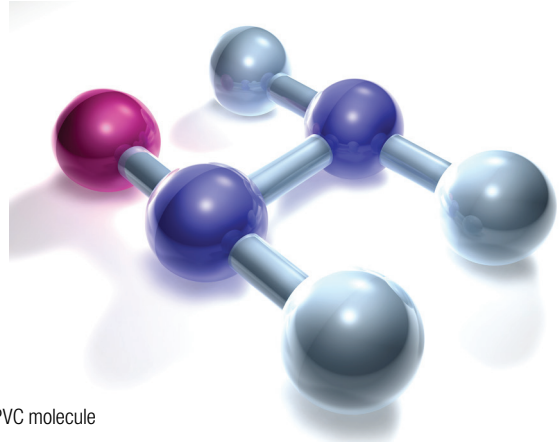
Accelerated Solvent Extraction of Plasticizers from Polyvinyl Chloride Polymer

Introduction

Polyvinyl 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 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.

Accelerated solvent extraction is a powerful technique that can be reliably used to extract plasticizers from PVC, as well as additives from other polymers. Accelerated solvent extraction 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. Accelerated solvent extraction is recognized as an official extraction method in U.S. EPA Method 3545.

This Application Note outlines the basic principles of using accelerated solvent extraction to extract plasticizers such as dioctyl adipate (DOA), trioctyl phosphate (TOP), dioctyl phthalate (DOP), and trioctyl trimellitate (TOTM) from PVC.



PVC molecule

Equipment

- Thermo Scientific™ Dionex™ ASE™ 200 Accelerated Solvent Extractor System* equipped with 11 mL extraction cells
- Thermo Scientific Dionex ASE Solvent Controller (optional)
- Thermo Scientific™ Dionex™ AutoASE™ Software (optional)
- Gas Chromatograph with a flame ionization detector
- Analytical balance
- Vials for collection of extracts (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
- Solvent Evaporator

*Dionex ASE 150 and 350 systems can be used for equivalent results.

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)

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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.

Cell Preparation

Inspect the extraction cells to verify the integrity of the PTFE 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 Dionex ASE 200 system and place the appropriate number of preweighed collection vials in the lower carousel.

Extraction Conditions

Enter the following conditions on the Dionex ASE 200 system and initiate the run.

Oven Temperature:	100 °C
Pressure:	1500 psi*
Solvent:	Petroleum ether
Cell Heat-Up 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

*Pressure studies show that 1500 psi is the optimum extraction pressure for all accelerated solvent extraction applications.

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

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Results

PVC samples were extracted using a 6-h Soxhlet extraction method (ASTM D 2124) and the accelerated solvent extraction 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.

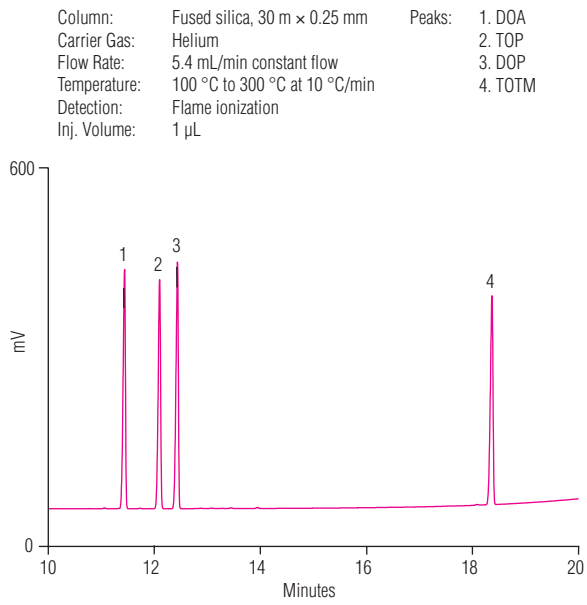

Figure 1. PVC extract chromatogram using accelerated solvent extraction.

Table 1. Weight percent of each plasticizer in PVC.

Plasticizer	Accelerated Solvent Extraction Recovery (n=3)	Soxhlet Recovery (ASTM D 2124) (n=2)	Accelerated Solvent Extraction 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

Discussion

Solvent Choice

As described in Application Note 331, Accelerated Solvent Extraction of Additives from Polymer Materials, accelerated solvent extraction was used to extract antioxidant additives from polyolefins. This Application Note recommended using the Hildebrand solubility parameter for choosing an appropriate accelerated solvent 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 the Dionex ASE system 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 accelerated solvent extraction or Soxhlet conditions described above.

Method Validation

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

Conclusion

This Application Note demonstrates that, for the extraction of the plasticizers discussed above, accelerated solvent extraction is equivalent to Soxhlet. Furthermore, the accelerated solvent extraction 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.

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AN70640_E 07/13S