Extraction of Polypropylene Additives and Their Analysis by HPLC

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Key Words

Column liquid chromatography
Polypropylene additives
Extraction methods
Antioxidants

Summary

The polypropylene additives were extracted by dissolution-precipitation and Soxhlet. The Soxhlet method was adapted for the extraction of phosphorous antioxidants. The RP HPLC method with quaternary gradient elution separated five chemical groups of additives: lower molecular mass di-tert-butyl phenol (D.T.B.P.), hindered amine light stabilizers (Tinuvin 326), hindered phenolic antioxidants (Irganox 1010) and phosphorous antioxidants (Irgafos 168 and Ultranox 626) with their degradation products.

Introduction

Polypropylene food packagings need the presence of additives during manufacture and use at levels ranging from 0,1 to 1 % [1]. Additives belong to several categories such as heat stabilizers, sterically hindered phenolic antioxidants, hindered amine light stabilizers, antiacids, antistatic agents and lubricant agents. Additives are potentially labile substances, so EEC program harmonization on food plastics [2] formulates the control of plastic composition. The extraction and analysis of additives are difficult due to the following reasons: the low concentration at which they are present in the polymer; a relatively insoluble matrix; the thermolability and reactivity of the additives which have a wide range of molecular weight (200–2000) and polarity. Direct methods of analysis such as ultraviolet absorption, infrared spectroscopy, fluorescence, phosphorescence and X-ray fluorescence have been reported [3–5]. However, these methods generally lack specificity [6]. Consequently, determination of additives needs a preliminary solid-liquid extraction [5]. Others methods have been developed such as microwave or ultrasonic extraction [7] and SFE [8, 9]. The extraction is followed by chromatographic analysis. Gas chromatography uses sensitive and universal detectors [10–12]. However, this technique is limited by the high molecular weight and polar groups of many antioxidants and light stabilizers which decompose at high temperature [13, 14]. Recently, some additives have been analysed by GC with column temperatures up to 420 °C [15, 16].

Many additives can be determined by high performance liquid chromatography [8, 17–20] but there is a lack of sensitive universal detectors [8, 18, 20]. Capillary SFC with carbon dioxide as the mobile phase exhibits high-resolution separation of non-volatile, thermally labile, high molecular weight and moderately polar additives [21–24] and can be coupled to various detectors including the universal flame ionization detector [21, 25]. The reproducibility of coupled SFE-SFC is improved by trapping the entire extract before injection onto the column [23, 24]; the pressure gradient used to analyse a complex mixture of additives needs more than 1 hour [26]. RP HPLC offers a separation of complex mixture by the use of gradient elution [14]. HPLC equipment is much more common than SFC in the laboratory. Thus, in this work, we optimized an HPLC method with a quaternary gradient to compare polypropylene additives and their degradation products obtained by dissolution-precipitation and Soxhlet methods.

Experimental

Chemicals

Trade names, chemical names, and suppliers are listed in Table I. Polypropylene was supplied by an EEC-sponsored experimental program (AIR 941025). All solvents were HPLC grade: Analychrom Tetrahydrofuran and Acetonitrile were obtained from Fisher-OSI (Elancourt, France), Methanol, Methylene chloride and Toluene were provided by Prolabo (Fontenay-sous bois, France). Deonized water was prepared by a

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Table I. Trade names and suppliers of standard additives.

Additives	Chemical name	Supplier
DBS	1,3,2,4-di-p-methyl-benzylidene sorbitol	Chemical Melicken
DTBP	2,4-di-tert-butyl phenol	–
Tinuvin 326	2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-2H-5-chloro-benzotriazole	Ciba-Geigy
Ultranox 626	Bis(2,4-di-tert-butylphenyl)pentaery-thritoldiphosphite	GE Silicon
Irganox 1010	Tetrakis methylene (3,5-di-tert-butyl-4-hydroxyhydro-cinnamate)methane	Ciba-Geigy
Irgafos 168	Tris(2,4-di-tert-butylphenyl)phosphite	Ciba-Geigy
Oxidized Irgafos 168	Tris(2,4-di-tert-butylphenyl)phosphate	Ciba-Geigy

Milli-Q plus (18,2 Ω), Millipore (Bedford, Massachusetts, USA).

Extraction

Dissolution-Precipitation

Polypropylene (5 g) was cut into small pieces (0.2 cm × 1 cm) and dissolved in 100 mL of refluxing toluene. Precipitation of high molecular weight material by addition of 250 mL methanol, was followed by filtration under vacuum through a glass fiber superimposed on a filter of 0.45 µm porosity and 47 mm diameter (GF/C Whatman filter, Maidstone, Kent, UK). The solution obtained was evaporated to dryness under reduced pressure. The residue was dissolved in 2 mL of THF.

Soxhlet Extraction

Polypropylene (5 g) was cut in small pieces and was placed in a 125 × 35 mm Schleicher & Schuell cellulose thimble (Keene, New Hamphire, USA) for extraction in a Soxhlet apparatus with 250 mL of methylene chloride (6 h, 50 °C). The extracting solvent was evaporated to dryness and the residue dissolved in 2 mL of THF. The THF solution was then filtred through a PTFE Nalgene filter of 0,2 µm pore size in order to remove undissolved material. 20 µL of filtred solution was analysed by HPLC.

High Performance Liquid Chromatography

The liquid chromatograph used for analysis consists of a Jasco 880 PU pump, (Tokyo, Japan), a Waters 990 photodiode array detector, (Milford, Massachusetts, USA), connected to a computer NEC power Mate 2 APC4. The refractive index detector (RI) was an HP 1047, Hewlett-Packard, (Wilmington, DW, USA). The separation used a reversed phase column 25 × 0.46 cm, packed with LiChrospher 5 µm, RP-Select B, Merck (Darmstadt, Germany). The eluent was a gradient consisting of a mixture of two solutions:

- A (THF : Acetonitrile : Methanol : Water, 40:10:10:40 (V/V)
- B (THF : Acetonitrile : Methanol, 40:30:30 (V/V).

The flow rate was 1 mL min^{-1}. The gradient varied during 35 min as following:

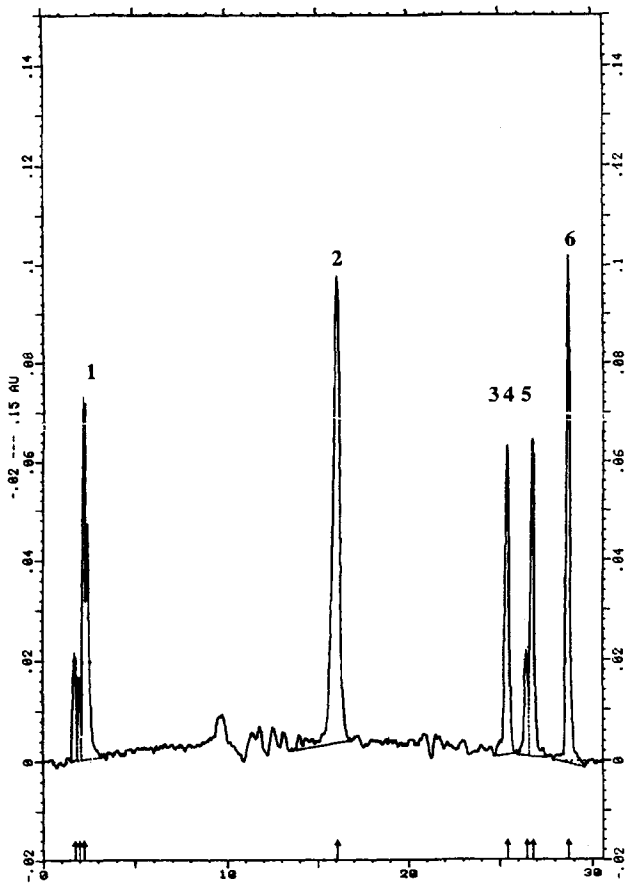


Figure 1

Chromatogram of standards additives, gradient elution, λ = 280nm: **1** = D. B. S., **2** = Tinuvin 326, **3** = Ultranox626, **4** = Oxidized Irgafos 168, **5** = Irganox 1010, **6** = Irgafos 168.

Time (min)	% solution A	% solution B
0	100	0
7	100	0
35	0	100

Mass Spectrometry

Mass spectrometric detection was performed in EI mode with a Nermag R 10–10 provided from Quad service (Poissy, France). The ion source and analyzer were at 10^{-3} and 10^{-7} Torr. The ion source temperature was 200 °C.

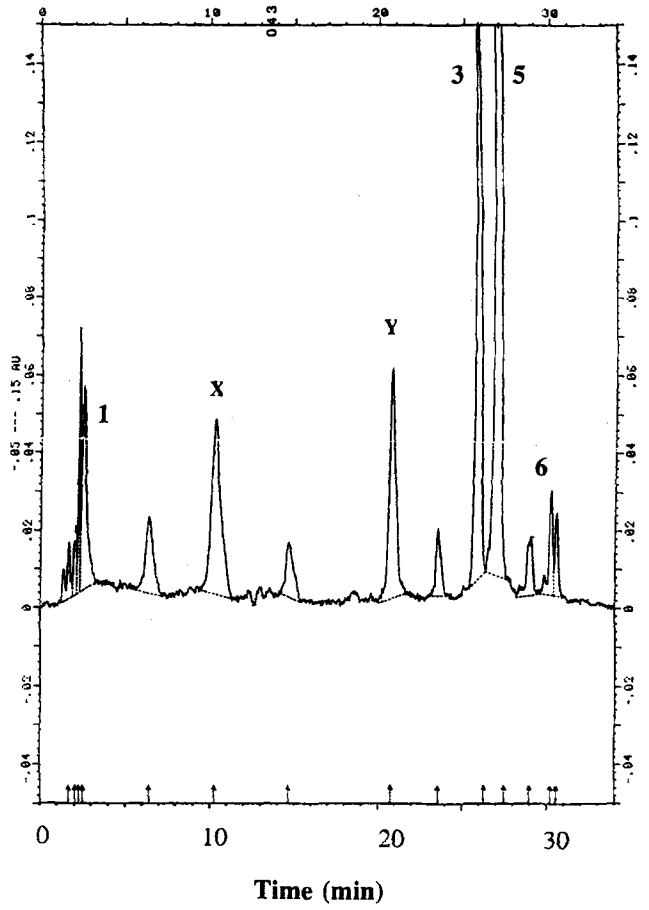


Figure 2
Chromatogram of Soxhlet extract, gradient elution, λ = 280 nm: **1** = D. B. S., **3** = Ultranox 626, **5** = Irganox 1010, **6** = Irgafos 168, **X** = D. T. B. P. (k = 3.56), **Y** = degradation product of Ultranox 626 (k = 8.23).

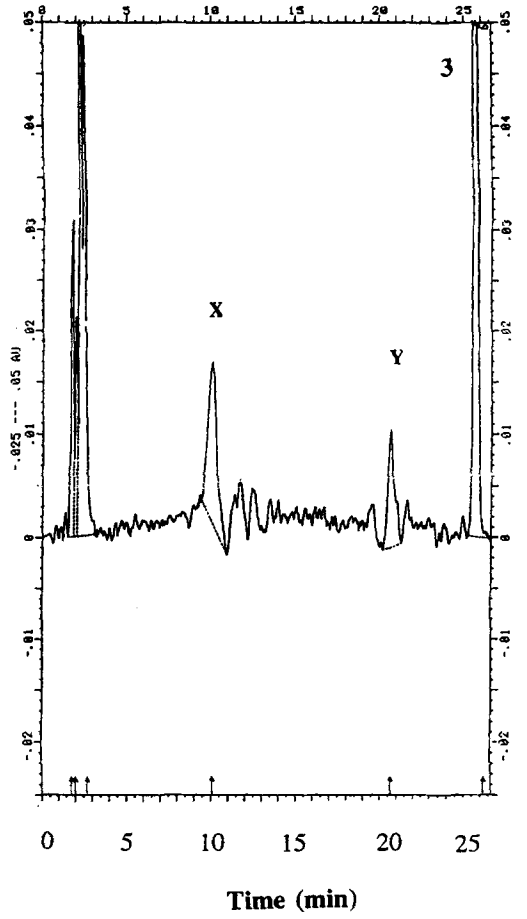


Figure 3
Chromatogram of Ultranox 626, gradient elution, λ = 280 nm: **3** = Ultranox 626, **X** = D. T. B. P. (k =3.52), **Y** = degradation product of Ultranox 626 (k = 8.30).

Results and Discussion

Figure 1 shows the chromatogram of the standard additives detected at 280 nm namely D.B.S., Tinuvin 326, Ultranox 626, Irganox 1010, Irgafos 168 and its oxidized product. Figure 2 shows the chromatogram of the Soxhlet extract.

The identified additives, by injection of standard samples, were Ultranox 626, Irganox 1010 and Irgafos 168. The Soxhlet extract contained two degradation products of the Ultranox 626. The first is D.T.B.P. identified by injection of a standard sample which eluted at k = 3.56 (10.26 min). The second is the chemical retained on the column until k = 8.23 (20.7 min), identified by the comparison with the retention time and UV spectrum as the degradation product present in the Ultranox 626 chromatogram (Figure 3). The mass spectrum of the Ultranox 626 standard (Figure 4) exhibits the molecular ion $M^{+\cdot}$ ($C_{33}H_{50}O_6P_2$) m/z 604 (product I, scheme I), and the adduct compounds which are ($C_{33}H_{50}O_6P_2$, H_2O) m/z 622 and ($C_{33}H_{50}O_6P_2$, $2H_2O$) m/z 640. This result is in agreement with Minagawa [27] who noted changes in weight due to water absorbed by Ultranox 626. The presence of the hydrated molecular ions in the sample, implies the existence of hydrolysis product such as du 2,4-di-tert-butyl phenol m/z 206 (product X, Scheme I). Its presence is confirmed by the fragment ion m/z 191, in Figures 4 and 5, which generated from 2,4-di-tert-butyl phenol by the loss of the methylic group. The Ultranox 626 degradation product eluted at k = 8.23 (20.7 min) (Figures 2, 3), is another derivative of the hydrolysis (product y, Scheme I). This absorbs at 275 nm which is due to its phenolic group.

Figure 6 shows the chromatogram of the dissolution-precipitation extract. It exhibits the same compounds previously identified (Ultranox 626, Irganox 1010, Irgafos 168). However, in this extraction, we have identified not only the Ultranox 626 degradation product (D.T.B.P.), but also, another compound eluted at k = 11.10 (26.5 min) corresponding to the oxidized Irgafos 168.

The qualitative comparison between these two polypropylene extracts shows that the dissolution-precipitation extract specifically exhibits the oxidized Irgafos 168 and unidentified product eluted at k = 11.6 (27.5 min),

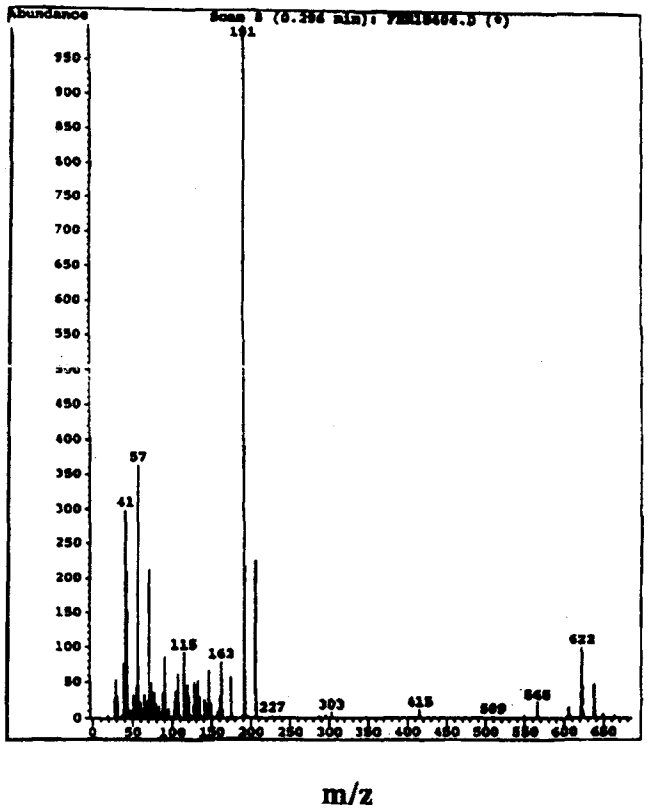


Figure 4
Mass spectrum of Ultranox 626.

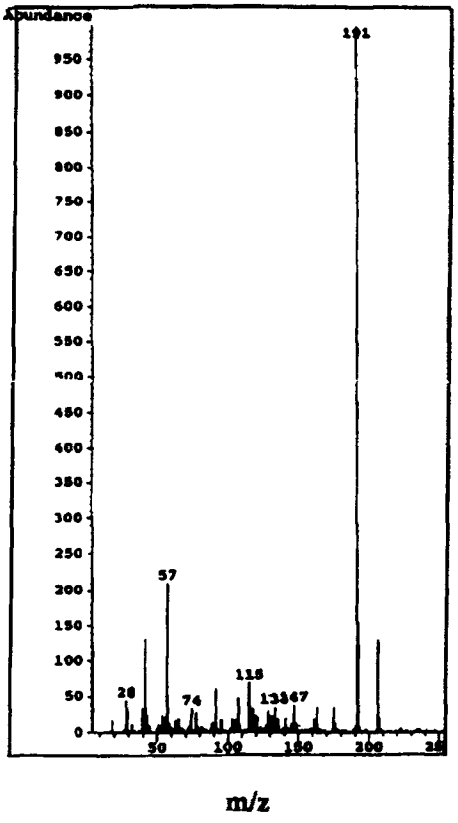
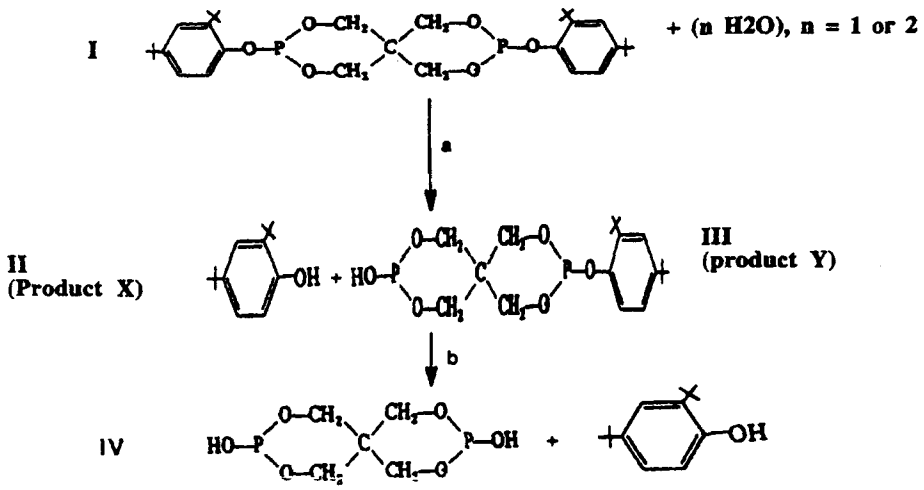


Figure 5
Mass spectrum of 2,4-di-t-butyl phenol.



Scheme I
Hydrolysis products of Ultranox 626.

whereas, the Soxhlet extract did not contain these compounds, but only contains the Ultranox 626 degradation product eluted at $k = 8.23$ (20.7 min). The high temperature (100 °C) of the dissolution-precipitation extraction can explain this difference. The presence of the oxidized Irgafos 168 in this type of extract confirms this hypothesis, since this compound exists only in some conditions of temperature and solvent. Effectively, we are looking at the phosphite stability, at 50 °C, in the extracting apolar solvents (Toluene and Dichloromethane) and in the polar solvent (Acetonitrile:Tetrahydrofuran 85:15 v/v). This latter solvent is choosen to have a minimal volume of THF to dissolve the Irgafos 168 because of its weak solubility in Acetonitrile. We observe that the Irgafos 168 degrades into the oxidized product in the THF-acetonitrile mixture. In contrast, in dichloromethane

and toluene, Irgafos 168 does not undergo any modification (Figure 7). This behaviour is due to the molecular interaction with polar solvents.

Before quantitative analysis, the HPLC method has been validated in terms of linearity, repeatability and detection limit for Ultranox 626, Irganox 1010 and Irgafos 168. Calibration curves were obtained using the least squares regression method. The linearity range was determined using the relative standard deviation of the response factor. All results are summarized in Table II. Three polypropylene extractions by dissolution-precipitation and by Soxhlet were performed to quantify the antioxidants. Table III summarizes the average of the concentration in ppm. The lack of information on the initial concentrations of additives in polymer did not permit the calculation of the yield of each extraction procedure. These results show that the level of the Irganox 1010 was approximately equal in both extracts, whereas, the quantity of the phosphite esters in the Soxhlet extract is larger than in the dissolution-precipitation extract. It confirms the degradation, of the phosphite esters, by heating at 100 °C. Also, it is noted that Ultranox 626 was more sensitive to heat than the Irgafos 168.

It is known that polypropylene contains other agents which are not absorbed in the UV region. An RP HPLC analysis achieved with an isocratic mobile phase and simultaneously RI and UV detection, confirms their presence in the polymeric matrix. So, a future study which couples RP HPLC-quaternary gradient-UV detection with light scattering diffusion, will be carried out in our laboratory, to detect all additives and their degradation products.

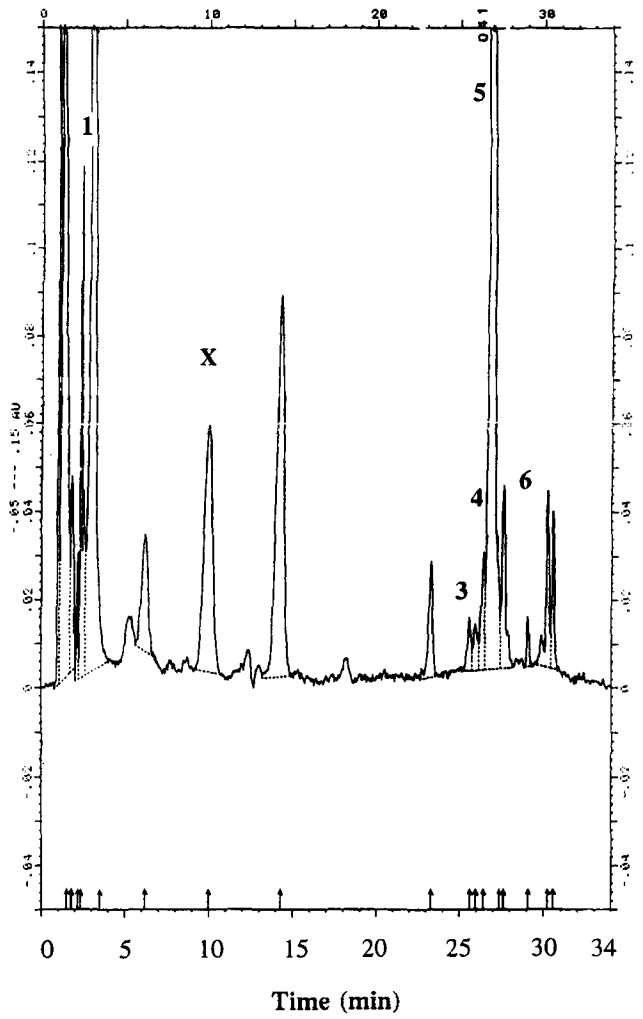


Figure 6
Chromatogram of dissolution-precipitation extract, gradient elution, λ = 280 nm: **1** = D. B. S., **3** = Ultranox 626, **4** = Oxidized Irgafos 168, **5** = Irganox 1010, **6** = Irgafos 168, **X** = D. T. B. P. (k = 3.54).

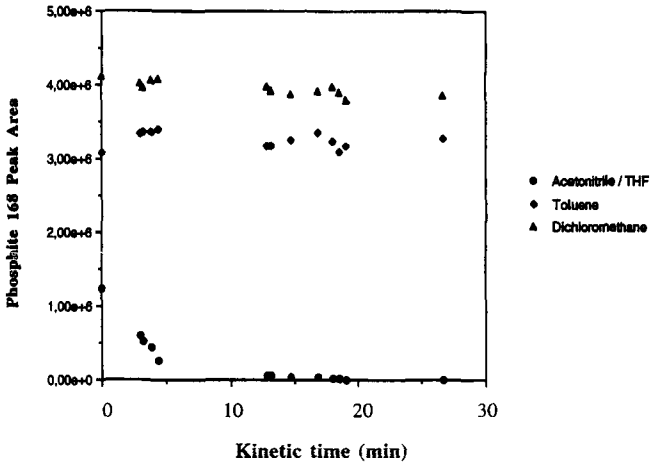


Figure 7
Kinetic curve of Irgafos 168 stability in THF : acetonitrile (15:85 v/v), toluene and methylene chloride.

Table II. Validation parameters of standard additives.

Additives	Calibration curves	% R. S. D.	Limit of detection mg mL^{-1}	Repetability % R. S. D.
Irganox 1010	$3{,}7447\ 10^{-4} + 0{,}11382\ x$	2.5	0.005	1.05
Ultranox 626	$-6.7020\ 10^{-4} + 4.4424\ x$	4	0.0045	2
Irgafos 168	$2.912610^{-6} + 7.6540\ 10^{-2} x$	4.8	0.005	2.3

Table III. Quantification of additives within polypropylene.

Additives	Dissolution-precipitation		Soxhlet	
	Amount (ppm)	%R.S.D.	Amount (ppm)	% R.S.D.
Irganox 1010	750	2	880	1.1
Irgafos 168	880	1.1	41	2.3
Ultranox 626	41	2.3	340	1.27

Conclusion

Soxhlet extraction with methylene chloride was the best technique to extract the phosphitic additives. RP HPLC separated selectively five chemical groups of additives: lower molecular mass (D.T.B.P.), hindered light amine stabilizers (Tinuvin 326), hindered phenolic antioxidants (Irganox 1010) and phosphitic esters anioxidants (Irgafos 168, Ultranox 626). Also, the latter chemicals were distinguishable from their degradation products. So HPLC can be employed to control the presence of additives after thermal processing and the quality of the polypropylene during its service life.

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