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Sample preparation

Investigation of thermal degradation during extraction by the EXTREVA ASE Accelerated Solvent Extractor

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Introduction

The Thermo Scientific™ EXTREVA™ ASE™ Accelerated Solvent Extractor (Figure 1) is a system based on many proprietary technologies including gas-assisted solvent delivery and parallel accelerated solvent extraction. This fully automated system combines the extraction and evaporation capabilities in one instrument, and it can be conveniently used for extracting and then concentrating/evaporating extracts from up to 16 solid and semi-solid samples. The system can use up to six different extraction solvents (or mixtures of them) and can extract up to four cells in parallel. The gas-assisted solvent extraction consists of the addition of mixed hot extraction solvents and nitrogen gas to the stainless-steel cell to reach the working pressure of 200 psi (~14 bar). The combined effect of temperature and pressure greatly increases the efficiency of the extraction process, significantly reducing the amount of time and solvent required for extraction when compared to traditional techniques such as Soxhlet. The evaporation process starts immediately after the completion of the extraction step without any user interaction if no offline cleanup of the extract is needed. The extracts can be evaporated to dryness or concentrated in 2 mL vials, with the final volume controlled by artificial intelligence machine vision hence the level sensing feature. The total workflow is fully automated and performed in parallel (up to 4 samples in parallel) for fast and automated extraction and/or evaporation with low solvent consumption. Moreover, most of the time the EXTREVA ASE system is on automation operating unassisted and hence frees up the analyst time to take care of other more demanding tasks such as data analysis.

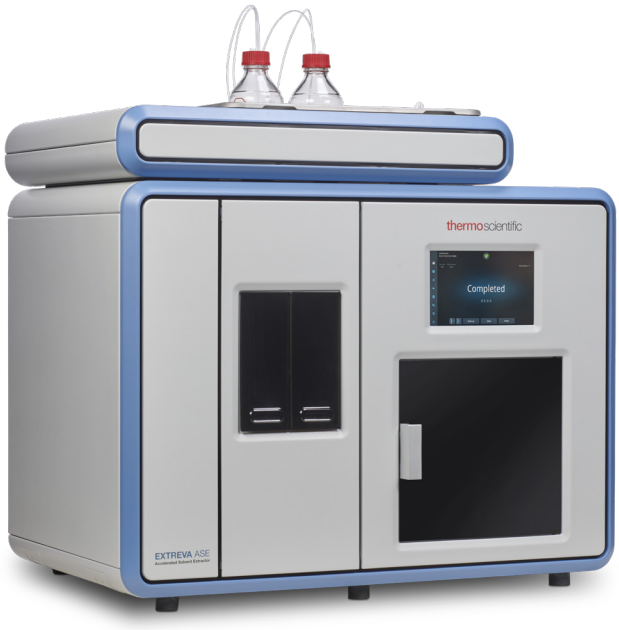

Figure 1. EXTREVA ASE Accelerated Solvent Extractor

Since elevated temperature is used to accomplish the extraction, the effect of thermal degradation was investigated to ascertain the viability of this technique for thermally labile compounds. The EXTREVA ASE system experiments reported here include monitoring the stability of thermally labile compounds during the parallel solvent extraction in gas-assisted mode at 100 °C as well as extractions done at higher temperatures (150 °C). The degradation of endrin and DDT during gas chromatography (GC) analysis is used as an indication of active sites or excessive thermal conditions. Endrin forms endrin aldehyde and endrin ketone, and dichlorodiphenyltrichloroethane (DDT) breaks down to dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE). These same compounds were used to determine if thermal decomposition can occur during the extraction with the EXTREVA ASE system.

Experimental

In these experiments, endrin and DDT were spiked on sand at 25 µg/kg (ppb). A cellulose filter was placed on a 10 mL body and the end cap was hand tightened. Two grams of clean loam soil were mixed in a glass beaker with an equal amount of diatomaceous earth (Thermo Scientific™ Dionex™ ASE™ Prep DE dispersant). The resulting mixture was poured carefully into the extraction cell and spiked with the appropriate amount of pesticide standard. Any empty volume was filled with ASE Prep DE with light tapping. After placing another cellulose filter on top of the cell body, the second end cap was hand tightened. The EXTREVA ASE system was programmed according to the optimized conditions of extraction and evaporation in one run, which was reported in organochlorine pesticides (OCP) Application Note AN001054. Before proceeding sample extraction, the system was rinsed with the extraction solvent (hexane-acetone 1:1, v/v). Hexane was used for solvent exchange (10 mL was added to the collection vessel before evaporation as "Pre-Rinse" and 1.6 mL was added during evaporation as "Rinse"). The spiked sand samples were extracted at 100 °C. Before analysis, the extracts were concentrated to a final volume of 1 mL by heating at 40 °C with a nitrogen gas stream (50 mL/min each concentration flask) under vacuum (8 psi/0.55 bar/422 torr). The final volume was controlled by artificial intelligence machine vision (level sensing feature). Pentachloronitrobenzene was added to the autosampler vials as an internal standard and the extracts were analyzed by a GC with an electron capture detector (ECD).

Results and discussion

Because soil samples are typically extracted at elevated temperatures (>100 °C), thermally labile analytes may partially degrade during the extraction phase. Out of the 20 OCP analytes used in the OCP study, endrin and 4,4'-DDT are the least thermally stable compounds. Therefore, soil samples spiked with endrin and 4,4'-DDT at 25 µg/kg were extracted to evaluate the presence of thermal degradation products.

The average recoveries are shown in Table 1. The average recoveries were 90.2% with 5.1% relative standard deviation (RSD) for endrin and 88.0% with 5.5% RSD for DDT with multiple extractions (n = 12) at 100 °C. The average recoveries were 92.2% with 4.0% RSD for endrin and 88.6% with 6.7% RSD for DDT with multiple extractions (n = 11) at 150 °C. These recoveries are similar to the results obtained with 20 OCP analytes used in the OCP study and reported in the OCP Application Note AN001054.

Table 1. Endrin and DDT recoveries at different extraction temperatures

Analyte	Recovery at 100 °C (%)	RSD	Recovery at 150 °C (%)	RSD
Endrin	90.2	5.1	92.2	4.0
DDT	88.0	5.5	88.6	6.7

Table 2 shows the thermal degradation results when the soil sample was extracted at 100 °C (n = 12) and 150 °C (n = 11). All breakdown percentages were well below the 15% criteria suggested by the U.S. EPA Method 8081b. For endrin, a 3.3% breakdown occurred in the GC injection port, as evidenced by injecting a control sample (n = 5, 0.05 ppm QC standard). The average breakdown of 4.0% and 3.2% for endrin at 100 °C (n = 12) and 150 °C (n = 11) can be attributed to the injection port

breakdown as evident from control samples. The DDT breakdown was very low for both the soil samples and the control samples. These data provide another indication that thermal degradation is not an issue during the extraction with the EXTREVA ASE system. However, when extracting a compound that is sensitive to elevated temperatures, it is prudent to choose a lower operating temperature.

Table 2. Endrin and DDT breakdown at different extraction temperatures

	Extraction temperature	Average breakdown (%)	
		Endrin	DDT
Samples	100	4.0	1.5
Samples	150	3.2	1.0
Controls	No extraction	3.3	0.1

Conclusion

In summary, the gas-assisted method of extraction followed by evaporation in the EXTREVA ASE system does not cause a significant breakdown for OCP analytes during the extraction process. Moreover, oxidative losses are minimized if the solvent is degassed, and oxygen is excluded. As the analytes are in the heated zone surrounded by solvent for short periods of time, thermal losses do not occur if appropriate temperatures are used for the extractions.

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