Application Note 332

Accelerated Solvent Extraction of Pesticide Residues in Food Products

Introduction

Residue analysis in crops and food products is routinely performed in regulatory and industrial laboratories around the world. Many of the traditional procedures used to perform these extractions are time-consuming and solvent-intensive. Accelerated solvent extraction is an extraction technique that speeds the extraction process and reduces the total amount of solvent used. The system uses conventional liquid solvents at elevated temperatures and pressures, which results in increased extraction kinetics. Extraction of samples ranging from 1 to 30 g typically requires 12–17 min and 15–50 mL of solvent.

In the environmental industry, accelerated solvent extraction has been compared extensively to traditional preparation techniques, and has been found to generate similar extracts in a more efficient manner. Accelerated solvent extraction is now widely used in environmental applications to replace time- and solvent-intensive techniques such as Soxhlet and sonication. The principles of accelerated solvent extraction technology are based on conventional liquid extraction theory, so the transfer of existing solvent-based extraction processes to accelerated solvent extraction is simple. In addition, the ability to extract up to 24 samples unattended can result in a dramatic increase in laboratory efficiency.

Equipment

Thermo Scientific Dionex ASE 200 accelerated solvent extraction system* equipped with 11, 22, or 33 mL cells

Thermo Scientific Dionex vials for collection of extracts (40 mL, P/N 049465; 60 mL, P/N 049466)

Cellulose filter disks (P/N 049458)

*Thermo Scientific Dionex ASE 150 and 350 accelerated solvent extraction systems can be used for equivalent results.

Reagents

Fisher Scientific Acetone, Optima grade

Fisher Scientific Acetonitrile, Optima grade

Fisher Scientific Hexane, Optima grade

Thermo Scientific Dionex ASE Prep DE (P/N 062819)

Fisher Scientific sodium sulfate, anhydrous added after extraction

Extraction Conditions

Temperature:	100 °C
Pressure:	1500 psi*
Heatup Time:	5 min
Static Time:	5 min
Flush Volume:	60%
Purge Time:	100 s
Static Cycles:	1–2
Total Extraction Time:	14–18 min per sample
Total Solvent Used:	15–45 mL per sample

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

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Sample Preparation

Weigh dry samples (1–20 g) and add directly to extraction cells containing a cellulose extraction filter. Grind wet samples (1–10 g) and mix with 6 g of Dionex ASE™ Prep DE (diatomaceous earth) using a mortar and pestle. Rinse the mortar and pestle with 2–3 mL of the extraction solvent. Add this volume to the sample in the extraction cell.

Extraction

Perform the sample extractions according to the outlined conditions. Following extraction, add 5 g of anhydrous sodium sulfate to the collection vial to absorb coextracted water. Shake the vial for 15 s and decant the water-free extract into a clean 60-mL vial. Rinse the original vial with 5 mL of the extraction solvent and decant this volume into a second vial. Concentrate the combined volume to approximately 10 mL under nitrogen.

Analytical

Analyze organochlorine pesticides using a gas chromatograph with a 30 m × 0.25 mm i.d. RTX-5 capillary column (Restek Corporation, Belefonte, USA). Set up a 1-µL splitless injection volume with the injector at 275 °C and the electron capture detector (ECD) maintained at 300 °C with a nitrogen atmosphere. Program the run from 140 °C (3 min) to 265 °C at 10 °C/min. Quantify results using endosulfan I or endrin aldehyde as the internal standard. Pass pesticide extracts through carbon or C18 cleanup cartridges prior to analysis. Quantify results by GC analysis with ECD detection (U.S. EPA Method 8151) or GC with MS detection (U.S. EPA Method 8270).

Results and Discussion

Samples (10 g) of raw potato and banana were spiked with 100 µL of a standard solution in hexane containing 12 organochlorine pesticides. Hexane with 10% acetone was chosen as the extraction solvent because it delivered good recoveries of the analytes with fewer interferences (co-extractables) than a 1:1 mixture. Resulting extracts were clear (after sodium sulfate treatment) upon concentration and suitable for GC/ECD analysis. The necessity of the drying step limits the amount of raw sample that can be extracted to 10 g. Results are presented in Tables 1 and 2. These results represent three extractions with duplicate GC injections of each extract.

Table 1. Recovery of Organochlorine Pesticides Spiked onto Raw Banana at the 100 ppm Level*

Compound	Av. Recovery (%)	SD (µg/kg)	RSD (%)
α-BHC	100.3	2.3	2.3
β-BHC	102.2	2.3	2.3
Υ-BHC	98.9	3.2	3.2
Heptachlor	89.2	7.6	8.5
Aldrin	89.4	2.2	2.5
Heptachlor Epoxide	93.5	2.1	2.2
Dieldrin	93.7	1.6	1.7
4,4'-DDE	92.1	1.8	1.9
2,4'-DDD	95.4	2.5	2.6
Endrin	94.4	2.7	3.0
4,4'-DDD	88.0	2.7	3.0
4,4'-DDT	89.6	5.8	6.4

* n = 3.

Table 2. Recovery of Organochlorine Pesticides Spiked onto Raw Potato at the 100 ppm Level*

Compound	Av. Recovery (%)	SD (µg/kg)	RSD (%)
α-BHC	96.3	6.3	6.6
β-BHC	108.6	2.3	2.1
Υ-BHC	97.4	6.6	6.8
Heptachlor	93.9	3.5	3.7
Aldrin	95.9	3.3	3.4
Heptachlor Epoxide	95.2	2.4	2.6
Dieldrin	97.1	0.55	0.57
4,4'-DDE	95.4	0.67	0.70
2,4'-DDD	95.7	0.85	0.89
Endrin	97.8	1.8	1.9
4,4'-DDD	93.7	1.8	1.9
4,4'-DDT	93.0	4.5	4.8

* n = 3.

Table 3. Recovery of Spiked Pesticides from Wheat by Accelerated Solvent Extraction

Compound	Spike Level (µg/kg)	Spike Level (µg/kg)
o-Methoate	74	85.4
Trifluralin	44	99.6
Dichlorvos	18	60.5
Phorate	18	92.8
Demeton	38	96.7
Dimethoate	58	87.8
Carbofuran	22	96.6
Atrazine	14	92.8
Diazinon	26	96.9
Disulfoton	22	87.9
Triallate	68	87.8
Parathion-methyl	40	115.7
Chlorpyrifos-methyl	8	115.4
Carbaryl	92	54.1
Linuron	102	83.6
Malathion	22	104.5
Phorate-sulfone	32	105.7
Parathion	84	101.2
Endosulfan-alpha	56	94.1
Disulfoton-sulfone	98	77.1
Imazalil	40	108.8
Endosulfan-beta	68	93.3
Endosulfan sulfate	20	77.0
Methoxychlor-*o,p*	48	89.9
Diclofop-methyl	36	81.8
Methoxychlor-*p,p'*	50	114.9
Azinphos-methyl	56	94.2

A 5-g sample of ground wheat grain was spiked with 100 µL of a standard solution containing 29 pesticides and herbicides at levels ranging from 8–102 ppb (see Table 3) and extracted at 100 °C with acetonitrile. Spike levels and recovery results are shown in Table 3. Recoveries ranged from 54.1–115.7%. The average recovery was 95.3% if the two outliers, dichlorvos and carbaryl, are excluded. Following the spike studies, 12 naturally incurred grain samples were extracted by the traditional wrist shaker extraction with acetonitrile, using post-extraction solid phase extraction (SPE) cleanup, and by accelerated solvent extraction using either acetone or acetonitrile as the extraction solvent. The accelerated solvent extraction took 12 min per sample and required 12–15 mL of solvent, while the shaker extraction took approximately 1 h per sample (including post-extraction SPE cleanup on carbon or C18) and used 130 mL of acetonitrile per sample. The accelerated solvent extraction extracts did not require post-extraction processing.

Extraction results for two compounds identified in these extracts, methyl chlorpyrifos and malathion, are shown in Table 4. The detected amounts compared well between the two techniques, with the accelerated solvent extraction values generally 10–20% higher. In all cases, samples with nondetectable levels (ND) were identified as such by both techniques. Acetonitrile and acetone appear to be good solvent choices for this application.

Table 4. Extraction of Incurred Pesticides in Wheat by accelerated solvent extraction and Conventional Wrist Shaker Extraction

Sample No.	Solvent	Sample Weight (g)	Methyl Chlorpyrifos (µg/kg)		Malathion (µg/kg)	
			Shaker	Accelerated Solvent Extraction	Wrist Shaker	Accelerated Solvent Extraction
1	Acetone	20.31	70	90	40	50
2	Acetone	19.78	80	100	40	50
3	Acetone	20.91	50	60	60	70
4	Acetone	10.13	ND	ND	ND	ND
5	Acetone	10.24	30	70	40	100
6	Acetone	9.93	ND	ND	ND	ND
7	Acetone	5.32	ND	ND	ND	ND
8	Acetone	5.39	ND	ND	ND	ND
9	Acetonitrile	19.85	60	80	60	80
10	Acetonitrile	20.4	70	90	60	70
11	Acetonitrile	5.30	ND	ND	ND	ND

ND = not detected.

Conclusion

Using accelerated solvent extraction, pesticide residue analysis laboratories can increase sample throughput while reducing overall solvent usage. The simplicity of the accelerated solvent extraction technique, combined with results showing excellent correlation to existing methods, have resulted in the rapid acceptance of accelerated solvent extraction for environmental analysis. The promulgation of U.S. EPA Method 3545 now provides a means for environmental test laboratories to take full advantage of accelerated solvent extraction technology. In addition to the wide range of target analytes covered under Method 3545 for organic pollutants in solid waste, accelerated solvent extraction has been applied successfully to the extraction of total petroleum hydrocarbons (TPH), dioxins, and furans from a variety of matrices. accelerated solvent extraction has also been applied to the extraction of explosives from soil, PCBs from fish and other marine tissues, and polyurethane foam (PUF) air sampling cartridges.

Suppliers

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275-1126 USA, Tel: 800-766-7000, www.fishersci.com.

Restek Corporation, 110 Benner Cir., Bellefonte, Pennsylvania, 16823 USA, Tel.: 814-353-1300, www.restekcorp.com.

"Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides Using Accelerated Solvent Extraction with Analytical Validation by GC/MS and GC/ECD" Document 116064.A, Dionex Corporation (now part of Thermo Fisher Scientific), June 16, 1994.

Thermo Scientific Dionex products are designed, developed, and manufactured under an ISO 9001 Quality System.

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