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Sample preparation

Investigation of carryover or cross-contamination in the EXTREVA ASE Accelerated Solvent Extractor

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Introduction

The Thermo Scientific™ EXTREVA™ ASE™ Accelerated Solvent Extractor (Figure 1) is a newly developed 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 concentrating/evaporating extracts from up to 16 solid and semisolid samples. The EXTREVA ASE system combines elevated temperatures and pressures with liquid solvents to achieve fast and efficient removal of analytes of interest from various matrices. The system can use up to six different extraction solvents (or mixtures of them) and extract up to four cells in parallel. The newly developed gas-assisted solvent extraction basically consists of the addition of 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. 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 in automated mode and hence frees up the user time to take care of other more demanding tasks.

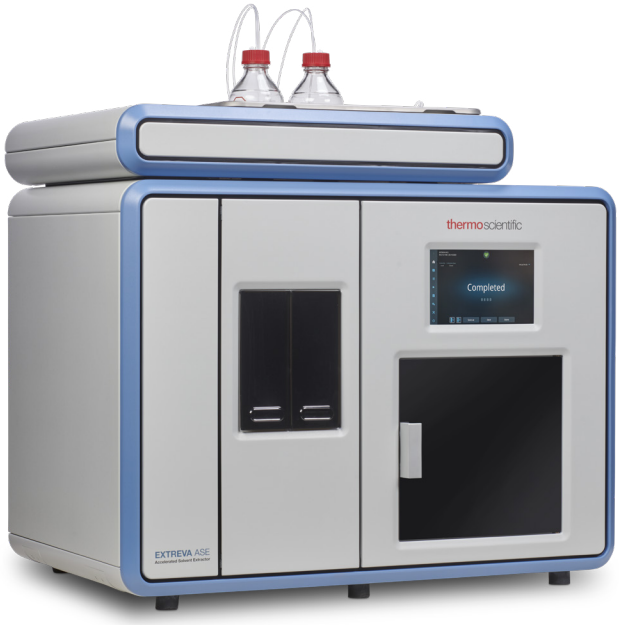

Figure 1. EXTREVA ASE Accelerated Solvent Extractor

The EXTREVA ASE system is a sample preparation technique that uses elevated temperature and pressure to increase extraction efficiency in solid and semi-solid samples. The EXTREVA ASE system uses gas-assisted solvent delivery and the parallel extraction technique significantly reduces the amount of time and solvent required for gas-assisted parallel extraction when compared to traditional techniques such as Soxhlet. This technique ensures a high degree of reproducibility by running each sample individually within parallel loading (up to 4 samples) under the same preset method conditions. This mode of operation uses an individual pathway to collect the extracts and carryover, or cross-contamination was investigated to ascertain the viability of this technique for multiple samples processed in a parallel run. The experiments performed included the extraction of heavily contaminated soil samples followed by extracting blank samples and the determination of target analytes in both extracts.

Two applications were run on soil contaminated with the highest level of polyaromatic hydrocarbons (up to 12,500 µg/kg) and organochlorine pesticides (250 µg/kg) respectively following the United States Environmental Protection Agency (U.S. EPA) Method 3545a and minimum carryover (less than 0.5%) was observed. These results demonstrate that the extractions with the EXTREVA ASE system are exhaustive, and all the compounds are removed from the fluidic pathway when using an optimized extraction method.

Experimental

In the first experiment, polyaromatic hydrocarbons (PAHs) were spiked on soil/DE samples at the 12,500 µg/kg (ppb) level. A cellulose filter was placed on a 10 mL cell 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 PAH standard. Any empty volume was filled with Dionex ASE Prep DE or sand while lightly tapping. After placing another cellulose filter on top of the cell body, the second end cap was hand tightened. All 4 cells with highly contaminated soil (spiked soil) were loaded into the EXTREVA ASE system for parallel extraction. The EXTREVA ASE system was programmed according to the optimized extraction conditions at 100 °C which are reported in PAH Application Note AN001106. Before proceeding to the extraction of the samples, as a part of the main extraction method each fluidic pathway of the system was rinsed with 10 mL extraction solvent (dichloromethane-acetone 1:1, v/v) as the user choice of pre-rinse. After the extraction, the extracts were collected into four concentration flasks. After the extraction, another set of 4 cells containing Ottawa Sand (clean) was loaded. A second extraction was performed using the same conditions and extract was collected in a second set of evaporation flasks. The extracted volumes were reduced at 40 °C with a nitrogen gas stream (50 mL/min each evaporation container) under vacuum (8 psi = 0.55 bar = 422 torr) in the EXTREVA ASE system evaporation to a fixed volume of 1 mL. The sand extracts were concentrated first, followed by the contaminated extracts. The final volume was controlled by artificial intelligence machine vision (level sensing feature). These steps were repeated with three separate new samples to determine reproducibility. The PAHs and blank samples were analyzed by GC-MS.

In the second experiment, organochlorine pesticides (OCPs) were spiked on soil/DE samples at the 250 µg/kg (ppb) level. A cellulose filter was placed on a 10 mL cell 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 (Dionex ASE Prep DE). The resulting mixture was poured carefully into the extraction cell and spiked with the appropriate amount of OCPs standard. Any empty volume was filled with Dionex ASE Prep DE or sand while light tapping. After placing another cellulose filter on top of the cell body, the second end cap was hand tightened. All 4 cells with highly contaminated soil (spiked soil) were loaded into the EXTREVA ASE system for

parallel extraction. The EXTREVA ASE system was programmed according to the optimized conditions of extraction at 100 °C, which were reported in OCP Application Note AN001054. Before proceeding to the extraction of the samples, as a part of the main extraction method each fluidic pathway of the system was rinsed with 10 mL extraction solvent (dichloromethane-acetone 1:1, v/v) as the user choice of pre-rinse. The extracts were collected into four concentration flasks. After the extraction, another set of four cells containing Ottawa Sand (clean) was loaded. A second extraction was performed using the same conditions and extract was collected in the second set of concentration flasks. Hexane was used for solvent exchange (10 mL added to collection vessel before evaporation and 1.6 mL added during evaporation). The extracted volumes were reduced at 40 °C with a nitrogen gas stream (50 mL/min each evaporation container) under vacuum (8 psi = 0.55 bar = 422 torr) in evaporation by the EXTREVA ASE system to 1 mL for the sand extract first and then contaminated extract before analysis. The final volume controlled by artificial intelligence machine vision (level sensing feature). These steps were repeated with three separate new samples to determine reproducibility. The OCPs and blank samples were analyzed by GC-ECD.

Results and discussion

The studies on the contaminated soil were performed to determine if any material remained and was not completely flushed from the tubing and valves that are in line with the extraction cell. With the small amount of solvent used relative to the sample size, carryover or cross-contamination could be potential concerns with the EXTREVA ASE Accelerated Solvent Extractor. To investigate these concerns, a heavily fortified contaminated soil sample (12,500 µg/kg) was extracted and concentrated under the conditions reported in PAH Application Note 1106. A second extraction was performed under the same conditions but using a new cell filled with Ottawa Sand. Between the two extractions, each flow path channel was rinsed with 10 mL of solvent that was part of extraction method. Results of the carryover test are shown in Table 1. The carryover percent was calculated by comparing the peak area ratio of the analyte between the spiked samples and the blanks. Good recoveries were observed, and carryover was less than 0.5% for all analytes which is negligible relative to the contamination of soil. These results demonstrate that the rinse implemented between the extractions was effective for minimizing carryover or cross-contamination. Moreover, the rinse volume (either pre-rinse or post-rinse) can be adjusted to remove residual contaminants from fluidic pathways to accommodate different sample sizes, matrices, and concentrations.

Table 1. Average recoveries of PAHs and carryover from soil samples with high spike level

Compound	Average recovery (%) (10 mL cell, n = 4)	RSD	Average recovery (%) (10 mL cell, n = 4)
Naphthalene	78	2.0	0.01
Acenaphthylene	85	2.3	0.01
Acenaphthene	84	2.6	0.01
Fluorene	85	2.4	0.01
Phenanthrene	92	2.4	0.01
Anthracene	98	2.1	0.01
Fluoranthene	102	3.2	0.02
Pyrene	99	2.2	0.02
Benzo[*a*]anthracene	104	1.8	0.02
Chrysene	100	2.2	0.02
Benzo[*b*]fluoranthene	101	1.2	0.02
Benzo[*k*]fluoranthene	100	1.4	0.01
Benzo[*a*]pyrene	100	2.3	0.01
Indeno[1,2,3-*cd*]fluoranthene	92	2.4	0.01
Dibenz[*a,h*]anthracene	88	2.1	0.01
Benzo[*ghi*]perylene	91	2.4	0.01

In the second application, a heavily fortified contaminated soil sample (250 µg/kg) was extracted and concentrated under the conditions reported in OCP Application Note AN001054.
A second extraction was performed under the same conditions but using a new cell filled with Ottawa sand. Between the two extractions, each flow path channel was rinsed with 10 mL of solvent. Results of the carryover test are shown in Table 2. The carryover percent was calculated by comparing the peak area ratio of the analyte between the spiked samples and the blanks.

Good recoveries were observed, and carryover was less than 0.5% for all analytes which is negligible compared to the contamination of soil. These results demonstrates that the rinse implemented between the extractions was effective for minimizing carryover or cross-contamination. Moreover, the rinse volume (either pre-rinse or post-rinse) can be adjusted to remove residual contaminants from fluidic pathways to accommodate different sample sizes, matrices, and concentrations.

Table 2. Average recoveries of OCPs and carryover from soil samples with high spike level

OCP	Average recovery % (10 mL, n = 4)	RSD	Average carryover % (10 mL, n = 4)
α-BHC	81.7	7.9	0.00
γ-BHC	83.1	6.5	0.19
β-BHC	93.9	5.7	0.07
δ-BHC	89.6	5.0	0.09
Heptachlor	90.1	7.0	0.33
Aldrin	86.9	6.9	0.00
Heptachlor epoxide	92.6	5.7	0.01
trans-Chlordane	92.9	5.0	0.00
cis-Chlordane	93.5	5.6	0.05
4,4'-DDE	86.6	5.8	0.06
Endosulfan I	90.6	5.1	0.00
Dieldrin	94.4	4.8	0.01
Endrin	102.2	4.3	0.02
4,4'-DDD	91.0	3.9	0.00
Endosulfan II	89.8	4.0	0.43
4,4'-DDT	91.7	3.8	0.02
Endrin aldehyde	83.8	5.1	0.03
Methoxychlor	98.6	4.4	0.14
Endosulfan sulfate	97.5	3.5	0.03
Endrin ketone	95.0	3.6	0.03

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