Extraction of Additives from Polymers

Abstract

The EDGE® automated extraction system is the most advanced extraction system available for the extraction of additives from polymers. The EDGE combines pressurized fluid extraction and dispersive solid phase extraction to dramatically reduce the sample preparation time and the potential of human error. The extraction is simple, repeatable, and fast, lasting less than 20 minutes, which includes sample cooling and system washing.

The extraction of polypropylene and polyethylene was performed with the EDGE and ASTM methods D6043-09 and D6953-11. Recovery results are published and discussed.

Introduction

It is important to know the composition of polymer materials from both quality and safety perspectives. Polymer materials are a staple in our world, and we have contact with these materials on a daily basis. From packaging to cell phone cases to medical devices, polymer materials are everywhere.

The performance of polymers can be affected by the amount of antioxidants and erucamide slip additives present in their forumlations. As manufacturers and consumers, it is important that we have confidence in the quality of our polymer products. Furthermore, from a safety perspective, it is important to ensure that no contaminants are leaching from these materials to which we are continuously exposed. The ability to extract additives from polymers with a quick and simple process is crucial to the polymers industry.

The extraction of additives from polymers is difficult for a number of reasons. The notably low melting point of the polymer makes it difficult to extract in a heated system. The polymer must be transformed to extract but not melted. Reaching that balance can be challenging. Furthermore, some traditional extraction techniques, such as soxhlet and sonication, can be time-consuming and require large volumes of solvent.

The EDGE is capable of producing a cooled extract that is ready for analysis in less than 20 minutes, using no more than 40 mL of solvent. The EDGE is also capable of cleaning the system of plastic additives, mitigating the risk of carryover.

Materials and Methods

Reagents

Polypropylene (P/N 427888) and polyethylene (P/N 427799) were sourced from Sigma Aldrich. ASTM D6042-96 Calibration Mix was sourced from Restek and used as the standard to calibrate and spike the samples. Tinuvin P (P/N 533203) was sourced from Sigma Aldrich and used as the internal standard. 2-Propanol (IPA) was used as the sonication, extraction rinse, and wash solvent.

Sonication Method

Either polypropylene or polyethylene (1 g) spiked with 0.7 mL of 50 ppm standard was sonicated in 20 mL of 2-Propanol (IPA) for 1 hour. The extract was then brought to dryness and reconstituted in 900 µL of 2-Propanol (IPA) with 100 µL of the internal standard. The sample was filtered through a 0.45 µm syringe prior to analysis.

Sample Preparation

Either polypropylene or polyethylene (1 g) was weighed into an assembled Q-Cup® containing a S1 Q-Disc® stack (C9+G1+C9 sandwich). The samples were spiked with 0.7 mL of 50 ppm standard. A Q-Screen™ was placed on top of each sample using a Q-Screen tool. The Q-Cups were placed in the EDGE removable rack (each with a 40 mL amber glass collection vial), and the rack was slid into position on the EDGE. The CEM-approved EDGE method for additives in the respective polymer was run. The extract was then brought to dryness and reconstituted in 900 µL of 2-Propanol (IPA) with 100 µL of the internal standard. If analysis is performed within ~30 minutes, additional filtration is not necessary. However, if additives begin to precipitate out, the sample can be filtered through a 0.45 µm syringe prior to analysis.

EDGE Method for Additives in Polypropylene

Q-Disc: S1 Q-Disc stack (C9+G1+C9 sandwich)

Cycle 1
Extraction Solvent: 2-Propanol (IPA)
Top Add: 30 mL
Bottom Add: 10 mL
Rinse: 0 mL
Temperature: 80 °C or 120 °C
Hold: 15:00 (mm:ss)

Wash 1
Wash Solvent: 2-Propanol (IPA)
Wash Volume: 15 mL
Temperature: 150 °C
Hold: 00:15 (mm:ss)

Wash 2
Wash Solvent: 2-Propanol (IPA)
Wash Volume: 15 mL
Temperature: - - -
Hold: - -:- -

EDGE Method for Additives in Polyethylene

Q-Disc: S1 Q-Disc stack (C9+G1+C9 sandwich)

Cycle 1
Extraction Solvent: 2-Propanol (IPA)
Top Add: 30 mL
Bottom Add: 10 mL
Rinse: 0 mL
Temperature: 90 °C
Hold: 15:00 (mm:ss)

Wash 1
Wash Solvent: 2-Propanol (IPA)
Wash Volume: 15 mL
Temperature: 90 °C
Hold: 00:15 (mm:ss)

Wash 2
Wash Solvent: 2-Propanol (IPA)
Wash Volume: 15 mL
Temperature: - - -
Hold: - -:- -

Analysis

A volume of 10 µL of each sample was injected into a Waters Acquity UPLC with a PDA detector for analysis. A Restek Ultra C8 column (5 µm, 150 x 4.6 mm) was used with a flow rate of 1 mL/min and a 16 minute ramp from 25% A (water) and 75% B (acetonitrile) to 100% B. The absorbance of the additives was monitored at 200 nm, and the standard addition method was used for quantification.

Results

The EDGE efficiently extracted the additives from both polypropylene and polyethylene in under 20 minutes, including sample cooling and system washing. **Figure 1** (page 4) is a representative HPLC chromatogram showing clean separation of the additives of interest. **Table 1** (page 3) contains the retention times and purpose of the standard compounds, which are common polymer additives. **Table 2** (page 3) shows the recovery data for the extraction of additives from polypropylene on the EDGE at two temperatures.

The data for the extraction of polypropylene at both 80 °C and 120 °C is shown in **Table 2**. It can be seen that no data was available for the extraction of BHT at 120 °C. BHT is known to be labile at higher temperatures, and a lower temperature must be used to extract BHT. Conversely, the higher temperature was needed to extract the erucamide. The extraction recoveries for remaining compounds were comparable at both temperatures. Depending on the analyte of interest, different temperatures may be optimal.

Table 3 (page 3) shows the recovery data for the extraction of additives from polypropylene using both the EDGE and sonication. **Table 4** (page 3) shows the recovery data for the extraction of additives from polyethylene using both the EDGE and sonication. It is clear that the EDGE performed better in the extraction of polypropylene and polyethylene for all compounds. The EDGE not only offered the benefits of automation but also yielded better results.

Conclusion

The extraction process used on the EDGE automated extraction system allowed for efficient extraction of additives from polymers. One simple extraction method with adjusted temperatures was utilized for all polymers, which greatly simplified the process. Additives were extracted more efficiently with the EDGE than with the traditional sonication because of the EDGE's rapid extraction and filtration capabilities, made possible with Q-Cup technology. No additional steps were required prior to analysis.

The focus of this study was the extraction of polypropylene and polyethylene. However, a similar method would be applicable for other polymer samples. The EDGE, with its efficient polymer extraction method, is ideal for manufacturers that want repeatable and reliable results for all samples.

Table 1. Standard Compound Information

Standard Compound	Retention Time (min)	Purpose
Tinuvin	3.3	Internal Standard
BHT	4.5	1° Antioxidant
Erucamide	7.8	Slip Agent
Irganox 3114	8.2	Antioxidant
Vitamin E	10.5	Antioxidant
Irganox 1010	10.8	1° Antioxidant
Irganox 1076	13.5	1° Antioxidant
Irgafos 168 OX Phosphite	13.9	
Irgafos 168	17.4	2° Antioxidant

Table 2. Recovery Data for the Extraction of Additives from Polypropylene

Standard Compound	80 °C (n=4)	RSD	120 °C (n=4)	RSD
BHT	90	34	N/A	N/A
Erucamide	N/A	N/A	90	4.2
Irganox 3114	86	5.6	81	3.1
Vitamin E	93	6.7	98	2.9
Irganox 1010	75	11	78	2.0
Irganox 1076	88	3.1	83	2.8
Irgafos 168 OX Phosphite	99	13	107	19
Irgafos 168	92	6.3	98	4.1
Irgafos Total	93	6.3	98	4.1

Table 3. Recovery Data for the Extraction of Additives from Polypropylene via the EDGE and Sonication

Standard Compound	ASTM (%)	EDGE (%)
BHT	79	91
Erucamide	65	90
Irganox 3114	58	86
Vitamin E	63	98
Irganox 1010	54	78
Irganox 1076	59	88
Irgafos 168 OX Phosphite	67	107
Irgafos 168	54	98
Irgafos Total	56	98

Table 4. Recovery Data for the Extraction of Additives from Polyethylene via the EDGE and Sonication

Standard Compound	ASTM (%)	EDGE (%)
BHT	62	111
Erucamide	48	86
Irganox 3114	58	91
Vitamin E	63	67
Irganox 1010	45	63
Irganox 1076	52	75
Irgafos 168 OX Phosphite	40	75
Irgafos 168	51	93
Irgafos Total	48	87

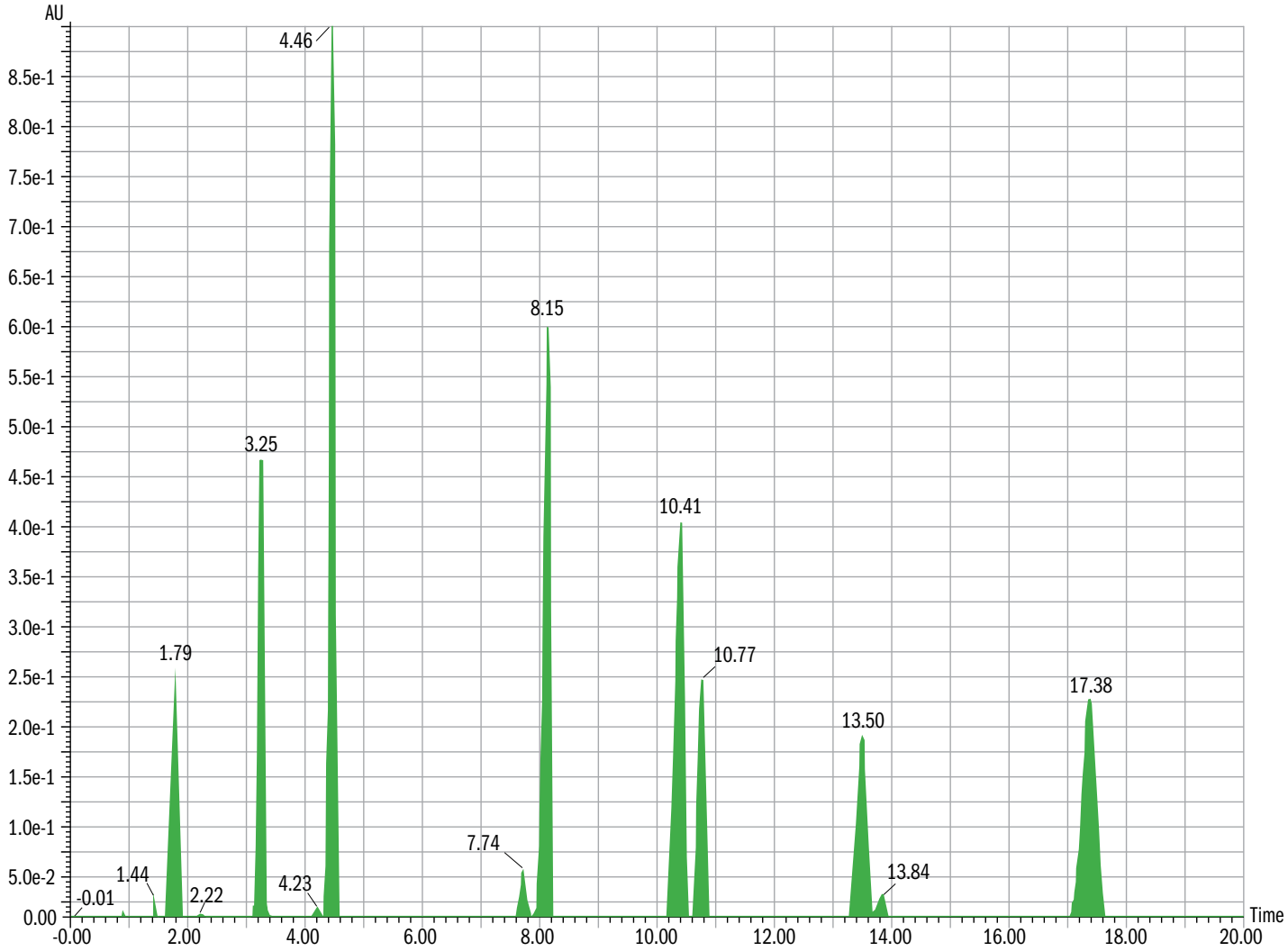

Figure 1. HPLC Chromatogram of Additives of Interest

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