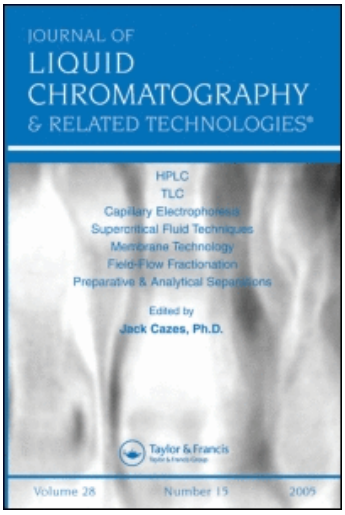

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Schabron, J. F. , Smith, V. J. and Ware, J. L.(1982) 'Determination of UV Absorbing Polyolefin Additives by Gradient and Isocratic Normal-Phase High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 5: 4, 613 — 624
To link to this Article: DOI: 10.1080/01483918208060573
URL: http://dx.doi.org/10.1080/01483918208060573

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(4), 613-624 (1982)

DETERMINATION OF UV ABSORBING POLYOLEFIN ADDITIVES BY GRADIENT AND ISOCRATIC NORMAL-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A method previously developed for the rapid extraction of BHT, Irganox 1076, and Irganox 1010 from polyethylene pellets was extended to include other ultraviolet absorbing additives in polyethylene and polypropylene matrices. These were Santonox R, Ethyl 330, Goodrite 3114, and Topanol CA. Polyolefin pellets were dissolved in decalin at 110°C followed by cooling to precipitate the polymer. The concentrations of the additives present were determined by normal-phase high-performance liquid chromatography of a portion of filtered extract. The HPLC stationary phase was μ-Porasil and the mobile phase was a heptane to methylene chloride gradient. The separation of some additives strongly retained with the gradient system was studied also using an isocratic methylene chloride mobile phase.

INTRODUCTION

Recently a rapid extraction and analysis method for the three most common polyolefin additives, BHT, Irganox 1076, and Irganox

1010 was described by Schabron and Fenska (1). A hot decalin extraction procedure was followed by high-performance liquid chromatography (HPLC) on μ-Porasil with a heptane to methylene chloride gradient. The gradient was used since BHT, Irganox 1076, and Irganox 1010 have significantly different polarities, and were not well separated by isocratic HPLC systems. With this type of a gradient system compounds with a wide range of polarity can be separated. Such a system is potentially useful not only for the analysis of various additives, but also for the rapid screening of unknown or competitors products for several ultraviolet absorbing additives with a single injection. Recently, Huber and Feher (2) showed that, in general, gradient elution is superior compared to optimized isocratic elution only in the separation of not too complex mixtures of widely different components and for pilot work to find a suitable mobile phase. Thus, for a separation of one or two components of similar polarity, an isocratic system should offer better precision and simplicity.

In the present work, the rapid extraction and analysis method for BHT, Irganox 1010, and Irganox 1076 (1) was studied with four additional UV absorbing hindred phenol type additives - Santonox R (bis-(2-methyl-4-hydroxy-5-tert-butylphenyl) thioether), Ethyl 330 (1,3,5-trimethyl-2, 4,6-tris [3,5-tert-butyl-4-hydroxybenzyl] benzene), Goodrite 3114 (tris (3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate), and Topanol CA (3:1 condensate of 3-methyl-6-tert-butylphenol with crotonaldehyde). Quantitative data from both the previously described HPLC system (1) and an isocratic HPLC system were obtained and compared.

MATERIALS AND METHODS

Instrumentation

The liquid chromatograph used in this study was a Waters Model 204 liquid chromatograph equipped with two model 6000A pumps

and a Model 660 solvent programmer. The Injector was a Valco 6000 psi injector with a 25 µL sample loop. Elution was monitored with a Waters Model 450 variable wavelength detector set at 280 nm and a 10 mV strip chart recorder. The column used was a 3.9 mm i.d. x 30 cm µ-Porasil column packed with 10 micron porous silica obtained from Waters Associates, Milford, Mass. To prevent clogging the analytical column with low molecular weight polymeric material when polypropylene extracts were injected, a 4mm i.d. x 3 cm guard column packed with 37-µm C_{18} Corasil was placed in line just prior to the analytical column (1). Thermolyne Type 1000 stir plates or Lab-Line Pyro-Magnestir No. 1268 six beaker stir plate were obtained from VWR Scientific.

The sample filtering apparatus is illustrated in Reference 1. A Waters 20-30 µm stainless steel solvent reservoir filter was connected to about a 5 inch length of 3-mm i.d. Teflon tubing. The other end of the Teflon tubing was connected to a 1 1/2 inch long blunt 16-gauge Luer-Lok needle with a 1/16 inch stainless steel nut and ferrule at the end of the needle. The needle was connected to a Hamilton No. 1010 W gastight 10-mL syringe with Teflon plunger.

Reagents

Heptane was distilled in glass obtained from Burdick and Jackson, Muskegon, Mich. Chloroform was Mallinkrodt AR grade from Scientific Products. Methylene chloride was Burdick and Jackson distilled in glass. The above mobile phase solvents were all filtered through Millipore Type F-H 0.5 µm filters prior to use. Eastman decalin from Sargent-Welch was purified prior to use by passing 500 g decalin through 120 g acidic aluminum oxide activity I (Fisher Scientific) in a 30 cm x 4 cm i.d. glass column with ground glass frit. This was necessary since significant amounts of polar aromatic impurities recently have been present in

decalins from various commercial sources. Recently purified decalin has been made available by special order from Burdick and Jackson.

Naugard BHT was obtained from Uniroyal Chemical, Naugatuck, Conn. Irganox 1076 and Irganox 1010 were obtained from Ciba-Geigy, Ardsley, N. Y. Santonox R was obtained from Monsanto, St. Louis, Mo. Ethyl 330 was obtained from Ethyl Corporation, Baton Rouge, La. Goodrite 3114 was obtained from B. F. Goodrich, Cleveland, Ohio. Topanol CA was obtained from ICI, Wilmington, Del. All additives were used without further purification.

Procedure

A 50-mL portion of a standard solution containing about 0.03 mg/mL each of Ethyl 330, Santonox R, Goodrite 3114 and Topanol CA was pipetted into a 100-mL beaker. A stirring bar was added and the solution was heated to 110°C with gentle stirring for 30 min. The solution was transferred to a cool stirrer and cooled to room temperature. This heated and cooled standard solution was used to obtain quantitative data on the sample extract solutions.

About 2g polyethylene or polypropylene pellets was weighed into a 100-mL beaker. A 50-mL portion of decalin was pipetted into the beaker and the mixture was heated to 110°C on a hot plate with gentle stirring for about 30 min. or until dissolution was complete. Usually polypropylene required about 45 min. The beaker was then transferred to a cool stirrer and cooled to room temperature with stirring to precipitate the polymer.

The precipitated polymer from the above extraction was pushed aside with a microspatula. The porous metal filter portion of the filter apparatus was inserted into the solution and about 5-10 mL of solution was drawn into the syringe. The Teflon tube was removed from the ferrule on the needle and the filtered solution was dispensed into a small vial. The filter apparatus was rinsed with acetone and dried between samples. After extensive use, the

metal filter became partially clogged and was regenerated by placing it in hot decalin and stirring.

For gradient runs the Model 660 solvent programmer was set at Program 6 (linear) going from 100% heptane to 100% methylene chloride in 5 min. The mobile phase gradient was started at the point of injection. For isocratic runs the mobile phase was methylene chloride. For both gradient and isocratic systems the total flow rate was 2mL/min. The UV detector was set at 0.2 or 0.4 absorbance unit sensitivity and the recorder chart speed was 1 cm/min. Duplicate injections of each of the standard and sample solutions were made. The retention volumes in the gradient system for BHT, Ethyl 330, Irganox 1076, Samtonox R, Goodrite 3114, Irganox 1010 and Topanol CA were 8.3, 9.8, 13.2, 14.4, 17.0, 21.4 and 24.9 mL, respectively. These are not the same as those previously reported (1) since a loop injector without 2 mL dead volume was used in this study. In the isocratic system the retention volumes for Santonox R, Goodrite 3114 and Topanol CA were 4.8, 5.7 and 10.8 mL, respectively. The amount of each additive was determined from each sample injection by comparing peak heights for samples and standards. A blank decalin injection was made to determine from what points on the baseline, peak heights should be measured. For the gradient runs, gradient reset was instantaneous, from 100% methylene chloride to 100% heptane. Sample injection could be made anytime after the appearance of a refractive index peak from the UV detector, signifying the emergence of heptane from the column.

RESULTS AND DISCUSSION

A gradient chromatogram of the four additives studied in this report and the three additives previously studied (1) is presented in Figure 1. All seven additives are completely separated. This illustrates the utility of this technique for separating a wide variety of UV absorbing polymer additives.

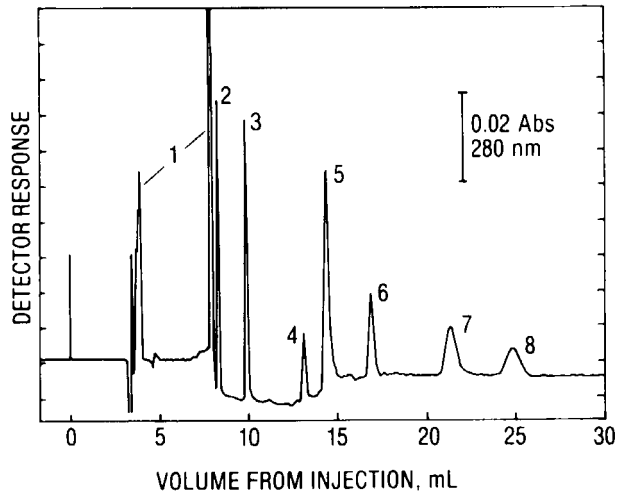

Figure 1. Separation of polyolefin additives: 1, in blank decalin; 2, 0.59 µg BHT; 3, 0.75 µg Ethyl 330; 4, 0.61 µg Irganox 1076; 5, 0.84 µg Santonox R; 6, 0.74 µg Goodrite 3114; 7, 0.64 µg Iragnox 1010; 8, 0.65 µg Topanol CA.

Accuracy

Spiking experiments were performed by dissolving polyolefin samples containing none of the additives under study in decalin containing known amounts of additives. The results of spiking 2 g portions of polyethylene and polypropylene are listed in Table I. The gradient HPLC separation was used. The results show good recovery of the additives Ethyl 330, Santonox R, Goodrite 3114, and Topanol CA at levels corresponding to 0.05% and 0.1% of each additive in the polymer. These good recoveries indicate that the additives were evenly distributed in the decalin both inside and outside the polymer "sponges" resulting from the extraction. Similar results were observed for BHT, Irganox 1076 and Irganox 1010 (1).

Sample Size

A polyethylene and a polypropylene sample, each containing the four additives, were each analyzed in duplicate at sample

TABLE I

RECOVERIES OF ETHYL 330, SANTONOX R, GOODRITE 3114 AND TOPANOL CA

Sample	Amount, g	Amount Added, mg				Amount Found, mg				Percent Recovered			
		Ethyl 330	Santonox R	Goodrite 3114	Topanol CA	Ethyl 330	Santonox R	Goodrite 3114	Topanol CA	Ethyl 330	Santonox R	Goodrite 3114	Topanol CA
PE	1.92	1.22	--	1.25	1.20	1.24	--	1.40	1.18	101	--	108	97
PE	1.86	1.22	--	1.25	1.20	1.24	--	1.38	1.22	101	--	106	101
PE	1.90	2.44	--	2.59	2.41	2.46	--	2.84	2.41	101	--	110	100
PE	2.13	2.44	--	2.59	2.41	2.44	--	2.82	2.40	100	--	109	99
PE	1.95	--	1.32	--	--	--	1.31	--	--	--	99	--	--
PE	1.98	--	1.32	--	--	--	1.30	--	--	--	98	--	--
PE	2.02	--	2.65	--	--	--	2.68	--	--	--	101	--	--
PE	2.28	--	2.65	--	--	--	2.54	--	--	--	96	--	--
PP	1.89	1.22	--	1.30	1.20	1.26	--	1.38	1.10	103	--	106	91
PP	2.20	1.22	--	1.30	1.20	1.24	--	1.34	1.12	102	--	104	93
PP	2.39	2.44	--	2.59	2.41	2.65	--	2.79	2.51	108	--	108	104
PP	2.02	2.44	--	2.59	2.41	2.58	--	2.86	2.28	106	--	110	99

amounts of about 1, 2 and 4 g, respectively. The results are listed in Table II. These data show the absence of significant constant error.

Precision

A polyethylene sample containing all four additives was analyzed in six replicate runs. The results are listed in Table III. These results show good precision for the method. A polypropylene sample containing the four additives, also was analyzed in six replicate runs. These results are listed in Table IV. They also show a good precision for the method.

The precision was slightly improved when the six polyethylene extracts (Table III) were injected using the isocratic HPLC system. These results are listed in Table V. Ethyl 330 could not be determined with a methylene chloride mobile phase because it elutes with the solvent front.

During the course of these precision studies, data comparing the precision for duplicate sample injections with the precision

TABLE II

SAMPLE SIZE VARIATION RESULTS WITH POLYETHYLENE AND POLYPROPYLENE

Sample	Amount, g	Amount Found, wt %: Ethyl 330	Santonox R	Goodrite 3114	Topanol CA
PE	1.01	0.074	0.063	0.090	0.086
PE	1.04	0.079	0.072	0.092	0.096
PE	2.16	0.080	0.078	0.100	0.095
PE	2.01	0.072	0.067	0.084	0.099
PE	4.01	0.072	0.070	0.091	0.082
PE	4.01	0.075	0.073	0.091	0.084
PP	1.00	0.070	0.051	0.091	0.094
PP	1.07	0.074	0.051	0.094	0.099
PP	2.02	0.076	0.058	0.097	0.096
PP	2.02	0.077	0.051	0.100	0.094
PP	4.01	0.072	0.059	0.093	0.090

TABLE III

RESULTS OF SIX REPLICATE DETERMINATIONS FOR A POLYETHYLENE SAMPLE, USING THE GRADIENT HPLC SYSTEM

Sample Amount,g	Amount Found, wt % Ethyl 330	Santonox R	Goodrite 3114	Topanol CA
1.97	0.082	0.073	0.100	0.093
2.09	0.079	0.074	0.094	0.086
2.01	0.078	0.072	0.092	0.088
2.00	0.074	0.071	0.088	0.086
2.01	0.072	0.068	0.084	0.091
2.06	0.080	0.076	0.096	0.090
$\bar{X}^a$ =	0.078	0.072	0.093	0.089
S =	0.0038	0.0029	0.0059	0.0030
95% Confidence	±0.0040	±0.0030	±0.0062	±0.0031
$\bar{X}^b$ =	0.078	0.074	0.092	0.087
	0.0040	0.0035	0.0063	0.0035
S =	±0.0042	±0.0037	±0.0066	±0.0037
95% Confidence				

a. Duplicate injection results.
b. Single injection results.

for single sample injections were obtained. These data are listed in Tables III, IV and V for polyethylene extracts separated by gradient HPLC, polypropylene extracts separated by gradient HPLC, and polyethylene extracts separated by isocratic HPLC, respectively. Generally, the precision drops somewhat when only single injections are made. The data show this precision drop to be slight and thus it should be possible to make single sample extract injection in cases when a relatively large number samples must be analyzed in a short period of time.

TABLE IV

RESULTS OF SIX REPLICATE DETERMINATIONS FOR A POLYPROPYLENE SAMPLE, USING THE GRADIENT HPLC SYSTEM

Sample Amount,g	Amount Found, wt % Ethyl 330	Santonox R	Goodrite 3114	Topanol CA
2.02	0.076	0.062	0.097	0.094
2.02	0.079	0.058	0.101	0.094
2.10	0.076	0.064	0.098	0.097
2.02	0.076	0.057	0.099	0.090
2.01	0.075	0.066	0.104	0.099
2.01	0.076	0.064	0.099	0.097
$\bar{x}$[a] =	0.076	0.062	0.099	0.095
S =	0.0014	0.0035	0.0025	0.0032
95% Confidence	±0.0015	±0.0037	±0.0026	±0.0034
$\bar{x}$[b] =	0.077	0.063	0.099	0.092
S =	0.0019	0.0031	0.0032	0.0033
95% Confidence	±0.0020	±0.0033	±0.0034	±0.0035

a. Duplicate injection results.
b. Single injection results.

Limits of Detection

The limits of detection for the additives were calculated based on 2-mm peak heights at 0.2 Abs. This corresponds to a S/N ratio of about 2. The limits of detection for a 25 µL extract from a 2 g polymer sample separated with the gradient HPLC system are 0.038 mg or 0.001% Ethyl 330, 0.058 mg or 0.002% Santonox R, 0.13 mg or 0.006% Goodrite 3114, and 0.32 mg or 0.016% Topanol CA. These limits are quite sufficient for the analysis of typical additive levels of about 0.05% or greater.

TABLE V

RESULTS OF SIX REPLICATE DETERMINATIONS FOR A POLYETHYLENE SAMPLE, USING THE ISOCRATIC HPLC SYSTEM

Sample Amount,g	Amount Found, wt % Santonox R	Goodrite 3114	Topanol CA
1.97	0.084	0.10	0.098
2.01	0.079	0.094	0.088
2.10	0.079	0.095	0.087
2.00	0.078	0.091	0.087
2.16	0.081	0.095	0.090
2.01	0.077	0.088	0.084
$\bar{x}$[a] =	0.080	0.094	0.089
S =	0.0025	0.0041	0.0048
95% Confidence	±0.0026	±0.0041	±0.0048
$\bar{x}$[b] =	0.080	0.093	0.089
S =	0.0027	0.0045	0.0052
95% Confidence	±0.0028	±0.0047	±0.0055

a. Duplicate injection results.
b. Single injection results.

CONCLUSION

The method described in this report, when combined with the method previously reported (1) for determining UV absorbing polymer additives by normal-phase HPLC on μ-Porasil following decalin extraction, provides a useful tool for quality assurance or lot certification analyses. The seven additives: BHT, Ethyl 330, Irganox 1076, Santonox R, Goodrite 3114, Irganox 1010 and Topanol CA can be determined individually or in any combination with a single HPLC system. Slight variations in the HPLC system also allow for the analysis of Tinuvin 144 (3) in polypropylene following decalin extraction. Other additives ammenable to the decalin extraction followed by separation on other normal-phase

HPLC systems are Irganox 1024 and UV 531. Work on these latter two additives is currently underway.

The decalin extraction followed by gradient normal-phase HPLC described in this report should provide a useful starting point for future analytical methods development work for other new UV absorbing additives, which may be used in polymer formulations.

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