

# Investigations of Thermal Degradation During Accelerated Solvent Extraction (ASE<sup>®</sup>)

## INTRODUCTION

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.

Because extractions are performed at elevated temperatures using ASE, 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 ASE 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<sup>1</sup>. 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 ASE. 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

Dionex ASE 200 Accelerated Solvent Extractor  
Gas chromatograph (GC) with electron capture detector (ECD)

Dionex DX-500 HPLC system with AD20 (UV detector)

## 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 ASE to current EPA extraction methodology<sup>2</sup>. 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 ASE 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 problem with ASE. 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<sup>3</sup>. 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<sup>3</sup>. 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.

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

**Table 1 Recovery of Dicumyl Peroxide (DCP) Using ASE 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

In summary, the results reported here demonstrate that thermal degradation does not occur during extractions with ASE under optimized conditions. With ASE, 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

1. *U.S. EPA SW-846*, 3rd ed.; Test Methods for Evaluating Solid Waste, Method 8080; U.S. GPO: Washington, DC, September 1986.
2. *U.S. EPA SW-846*, 3rd ed., Update III; Test Methods for Evaluating Solid Waste, Method 3545; U.S. GPO: Washington, DC, May 1995.
3. "Half-life," peroxide decomposition software, file no. 99021, Atochem North America, NY, 1991.
4. "Extraction of Oils from Oilseeds by Accelerated Solvent Extraction (ASE)," Application Note 325, Dionex Corporation.



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\* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.



LPN 0765-01 SM 5/01  
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