Accelerated Solvent Extraction (ASE®) of Plasticizers from Poly(vinyl chloride) Polymer

INTRODUCTION

Poly(vinyl chloride) (PVC) is a popular, versatile polymer used in many different products, including water pipes, toys, and shower curtains. PVC is typically composed of resins, stabilizers, pigments, and plasticizers. Plasticizers soften the polymer, aid in the manufacturing process, and provide form and function to various PVC materials. Plasticizers may account for 30–35% of the PVC formulation. Extraction and determination of plasticizers in a PVC material are critical steps in evaluating a polymer for an intended use. Traditionally, plasticizers are extracted from PVC using a 6-h Soxhlet method and identified using infrared spectrometry or gas chromatography.

ASE is a powerful technique that can be reliably used to extract plasticizers from PVC, as well as additives from other polymers. ASE uses organic solvents at temperatures above their atmospheric boiling points to deliver extractions equivalent to traditional extraction techniques, but with faster extraction times, reduced solvent use, and automation of the extraction process. ASE is recognized as an official extraction method in U.S. EPA Method 3545.

This application note outlines the basic principles of using ASE to extract plasticizers such as dioctyl adipate (DOA), trioctyl phosphate (TOP), dioctyl phthalate (DOP), and trioctyl trimellitate (TOTM) from PVC.

EQUIPMENT

ASE 200 Accelerated Solvent Extractor equipped with 11-mL extraction cells

ASE Solvent Controller (optional)

AutoASE™ Software (optional)

Gas Chromatograph with a flame ionization detector

Analytical balance

Dionex vials for extract collection (40 mL, P/N 49465)

Cellulose extraction thimbles (19 × 37 mm, P/N 55708)

Polymer grinder (SPEX CertiPrep, 6750 freezer/mill)

Oven for drying extracts

TurboVap® solvent evaporation system (Caliper Life Sciences) or equivalent

REAGENTS AND STANDARDS

Petroleum ether (pesticide quality or equivalent)

Methylene chloride (pesticide quality or equivalent)

Bis (2-ethylhexyl) adipate (DOA)

Tris (2-ethylhexyl) phosphate (TOP)

Bis (2-ethylhexyl) phthalate (DOP)

Trioctyl trimellitate (TOTM)

EXTRACTION PROCEDURE

The following procedure provides high extraction efficiencies for plasticizer additives such as DOA, TOP, DOP, and TOTM. However, each polymer formulation is unique, so the procedure may need modifications for additives not included in the above list. Analysts should use the method validation technique outlined below to evaluate the success of method modification.

Extraction Cell Preparation

Inspect the extraction cells to verify the integrity of the Teflon® O-Ring and PEEK seals in the cell caps.

Sample Preparation

Grind the polymer sample to a size of 10 mesh or finer using a liquid-nitrogen-cooled grinder. For this work a SPEX CertiPrep 6750 freezer/mill was used. Accurately weigh approximately 0.5–1.0 g of the ground PVC sample into a cellulose extraction thimble and place the thimble into an extraction cell. Place a cell cap on the outlet end of the cell and hand-tighten. Preweigh enough collection vials (without the caps) to collect the extracts. After extraction, the solvent is evaporated under a stream of nitrogen and the collection vials are reweighed to determine the extraction recovery. Place the cells in the upper carousel of the ASE 200 and place the appropriate number of preweighed collection vials in the lower carousel.

Extraction Conditions

Enter the following parameters on the ASE 200 extractor and initiate the run.

Oven Temperature:	100 ºC
Pressure:	1500 psi
Solvent:	Petroleum ether
Cell Heatup Time:	5 min
Static Time:	1 min
Flush Volume:	100% of cell volume
Static Cycles:	3
Purge Time:	120 s
Total Volume:	20 mL
Total Time:	12 min

At the completion of the extraction, the extracts were taken to dryness in a TurboVap evaporation workstation and then dried to a constant weight in a vacuum oven heated at 50 ºC. The extracts were then reconstituted using 10 mL of methylene chloride and reserved for chromatographic analysis.

GAS CHROMATOGRAPHY

DOA, TOP, DOP, and TOTM were extracted from PVC using the procedure described above and identified using gas chromatography. Gas chromatographic conditions were as follows:

Instrument:	HP 6890 Gas Chromatograph
Column:	30 m × 0.25-mm i.d., SP-1 (Supelco), film thickness 0.25 mm
Carrier Gas:	Helium, constant flow
Detector	
	Temperature: 350 ºC
Column	
	Temperature: 100 ºC ramp to 300 ºC at 10 ºC/min
Flow Rate:	5.4 mL/min
Injector	
	Temperature: 350 ºC
Injection:	Split
Split Ratio:	75:1
Injection Volume:	1 µL

RESULTS

PVC samples were extracted using a 6-h Soxhlet extraction method (ASTM D 2124) and the ASE method described above. Both methods used petroleum ether as the extraction solvent. Each extract was thoroughly dried, reconstituted using methylene chloride, and analyzed using the GC method described above. A representative chromatogram is shown in Figure 1. Table 1 compares the extraction efficiency of the two methods.

Table 1. Weight Percent of Each Plasticizer in PVC

Plasticizer	ASE Recovery n = 3	Soxhlet Recovery (ASTM D 2124) n = 2	ASE Recovery (%)
DOA	9.81	9.56	102.6*
TOP	9.50	9.28	102.4*
DOP	9.42	9.35	100.7*
TOTM	9.17	9.05	101.3*

* % recovery vs. Soxhlet

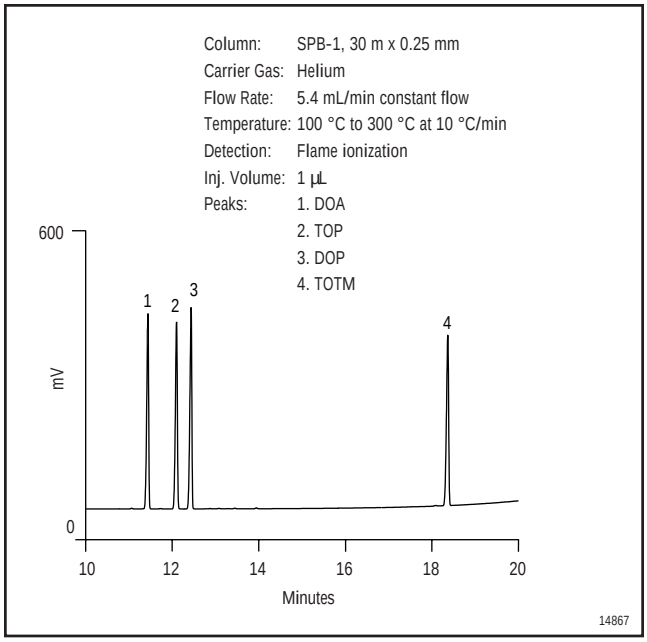

***Figure 1**. ASE PVC extract chromatogram.*

DISCUSSION

Solvent Choice

As described in Dionex Application Note 331, *Accelerated Solvent Extraction of Additives from Polymer Materials*, we used ASE to extract antioxidant additives from polyolefins. In that application we recommended using the Hildebrand solubility parameter for choosing an appropriate ASE extraction solvent. The Hildebrand approach was used to reduce the amount of matrix co-extractable material found in polyolefins.

In contrast, petroleum ether is recommended for both ASE and Soxhlet extraction of plasticizers from PVC. In addition to plasticizers, PVC formulations contain resins, stabilizers, and fillers. The traditional Soxhlet method for the extraction of plasticizers is aimed at removing these compounds from the PVC matrix so additional analyses can be performed on the resin and stabilizer portions of the polymer. Petroleum ether does not appear to solubilize the PVC matrix under the ASE or Soxhlet conditions described above.

Method Validation

When developing extraction methods, one way to validate extraction efficiency is to reextract the same sample and check for remaining analytes. The ASE system allows the analyst to automate reextraction for easy method validation.

CONCLUSION

This application note demonstrates that, for the extraction of the plasticizers discussed above, ASE is equivalent to Soxhlet. Furthermore, the ASE method requires only 12 min per sample and approximately 20 mL of extraction solvent, whereas the Soxhlet method requires 6 h and 120 mL solvent.

SUPPLIERS

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