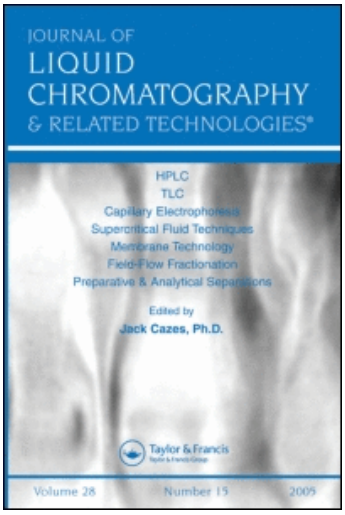

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Recent Advances in Polyolefin Additive Analysis

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RECENT ADVANCES IN POLYOLEFIN ADDITIVE ANALYSIS

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ABSTRACT

The extraction and quantitation of polymer additives continues to be a very important procedure in polymer deformulation. We have previously shown ultrasonic and microwave oven techniques to extract out antioxidants and slip agents from polyolefins in much less time than conventional methods such as Soxhlet extraction. The ability to reproducibly extract these materials out of polymer matrices at a high level (>90%) is desirable to ensure that the correct amount of material is in the formulation to afford the necessary protection during processing and end use. This paper will emphasize the ultrasonic bath extraction and recovery of the phosphite ester, Irgafos 168, using various extraction solvents in high density polyethylene (HDPE). The phosphite esters will hydrolyze in extraction solvents containing alcohols (such as isopropanol, a common polyolefin extraction solvent), and also will undergo hydrolysis during the reverse phase gradient LC run if exposed to water for too long a period. The hydrolysis products will result in multiple peaks eluting in the chromatogram, which make the precision of the integration (by adding the multiple peak areas) quite poor. Also, the presence of these multiple peaks will co-elute with other antioxidants, such as Irganox 1076. The use of solvents such as cyclohexane and methylene chloride with an ultrasonic bath provides for a fast, reproducible method to extract these phosphite esters out without risking hydrolysis breakdown. Conventional acetonitrile/water reverse phase gradient techniques are discussed, as well as the use of normal phase, isocratic separations in under seven

minutes. Also, flow programming is demonstrated to illustrate the use of this technique in further optimizing the LC analysis to improve selectivity and resolution.

INTRODUCTION

The ability to reproducibly extract out the additive package present in polyolefins has been a major concern to resin manufacturers, fabricators and end users. The use of HPLC has proven to be a very fast, accurate, reproducible means of identifying and quantitating the components present, provided that the extraction technique successfully migrated the materials out of the polymer matrix. Some of the early HPLC work used normal phase techniques (1,4,5) for the separations, which did not prove to be as selective as reverse phase techniques, (2). Some of the earlier reverse phase work (6) was isocratic, which showed an improvement over normal phase, but still did not show very good resolution. For a long period of time, Soxhlet extraction was the method of choice for migration of the additives out of the polymer matrix (3). This technique proved to be very time consuming, taking up to 15 hours in some cases to extract some of the higher molecular weight antioxidants such as Irganox 1010. In some relatively recent work (7), the use of the ultrasonic bath cleaner was described, which greatly reduced the time taken to extract out the additives. Last year, a comparison was done examining the time needed and the recoveries obtained for extraction of polyolefins with Soxhlet, ultrasonic bath, and microwave oven, (8).

The use of cyclohexane/2-propanol (IPA) as an extraction media for polyolefin additives has been used successfully for some time now. The cyclohexane swells the polymer and the IPA helps the migration of the additive out of the polymer matrix. Butyl alcohol has also been used with success, but both of these alcohols will promote hydrolysis of the phosphite esters when used for the extraction. The use of alternative solvent mixtures such as methylene chloride/cyclohexane will extract the antioxidants at a high level of recovery without risk of degrading the phosphites. Also, using a gradient profile that minimizes the time that the phosphites are in contact with water helps to minimize the possibility of hydrolysis.

EXPERIMENTAL

Materials: Table I lists the antioxidants used in this study.

Instrumentation - A Waters Model 600 Gradient Controller was used for the LC analysis. This consisted of a model 600E solvent delivery system, with an M490 variable wavelength UV detector, Model 717 Autoinjector

TABLE I

ANTIOXIDANTS

COMMON NAME	CHEMICAL NAME/FORMULA	MANUFACTURER
BHT	2,6-di-tert-butyl-p-cresol	Many
BHEB	2,6-di-tert-butyl-4-ethyl phenol	Many
MD 1024	$C_{34}H_{52}N_2O_4$	Ciba-Geigy
Isonox 129	$C_{30}H_{46}O_2$	Schenectady Chemicals, Inc.
Irgafos 168	Tris(2,4-di-t-butylphenyl)phosphite	Ciba Geigy
Irganox 1010	Tetrabis(methylene(3,5-di-t-butyl 4-hydroxyhydrocinnamate))	Ciba-Geigy
Irganox 1076	Octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate	Ciba-Geigy
Cyasorb UV 531	2-hydroxy-4-n-octabenzophenone	American Cyanamid
AM 340	Hindered Phenol	Ferro Corp.

Note: Some of the materials above are also manufactured by other companies. Many of these chemicals have registered trademarks owned by the manufacturer.
All solvents were Burdick and Jackson distilled-in-glass, and the water used for the analysis was Milli-Q water (Millipore Corp., Bedford, MA).

and a 991 photodiode array detector. The columns used for the separations were 15cm. x 3.9mm. Nova-Pak (4 micron) C18 and silica columns. The data system for collection and quantitation was a Waters model 860 Vax Station with ExpertEase software (Waters Chromatography Div./Millipore Corp., Milford, MA). The ultrasonic bath used for the extractions was a Branson B-52 (240W) unit, manufactured by Branson Cleaning Equipment Co., Shelton, CT. The Wiley Mill was obtained from VWR Scientific Co., (Westwood, MA), model #3383-L10.

TABLE II

RESIN	ANTIOXIDANTS/AMOUNTS (ppm)
"A"	BHT, BHEB, IRGANOX 1010, IRGANOX 1076, (200 ppm each)
"B"	BHT, 1010, 1076, (800 ppm each)
"C"	MD-1024, ISONOX 129, IRGAFOS 168, (200 ppm each)
"D"	BHEB, 129, 168, (800 ppm each)

RESULTS AND DISCUSSION

The four high density polyethylene resins were labelled "A" through "D", with the antioxidants being compounded in at levels with a precision of approximately 3%. Table II lists the levels of each of the antioxidants present in the four resins.

Figure 1 shows a typical reverse phase gradient chromatogram of the seven antioxidant standards: MD-1024, BHT, BHEB, Isonox 129, 1010, 1076, and Irgafos 168. The eluent was initially at 60:40 acetonitrile/water, with the final conditions being 100% acetonitrile. The gradient profile was linear, with 100% acetonitrile being reached in 6.0 minutes. The flow rate was 1.50 mL/min., and the Nova-Pak C18 column was held at 50C. The UV was set at 225nm.

Sample Preparation: Once the standards have been run (known amounts individually to obtain the response factors for each), each sample is ground in the Wiley Mill to a 20 mesh under liquid nitrogen cooling. Five grams of the ground sample are then added to a beaker containing 50 mls. of the extraction solvent. The beakers are then placed in the ultrasonic bath containing a suitable solvent (such as 2-propanol). It is advisable to allow for mixing or stirring of the solutions while they are undergoing the ultrasonic extraction. Constant stirring is best, but occasional vigorous stirring with a glass rod for a minute works well also. After the extraction period, the solution is filtered through a #1 Whatman filter paper to remove the extracted polyolefin. The extracted resin is then rinsed with warm extraction solvent. The solution is then allowed to evaporate (a nitrogen stream is preferable to reduce any risk of oxidation). The dried extract residue is next taken up in warm (~45C) acetonitrile and allowed to cool. The solution is then transferred to a 25

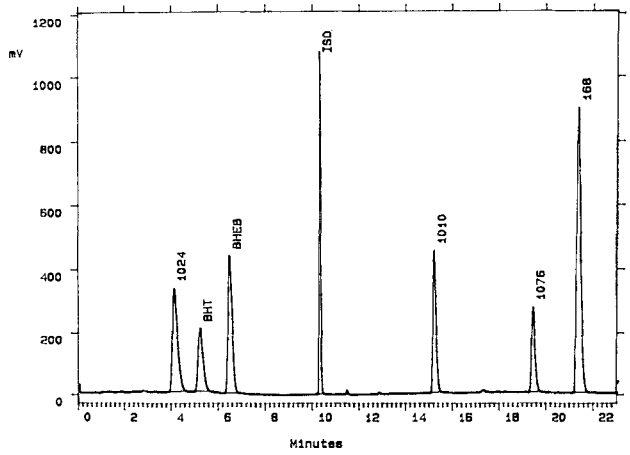

FIGURE 1. Chromatogram of the seven antioxidants (standards) used in the HDPE extraction study. The reverse phase separation was carried out with a 15 cm. Nova-Pak C18 column maintained at 50C. The eluent was initially a 60:40 acetonitrile/water mixture, with the final eluent conditions being 100% acetonitrile (a 6.0 minute linear gradient). The flow rate was maintained at 1.50 mL/min. Detection by UV at 225nm.

or 50 mL volumetric flask. During this transfer, the solution is filtered through a 0.45μ fuorocarbon filter to remove any insoluble waxes. The solution is then ready for injection (~10-15 μL). Figure 2 shows the reverse phase gradient (same conditions as for Figure 1) chromatogram for the ultrasonic extract from the "B" HDPE resin, with BHT, 1010 and 1076 being recovered. The extraction solvent mixture was 50:50 cyclohexane/IPA. When the 1010 is present, an extraction time of 60 minutes is used. Otherwise, 30-40 minutes is sufficient to extract most of the other antioxidants at high (>90%) recoveries. Table III below lists the recoveries in ppm (in triplicate*) for the "A" and "B" resins using the 50:50 cyclohexane/IPA mixture for 60 minutes.

The extraction recoveries are >89% for the four antioxidants, and the precision is better than 3%. The 50/50 cyclohexane/2-propanol mixture does a very good job at extracting these materials from HDPE. To speed up the extraction time, the solvent in the ultrasonic bath unit (we use 2-propanol) is allowed to heat up by turning the bath on for 30 minutes prior to placing the beakers containing the extraction solvent and ground resin inside. Figure 3 shows the reverse phase chromatogram (same conditions

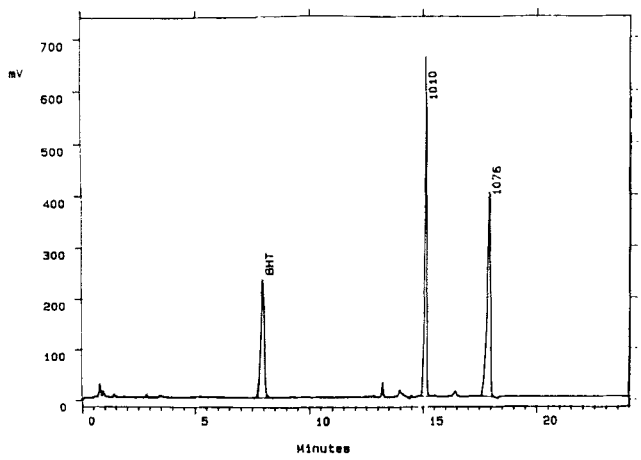

FIGURE 2. Chromatogram of the ultrasonic bath extraction for the "B" resin using 50:50 cyclohexane/2-propanol. Same reverse phase conditions as in FIGURE 1.

TABLE III

RECOVERIES FOR HDPE RESINS (ppm)

50:50 CYCLOHEXANE/2-PROPANOL

RESIN	BHT	BHEB	1010	1076
A - 1	174	188	170	183
A - 2	182	183	177	176
A - 3	177	181	172	184
B - 1	753	-	709	739
B - 2	744	-	716	732
B - 3	741	-	702	741

*Note: The triplicate analyses throughout this work represent three separate extractions on three different days.

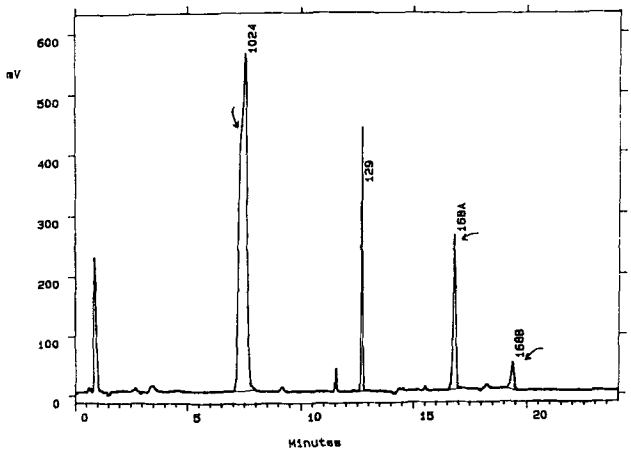

FIGURE 3. Chromatogram of the extraction for the "C' resin using 50:50 cyclohexane/2-propanol. Same reverse phase conditions as in FIGURE 1.

as for Figure 2) for the "C" resin using the 50:50 cyclohexane/2-propanol mixture. Notice how the Irgafos 168 has split into two peaks, and the MD-1024 has a significant shoulder present. The peak areas were added for the 168 to obtain the recovery data, but the peak height had to be used for the MD-1024, as using the peak area resulted in recoveries over 110%. The Irgafos 168 has degraded into hydrolysis products, but we are not sure as to what has happened to the MD-1024. Table IV shows the recovery data for the "C" and "D" resins (in ppm) using the 50:50 cyclohexane/2-propanol extraction mixture.

Since the results for the MD-1024 and the Irgafos 168 using the cyclohexane/2-propanol mixture were questionable at best, a 75:25 methylene chloride/cyclohexane mixture was used. Figure 4 illustrates the reverse phase gradient chromatogram for the antioxidants extracted from the "C" resin using the methylene chloride/cyclohexane mixture. Notice how the symmetry of the MD-1024 peak is much improved, and the Irgafos 168 peak is a single symmetrical peak, with no indication of degradation. Table V lists the recovery data for the "C" and "D" resin (in ppm) using this solvent extraction mixture.

The recoveries are all ~90% or better, with the worst precision being better than 3%. Figure 5 shows the chromatogram for the antioxidants extracted from the "D" resin. Once again, the Irgafos 168 is split into two peaks, which resulted in the recoveries being >100% as shown in Table IV.

TABLE IV

RECOVERIES FOR HDPE RESINS (ppm)

50:50 CYCLOHEXANE/2-PROPANOL

RESIN	BHEB	MD-1024	ISO-129	FOS-168
C - 1	-	174	183	169
C - 2	-	169	171	163
C - 3	-	179	180	174
D - 1	780	-	774	803*
D - 2	785	-	763	814*
D - 3	766	-	759	807*

*Adding the peak areas for the Irgafos 168 yields >100% recoveries for the "D" resin. It is interesting to note that the recovery for the 168 in the "C" resin is only ~84% adding the peak areas.

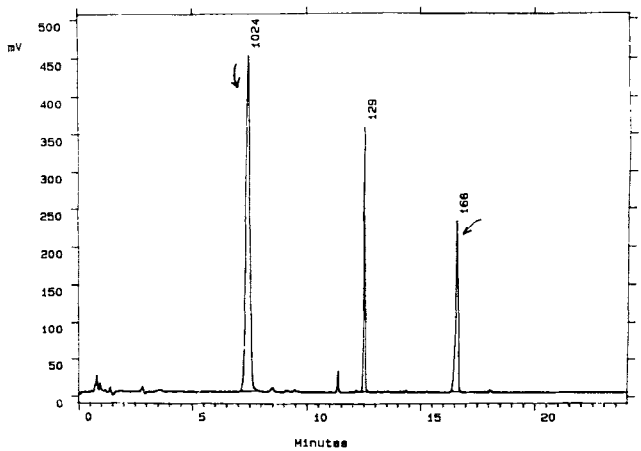

FIGURE 4. Chromatogram of the extraction for the "C" resin using the 75:25 methylene chloride/cyclohexane mixture. Same reverse phase conditions as for FIGURE 1.

TABLE V

RECOVERIES FOR HDPE RESINS (ppm)

75:25 METHYLENE CHLORIDE/CYCLOHEXANE

RESIN	BHEB	MD-1024	ISO-129	FOS-168
C - 1	-	184	188	174
C - 2	-	189	181	177
C - 3	-	178	183	180
D - 1	788	-	769	764
D - 2	779	-	774	768
D - 3	773	-	781	771

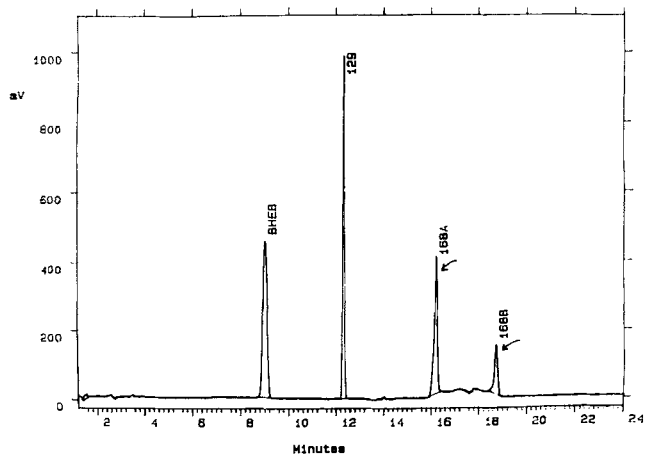

FIGURE 5. Chromatogram of the extraction for the "D" resin using the 50:50 cyclohexane/2-propanol solvent mixture. Same reverse phase conditions as for FIGURE 1.

A reproducibilty study was done on the Irgafos 168 phosphite antioxidant for the "C" resin (contains 200 ppm originally). An extraction was done once each day on eight different days, in addition to the triplicate analysis reported in Table V. The study represents eight different grindings on the Wiley Mill, followed by separate extractions in the 75:25 methylene chloride/cyclohexane solvent mix, and then separate LC analyses. The results (including the original triplicate data from Table V above) are shown in Table VI as follows:

TABLE VI

"C" RESIN EXTRACTION REPRODUCIBILITY STUDY

EXTRACTION #	CONCENTRATION 168 (ppm)
1 *	174
2 *	177
3 *	180
4	177
5	180
6	185
7	182
8	179
9	184
10	180
11	175

* Data from Table V.

The precision for the eleven measurements is better than 3%, with the recovery averaging out to 90%.

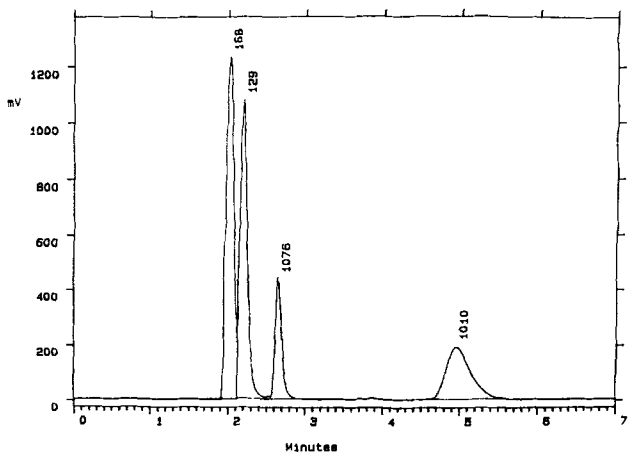

FIGURE 6. Chromatogram of four additive standards separated using normal phase with flow programming. Separation is carried out using a 15 cm. Nova-Pak silica column, maintained at 30C. Eluent is 80:20 n-butyl chloride/methylene chloride (isocratic), initially at 0.75 mL/min., then flow programmed to 1 mL/min. after 2.50 minutes, then to 2.0 mL/min. after 4.0 minutes, (linear program). UV detection is at 230nm.

FLOW PROGRAMMING:

The last section of this paper discusses the use of normal and reverse phase LC analysis with flow programming. Figure 6 shows a normal phase, isocratic separation with flow programming for Irgafos 168, Isonox 129, Irganox 1076, and Irganox 1010, in under 5.5 minutes. One can do an exponential skim integration on the first two peaks to obtain area quantitation, or use the heights. The results obtained using the normal phase analysis were nearly as good for recovery and precision as the reverse phase analysis. The eluent is 80:20 n-butyl chloride/methylene chloride at 0.75 mL/min. initially, then increased to 1.0 mL/min. after 2.50 minutes, then to 2.0 mL/min. after 4.0 minutes, (all linear transitions). The separation was carried out using a 15 cm. Nova-Pak silica column at 30C. The UV detection was made at 230nm. If the additive formulation is relatively simple, the normal phase procedure will save a lot of time over the reverse phase gradient.

Figure 7 illustrates a reverse phase gradient program without any flow program (flow is constant at 1.50 ml/minute) for 12 additives: Tinuvin P, MD1024, BHT, BHEB, Irganox 1330, Cyasorb UV 531, Isonox 129, AM 340,

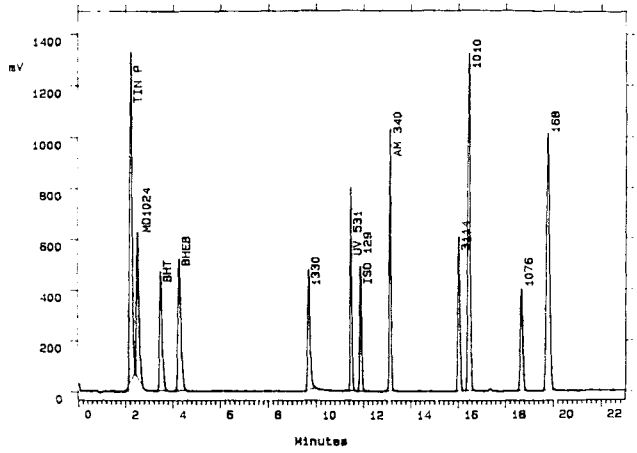

FIGURE 7. Chromatogram of 12 additive standards separated by reverse phase gradient using a 15 cm. Nova-Pak C18 column, maintained at 50C. Eluent is initially 70:30 acetonitrile/water, and is 100% acetonitrile after 8.0 minutes (linear gradient). Flow Rate is 1.50 mL/min., and UV detection is at 225nm.

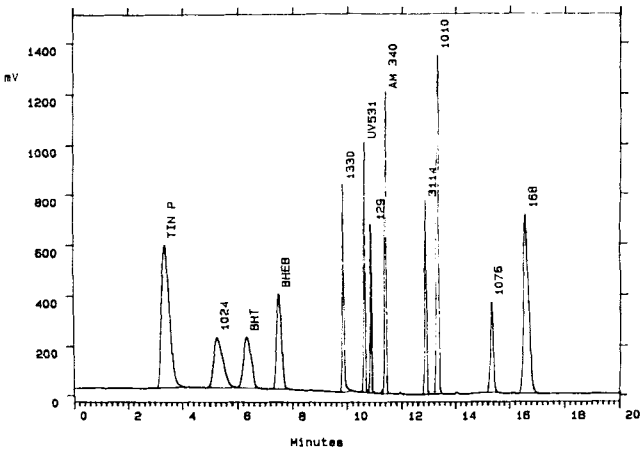

FIGURE 8. Chromatogram of the same 12 standards as in FIGURE 7, using the same gradient profile. Flow programming is also used, beginning initially at 0.80 mL/min., then increasing to 1.50 mL/min. after 7.0 *minutes*, (program curve 10), then finally to 2.0 mL/min. after 12.0 minutes (linear curve).

Irganox 3114, 1010, 1076, Irgafos 168. The eluent is initially 70:30 acetonitrile/water, and is 100% acetonitrile after 8 minutes, (linear gradient). The separation shows partial separation of Tinuvin P and MD1024. Figure 8 shows the same additive standards separated using the same gradient but with a flow program. The initial flow rate is 0.80 mL/min., increasing to 1.50 mL/min. after 7 minutes (curve 10 on the program), then to 2.0 mL/min. after 12 minutes (linear curve on the program). The Tinuvin P is baseline separated from the MD1024 in this chromatogram, and the last peak eluting (Irgafos 168) has a retention time under 17 minutes, compared to ~20 minutes for the chromatogram without the flow program. The combination of solvent gradient with flow programming provides a means of optimizing the separation of numerous components in a shorter analysis time.

CONCLUSIONS

For a polyolefin additive package that contains typical hindered phenol type antioxidants, the use of cyclohexane with 2-propanol works very well at extracting out the additives with the ultrasonic bath and obtaining good recovery data. If a phosphite ester is present in the formulation, the use of alcohols in the extraction solvent mixture will most likely cause degradation of the phosphite, resulting in multiple peaks in the chromatogram. The peak areas must be added together, resulting in poor reproducibility (precision) and questionable recovery data (accuracy). Also, the multiple peaks present interfere with other eluting species, such as Irganox 1076. We also noticed that the MD1024 (amine type of antioxidant) had a shoulder present on the peak when the 2-propanol was used. These problems were eliminated when methylene chloride/cyclohexane was used as the extraction solvent mix. Another thing to keep in mind is the fact that the time the sample is in contact with water used in the gradient (water/acetonitrile - initial conditions) should be kept to a minimum (under 7 minutes), otherwise, risk of hydrolysis is again of concern. The other alternative is to use the normal phase procedure, where the phosphite esters may be separated from 1010, 1076, Isonox 129, etc. in under six minutes without risk of hydrolysis. We have also extracted Ultranox 626 (a phosphite additive manufactured by Borg Warner) from HDPE and obtained very good recoveries with both the reverse phase and normal phase separations.

The use of flow programming with both the reverse phase gradient and the normal phase isocratic separations provides an excellent way to maximize resolution and optimize the analysis time.

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