

Accelerated Solvent Extraction for Additives in Polymer Materials

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Executive Summary

Accelerated solvent extraction is a sample preparation technique that is beneficial to laboratories extracting additives from polymer materials. This technique uses elevated temperature and pressure to improve extraction efficiency for samples that are difficult to extract. The extraction efficiencies of the accelerated solvent extraction technique are equivalent to Soxhlet for polymer samples but require only 12 min of extraction time and approximately 40 mL of solvent per sample. Since Soxhlet extraction requires up to six hours and more than 500 mL of solvent per sample, use of the accelerated solvent extraction technique for additive extraction from polymers can significantly reduce the amount of time and solvent required for sample preparation.

Keywords

Accelerated solvent extraction, plasticizers, polyvinyl chloride, PVC, Soxhlet extraction, extraction thimbles, GC-MS, HPLC



Introduction

Synthetic polymers are large organic molecules with a range of applications that far exceeds any other class of material.¹ Current applications extend from adhesives, coatings, foams, and packaging materials to textile and industrial fibers, composites, electronic devices, biomedical devices, optical devices, and precursors for newly developed high-tech ceramics. Due to the diversity of these applications, polymers are manufactured to meet the intended application through the addition of compounds that reduce oxidation, stabilize the polymer for environmental exposure (e.g. heat or light), and soften the polymer. Compounds, such as heat stabilizers, light stabilizers, slip agents, plasticizers, and antioxidants represent some of the most common classes of additives used to tailor polymers for use.²

Extraction and chromatographic analysis of these additives are required to monitor their formulation levels and are critical steps in evaluating a polymer for its intended use. While chromatographic analysis can be automated, the extraction process is accomplished using the Soxhlet technique, which is time consuming, and requires large amounts of solvents. Laboratories testing additives in polymers are required to process multiple samples, which are difficult to extract, on a daily basis. Consequently, the process of sample preparation is often a severe bottleneck in the analytical workflow. The accelerated solvent extraction technique provides fast extraction times and low solvent usage to benefit laboratories extracting additives from polymer materials.

Accelerated Solvent Extraction

The accelerated solvent extraction technique improves the extraction efficiency of plasticizers from polymers by using elevated temperature and pressure. Many of the organic solvents used in these extractions boil at relatively low temperatures at atmospheric pressure (e.g., acetone boils at 56 °C). By exerting a pressure of 1500 psi (10 MPa) on the solvent, the boiling point is elevated and the extraction solvent remains in a liquid state. When extractions occur at temperatures ranging from 50–200 °C, several factors contribute to improved speed and efficiency (Table 1).

Table 1. Parameters that improve extraction efficiency.

Parameter	Effect on the Extraction Process
Temperature	Elevated temperature increases analyte diffusion from the matrix and improves analyte solubility in the extraction solvent (e.g. petroleum ether) for plasticizer extraction.
Analyte Solubility	Increases as temperature increase to improve extraction efficiency.
Solvent Viscosity	Decreases as temperature increases, improving solvent migration through the matrix to increase extraction efficiency.
Solvent Surface Tension	Decreases as temperature increases. Allows solvent to better coat the matrix and helps improve analyte diffusion.

Table 2 shows the results of the accelerated solvent extraction technique to Soxhlet extraction. Polyvinyl chloride (PVC) samples were extracted using a six-hour Soxhlet extraction method (ASTM D-2124) and the accelerated solvent extraction technique. The extracts were analyzed using gas chromatography with flame ionization detection and the extraction efficiencies of four plasticizers were compared. The accelerated solvent extraction technique produced equivalent performance to Soxhlet but required approximately 40 mL of solvent and 12 min of extraction time per sample. The Soxhlet extractions required six hours and 120 mL of solvent per sample.³

Table 2. Weight percent of each plasticizer in PVC.

Plasticizer	Accelerated Solvent Extraction Technique Recovery (n=3)	Soxhlet Extraction Recovery (n=3)	Accelerated Solvent Extraction Technique 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

Advantages of Using Accelerated Solvent Extraction Technique

True Walk-Away Automation

The Thermo Scientific™ Dionex™ ASE™ 150/350 Accelerated Solvent Extraction system is designed to provide walk-away automation and can extract 1–24 samples in a single batch. An entire set of 24 samples can be set up at the beginning of the day and another set of 24 samples can be set up to run overnight, with extracts that are ready for analysis first thing in the morning. The Dionex ASE 150/350 system performs a sequential extraction wherein one sample is extracted at a time. This strategy is advantageous because it ensures that each sample is subjected to the precisely the same conditions during within the extraction and there is no variation in temperature and pressure between samples. Sequential extraction allows each sample, or sets of samples, to be extracted using different conditions and permits the use of multiple sample sizes within an extraction batch.

Multiple Extraction Methods

Polymer formulations are unique and there is no universal extraction method that works for every sample type. Analysts may be tasked with developing extraction methods that vary the temperature, solvent composition, and extraction time. Additionally, the extraction efficiency of new or modified methods is validated by analyzing multiple extracts to ensure the method is exhaustive. The Dionex ASE 150/350 systems can store up to 24 extraction methods, allowing the analyst to process multiple sample types. The accelerated solvent extraction systems offer both front panel and the Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System software control to greatly simplify operation when extracting polymer samples.

Flow-Through Design with Disposable Thimbles

The Thermo Scientific™ Dionex™ ASE™ extraction cells are designed for a solvent to enter the top of the cell and exit at the bottom with the extracted analytes. This design permits the analyst to add thimbles to the cell in order to prevent plugging the fluid path. When a polymer is extracted under pressure, there is a tendency for it to melt at a point lower than its atmospheric melting point. This can result in the polymer extruding from the extraction cell and plugging the system.

Extraction thimbles have been shown to retain melted polymers and enable use of elevated pressure and temperature to improve extraction efficiency. These thimbles have been optimized to fit the Dionex ASE extraction cells to improve ease of use when extraction polymer samples and eliminate the need to clean melted polymer from the extraction cell walls.⁴

Dynamic and Static Extractions

The Dionex ASE 150/350 system is capable of performing both a dynamic and static extraction cycle in the same run. Dynamic extraction is defined as the ability to introduce fresh solvent during the extraction process. This is important because it ensures that the extraction solvent will not become saturated with the analyte which decreases its ability to remove more analyte from the matrix.

Since the diffusion of additives from polymers may be limited, bringing fresh solvent to the surface of the polymer particle enhances extraction efficiency. Static extraction is defined as holding the extraction solvent and sample for a set period of time to maximize the solubility of the analytes. Performing both dynamic and static extractions allows the accelerated solvent extraction technique to be exhaustive and ensures maximum analyte recoveries with minimal solvent consumption. This functionality ensures that the quantities of components present in each sample are determined with a high degree of accuracy.

Application Notes Summary

AN 331: Accelerated Solvent Extraction of Additives from Polymer Materials

This application note summarizes the work of researchers at the University of Leeds, U.K., using the accelerated solvent extraction technique for extracting the polymer additives Irganox® 1010, Irganox® 1330, Irganox® 1076, and Irgafos® 168 antioxidants from polypropylene and polyethylene.⁵ These polymer additives were extracted using approximately 30 mL of solvent with an extraction time of 20 min per sample. The extracts analyzed using HPLC with UV detection and the additives were resolved in 18 min using a C18 column. Cellulose extraction thimbles were used to prevent plugging of the extraction cell and enable extraction of the polymeric components at elevated temperature and pressure. Since polymer formulations are unique, this application note provides additional guidance for extraction method optimization using the accelerated solvent extraction method and serves as a useful reference for laboratories performing additive extraction from polymer materials.

AN 336: Accelerated Solvent Extraction of Plasticizers from Polyvinyl Chloride Polymer

The accelerated solvent extraction technique is compared to Soxhlet for the extraction plasticizers (dioctyl adipate (DOA), trioctyl phosphate (TOP), dioctyl phthalate (DOP), and trioctyl trimellitate (TOTM)) from polyvinyl chloride polymer (PVC) in this application note. These plasticizers were extracted from PVC using Soxhlet according to ASTM D-2124, a method requiring six hours of extraction time per sample. Use of the accelerated solvent extraction method was compared to the ASTM method and was demonstrated to yield equivalent performance on the basis of analyte recovery. The accelerated solvent extraction method used approximately 40 mL of solvent and required only 12 min of extraction time per sample. Analysis of the extracts was performed using GC-FID with all four plasticizers being resolved in 20 min. This application note demonstrates use of cellulose thimbles to prevent plugging of the solvent flow path.

AN 354: Accelerated Solvent Extraction of Extractables from Polymeric Components Used in Precision Drug Delivery Devices

Use of the accelerated solvent extraction technique for extracting compounds such as cross-linking agent residues and by-products of the cross-linking process from elastomeric drug delivery device is demonstrated in this application note. The work reported here was performed by John Colwell at Bepak Europe, Ltd. and used a GC-MS system to identify four proprietary compounds in the elastomeric device. The accelerated solvent extraction technique was compared against the current extraction method (Soxhlet) and was found to reduce extraction time from 24 hours to 1 hour per sample. Additionally, the accelerated solvent extraction technique reduced solvent consumption by approximately 70% when compared to Soxhlet and enabled the samples to be extracted unattended overnight.

References

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