Application Note 328

Extraction of Explosives from Soils by Accelerated Solvent Extraction (ASE)

INTRODUCTION

Compounds used in high explosives may be toxic, carcinogenic, and are found on the Resource Conservation and Recovery Act (RCRA) list. These compounds and their metabolites are monitored in soils and ground waters to ensure compliance with U.S. EPA regulations. With many military production and testing sites throughout the world becoming decommissioned and returning to the private sector, and with the planned destruction of munitions through open-air burning and detonation, there is an increased need for the analytical determination of compounds used in high explosives. Current methods to remove explosive compounds from soils and other solid matrices prior to analytical determinations are sonication and Soxhlet extraction. These methods use large quantities of solvent and are very time-consuming.

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.

ASE has been demonstrated to be equivalent to existing extraction methodologies for most RCRA analytes from solid and semisolid samples, and meets the requirements of U.S. EPA Method 3545. Method 3545 includes the semivolatiles (BNAs), organochlorine and organophosphorus pesticides (OCPs and OPPs), polychlorinated biphenyls (PCBs), and chlorinated herbicides.

This application note reports on the use of ASE for the extraction of explosive compounds such as HMX, RDX, 2,4,6-trinitrotoluene (TNT), and some of their known metabolites from soils. Compound recovery was determined for spiked soil samples. Sample-to-sample precision was determined for soil samples obtained from the sites of munitions plants in Germany.

EQUIPMENT

Dionex ASE 200 Accelerated Solvent Extractor*

Dionex DX 500 HPLC with AD20
(UV/Vis Absorbance Detector)

Gas Chromatograph with Electron Capture Detector
(GC-ECD)

**ASE 150 and 350 can be used for equivalent results.*

SOLVENTS (PESTICIDE GRADE)

Methanol

Acetone

ASE CONDITIONS

System Pressure: 1500 psi*
Oven Temperature: 100 °C
Sample Size: 2.5 to 30 g
Oven Heat-up Time: 5 min
Static Time: 5 min
Flush Volume: 60%
Solvent: Acetone or Methanol
Purge: 1 MPa (150 psi) Nitrogen for 200 s
Static Cycles: 1
Total Extraction Time: 14 min
Solvent Usage: 17 to 50 mL per sample

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

SAMPLE INFORMATION

Clean soil samples from Environmental Resource Associates (Arvada, CO) were used for the spiking experiments. A second and third set of soil samples were taken from munitions plants in Germany that were used in both World Wars. In one case, the soils were taken in large quantities (2 kg), dried, ground, and sieved to less than 1 mm particle size. For the wet soil, the sample was used as it was collected. A quantity of 2.5 g of wet soil was mixed with 0.8 g of diatomaceous earth and then placed in the extraction cell.

The following conditions were used for the sonication and automated Soxhlet methods.

Sonication

Sample Size: 10 g
Solvent: 10 mL Methanol
Extraction Time: 15 min

Automated Soxhlet

Sample Size: 50 g
Solvent: 150 mL Methanol
Extraction Time: 2 h

ANALYSIS CONDITIONS

The following conditions were used for the analysis of the extracts from the spiked soil (Table 1). An isocratic method was used because only HMX, RDX, TNT, and DNT (2,4-dinitrotoluene) were spiked on the soil.

Table 1. Recovery from Spiked Soil at the 3 mg/kg Levels

Sample	HMX mg/kg	RDX mg/kg	TNT mg/kg	DNT mg/kg
1	3.07	3.06	3.03	3.14
2	2.99	2.89	3.02	3.07
3	2.99	2.86	2.92	3.06
4	2.84	2.74	2.81	2.97
Average	2.97	2.89	2.95	3.06
Recovery (%)	99.0	96.3	98.3	102
RSD (%)	3.2	4.6	3.5	2.3

Column: C18, 25 cm ħ 4.6 mm i.d., 5 Õm
Mobile Phase: 5% Isopropanol in methanol:water (32:68)
Flow Rate: 2.0 mL/min
Detection: UV, 254 nm
Injection Vol.: 25 µL

The extracts obtained by ASE and sonication for the incurred samples (Tables 2–6) were analyzed by HPLC for direct comparison. The ASE and Soxhlet extracts obtained from the same samples were analyzed by GC-ECD for comparison. A gradient was used for the HPLC method because several of the metabolites were quantified, and the gradient was needed to separate all of the compounds.

Column: C18, 25 cm x 1.0 mm i.d., 7 µm
Mobile Phase: Methanol/Water, 40% methanol to 56% methanol in 30 min
Flow Rate: 0.8 mL/min
Detection: UV, 254 nm
Injection Vol.: 20 µL

Table 2. Results from Soil A, HPLC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2,6-dinitrotoluene	n.d.	n.d.
2,4-dinitrotoluene	0.198	0.253
TNT	103	128
1,3,5-trinitrobenzene	2.35	3.45
4-amino-2,6-dinitrotoluene	5.34	9.30
2-amino-4,6-dinitrotoluene	6.09	9.39
Hexogene (RDX)	26.5	93.0

Table 3. Results from Soil B, HPLC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2,4-dinitrotoluene	0.026	0.023
TNT	30.1	45.6
1,3,5-trinitrobenzene	0.273	0.320
4-amino-2,6-dinitrotoluene	0.372	0.674
2-amino-4,6-dinitrotoluene	0.474	0.677
Hexogene (RDX)	0.154	0.609

Table 4. Results from Soil C, HPLC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2,6-dinitrotoluene	n.d.	n.d.
2,4-dinitrotoluene	0.095	0.186
TNT	4.55	4.74
1,3,5-trinitrobenzene	n.d.	0.069
4-amino-2,6-dinitrotoluene	1.68	3.64
2-amino-4,6-dinitrotoluene	2.05	3.36
Hexogene (RDX)	n.d.	n.d.

Table 5. Results from Soil D, HPLC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2,6-dinitrotoluene	n.d.	n.d.
2,4-dinitrotoluene	0.164	0.165
TNT	83.9	95.4
1,3,5-trinitrobenzene	3.38	3.87
4-amino-2,6-dinitrotoluene	1.03	1.44
2-amino-4,6-dinitrotoluene	1.81	2.12
Hexogene (RDX)	0.436	2.15

Table 6. Results from Soil E, HPLC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2-nitrotoluene	2.51	3.80
3-nitrotoluene	0.136	0.312
4-nitrotoluene	0.384	0.914
2,6-dinitrotoluene	0.295	0.588
2,4-dinitrotoluene	0.172	0.335
TNT	18.1	26.8
1,3,5-trinitrobenzene	0.814	1.62
4-amino-2,6-dinitrotoluene	1.46	3.23
2-amino-4,6-dinitrotoluene	0.890	1.90
Hexogene (RDX)	20.7	82.5

The conditions of the GC analysis (Tables 7–9) are given below. It should be noted that no results for hexogene (RDX) were obtained under GC conditions because the compound decomposes in the GC injector port.

Column:	30 m × 0.25 mm i.d., 0.25 µm film
Injector:	Split (50:1) at 250 °C, 1 µL
Detector:	ECD, 300 °C
Temperature Program:	40 °C, 2 min hold, to 250 °C at 10 °C/min, 5 min hold
Carrier:	Helium, 2 cm/s

Table 7. Results from soil B, GC analysis

Compound	Sonication mg/kg	ACE mg/kg
2,4-dinitrotoluene	0.036	0.16
TNT	30.7	39.4
1,3,5-trinitrobenzene	0.434	1.32
4-amino-2,6-dinitrotoluene	3.41	3.16
2-amino-4,6-dinitrotoluene	3.51	2.96

Table 8. Results from Soil D, GC Analysis

Compound	Sonication mg/kg	ACE mg/kg
2,6-dinitrotoluene	0.019	n.d.
2,4-dinitrotoluene	0.218	0.333
TNT	73.4	74.4
1,3,5-trinitrobenzene	4.56	9.72
4-amino-2,6-dinitrotoluene	7.20	12.5
2-amino-4,6-dinitrotoluene	7.69	11.5

Table 9. TNT from Wet, Heavily Contaminated Soil

Sample	TNT Recovery, mg/kg
1	3650
2	3530
3	3290
4	3200
Average	3420
RSD (%)	6.1

RESULTS

Soil samples were spiked at the 3 mg/kg (ppm) level by the addition of a 1 mL standard solution of HMX, RDX, TNT, and DNT (2,4-dinitrotoluene) in acetone onto 30 g of soil. The results represent the average of two HPLC injections performed on each of four replicate extractions.

The recoveries were quantitative with good precision. After these experiments, work proceeded on incurred samples. The results for the soil samples from the munitions plants are given below in the following tables. The "n.d." designation means that these compounds were not detected in the analysis.

As can be seen, ASE provides equivalent or superior recovery to existing extraction procedures for these compounds.

The final set of data shows the recovery of TNT from a wet, heavily contaminated soil that was collected near a munitions plant in Germany. ASE conditions remained the same as previous analyses, except the oven temperature was set to 125 °C and the pressure was 14.0 MPa (2000 psi). Four extractions were performed, and duplicate injections of each extract were analyzed using the GC.

CONCLUSION

The data presented here demonstrate that ASE is equivalent or superior to sonication and Soxhlet extraction for the determination of explosives and their metabolites in soils. ASE provides these results in a short period of time (less than 15 min per sample) and with minimum solvent usage (less than 15 mL for a 10 g sample). With the ASE 200, all of the sample extractions (up to 24 samples in a batch) can be done without operator intervention once the instrument is loaded and started.

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