

Extraction of Organophosphorus Pesticides Using Accelerated Solvent Extraction (ASE[®])

Meets the requirements of U.S. EPA Method 3545 (Proposed)

INTRODUCTION

Accelerated Solvent Extraction (ASE[®]) is an 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 extractions with low solvent consumption.

Extraction is the first step in the analysis of organophosphorous pesticides (OPP) in soils, sludge, and other solid wastes. This step previously required large amounts of solvents. Soxhlet, for example, can use from 250 to 500 mL of solvent for the extraction of OPPs at trace levels from a soil matrix. Recent and anticipated changes in environmental regulations will cause severe restrictions on the amount of solvent usage in laboratories worldwide. For example, in the United States, a recent executive order calls for a 50–90% reduction of solvent usage in all federal laboratories. ASE was developed by Dionex to meet the new requirements for reducing solvent usage in the preparation of solid waste samples.

The use of ASE in the extraction of OPP compounds from solid wastes is a more convenient, faster, and less solvent-intensive method than previously available. OPP recoveries by ASE are equivalent to recoveries from Soxhlet and other methods. 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 U.S. EPA Method 3545A. This method is applicable to the extraction of water-insoluble or slightly water-soluble organophosphorus pesticides in preparation for gas chromatographic measurements. This method is applicable to soils, solid wastes, and sediments containing 250–2500 µg/kg of OPPs.

EQUIPMENT

ASE 200 Accelerated Solvent Extractor with 11- or 22-mL stainless steel extraction cells
Suitable GC with nitrogen phosphorous detector (NPD)
Dionex vials for collection of extracts
(40 mL P/N 49465; 60 mL P/N 49466)

SOLVENTS

Dichloromethane
Acetone

ASE 200 CONDITIONS

Oven Temperature: 100 °C
Pressure: 14 MPa (2000 psi)
Oven Heatup Time: 5 min
Static Time: 5 min
Flush Volume: 60% of extraction cell volume
Nitrogen Purge: 1 MPa (150 psi) for 60 s
Solvent: Dichloromethane/acetone
(1:1 v/v)

SAMPLE INFORMATION

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 Soxhlet. Extracts collected from ASE 200 were approximately 13–15 mL. A solvent exchange to hexane was performed and the hexane solution was brought to a final volume of 10 mL. Extracts were analyzed by U.S. EPA SW-846 Method 8141.

Note: All extractions and analytical work were performed by DataChem Laboratories, Salt Lake City, UT, USA. Matrix blanks, spikes, and spike duplicates were included for each matrix.

PROCEDURE

The procedure used in this application note follows the detailed method as described in U.S. EPA Method 3545A.

Dried sediment, soil, and dry waste samples can be ground or otherwise subdivided to pass through a 1-mm sieve. Introduce sufficient sample into the grinding apparatus to yield 10–20 g after grinding. Air dry the sample or mix with ASE Prep DE (diatomaceous earth) (P/N 062819) until a free-flowing powder is obtained. Air drying is not appropriate for the analysis of the more volatile organophosphorus pesticides.

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

Place extraction cells into the upper sample 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

Results from the extraction of two spiking levels in three different soil types are summarized in Tables 1 and 2. These results illustrate the effectiveness of the ASE technique in obtaining recoveries of analytes equivalent to Soxhlet.²

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. and Felix, D. “Single Laboratory Method Validation Report: Extraction of Organophosphorus Pesticides, Chlorinated Herbicides, and Polychlorinated Biphenyls Using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/NPD and GC/ECD,” Document 101124, Dionex Corporation, December 2, 1994.

Table 1. Average recovery of organophosphorus pesticides from three soil types — ASE compared to Soxhlet^a

OPP Target Compound	Average Recovery (% of Soxhlet)
Dichlorvos	112.7
Mevinphos	100.3
Demeton O & S	108.7
Ethoprop	96.7
TEPP	100.0
Phorate	98.5
Sulfotep	111.3
Naled	100.0
Diazinon	98.2
Disulfoton	96.8
Monocrotophos	100.0
Dimethoate	92.8
Ronnel	95.3
Chlorpyrifos	96.7
Parathion Methyl	96.6
Parathion Ethyl	96.3
Fenthion	96.5
Tokuthion	97.4
Tetrachlorvinphos	103.5
Bolstar	99.9
Fensulfothion	90.0
EPN	94.5
Azinfos Methyl	93.1
Coumaphos	97.0

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

Table 2. Average recovery and precision for OPP extractions from three soil types

Matrix ^a	ASE (% of Spike)	ASE ^b (RSD, %)	Soxhlet (% of Spike)	Soxhlet ^b (RSD, %)	ASE as % of Soxhlet
Clay (low)	55.0	6.2	56.4	7.6	98.8
Clay (high)	69.2	5.2	72.3	16.3	96.3
Loam (low)	61.3	11.6	60.4	8.6	103.6
Loam (high)	61.4	7.8	64.2	6.3	96.5
Sand (low)	59.0	13.0	63.3	6.7	95.0
Sand (high)	64.1	11.9	63.2	4.8	101.2

^a Low spiking level is approximately 250 µg/kg.

High spiking level is approximately 2500 µg/kg.

^b Each recovery and precision (%RSD) value is the average of seven replicate measurements for each compound, then averaged for all compounds.



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* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.

