

# Accelerated Solvent Extraction of Additives from Polymer Materials

## Introduction

Additives such as heat stabilizers, light stabilizers, slip agents, plasticizers, and antioxidants represent some of the most common classes of compounds used to tailor polymer properties for specific applications. Extraction and analysis of these additives are required to monitor their formulation levels.

Accelerated solvent extraction is a powerful technique that can be used to reliably extract additives from polymer materials. Accelerated solvent extraction uses organic solvents at temperatures above their atmospheric pressure 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 the Thermo Scientific™ Dionex™ ASE™ Accelerated Solvent Extractor system to extract polymer additives such as Irganox® 1010 (Ciba Specialty Chemicals) from polypropylene or polyethylene.

## Equipment

- Dionex ASE 200 Accelerated Solvent Extractor System\* equipped with 11 mL cells
- Thermo Scientific™ Dionex™ ASE Solvent Controller (optional)
- Thermo Scientific™ Dionex™ AutoASE™ software (optional)
- Thermo Scientific™ Dionex™ Dionex DX-500 HPLC system equipped with an AD20 Absorbance Detector
- Analytical balance
- Vials for extract collection (40 mL, P/N 49465)
- Cellulose filter disks (P/N 49458)
- Cellulose extraction thimbles (P/N 055708 11 mL, 055999 22 mL)
- Sand (Ottawa Standard, Fisher Scientific, Cat. No. S23-3)
- Polymer grinder (Spex CertiPrep, 6750 Freezer Mill)
- Disposable syringe filter, 13 mm, nylon, 0.45 µm

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

## Solvents

- Isopropyl alcohol (pesticide quality or equivalent)
- Cyclohexane (pesticide quality or equivalent)
- Extraction solvent: 2.5% (v/v) cyclohexane in isopropyl alcohol (IPA)

## Extraction Procedure

The following procedure provides high extraction efficiencies for a number of polymer additives such as the Irganox products (Irganox 1010, Irganox 1076, Irgafos 168, etc.). However, each polymer formulation is unique, so the procedure may need modifications to optimize extraction speed and efficiency. Analysts should use the Method Validation technique outlined below to evaluate the success of method modifications.

### Cell Preparation

Insert a cellulose extraction thimble into the cell.

### Sample Preparation

Grind the polymer sample to a size of 10 mesh or finer using a liquid-nitrogen-cooled grinder. Weigh approximately 0.5 g of ground sample and mix it with enough sand to fill the extraction thimble. Quantitatively transfer the polymer/sand mixture to the extraction thimble in the cell and place a cell cap on the inlet end of the cell. Place the cell in the upper carousel of the Dionex ASE 200 extractor and place the appropriate number of vials in the lower carousel.

### Extraction Conditions

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

Oven Temperature:	140 °C
Pressure:	1500 psi*
Solvent:	2.5% cyclohexane in isopropyl alcohol
Cell Heatup Time:	6 min
Static Time:	3 min
Flush Volume:	100% of cell volume
Static Cycles:	3
Purge Time:	60 s
Total Volume:	30 mL
Total Time:	20 min

### Additive Analysis

Irganox 1010 was extracted from polypropylene using the procedure described above. Additives were determined using reversed-phase HPLC. HPLC conditions were as follows:

Column:	C18, 3.9 × 150 mm
Mobile Phase:	10 min linear gradient from acetonitrile: H <sub>2</sub> O (85:15) to 100% acetonitrile. Hold for 8 min or until other additive components elute.
Flow Rate:	1.5 mL/min
Temperature:	40 °C
Inj. Vol.:	10 µL
Detection:	UV, 200 nm

The IPA/cyclohexane extract is suitable for HPLC analysis, but the Irganox 1010 peak may exhibit some fronting, as shown in Figure 1. Evaporating the extract to near dryness and then redissolving the extracted additive in methanol will yield greater peak symmetry when analyzing by HPLC.

Extracts are sometimes cloudy due to a small amount of polymer being extracted from the sample. Accordingly, the extract injected onto the HPLC column was filtered with a 0.45 µm nylon syringe-mounted filter.

Quantification of the Irganox 1010 was done relative to an internal standard (Irganox 1330), which was added to the finished extract. A typical chromatogram using the recommended extraction solvent is shown in Figure 1.

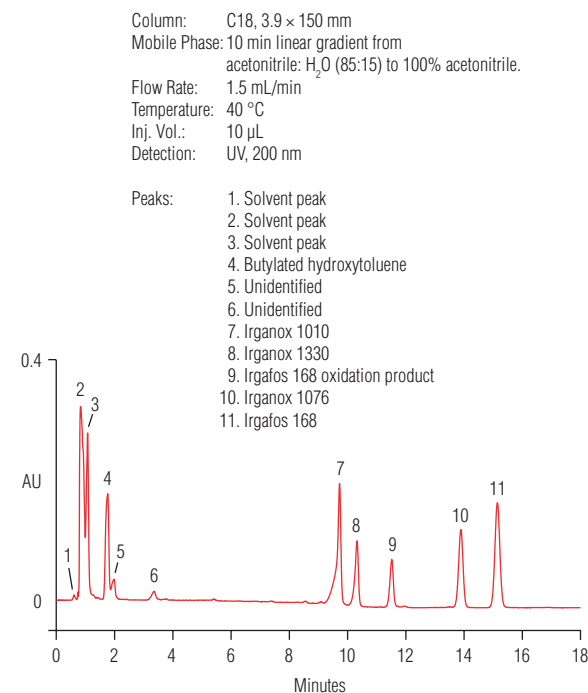


Figure 1. Typical HPLC chromatogram of additives in a polyethylene sample when extracted and analyzed under the conditions outlined in this application note. Irganox 1330 is an internal standard.

## Results

A polypropylene sample\* formulated to be 0.137% in Irganox 1010 was freeze ground and extracted according to the Dionex ASE 200 system operating conditions outlined above. Table 1 shows the benefits of lengthening the extraction time while using three static cycles: higher recovery (94.1%)\*\* and improved precision (S.D. of 0.87%). These results were achieved in 20 min per extraction using only 30 mL of solvent. A recovery of greater than 90% is considered acceptable given that there is some uncertainty in the formulation value.

Table 1. Benefits of Lengthening the Extraction Time Using Three Static Cycles

Static Time (min)	Static Cycles	% Recovery <sup>a</sup>	S.D. <sup>b</sup> (n = 3)
1	3	86.6%	2.20%
2	3	87.0%	2.50%
3	3	94.1%	0.87%

<sup>a</sup> Relative to nominal formulation value.

<sup>b</sup> S.D. = Standard Deviation

## Discussion

### Solvent Choice

When using Dionex ASE system, the goal is to use a solvent that will dissolve the analytes of interest (e.g., the additives) but not the matrix (e.g., the polymer). It is also helpful to use a solvent that is compatible with the preferred analytical finish (e.g., HPLC). Isopropyl alcohol (IPA) is a good choice for dissolving the analytes of interest. Using the Hildebrand solubility index as a guide, IPA is among the solvents least likely to dissolve a polymer such as polypropylene, and is compatible with HPLC analysis of the extracted additives.

Cyclohexane (2.5%) is added to the IPA to cause the polymer to swell, thus increasing extraction efficiency. Caution: accelerated solvent extraction are done in a closed system, so an excess amount of swelling agent may cause the polymer to extrude out of the system.

### Grinding and Dispersion

Reducing the polymer particle size by grinding will greatly increase the extraction rate. Dispersion in sand will keep the polymer particles from agglomerating when heated to ensure efficient extraction.

### Extraction Thimbles

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 cell and plugging the system. Extraction thimbles have been shown to retain melted polymers and thus provide valuable preventative maintenance.

## Extraction Temperature

The temperature chosen in this procedure (140 °C) is high enough to efficiently extract most additives, yet is lower than the melting point of polymers such as polypropylene or polyethylene. Higher temperatures did not increase the extraction efficiency of Irganox 1010.

## Repetitive Cycles

The extraction of additives from polymers tends to be diffusion-limited. Bringing fresh solvent to the surface of the polymer particle enhances extraction efficiency by providing a favorable concentration gradient. In the extraction procedure outlined here, it was found that three repetitions of the 3 min static cycle were sufficient to achieve reliable recovery. The Dionex ASE system can be automatically programmed for up to five static cycles.

## Method Validation

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

## Conclusion

This application note provides the following general principles for the extraction of additives from polymers:

- Use a main solvent (e.g., IPA) that can dissolve the additives but not the polymer.
- Add to the main solvent a small amount of another solvent (e.g., cyclohexane) that will cause the polymer to swell.
- Disperse the ground polymer sample with sand to prevent the particles from agglomerating.
- Use a cellulose thimble in the extraction cell to prevent plugging.
- Use multiple static cycles to maximize concentration gradients.
- Use sample reextraction as needed as an easy way to confirm completeness of extraction, especially when making method modifications.

## Suppliers

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA  
15275-1126, USA, Tel: 1-800-766-7000,  
www.fishersci.com.

Spex CertiPrep, Sample Preparation Division, 203  
Norcross Avenue, Metuchen, NJ 08840 USA,  
Tel: 800-LAB-SPEX, www.spexcsp.com.

Ciba Specialty Chemicals, 540 White Plains Road,  
Tarrytown, NY 10591 USA, Tel: 914-785-2000,  
www.cibasc.com.

## Acknowledgement

We would like to thank Dr. Harold Vandenburg of the University of Leeds, UK, for his valuable contribution to the development of the extraction method and for the data presented in this Application Note.

For more detailed information see the following literature:  
Vandenburg, H. et al. Analyst, 1999, 124, 1707, 1710.

## [www.thermoscientific.com/samplepreparation](http://www.thermoscientific.com/samplepreparation)

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