

# **Extraction of Total Petroleum Hydrocarbon Contaminants (Diesel and Waste Oil) in Soils by Accelerated Solvent Extraction (ASE<sup>®</sup>)**

## **INTRODUCTION**

Underground storage tanks containing hydrocarbon-based fuels are found worldwide. Many of these tanks have leaks, allowing gasoline, diesel, oil, or other hydrocarbon materials to contaminate the surrounding soil. In 1992, only 2 million of the 5 million tanks in the U.S. were monitored for leaks. However, underground storage tanks represent only one of many sources of hydrocarbon contamination in soils. Obviously, the ability to determine the level of hydrocarbon contamination in soils is important.

In the United States, U.S. EPA Methods 3540 (Soxhlet) and 3550 (ultrasonic) are presently used for the extraction of hydrocarbons from soils prior to the 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. Ultrasonic extraction requires 150–500 mL of solvent and is a labor-intensive method requiring multiple extractions, decanting, and filtering steps for each sample.

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 compared to conventional sample extraction techniques such as Soxhlet and 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. ASE meets the requirements of U.S. EPA Method 3545, Pressurized Fluid Extraction. The analytes included in Method 3545 are the semivolatiles (BNAs), organochlorine and organophosphorus pesticides (OCPs and OPPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and chlorinated herbicides. This application note reports on the use of ASE for the extraction of diesel range organics (DRO), waste oil organics (WOO), and total petroleum hydrocarbons (TPH, the sum of DRO and WOO) from soils.

## **EQUIPMENT**

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

Gas chromatograph with flame ionization detector (GC-FID)

Analytical balance

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

Glass fiber cell filters (P/N 47017)

TurboVap<sup>®</sup> II concentrator (Caliper Life Sciences)

Screw-on cell funnel (P/N 49288)

100-mL beakers

Spatula

10 × 250 mm chromatographic columns or disposable pipettes

Silanized glass wool

## REAGENTS AND SOLVENTS

Acetone

Methylene chloride

ASE Prep DE (diatomaceous earth) (P/N 062819)

Ottawa sand (Fisher Scientific)

Sodium sulfate (anhydrous) used after extraction

Silica gel

*n*-Tricosane (C<sub>23</sub>) as surrogate

*Note: The drying agent (ASE Prep DE) should be purified by heating at 400 °C for 4 h in a shallow tray or by extraction with methylene chloride. The silica gel should be activated by heating for at least 16 h at 130 °C in a shallow glass tray, loosely covered with foil.*

## EXPERIMENTAL

### Extraction Conditions

Sample Size:	3–20 g
Solvent:	Methylene chloride/acetone (1:1, v/v)
Temperature:	175 °C
Pressure:	2000 psi
Heatup Time:	8 min
Static Time:	5 min
Flush Volume:	75%
Purge Time:	60 s
Cycles:	1
Total Extraction Time:	17 min per sample
Total Solvent Used:	17 mL per sample (11-mL cell)

### Sample Description

Soils from Environmental Resource Associates (ERA) with certified values of TPH were used for methods development. The level of TPH in these samples was approximately 2000 mg/kg. Soils were first extracted as received at various temperatures and with various solvents. Then, to mimic wet samples, water was added to the certified soils (50% w/w) and the experiments were repeated.

After determining the optimal conditions, soils containing certified levels of diesel and motor oil (purchased from ERA) were extracted and analyzed as part of the method validation. All of the analytical work on these samples was done by an outside contract laboratory (Mountain States Analytical). These soils represented three matrices (clay, loam, and sand) and

were spiked at two concentration levels (5 and 2000 mg/kg for both DRO and WOO, therefore 10 and 4000 mg/kg for TPH). Blanks and spiked blanks were also analyzed and included in the sample set. Seven replicates of each matrix at each concentration were performed. The bias (percent recovery) and precision (relative standard deviation) were determined for each matrix and concentration. The seven replicates at the low level were used to calculate the method detection limit (MDL) and the reliable quantitation limit (RQL).

### Sample Preparation and Extraction

All samples were inspected prior to extraction by ASE. Large rocks and sticks were removed. Samples that appeared dry were loaded directly into the extraction cells containing glass-fiber filters at the outlet end. The extraction cells with a screw-on filter were tared on the analytical balance and the dry samples were weighed directly into the cells. Wet samples were weighed into a 100-mL beaker and mixed thoroughly with ASE Prep DE using a spatula until a free-flowing mixture resulted. These samples were then placed into the extraction cell through the screw-on funnel. A 1-mL aliquot of the surrogate solution (*n*-tricosane) was added just prior to closing the cells and loading them in the ASE carousel. The samples were then extracted using the conditions cited above.

### Quantification

After collection, 10 mL of methylene chloride was added to each extract to enhance phase separation. The extracts were visually inspected for water that appeared as cloudiness in the extract or as a distinct water layer on top. If water was present in the extracts, sodium sulfate was added directly to the vial. The extracts were passed through pipettes or glass chromatographic columns containing silanized glass wool in the outlet end and loaded with approximately 4 g of silica gel and 4 g of sodium sulfate. Two 10-mL portions of methylene chloride/acetone were used to rinse the vials (and the sodium sulfate remaining in the vials) and the cleanup columns. All of the extract and rinsate were collected together. The resulting solutions were concentrated to 1 mL (in a TurboVap) for the low concentration level or diluted to 100 mL for the high concentration level prior to analysis.

Analytical determinations of the hydrocarbons in the soil extracts were performed by gas chromatography with flame ionization detection. The procedure used was similar to that in American Petroleum Institute (API) Publication Number 4599. The conditions were as follows: 30-m  $\times$  0.32-mm i.d. Rt<sub>x</sub>-1 (Restek) capillary column (0.25- $\mu$ m film), FID at 350 °C, splitless injector at 330 °C, 2.0- $\mu$ L injection, temperature programmed from 40 to 330 °C at 12 °C/min after a 5-min hold with a 12-min hold at the final temperature. The flow was programmed from 1.0 to 6.0 mL/min at 0.5mL/min/min after a 20-min hold. These conditions differed from those specified by API in that flow programming and higher temperatures were used for the injector, detector, and final oven setpoint. These changes were made to facilitate the elution of heavier hydrocarbons. The DRO are in the range of C<sub>10</sub> to C<sub>28</sub> (12.25 to 25.7 min under GC conditions used). The WOO are in the range beyond C<sub>28</sub> to the end of the chromatographic analysis (25.71 to 41.0 min). Calibration standards were prepared from #2 diesel and 30w motor oil in methylene chloride. TPH values were calculated as the sum of the DRO and WOO results. Figure 1 shows a typical chromatogram obtained from a soil extract.

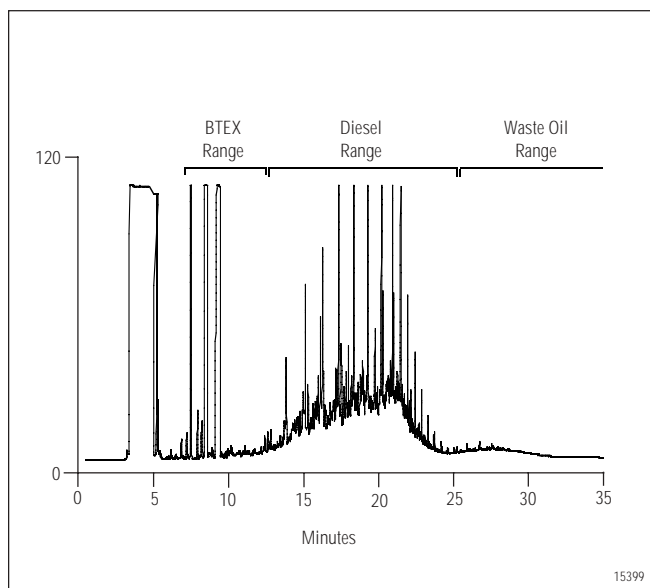


Figure 1. Typical gas chromatogram from a soil extract.

## RESULTS

Tables 1–4 show the summaries of the results of the method validation work. (MDL was calculated as  $3.143 \times \sigma$  for the seven low-level replicates. RQL was calculated as  $4 \times \text{MDL}$ .) ASE gives good recovery of DRO, WOO, and TPH with good precision. The recovery of the surrogate from all of these studies ranged from 90–147%.

Table 1. Results for All Hydrocarbon Groups (Average of TPH, DRO, WOO)

Matrix and Concentration	Bias <sup>1</sup>	Precision <sup>2</sup>	MDL (mg/kg)	RQL
Clay, low	123.8	19.7	5.0	20.0
Clay, high	111.0	18.5	NA <sup>3</sup>	NA
Loam, low	124.6	21.6	5.6	22.2
Loam, high	100.8	7.9	NA	NA
Sand, low	123.6	21.5	5.2	21.0
Sand, high	108.6	12.2	NA	NA
Average	115.4	16.9	5.3	21.1

<sup>1</sup> Bias was calculated as recovery of ASE as a percent of the spike.

<sup>2</sup> Precision was calculated as the RSD (%) of ASE recovery from the spiked soils.

<sup>3</sup> NA = not applicable.

Table 2. TPH Results

Matrix and Concentration	Bias <sup>1</sup>	Precision <sup>2</sup>	MDL (mg/kg)	RQL
Clay, low	123.8	17.6	6.9	27.4
Clay, high	111.0	18.1	NA <sup>3</sup>	NA
Loam, low	124.6	20.3	8.0	32.0
Loam, high	100.8	7.8	NA	NA
Sand, low	123.6	16.1	6.3	25.1
Sand, high	108.6	12.2	NA	NA
Average	115.4	15.3	7.0	28.2

<sup>1</sup> Bias was calculated as recovery of ASE as a percent of the spike.

<sup>2</sup> Precision was calculated as the RSD (%) of ASE recovery from the spiked soils.

<sup>3</sup> NA = not applicable.

**Table 3. DRO Results**

Matrix and Concentration	Bias <sup>1</sup>	Precision <sup>2</sup>	MDL (mg/kg)	RQL
Clay, low	127.8	23.6	4.8	19.0
Clay, high	111.8	19.2	NA <sup>3</sup>	NA
Loam, low	137.5	20.7	4.5	17.9
Loam, high	94.2	4.6	NA	NA
Sand, low	127.2	25.4	5.1	20.4
Sand, high	108.6	10.7	NA	NA
Average	117.8	17.4	4.8	19.1

<sup>1</sup> Bias was calculated as recovery of ASE as a percent of the spike.

<sup>2</sup> Precision was calculated as the RSD (%) of ASE recovery from the spiked soils.

<sup>3</sup> NA = not applicable.

**Table 4. WOO Results**

Matrix and Concentration	Bias <sup>1</sup>	Precision <sup>2</sup>	MDL (mg/kg)	RQL
Clay, low	119.8	17.9	3.4	13.5
Clay, high	110.3	18.2	NA <sup>3</sup>	NA
Loam, low	111.8	23.8	4.2	16.8
Loam, high	107.3	11.3	NA	NA
Sand, low	120.1	23.0	4.4	17.5
Sand, high	108.6	13.8	NA	NA
Average	113.0	18.0	4.0	15.9

<sup>1</sup> Bias was calculated as recovery of ASE as a percent of the spike.

<sup>2</sup> Precision was calculated as the RSD (%) of ASE recovery from the spiked soils.

<sup>3</sup> NA = not applicable.

**Table 5. Reported MDL Values for Selected States' Hydrocarbon Methods**

State	MDL (mg/kg)	Analyte
Arizona	30	DRO
	50	WOO
	100	TPH
Connecticut	10	TPH
Florida	4	TPH
Oregon/Washington	50	DRO
	100	WOO
Texas	50	DRO
API Method 4599	12–20	DRO

For comparison, Table 5 lists some of the MDL values for TPH methods used in selected states. These states' methods use either sonication or Soxhlet extraction coupled with GC analysis of the extracts. The optimized ASE conditions along with GC analysis give MDL values similar to Soxhlet and sonication extraction combined with GC analysis. The action level for all states for hydrocarbon groups such as DRO, WOO, and TPH are in the range of 50–100 mg/kg. The control limits for all state methods currently are 75–125% recovery for the hydrocarbon groups and 50–150% recovery for the surrogate. The optimized ASE method detailed in this application note meets these acceptance criteria for bias values.

In conclusion, ASE is equivalent to existing extraction methods (Soxhlet, automated Soxhlet, and ultrasonic extraction) for the removal of hydrocarbons from solid matrices like soils and sludges. ASE uses less solvent than conventional techniques (<15 mL for 10-g dry samples) and extraction times are shorter (<15 min per sample).

Although methylene/acetone was used for the validation work, method development was done with hexane/acetone (1:1) and heptane/acetone (1:1). Comparable results can be achieved using any of these three solvent systems with wet or dry samples using the conditions given here.

## ACKNOWLEDGMENTS

The work of Matt Sorensen and his colleagues at Mountain States Analytical is gratefully acknowledged.

## SUPPLIERS

Caliper Life Sciences, 68 Elm Street, Hopkinton, MA 01748 USA, Tel: 508-435-9500, [www.caliperls.com](http://www.caliperls.com).

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275-1126 USA, Tel: 800-766-7000, [www.fishersci.com](http://www.fishersci.com).



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**Dionex Corporation**  
1228 Titan Way  
P.O. Box 3603  
Sunnyvale, CA  
94088-3603  
(408) 737-0700

**Dionex Corporation**  
Salt Lake City Technical Center  
1515 West 2200 South, Suite A  
Salt Lake City, UT  
84119-1484  
(801) 972-9292

**Dionex U.S. Regional Offices**  
Sunnyvale, CA (408) 737-8522  
Westmont, IL (630) 789-3660  
Houston, TX (281) 847-5652  
Atlanta, GA (770) 432-8100  
Marlton, NJ (856) 596-06009

**Dionex International Subsidiaries**  
Australia 61 (2) 9420 5233 Austria (01) 616 51 25 Belgium (03) 353 42 94 Canada (905) 844-9650 China (852) 2428 3282  
France 01 39 30 01 10 Germany 06126-991-0 Italy (06) 66 51 50 52 Japan (06) 6885-1213 Korea 82 2 2653 2580  
The Netherlands (0161) 43 43 03 Switzerland (062) 205 99 66 United Kingdom (01216) 691722  
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