and sludges. ASE uses less solvent than conventional techniques (<15 mL for 10 g dry samples), and the time needed for extraction is shorter (<15 min per sample). The recommended conditions for the extraction of hydrocarbons from soil are listed in Table 2.

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SUPPLIERS

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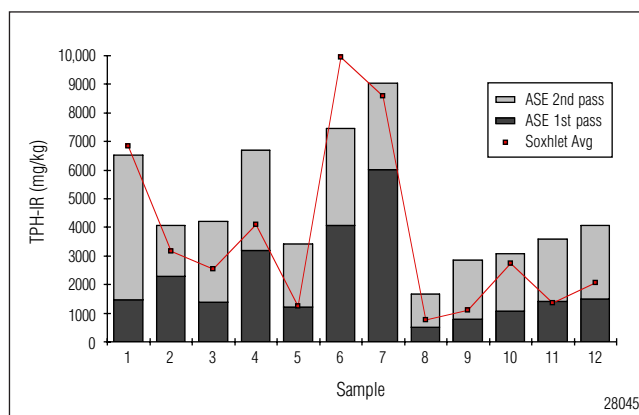


Figure 2. Soxhlet and ASE on wet clay samples, two complete ASE extractions.

Table 2. Recommended Conditions for Hydrocarbon Extractions with ASE	
Sample Size:	3–20 g, mixed 1:1 with ASE Prep DE (diatomaceous earth) if > 40% water
Solvent:	Perchloroethylene (IR determination); hexane/acetone, 1:1 vol (GC determination)
Temperature:	200 °C
Pressure:	10.3 MPa (1500 psi)
Heatup Time:	9 min
Static Time:	5 min
Flush Volume:	60%
Purge Time:	60 s

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