Investigations of Thermal Degradation During Accelerated Solvent Extraction (ASE)

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Key Words
Accelerated Solvent Extraction, ASE, DDT, Endrin, Dicumyl Peroxide, Method Optimization, Thermally Labile Compounds

Goal

To demonstrate that the accelerated solvent extraction technique can be used to extract thermally labile compounds with proper method optimization.

Executive Summary

Accelerated solvent extraction is a sample preparation technique that uses elevated temperature and pressure to increase extraction efficiency in solid and semi-solid samples. This technique significantly reduces the amount of time and solvent required for extraction when compared to traditional techniques such as Soxhlet. 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. Thermal degradation was not observed for DDT, endrin, and dicumyl peroxide in spiked sand samples at temperatures as high as 150 °C. These results demonstrate the versatility of the accelerated solvent extraction method and show that thermally labile compounds can be extracted in an optimized extraction method.

Introduction

Accelerated lower case these two 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.

Because extractions are performed at elevated temperatures using the accelerated solvent extraction method, thermal degradation could be a concern. This has been investigated, and no evidence of degradation has been seen. The experiments reported here include monitoring the stability of thermally labile compounds during standard accelerated solvent extraction conditions (100 °C) as well as extractions done at higher temperatures (150 °C).

The degradation of DDT and endrin during GC analysis is used as an indication of active sites or excessive thermal conditions.[1] DDT breaks down to DDD and DDE, and endrin forms endrin aldehyde and endrin ketone. These same compounds were used to determine if thermal decomposition can occur during the accelerated solvent extraction method. Another temperature sensitive compound was also used as a probe to measure thermal and oxidative decomposition. Dicumyl peroxide (DCP) is used as a free radical generator in polymerization, and it is very sensitive to thermal degradation.

Instrumentation

- Thermo Scientific™ Dionex™ ASE™ 200 Accelerated Solvent Extractor system
- Gas chromatograph (GC) with electron capture detector (ECD)
- Thermo Scientific™ Dionex™ DX-500 HPLC system with AD20 (UV detector)

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Experimental

In separate experiments, DDT and endrin were spiked on sand at the 5 µg/kg (ppb) level. The spiked sand samples were extracted at 150 °C (normal extraction temperature for these compounds is 100 °C), and the extracts were analyzed by GC with ECD. Dieldrin was added to the collection vials as an internal standard, and the volumes were reduced with a nitrogen gas stream to 1 mL before analysis.

Experiments with DCP as the analyte were also conducted to investigate thermal degradation. A 0.5 mL aliquot of a 2 mg/mL solution of DCP was spiked on sand in an extraction cell. The extraction conditions were as follows: Hexane at 100 and 150 °C extraction temperatures, 17.22 MPa (2500 psi), 5 minute heat-up and 5 minute static, 60% flush volume, and nitrogen purge for 60 seconds. HPLC was the analytical method, and naphthalene was used as an internal standard and was spiked in the collection vial after extraction.

Results and Discussion

The average recoveries were 103% with 3.9% RSD for DDT and 110% with 2.4% RSD for endrin with three extractions and duplicate injections of each. No evidence was seen for the presence of DDE or DDD in the experiments with DDT, and neither endrin aldehyde nor endrin ketone was observed in the experiments with endrin. The minimum detectable quantity for these analytes was 0.1 µg/kg. These results were confirmed by an environmental contract laboratory as part of the study which demonstrated the equivalency of the accelerated solvent extraction method to current EPA extraction methodology.[2] In this study, the recoveries of other temperature-sensitive compounds such as *o*-toluidine and 3,3'-dichlorobenzidine were carefully monitored. The average recoveries of these compounds by accelerated solvent extraction method were 110.3% and 116.5%, respectively, relative to automated Soxhlet extraction. The integrity of DDT and endrin was measured, and no degradation was observed. These data provide another indication that thermal degradation is not a an issue with the accelerated solvent extraction method. However, when extracting a compound that is sensitive to elevated temperatures, common sense should be used when choosing an operating temperature.

Dicumyl peroxide (DCP) is used as a free radical generator, and based on half-life calculations, 30% will decompose in 7.5 minutes at 150 °C.[3] Table 1 summarizes the results of the experiments with DCP. At 100 °C, the recovery of the DCP was 101% with 5.9% RSD for duplicate extractions with duplicate injections. At 150 °C, the recovery was 77.0% with 3.2% RSD. This agrees well with the literature values for decomposition at this temperature.[3] However, when the solvent was degassed and blanketed with nitrogen instead of air, the recovery at 150 °C increased to 91.1% with 0.83% RSD. This indicates that some of the measured thermal decomposition may be oxidative decomposition.

Table 1. Recovery of dicumyl peroxide (DCP) using accelerated solvent extraction method while varying temperature/degas conditions.

Conditions	Recovery (%)	RSD (%)
100 °C, no degas, air pressurization	101	5.9
150 °C, no degas, air pressurization	77.0	3.2
150 °C, solvent degassed, nitrogen pressurization	91.1	0.83

Additional work with triglycerides containing unsaturated fatty acids has shown that thermal degradation and oxidation with accelerated solvent extraction method (at temperatures up to 130 °C) are the same as with Soxhlet extraction[4] in which the extractions are done only slightly above room temperature.

In summary, the results reported here demonstrate that thermal degradation does not occur during extractions with the accelerated solvent extraction method under optimized conditions. With this method, the sample is surrounded by solvent; thus, oxidative losses are minimized if the solvent is degassed and oxygen is excluded. Since the analytes are in the heated zone for short periods of time, thermal losses do not occur if appropriate temperatures are used for the extractions.

References

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