

A Case Study: Polymer Additives



The properties of plastic and rubber materials are altered in very important ways by the inclusion of appropriate additives packages. The additives can include fillers, antimicrobials, antioxidants, antistats, colorants and pigments, flame retardants, heat stabilizers, light stabilizers, lubricants, and plasticizers. A large amount of quality control and specification testing involves the evaluation of the additives packages in fully formulated polymer systems. The analysis can verify that the intended additives package, including the desired initial concentration of each additive, was utilized. Analysis can also be used to monitor the fate of the additives as a function of time and environmental exposure. This case study provides general analytical information pertaining to the analysis of plastic materials, as manufactured, that contain heat stabilizers, light stabilizers, antioxidants, and phthalate plasticizers.

The Approach

The analysis of additives that are a portion of the composition of polymer samples requires multiple analytical methods. The methods selected are influenced by the specific additives that are to be characterized and the physiochemical properties of these additives. Hindered phenolic antioxidants and phosphite antioxidants have been evaluated using high performance liquid chromatography. Gas chromatography coupled with mass spectrometry (GC-MS) is applied to the analysis of some hindered amine light stabilizers (HALS), antioxidants, other light stabilizers, and plasticizers. Higher molecular weight oligomeric hindered amine light stabilizers are analyzed using a combination of analytical techniques.

HPLC Analysis of Antioxidant Content

The levels of the antioxidants Irganox 1010, Irganox 3114, and Irgafos 168 were determined using reverse-phase HPLC, according to a procedure very similar to that described in ASTM D6042. The samples were ground to a 20 mesh particle size prior to solvent extraction. A 1-g portion of each ground sample was extracted in an ultrasonic bath for 60 minutes. Prior to the extraction, a known amount of Tinuvin P was added to each sample as an internal standard. The extract was then diluted and injected on an HPLC system equipped with a reverse-phase HPLC column and a photodiode array (PDA) detector. Peak detection and integration was performed at a wavelength of 220 nm with a 10-nm bandwidth. An example HPLC chromatogram is shown in Figure 1.

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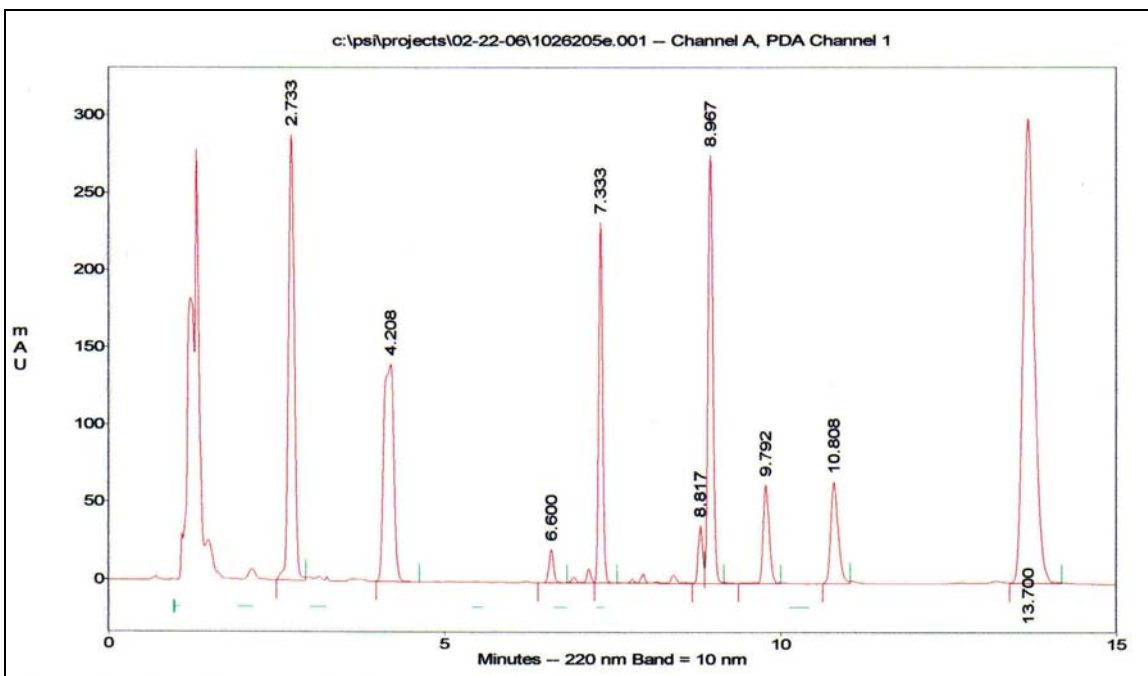


Figure 1. HPLC chromatogram of the extract of a polypropylene pellet.

Analysis of commercially available additive samples can be used to assign the probable identity of an additive based on chromatographic retention time. In addition, a range of solution concentrations can be used to prepare standards. Using these standards the detector response can be calibrated so that absolute concentration values can be performed. This is the basic procedure that yields quantitative additives analysis and results similar to what is shown in Table 1.

Table 1. HPLC Antioxidant Results for the extract of a polypropylene pellet.

Compound	Retention Time (minutes)	Peak Area	Amount Detected (wt. %)
Tinuvin P (Internal Standard)	2.73	1,732,340	-
Irganox 3114	7.33	979,327	0.082
Irganox 1010	8.97	1,323,517	0.140
Irgafos 168	13.7	3,498,254	0.177

It is possible to identify the peak associated with the oxidation product of Irgafos 168. The original phosphite form of Irgafos 168 is oxidized to a phosphate during melt processing of the polymer. This is an example of the additives analysis including the detection of chemically modified versions of the original additive compound. Often these chemicals are referred to as “daughter compounds”. The relative amount oxidized Irgafos 168 can be estimated based on peak area ratios.

GC-MS Analysis of Hindered Amine Light Stabilizer

Tinuvin 622, an oligomeric hindered amine light stabilizer, was detected using gas chromatography coupled with mass spectrometry (GC/MS). Portions of sample pellets weighing 0.5 g (about 30 pellets) were extracted and derivitized. The concentration of Tinuvin 622 in the extract is determined via analysis of the chemically derivitized product. An example chromatogram of the derivitized products is shown in Figure 2. Typical results for the concentration of this additive in a series of polymers is shown in Table 2.

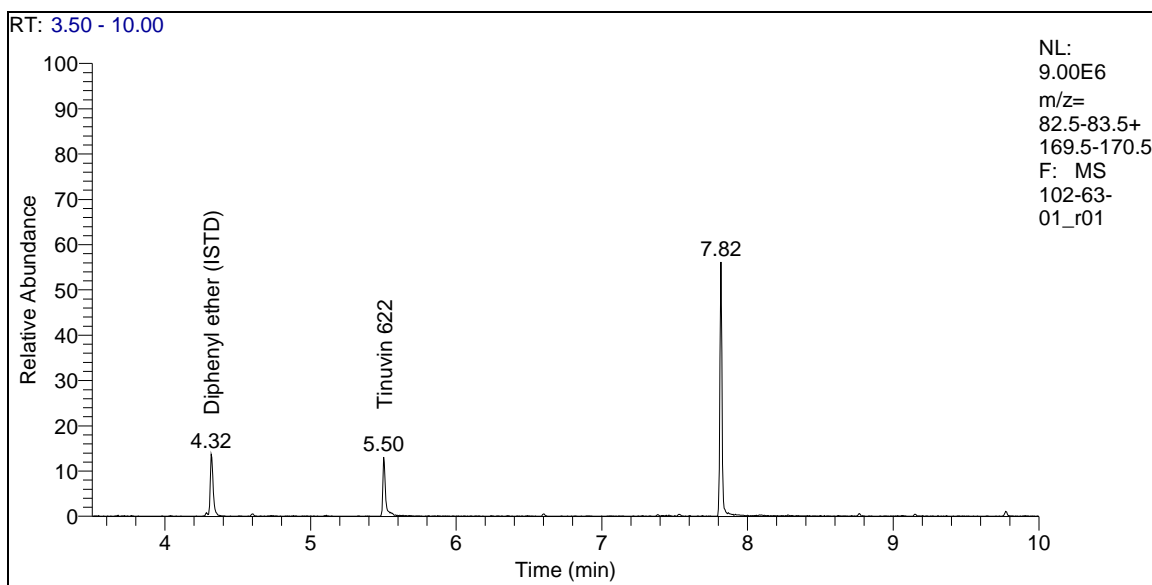


Figure 2. GC/MS chromatogram of the Tinuvin 622 extracted from a polypropylene pellet.

Table 2. Amounts of Tinuvin 622 Detected in Polypropylene Samples.

Sample	Amount Detected (wt. %)
A	0.356
B	0.429
C	0.307
D	0.342

SEC (GPC) Analysis of Oligomeric HALS

The quantity of the oligomeric hindered amine light stabilizer (HALS) present in a polyolefin sample was determined using size exclusion chromatography (SEC) with photodiode array (PDA) detection. The sample was extracted, and dissolved in the SEC mobile phase, which was modified tetrahydrofuran (THF). One 50-Angstrom pore size SEC column and one 100-Angstrom pore size SEC column were connected in series and used for the chromatographic separation.

A wavelength of 234 nm was chosen for quantification of Cyasorb UV-3346. An example chromatogram is shown in Figure 3. Other stabilizers present in the sample extract also contributed peaks at 234 nm, in the retention time range of the Cyasorb UV-

3346. The effect of this interference was removed by also monitoring the UV absorbance chromatogram at a wavelength of 273 nm (Figure 4). Other stabilizers absorb strongly at 273 nm, but Cyasorb UV-3346 does not absorb at this wavelength. The peak area ratios (234 nm/273 nm) were determined for injections of single-component solutions of the other stabilizers. These peak area ratios were used to subtract the contributions of these other additives from the 234 nm chromatogram of the sample extract. The amount of Cyasorb UV-3346 detected in the sample was 0.252 weight percent.

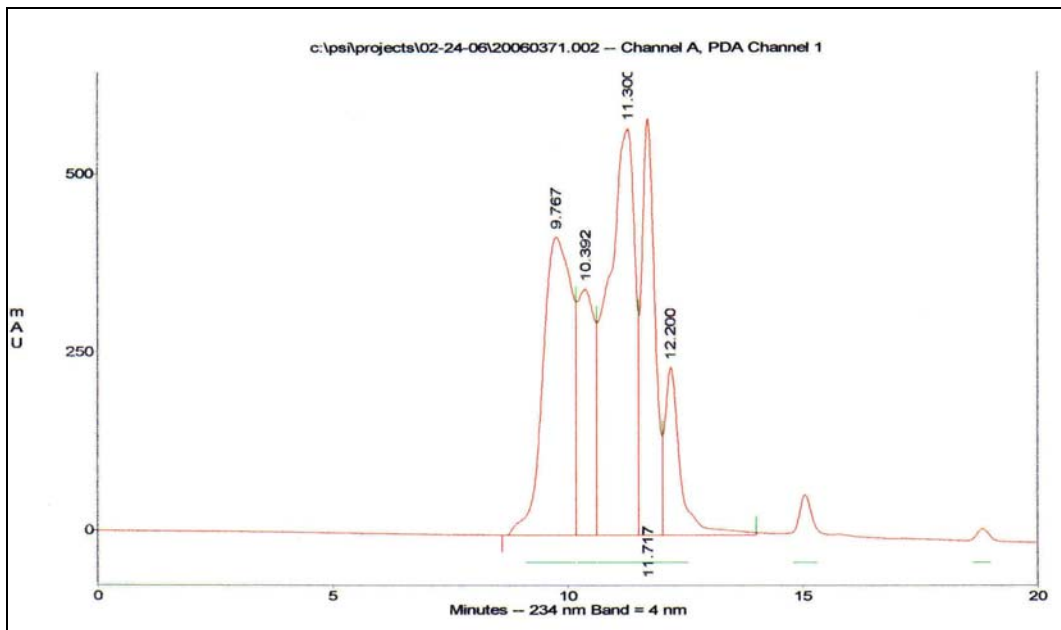


Figure 3. SEC-UV chromatogram at 234 nm for the extract of a polyolefin sample.

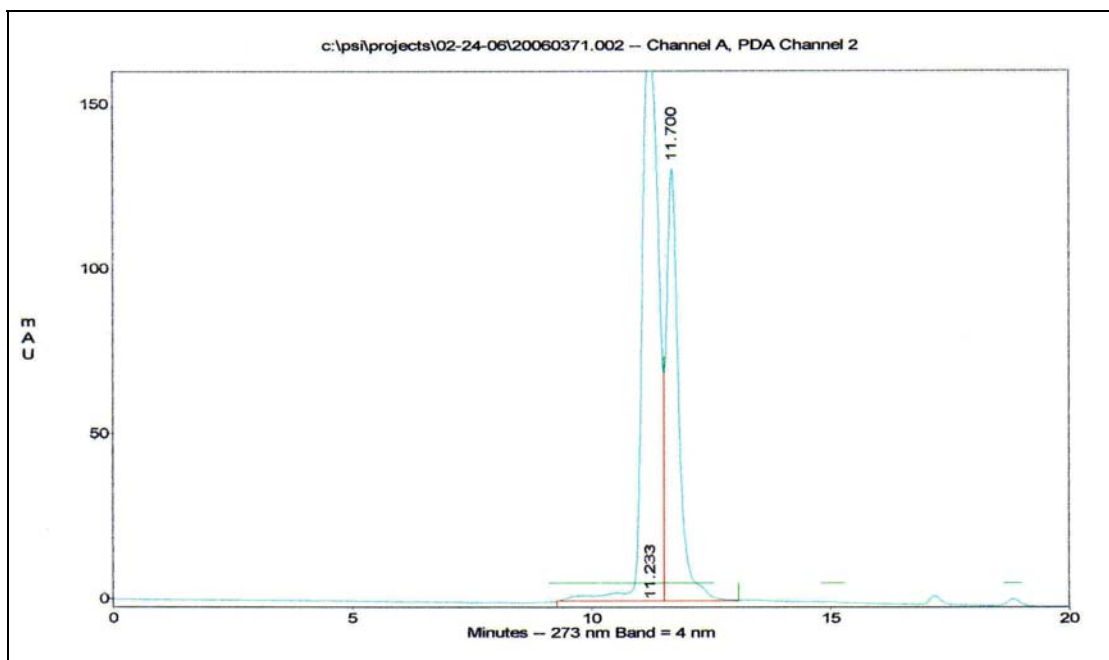


Figure 4. SEC-UV chromatogram at 273 nm for the extract of a polyolefin sample.

GC-MS Analysis of Plasticizers

Three polyvinyl chloride (PVC) thick film samples were analyzed to determine the type and quantity of plasticizer that was present in each film. The method of analysis, well suited for this determination, is gas chromatography coupled with mass spectrometry (GC-MS).

Samples were prepared by dissolving the PVC films and treating them for analysis. Initial GC/MS library searches indicated that all three thick film samples contain phthalate ester plasticizers. Figure 5 shows the total ion chromatogram for Sample E and Sample G. The patterns of plasticizer peaks were identical for E and G, indicating that the two samples contained the same plasticizer. Library searching and careful examination of the mass spectra indicated that E and G contain a dinonyl phthalate plasticizer; that is, a phthalic acid diester based on 9-carbon (C_9) alcohols. The pattern of peaks in the chromatograms in Figure 5 indicates that the C_9 alcohols in this plasticizer are predominantly linear, not branched.

Figure 6 shows the GC/MS total ion chromatogram for Sample F, along with the selected ion chromatograms for $m/z = 265$, $m/z = 293$, and $m/z = 321$. These three selected ion chromatograms are specific for C_7 , C_9 , and C_{11} alcohol side chains, respectively, on the phthalate ester. The GC/MS data indicate that the plasticizer in Sample F is a phthalate plasticizer based on a mixture of predominantly linear C_7 , C_9 , and C_{11} alcohols. Some of the phthalate ester molecules are homogeneous, containing two C_7 , two C_9 , or two C_{11} side chains, while some are heterogeneous, containing one C_7 and one C_9 side chain, one C_7 and one C_{11} side chain, or one C_9 and one C_{11} side chain. This indicates that the plasticizer is a single product produced from a mixture of C_7 , C_9 , and C_{11} alcohols, and is not a mixture of separately-prepared diheptyl phthalate, dinonyl phthalate, and diundecyl phthalate. A commercially available product, similar to the plasticizer found in Sample F, is Palatino[®] 711P.

Table 3 summarizes the plasticizer types in the PVC film samples, and also lists the weight percent plasticizer in each sample as determined via GC-MS. The GC-MS response was calibrated by injecting known concentrations of diisooheptyl, diisononyl, and diundecyl phthalates. Samples E and G had somewhat higher plasticizer contents than Sample F. It should be noted that the GC-MS analysis is incapable of detecting polymeric plasticizers because the GC-MS method requires that the analytes be volatile.

Table 3. Plasticizer Type and Content in Thick Film PVC Samples.

Sample	Plasticizer Type	Amount in Sample (wt. %)
E	Predominantly linear phthalate ester based on C_9 alcohols	36.4
F	Predominantly linear phthalate ester based on C_7 , C_9 , and C_{11} alcohols	29.2
G	Predominantly linear phthalate ester based on C_9 alcohols	31.8

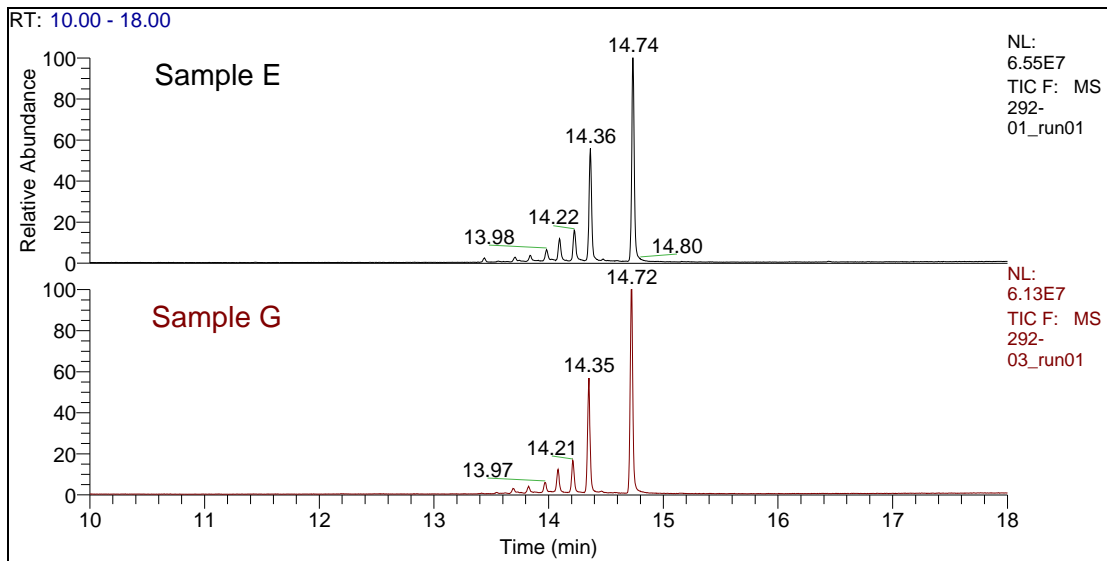


Figure 5. GC/MS total ion chromatograms for Sample E (top) and Sample G (bottom).

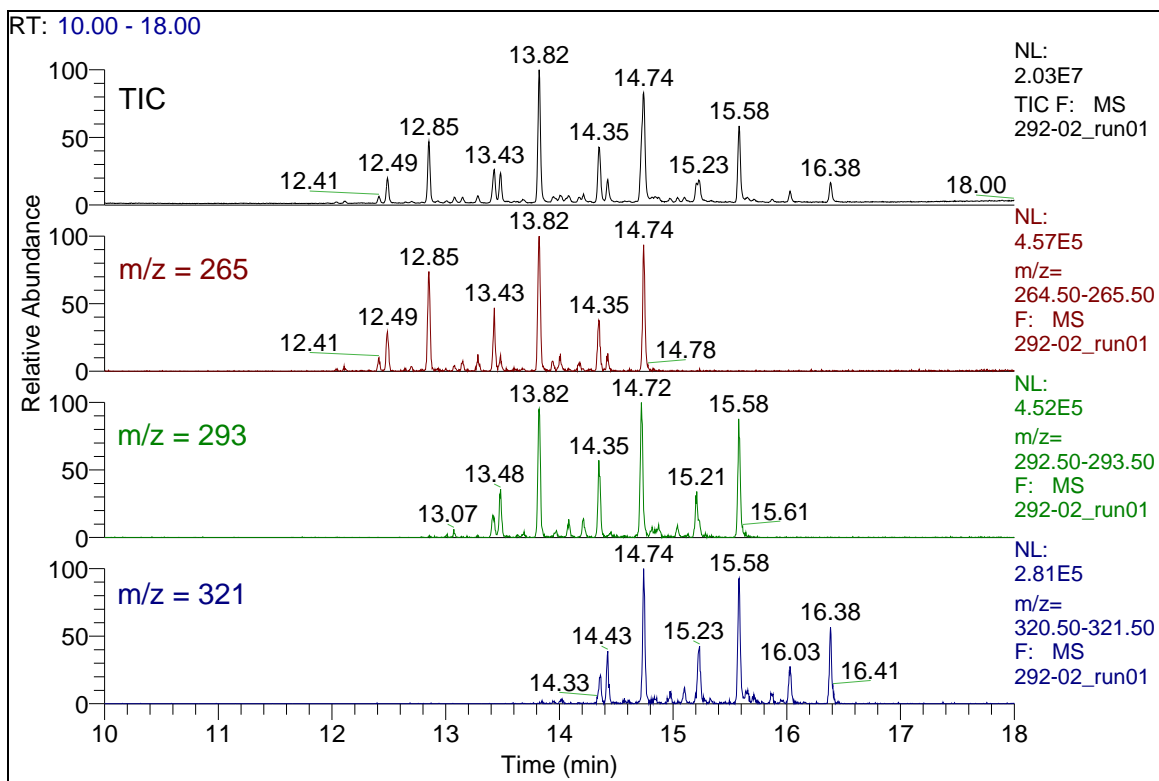


Figure 6. GC/MS total ion chromatogram of Sample F (top) and selected ion chromatograms for m/z = 265 (C7 alcohol), m/z = 293 (C9 alcohol), and m/z = 321 (C11 alcohol).