

Extraction of Chlorinated Pesticides Using 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 chlorinated pesticides from soils, sludge, and other solid wastes consumed large amounts of solvents. Soxhlet, for example, can use from 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 chlorinated pesticides from environmentally important samples. Recoveries of these analytes by ASE are equivalent to or better than other more solvent intense methods such as Soxhlet. ASE also avoids the problem of multiple washing procedures associated with sonication. ASE can extract 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 sample extraction as prescribed by EPA Method 3545. This method is applicable to the extraction of water-insoluble or slightly water-soluble volatiles and semivolatiles in preparation for gas chromatographic or GC/MS measurement. The method is applicable to the extraction of chlorinated pesticides from soils, clays, wastes, and sediments containing from 5 to 250 µg/kg of the target compounds.

EQUIPMENT

ASE 200 Accelerated Solvent Extractor* with 11 or 22 mL stainless steel extraction cells
GC or GC/MS

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

Acetone (pesticide quality or equivalent)
Hexane (pesticide quality or equivalent)

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ASE 200 CONDITIONS

| | |
|-------------------|-------------------------------|
| Oven Temperature: | 100 °C |
| Pressure: | 1500 psi* |
| Oven Heatup Time: | 5 min |
| Static Time: | 5 min |
| Flush Volume: | 60% of extraction cell volume |
| Solvent: | Acetone/hexane (1:1 v/v) |

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

SAMPLE INFORMATION

Spiking concentrations ranged from 5 to 250 µg/kg. All spiked soils were prepared and certified by ERA (Environmental Resource Associates, Arvada, Colorado, USA). Spiked samples were extracted both by the ASE 200 system and by a Perstorp Environmental Soxtec® (automated Soxhlet). Matrix blanks, spikes, and spike duplicates were included for the low-level spikes; matrix spikes were included for all other concentrations. Collected extracts from ASE 200 were approximately 13–15 mL from the 11 mL extraction cells and approximately 26–30 mL from the 22 mL cells. Extracts can be further cleaned up or directly analyzed depending on the extent of interfering co-extractives. For the examples shown in this application note, extracts were analyzed by SW-846 Method 8080.

Note: All extractions and analytical work were performed by Mountain States Analytical, Inc. (Salt Lake City, Utah, USA).

SAMPLE PREPARATION

The sample is ground to 100–200 mesh (150–75 µm). Wet samples are mixed with either ASE Prep DE (diatomaceous earth), P/N 062819 (1:1, w/w), or air dried.¹ After grinding, a weighed sample is transferred to either a 11 or 22 mL extraction cell.

PROCEDURE

Mix sample thoroughly, especially composite samples. Dried sediment, soil, and dry waste samples should be ground or otherwise subdivided so that it passes through a 1 mm sieve. Introduce sufficient sample into the grinding apparatus to yield at least 10–20 g after grinding. Air dry the sample at room temperature for 48 h in a glass tray or on hexane cleaned aluminum foil, or dry the sample by mixing with ASE Prep DE until a free-flowing powder is obtained. Air drying is not appropriate for the analysis of the more volatile organochlorine pesticides (e.g., the BHCs), because of losses during the drying process. For sediment and soils (especially gummy clay) that are moist and cannot be air-dried because of loss of volatile analytes, mix 5–10 g of sample with an equal amount of ASE Prep DE in a small beaker using a spatula. Use this approach for any solid sample that requires dispersion of the sample particles to ensure greater solvent contact throughout the sample mass.

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

Place a cellulose disk at the outlet end of the extraction cell. Weigh approximately 10 g of each sample into 11 mL extraction cells, or approximately 20 g into 22 mL cells. 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. Set the method conditions on the ASE 200 system and initiate the run.

DISCUSSION AND RESULTS

Examples of extraction of selected environmental samples including both spiked and incurred samples are shown. These examples illustrate the effectiveness of the ASE technique in obtaining recoveries of analytes equivalent to Soxtec.² Results of this study are summarized in Tables 1 and 2 for chlorinated pesticides spiked at three different levels in three different soil types.

Table 1. Average Recovery of Pesticides from Three Soil Types^a—ASE Compared to Automated Soxhlet^a

| Pesticide | Average Recovery (% of Soxhlet) |
|--------------------|---------------------------------|
| Alpha BHC | 93.3 |
| Gamma BHC-Lindane | 95.6 |
| Beta BHC | 98.6 |
| Heptachlor | 88.0 |
| Delta BHC | 99.5 |
| Aldrin | 94.9 |
| Heptachlor Epoxide | 100.7 |
| Gamma Chlordane | 99.5 |
| Alpha Chlordane | 102.0 |
| Endosulfan 1 | 100.3 |
| p,p'-DDE | 98.6 |
| Dieldrin | 101.2 |
| Endrin | 97.2 |
| p,p'-DDD | 104.6 |
| Endosulfan II | 105.6 |
| p,p'-DDT | 74.9 |
| Endrin Aldehyde | 104.0 |
| Endosulfan Sulfate | 105.2 |
| Methochlor | 79.6 |
| Endrin Ketone | 102.9 |

^aAverages from extraction of sand, loam, and clay soils.

REFERENCES

1. U.S. Environmental Protection Agency. U.S. EPA Method 600/4-81-055, *Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue*, Section 3.1.3.
2. 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.

Table 2. Average RSD (%) for Chlorinated Pesticides

| Matrix | ASE | Automated Soxhlet |
|--------|------|-------------------|
| Clay | 0.5 | 9.7 |
| Loam | 7.8 | 6.2 |
| Sand | 12.0 | 10.1 |

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ASE is a registered trademark of Dionex Corporation.

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