

Extraction of PAHs from Environmental Samples by Accelerated Solvent Extraction (ASE)

Meets the requirements of U.S. EPA Method 3545

INTRODUCTION

Accelerated Solvent Extraction (ASE[®]) is a new extraction method that significantly streamlines sample preparation. A commonly used solvent is pumped into an extraction cell containing the sample, which is then brought to an elevated temperature and pressure. Minutes later, the extract is transferred from the heated cell to a standard collection vial for cleanup or analysis. The entire extraction process is fully automated and performed in minutes for fast and easy extraction with low solvent consumption.

Previously, the extraction of PAH compounds from environmental materials including soils, sludge, and other solid wastes typically required large amounts of solvents. Soxhlet, for example, can use 250 to 500 mL of solvent for most environmental samples. Recent and anticipated changes in environmental regulations will cause severe restrictions on the amount of solvent usage in laboratories worldwide. ASE was developed to meet the new requirements for reducing solvent usage in the preparation of solid waste samples.

ASE provides a more convenient, faster, and less solvent intensive method than previously available for the extraction of PAHs from solid wastes. PAH recoveries by ASE are equivalent to other more solvent intense methods such as Soxhlet or sonication. ASE also avoids the problem of multiple washing procedures associated with sonication. ASE extracts from a 10 g sample of a typical soil in about 12 min with a total solvent consumption of approximately 15 mL.

The procedures described in this application note meet the requirements for the extraction of PAHs from solid waste as described in U.S. EPA Method 3545. This method is applicable to solid wastes including soils, sludges, and sediments.

EQUIPMENT

ASE 200 Accelerated Solvent Extractor* with 11-mL or larger stainless steel extraction cells

Dionex HPLC system

SUPELCO[™] LC-PAH Column, 15 cm × 4.6 mm
(Supelco, Inc., Bellefonte, Pennsylvania, USA)

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.*

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SOLVENTS

Dichloromethane

Acetone

Acetonitrile

ASE 200 CONDITIONS

System Pressure: 1500 psi*

Oven Temperature: 100 °C

Sample Size: 7 g

Oven Heatup Time: 5 min

Static Time: 5 min

Solvent: Dichloromethane/acetone
(1:1), (v/v)

Flush Volume: 60% of extraction cell volume

Nitrogen Purge: 1 MPa (150 psi) for 60 s

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

SAMPLE INFORMATION

PAH-contaminated soils were prepared and certified by Resource Technology Corp. (SRS100-103, lot number AQ103 and RQ103). A marine sediment containing PAHs at certified levels was obtained from the National Research Council of Canada (HS-3). Sample extracts from the contaminated soil were analyzed by HPLC.

Note: Extracts from the marine sediment sample were analyzed by GC/MS by Mountain States Analytical, Inc. (Salt Lake City, Utah, USA).

SAMPLE PREPARATION

Samples should be dry and ground before filling the extraction cells. Samples that contain water (greater than 10%) should be mixed in equal proportions with ASE Prep DE (diatomaceous earth) (P/N 062819). Introduce a sufficient amount of sample into the grinding apparatus to yield at least 10–20 g after grinding.

Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise separated to allow for mixing and maximum exposure of the sample surfaces for extraction. If grinding of these materials is preferred, the addition and mixing of ASE Prep DE with the sample (1:1) may improve grinding efficiency.

Place a cellulose disk at the outlet end of the extraction cell. Weigh approximately 10 g of each sample into a 11 mL extraction cell or approximately 20 g into a 22 mL extraction cell. For samples mixed with ASE Prep DE, transfer the entire contents of the beaker to the extraction cell. Surrogate spikes and matrix spikes may be added to the appropriate sample cells.

Place extraction cells into the autosampler tray and load the collection tray with the appropriate number (up to 24) of 40 mL, precleaned, capped vials with septa.

HPLC ANALYTICAL CONDITIONS

The sample extract as received from ASE was diluted or concentrated as needed for analysis by HPLC. HPLC was performed with a SUPELCO SIL 15 cm × 4.6 mm LC-PAH column at a flow rate of 1.5 mL/min. The mobile phase consisted of 60% water, 40% acetonitrile for 5 min, followed by a linear gradient to 100% acetonitrile over 25 min. Detection combined UV at 254 nm and fluorescence detection with 300 nm excitation and 410-nm emission. Quantification was performed by external standard calibration.

GC/MS ANALYTICAL CONDITIONS

Extracts obtained by ASE were concentrated to 4 mL for analysis by U.S. EPA Method 8270. A GC equipped with a split-splitless injector, autosampler, and mass-selective detector were used for the analyses. Sample injection volume was 1 µL. A 30 m × 0.25 mm i.d. XTI-5 Capillary Column (Restek, Bellefonte, Pennsylvania, USA) was used without a guard column. The injector was maintained at 270 °C and the transfer line at 300 °C. A three-ramp oven program was used: 50 to 310 °C at 10 °C/min after a 3-min hold, then to 326 °C at 4 °C/min, then to 350 °C at 10 °C/min with a 10 min final hold. Helium was used as the carrier gas at a linear velocity of approximately 30 cm/s. The multiplier voltage on the mass spectrometer was held at 2000 eV, and the system was scanned from 35 to 500 amu.

ANALYTICAL RESULTS

Results of the extractions of PAH from soil and marine sediment by ASE are shown in Tables 1 and 2. The recoveries from all matrices compared well with the certified values that had been obtained from 8- to 18-h Soxhlet extractions as shown in Table 1.¹ The recoveries for benzo[*b*]fluoranthene and benzo[*k*]fluoranthene are reported as the sum of the two compounds to be consistent with the way in which the certified values were reported. The HPLC method could not be used to quantify compounds lighter than fluorene. In addition, since the soil was not certified for compounds larger than benzo[*a*]pyrene, results are not given for compounds outside of this range for the soil.

Results for extractions of the Canadian marine sediment sample are presented in Table 2. Only four of the compounds are outside the 90% confidence interval (CI) for the certified values: anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and dibenz[*a,h*]anthracene. The average recovery for anthracene was lower than the certified value, while the results for the other three compounds are higher than the certified values.

The results indicate that the ASE technique provides equivalent or superior extraction of PAH compounds as compared to the traditional Soxhlet method.

ASE meets the requirements for PAH analysis as described in U.S. EPA SW-846 Method 3545 (Proposed).

Table 1. Recovery of PAHs from Contaminated Soil (SRS 103-100)^a

Compound	Average Recovery, n = 8 (as % of Soxhlet)	RSD (%)
Fluorene	83.4	1.6
Phenanthrene	119.2	1.9
Anthracene	88.0	6.6
Fluoranthene	101.2	14
Pyrene	104.8	18
Benz[<i>a</i>]anthracene	93.6	10
Chrysene	121.8	15
Benzo[<i>b,k</i>]fluoranthene ^b	142.3	8.1
Benzo[<i>a</i>]pyrene	100.3	15

^a Analyte concentration range: 20–1400 mg/kg per component

^b Sum of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene

Table 2. PAHs from Marine Sediment HS-3 (mg/kg)

Compound	Average Recovery (n = 4)	Standard Deviation	Certified Value	90% CI ^a
Naphthalene	8.87	1.00	9.0	0.7
Acenaphthalene	ND ^b	NA ^c	0.3	0.1
Acenaphthene	4.89	0.51	4.5	1.5
Fluorene	10.09	1.26	13.6	3.1
Phenanthrene	68.80	6.44	85.0	20
Anthracene	7.73	0.57	13.4	0.5
Fluoranthene	54.73	4.82	60.0	9
Pyrene	33.70	2.83	39.0	9
Benz[<i>a</i>]anthracene	12.40	1.07	14.6	2
Chrysene	14.95	1.52	14.1	2
Benzo[<i>a</i>]pyrene	6.27	0.65	7.4	3.6
Benzo[<i>b</i>]fluoranthene	11.46	1.27	7.7	1.2
Benzo[<i>k</i>]fluoranthene	10.16	1.28	2.8	2
Benzo[<i>ghi</i>]perylene	4.14	0.69	5.0	2
Dibenz[<i>ah</i>]anthracene	2.58	0.33	1.3	0.5
Indeno[<i>1,2,3-cd</i>]pyrene	4.30	0.77	5.4	1.3

^a CI = Confidence interval of the mean

^b ND = Not detectable at the level of detection (1.5 mg/kg)

^c NA = Not applicable

REFERENCES

1. Richter, B.; Ezzell, J.; Felix, D. *Single Laboratory Method Validation Report: Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides Using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD* Document 116064.A, Dionex Corporation, June 16, 1994.

SUPPLIERS

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