DIONEX

Application Note 318

Extraction of Chlorinated Herbicides 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.

Analysis of soils, sludge, and other solid wastes for chlorinated herbicides first requires extraction of the analytes from the matrix. Previously, this step usually required large amounts of solvents. 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 chlorinated herbicides from solid wastes is more convenient, faster, and less solvent-intensive than previous methods. U.S. EPA Method 8150A for the analysis of chlorinated herbicides uses a wrist-shaking technique that requires 300 mL of acetone and diethyl ether following acidification to pH 2 with HCl. In the method reported in this application note, chlorinated herbicide recoveries by ASE are equivalent to recoveries from the wrist-shaking method recommended in Method 8150A. 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 3545. This method is applicable to the extraction of water-insoluble or slightly water-soluble chlorinated herbicides in preparation for gas chromatographic measurements.

EQUIPMENT

ASE 200 Accelerated Solvent Extractor,* with 11 or 22 mL stainless steel extraction cells

Gas chromatograph (GC) with ECD

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

Dichloromethane
Acetone
Phosphoric acid

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
Nitrogen Purge:	1 MPa (150 psi) for 60 s
Solvent:	Dichloromethane/acetone (1:2, v/v), with 4% (v/v) H_3PO_4/H_2O (1:1)

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

SAMPLE INFORMATION

All spiked soils were prepared and certified by ERA (Environmental Resource Associates). Spiked samples were extracted both by the ASE 200 system and by the wrist-shaking technique. The extract was treated using the postextraction steps as outlined in U.S. EPA Method 8150A. These steps include treatment with acidic Na_2SO_4, base hydrolysis, concentration, and esterification with diazomethane. Extracts were analyzed by SW-846 Method 8150A using GC/ECD.

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

SAMPLE PREPARATION

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

PROCEDURE

The procedure used in this application note follows the detailed method as described under the U.S. EPA SW-846 Method 3545.

Dried sediment, soil, and dry waste samples should be ground or otherwise subdivided to pass through a 1 mm sieve. Wet samples are mixed with ASE Prep DE until a free-flowing powder is obtained. Introduce a sufficient amount of sample into the grinding apparatus to yield 10–20 g after grinding. Dry the sample or mix. Air drying is not appropriate for the analysis of the more volatile chlorinated herbicides.

Place a cellulose disk at the outlet end of the ex-traction cell. Weigh 10 g of each sample into 11 mL extraction cells or 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

Results from the extraction of two spiking levels in three different soil types are summarized in Tables 1 and 2. These results illustrate that the ASE technique obtains analyte recoveries equivalent to the Method 8150A wrist-shaking procedure for the extraction of chlorinated herbicides from solid waste.[2]

REFERENCES

1. *Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue*; U.S. EPA Method 600/4-81-055, Section 3.1.3.
2. Richter, B.; Ezzell, J.; Felix, D. *Single Laboratory Method Validation Report: Extraction of Organophosphorous 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 Chlorinated Herbicides from Three Soil Types[a]—ASE Compared to Wrist-Shaking Method

Chlorinated Herbicide Target Compound	Average Recovery (% of Shaking Method)
2,4-D	116.2
2,4-DB	112.9
2,4,5-T	106.6
2,4,5-TP	117.4
Dalapon	101.8
Dicamba	108.1
Dichlorprop	107.7
Dinoseb	118.4

[a] Averages from extraction of sand, loam, and clay soils.

Table 2. Average Recovery and Precision for Extraction of Chlorinated Herbicides from Three Soil Types by ASE

Matrix[a]	ASE (% of Spike)	ASE[b] (RSD,%)	Shaking (% of Spike)	Shaking[b] (RSD,%)	ASE as % of Shaking
Clay (low)	36.1	54.5	42.2	25.2	89.8
Clay (high)	71.1	15.0	61.6	21.6	112.8
Loam (low)	56.7	11.2	36.9	78.7	126.6
Loam (high)	59.9	14.1	43.9	14.7	132.8
Sand (low)	51.1	12.6	49.7	13.3	111.2
Sand (high)	69.2	39.5	66.3	35.5	104.4

[a] Low spiking levels ranged from 50 to 500 µg/kg. High spiking levels ranged from 500 to 5000 µg/kg.

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

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