

## Short Communication

# Determination of the polymeric light stabilizer Chimassorb 944 in polyolefins by isocratic high-performance liquid chromatography

R. Matuška, L. Preisler and J. Sedlář

*Chemopetrol, Litvínov, Research Institute of Macromolecular Chemistry, 656 49 Brno (Czechoslovakia)*

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### ABSTRACT

A procedure is described for the determination of Chimassorb 944 in polyolefins. The method is based on high-performance liquid chromatographic (HPLC) analysis of an extract obtained through disintegration of the polymer sample in boiling toluene. The dissolved polymer is then precipitated with methanol, containing triethylamine which prevents sorption of Chimassorb 944 on laboratory glassware and filter-paper. The HPLC determination employs the calibration line method. If the calibration is carried out with Chimassorb 944–Irganox 1010 mixture then an accurate determination of both additives is possible. The detection limit is 0.02% (w/w), the relative standard deviation being lower than 10%.

### INTRODUCTION

Hindered amine light stabilizers (HALSs) have been widely applied in the plastics industry to protect polymers against photooxidation. New types of stabilizers are being developed with the aim of suppressing their volatility and extractability from polymers. Chimassorb 944 (Fig. 1) stabilizer may serve as an example of this type of additive. It is an oligomer with a molecular mass of 2500–3000.

Compared with monomeric stabilizers, the determination of such oligomeric structures in polymer matrices usually represents a serious analytical problem. Methods for determining Chimassorb 944

are mainly based on the determination of the nitrogen content in the polymer (polyolefin) by Kjeldahl digestion [1] or on the hydrogenolysis [2] of the sample. This is applicable only when the stabilizer is the only nitrogen-containing component in the system. Another approach makes use of the measurement

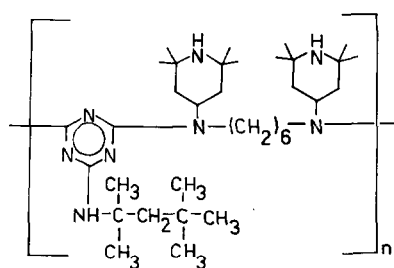


Fig. 1. Structure of Chimassorb 944.

Correspondence to: Dr. R. Matuška, Chemopetrol, Litvínov, Research Institute of Macromolecular Chemistry, 656 49 Brno, Czechoslovakia.

of the UV absorbance of the polymer dissolved in decalin and extracted with sulphuric acid [3] or the measurement of the IR absorption of the stabilizer triazine group [4,5]. Chromatographic methods include pyrolysis–gas chromatography [6] or high-performance liquid chromatography (HPLC) using Styragel and Ultragel columns with the flame ionization detection [7] and reversed-phase gradient elution HPLC [8].

This paper describes a simple isocratic elution HPLC method using a size-exclusion column and UV detection. Particular attention has been paid to the elimination of the adsorption of Chimassorb 944 on the polymer and the filter during the sample preparation. In this way, an almost complete recovery has been attained.

## EXPERIMENTAL

### Apparatus

A Hewlett-Packard Model 1050 liquid chromatograph equipped with a Rheodyne Model 7125 sampling valve (20- $\mu$ l sample loop), a UV detector operated at 244 nm, sensitivity 0.5 AUFS, and a Hewlett-Packard Model 3396 A integrator was used. The analytical columns (250  $\times$  7 mm I.D.), made of stainless steel and packed with LiChrogel PS4 and PS1, were connected in series and operated at room temperature (gel permeation chromatographic exclusion limits  $2 \cdot 10^3$  D for LiChrogel PS1 and  $5 \cdot 10^3$  D for LiChrogel PS4). A 1.5 g/l solution of diethanolamine (DEA) in tetrahydrofuran (THF) (inlet pressure 40 bar, flow 1 ml/min) was employed as a mobile phase.

### Solvents and chemicals

Toluene, methanol (analytical-reagent grade), triethylamine (TEA), DEA (both of technical grade) were obtained from Lachema (Brno, Czechoslovakia). The TEA was dried with molecular sieve 5A and distilled before use. THF stabilized with 0.025% of 2,6-ditertiarybutyl-4-methylphenol (BHT) was obtained from Merck (Darmstadt, Germany) and Chimassorb 944 from Ciba-Geigy (Basle, Switzerland). The calibration solution was prepared by dissolving 100 mg of Chimassorb 944 in 250 ml of THF. Three model samples of polypropylene with known stabilizer content (0.05% BHT and 0.05%, 0.1% and 0.3% of Chimassorb 944) were also prepared.

### Procedure

A 1-g polyolefin sample was placed in a 250-ml round-bottomed flask and disintegrated by refluxing with 30 ml of toluene for 40 min on an oil-bath at 130°C. After cooling to about 60°C, 75 ml of 1% TEA solution in methanol were added through the reflux condenser. The mixture was agitated, allowed to cool to laboratory temperature and filtered through a filter-paper impregnated with 1% TEA solution in methanol. The filter cake was washed twice with 10 ml of the same TEA solution. The combined filtrate was evaporated to dryness and the residue dissolved in 5 ml of THF or in 5 ml of THF–toluene (1:1) when the stabilizers were incompletely dissolved in THF alone. A volume of 20  $\mu$ l of this solution was injected into the chromatograph. A typical chromatogram is shown in Fig. 2.

The Chimassorb 944 content in the polymer sample was calculated by comparing the peak heights of the calibration solution with those of the sample solution.

## RESULTS AND DISCUSSION

It is not possible to separate polymeric HALSs (Chimassorb 944, Tinuvin 622) quantitatively from

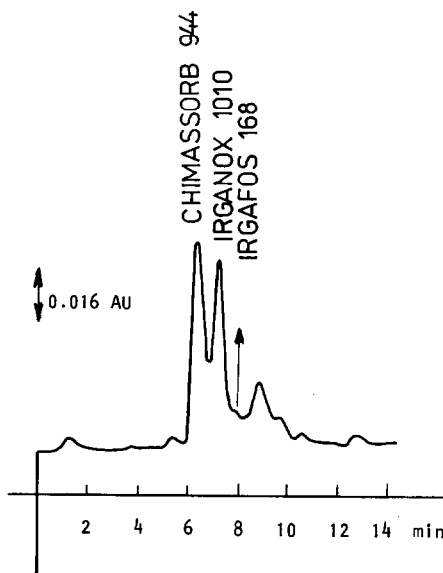


Fig. 2. Typical chromatogram of sample containing 0.3% Chimassorb 944, 0.3% Irganox 1010 and 0.3% Irganox 168. Sample after exposure for 1000 h at 80°C.

TABLE I

INFLUENCE OF TEA ADDITION ON THE RECOVERY OF CHIMASSORB 944 FROM A POLYMER MATRIX

Model Sample	Treatment			
	Without TEA		With TEA	
	Chimassorb 944 found (%)	$s_R^a$	Chimassorb 944 found (%)	$s_R^a$
Ch 05: 0.05% Chimassorb 944, 0.05% BHT in PP <sup>b</sup>	0.041	0.004	0.049	0.005
Ch 1: 0.10% Chimassorb 944, 0.05% BHT in PP	0.087	0.005	0.103	0.004
Ch 3: 0.30% Chimassorb 944, 0.05% BHT in PP	0.265	0.005	0.308	0.007

<sup>a</sup>  $s_R$  = Standard deviation =  $K_n \cdot R$  ( $n = 6$ ).

<sup>b</sup> PP = polypropylene.

the polymer matrix by a simple extraction. To achieve this, it is necessary to boil the sample containing Chimassorb 944 in toluene or decalin and after its disintegration to precipitate the polymer (e.g., with methanol). The precipitated polymer, however, can sorb the stabilizer on its large surface. The stabilizer can also be sorbed on the glass walls of vessels and on a filter during the sample treatment.

The phenomena caused a lowering of the results when model samples were analysed. Our observations correspond well with those published by Freitag [8], who achieved only an 83% recovery in analyses where 0.05% Chimassorb was present in polypropylene. We have found that the recovery of Chimassorb 944 after its separation from polyolefin can be considerably increased by using TEA and inducing competitive sorption. For this reason, we impregnated with TEA all the glassware and the filter used in handling the stabilizer extract. TEA was also added to the methanol used for the polymer precipitation. The results of analyses obtained both in the presence and in the absence of TEA are shown in Table I. The results indicate that the TEA treatment permits the quantitative recovery of HALSs.

To separate Chimassorb 944 from polyolefin oligomers and from other components of the stabilizing system we used LiChrogel packings. For these gels (styrene-divinylbenzene copolymers) mobile phases such as THF, acetone, dimethylformamide and chloroform are generally recommended. However, the use of THF alone as a mobile phase did

not lead to the elution of Chimassorb 944. This was rendered possible only after the addition of DEA to the mobile phase.

An increase in the DEA concentration in THF progressively reduced the retention time and improved the Chimassorb 944 peak symmetry. The former phenomenon was observable up to a concentration of 0.5 g/l of DEA in THF in the mobile phase. Further increase in DEA concentration led only to the improvement of the Chimassorb 944 peak shape. A concentration of DEA of 1.5 g/l in THF was chosen as the optimum in the mobile phase.

THF used for the mobile phase was stabilized with 0.025% of 2,6-di-*tert*-butyl-4-methylphenol and the UV spectra show that the absorbance minimum of the mobile phase can be matched satisfactorily with the absorbance maximum of Chimassorb 944 (244 nm). The recommended values of the wavelength and the mobile phase composition are optimum also from the viewpoint of demands on the sensitivity of the method and the separation of Chimassorb 944 from the other stabilizers, especially Irganox 1010.

When determining Chimassorb 944 in the presence of a phenolic component, such as Irganox 1010, it is recommended that the sample size taken for analysis is as small as possible. Another possibility is to carry out the calibration with Chimassorb 944–Irganox 1010 mixture in a ratio corresponding to that used in the stabilizer package. In this way the interference of the phenolic component is min-

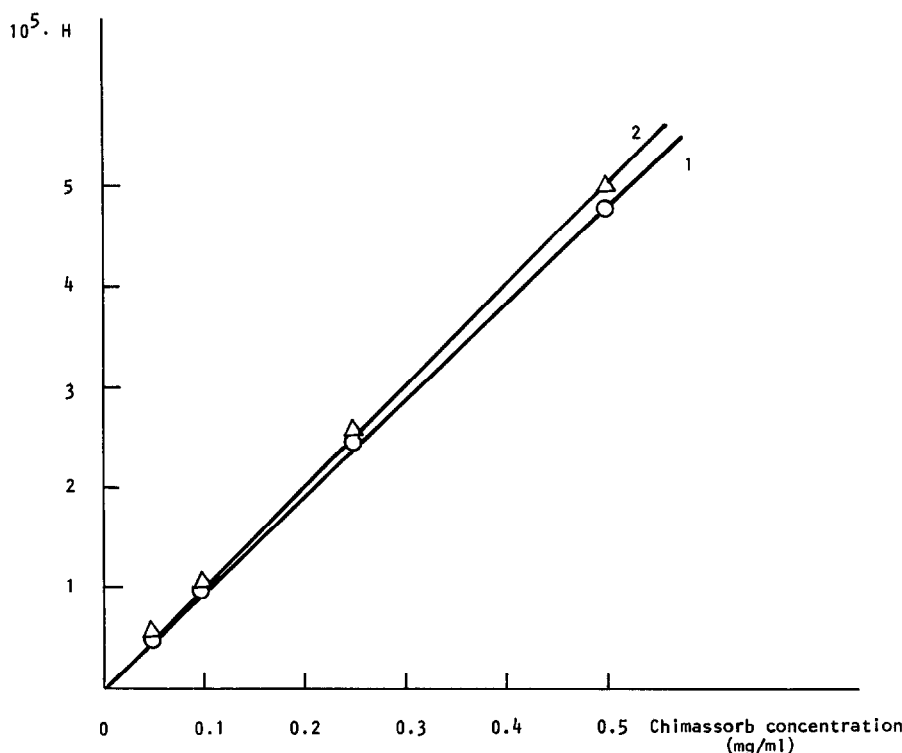


Fig. 3. Effect of addition of Irganox 1010 on the slope of the Chimassorb 944 calibration curve. 1 = Without addition Irganox 1010; 2 = Chimassorb 944 + Irganox 1010 (1:3, w/w).  $H$  = height of peaks.

imised (see Fig. 3). When the calibration is carried out in the absence of Irganox 1010 then the systematic error of Chimassorb 944 determination may be as high as 10%, the overall stabilizer concentration being within the range 0.1–0.5% (w/w). The following example illustrates the analysis of commercial

fibre-grade polypropylene Tatren (Slovnaft, Bratislava, Czechoslovakia). The concentration of Chimassorb 944 was determined both in pellets and in the corresponding fibre (see Table II). The presence of other components of the stabilizer package (*i.e.*, phenolics and phosphites) did not interfere with the analysis.

Although the scatter of experimental values was higher in the case of fibre, the accuracy of the determination was still sufficient to show the effect of processing on the concentration of HALSs in the final product. The demanding operations connected with the conversion of pellets into fibre and subsequent thermal treatment of the latter reduce the stabilizer concentration. This decrease is, however, far less pronounced than with low-molecular-mass (monomeric) HALSs.

#### CONCLUSION

The proposed method represents a very simple

TABLE II

DETERMINATION OF CHIMASSORB 944 IN THE COMMERCIAL POLYPROPYLENE TATREN AND FIBRE MADE THEREFROM

	Chimassorb 944 (% w/w)	
	Pellets	Fibre
	0.123	0.093
	0.116	0.112
	0.121	0.097
Mean	0.120	0.100
$s_R$	0.004	0.011

way of determining Chimassorb 944 by HPLC in a basic instrumental configuration. No special detector, gradient elution system or device for baseline subtraction is necessary. The method can be used to determine 0.02–1.0% (w/w) of Chimassorb 944 in polyolefins. No interferences from other additives currently used for the stabilization of polyolefins were noted.

In practice, phenolic and phosphite stabilizers are most likely to be present in the stabilizer package containing Chimassorb 944. Their concentration is usually of the same order of magnitude as that of Chimassorb 944. Frequently, their level is even lower than that of HALSs. Chimassorb 944, being a typical stabilizer of choice for fibre-grades PPs, is unlikely to be combined with UV screeners such as Tinuvin 327 or benzophenones. For this reason only the above-mentioned phenol–phosphite combi-

nations with Chimassorb 944 were analysed in the test runs. The results showed a good separation of this HALS from other components even when the latter were present in a threefold excess.

#### REFERENCES

- 1 *Chimassorb 944 Determination in Polypropylene, High Density Polyethylene and Low Density Polyethylene by the Total Nitrogen Content; Analytical Method KC-65/1*, Ciba-Geigy, Basle 1980.
- 2 V. Mika, L. Preisler and J. Sodomka, *Polym. Degrad. Stabil.*, 28 (1990) 215.
- 3 W. Freitag, *Fresenius' Z. Anal. Chem.*, 316 (1983) 495.
- 4 Li, Peiji et al., *Fenxi Huaxue*, 13 (1985) 664; *C.A.*, 104 (1986) 51459e.
- 5 *Chimassorb 944 and Chimassorb 81 Determination in Polyolefins*, Analytical Method KC-71/2, Ciba-Geigy, Basle, 1982.
- 6 P. Perstein and P. Orme, *J. Chromatogr.*, 325 (1983) 87.
- 7 S. G. Gharfeh, *J. Chromatogr.*, 389 (1987) 211.
- 8 W. Freitag, *J. Chromatogr.*, 450 (1988) 430.