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Determination of polymeric hindered amine light stabilizers in polyolefins by high-performance liquid chromatography

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ABSTRACT

Thin-layer and high-performance liquid chromatography procedures were used for the identification and quantitative determination of the polymeric hindered amine light stabilizers Chimassorb 944 and Cyasorb UV 3346 in polyolefins. After extraction from the polymer by the appropriate solvents, the hindered amine light stabilizers solution was qualitatively tested by thin-layer chromatography and successively analysed with a separation technique described as size-exclusion non-aqueous reversed-phase chromatography using traditional high-performance liquid chromatography equipment. The stationary phase was a non-polar styrene–divinylbenzene copolymer. The mobile phase was tetrahydrofuran containing diethanolamine. Both hindered amine light stabilizers were eluted at times ranging from 10 to 19 min and detected by UV at 239 nm, also showing a specific molecular mass distribution of their telomers. Interference due to other stabilizers was determined by a second elution of the same extraction solution after selective treatment on silica-gel cartridge.

INTRODUCTION

Since the commercial introduction of hindered amine light stabilizers (HALSs), increasing interest has been shown in studies of their protective mechanisms and of their practical use in industrial stabilizing packages for polyolefins, even at low concentrations and in the presence of other types of additives. Several analytical investigations aiming at their identification and quantitative determination in polymers have been carried out. Among the various analytical techniques, the liquid chromatographic approach appears to be one of the most adequate for both specificity and sensitivity.

In the case of monomeric HALSs, several methods have appeared in the literature concerning common commercial products [1–4]. In the field of polymeric HALSs, some spectroscopic [5,6], pyrolysis–gas chromatographic (GC) [7] and, more recently, high-performance liquid chromatographic (HPLC) [8–10] procedures have been proposed for the commercial stabilizers Chimassorb 944 and Tinuvin 622 (Ciba-Geigy, Basle, Switzerland).

This paper describes liquid chromatographic procedures suitable for identification and quantitative determination of Chimassorb 944 and Cyasorb UV 3346 (Cyanamid) polymeric HALSs in crystalline polyolefins. The proposed procedures provide considerable advantages in comparison with other available methods, such as:

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the requirement for traditional thin-layer chromatographic (TLC) and HPLC equipment (isocratic conditions and UV detector); the low detection limit (down to 1.0 μg of Chimassorb 944 and 0.5 μg of Cyasorb UV 3346, corresponding to a concentration of 10 and 5 ppm in the polymer sample, respectively) as well as good recovery (about 95%) from the polymer; the removal of interference from other additives used along with polymeric HALSs commercial stabilization packages; and qualitative information on the molecular mass distribution profile of the HALSs as produced, and after polymer extraction.

EXPERIMENTAL

HPLC apparatus

A Varian Model 5500 liquid chromatograph was employed, equipped with a Rheodyne 7125 injection valve and a selection of 100-, 200- or 500-μl loops, a diode array Varian Polychrome 9060 detector, and a DS 651 data station. The analytical columns were Waters Ultrastyragel 1000 Å (30 × 0.78 cm I.D.; code 8552) and Waters Ultrastyragel 500 Å (30 × 0.78 cm I.D.; code 8551) connected in series. Moreover, the injection system may include a direct injection pre-selective silica-gel cartridge (Alltech code 20974) and a Luer-Hub syringe (5 ml).

TLC apparatus

Pre-coated TLC plates (20 × 20 cm) with a layer thickness of 0.25 mm of silica gel 60 F254 (code 11798, Merck, Darmstadt, Germany) were used. A Camag Linomat IV sample application device was employed for sample deposit.

Reagents

Chimassorb 944 and Tinuvin 770 are commercial products supplied by Ciba-Geigy; Chimassorb 905 is a monomeric HALS not commercially available and was provided by Ciba-Geigy; Cyasorb UV 3346 is a commercial product supplied by Cyanamid (Wayne, NJ, U.S.A.). *n*-Hexane, ethyl acetate, chloroform, 2-propanol, methanol, ammonium hydroxide, xylene, tetrahydrofuran (THF) (stabilized) and diethanolamine were all reagent grade obtained from C. Erba (Milan, Italy). Tetrahydrofuran (unstabilized), HPLC grade, was supplied by Merck.

Extraction procedure

A weighed polymer sample (2.5 g) is dissolved in 80 ml of xylene by refluxing for 30 min under stirring. After cooling to about 100°C, 160 ml of 2-propanol are added through the condenser under vigorous stirring. The precipitated polymer is filtered at room temperature under vacuum, and washed with xylene–2-propanol (1:2, v/v). The filtered solution is evaporated to dryness in Rotavapor and the residue dissolved and brought to 10 ml with tetrahydrofuran (stabilized). If the polymer sample is in the form of fibers, powders or flakes, a simplified extraction procedure might be applied, as follows: 10 g of polymer are extracted with 50 ml of tetrahydrofuran at room temperature under stirring for about 1 h; this solution may be directly injected into the chromatograph.

TLC qualitative analysis

A portion (5–50 μl, according to the expected sample concentration) of extraction solution and equivalent amounts of standard solutions of pure additives are spotted on a pre-coated TLC plate. The plate is eluted in the ascending mode with *n*-hexane–ethyl acetate (7:3, v/v), and after drying at room temperature eluted again with chloroform–methanol (92.5:7.5, v/v), which has been previously saturated by shaking it with a 28° Bè ammonium hydroxide solution.

The first elution run (16–17 cm) removes interferences from extracted oligomers and other stabilizers such as phenols, phosphites, phosphonites, thioesters etc. The second elution run (10–11 cm) allows Chimassorb 944 and Cyasorb UV 3346 to separate.

After drying, the chromatograms are developed by chlorination with chlorine gas or *tert.*-butyl hypochlorite, and then sprayed with a potassium iodide (0.5%, w/v) and soluble starch (0.5%, w/v) mixed acqueous solution [11,12]. Dark violet–blue spots appear on a pale blue background. Chimassorb 944 and Cyasorb UV 3346 are identified as sequences of spots at R_F = 0.3–0.75 and R_F = 0.12–0.5, respectively.

HPLC analysis

The sample solution and proper external standard solutions in THF were injected into the chromatograph by means of a sample loop. The chromatographic conditions were as follows. Mobile phase: 0.02 *M* diethanolamine in HPLC-grade THF. Flow-rate: 1.0 ml/min. Column temperature: 40°C. Detector wavelength: 239 nm. Data station: area integration in the "group peaks" mode from 10 to 16.5 min elution time and "horizontal forward baseline" from 10 to 22 min. Typical chromatograms of two Chimassorb 944 are shown in Fig. 1. Fig. 2 shows the chromatogram of the extracted solution of an actual stabilized polymer including Chimassorb 944 and some additional antioxidants.

Retention times of Chimassorb 944 range from 10 to 19 min. On the other hand, the most frequently used antioxidants in commercial polymers have retention times of 14–20 min for instance Irganox 1010 is eluted at about 14 min retention time.

RESULTS AND DISCUSSION

As clearly shown in Fig. 2A, interference may arise from several common polymer additives. When this is the case, accurate quantitative evaluation of Chimassorb 944 requires removal of these interfering peaks. To this purpose, a second injection of the extracted solution is performed under exactly the same chromatographic conditions, but after selective treatment of the solution on a silica cartridge (see Experimental). One cartridge is used for each sample injection. Such treatment causes Chimassorb 944 to be completely retained on silica but allows elution of all the other stabilizers, thus quantitatively evaluated as the overall interfering peak area.

Fig. 2B shows the same sample as Fig. 2A after silica cartridge pre-treatment.

The concentration of Chimassorb 944 is calculated by subtracting the total interfering area originating from the second sample injection from the total area of the first, and by then comparing the resulting difference with the standard area, following the usual external standard method.

The same experimental conditions can be applied to the qualitative and

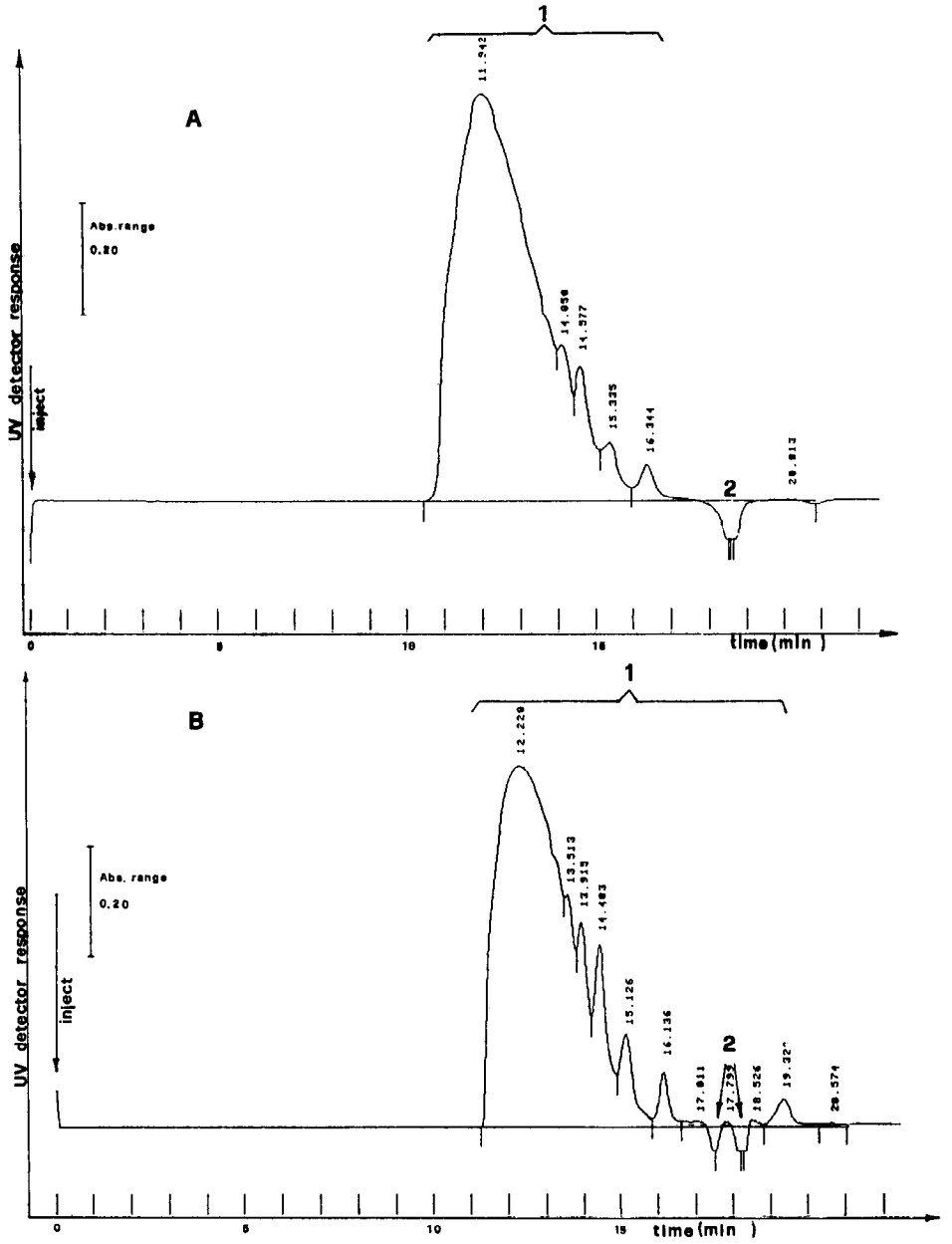

Fig. 1. (A) Chromatogram of Chimassorb 944 (commercial product A), 125 μg. (B) Chromatogram of Chimassorb 944 (commercial product B), 125 μg. Peaks: 1 = Telomers of Chimassorb 944; 2 = THF solvent (negative peak).

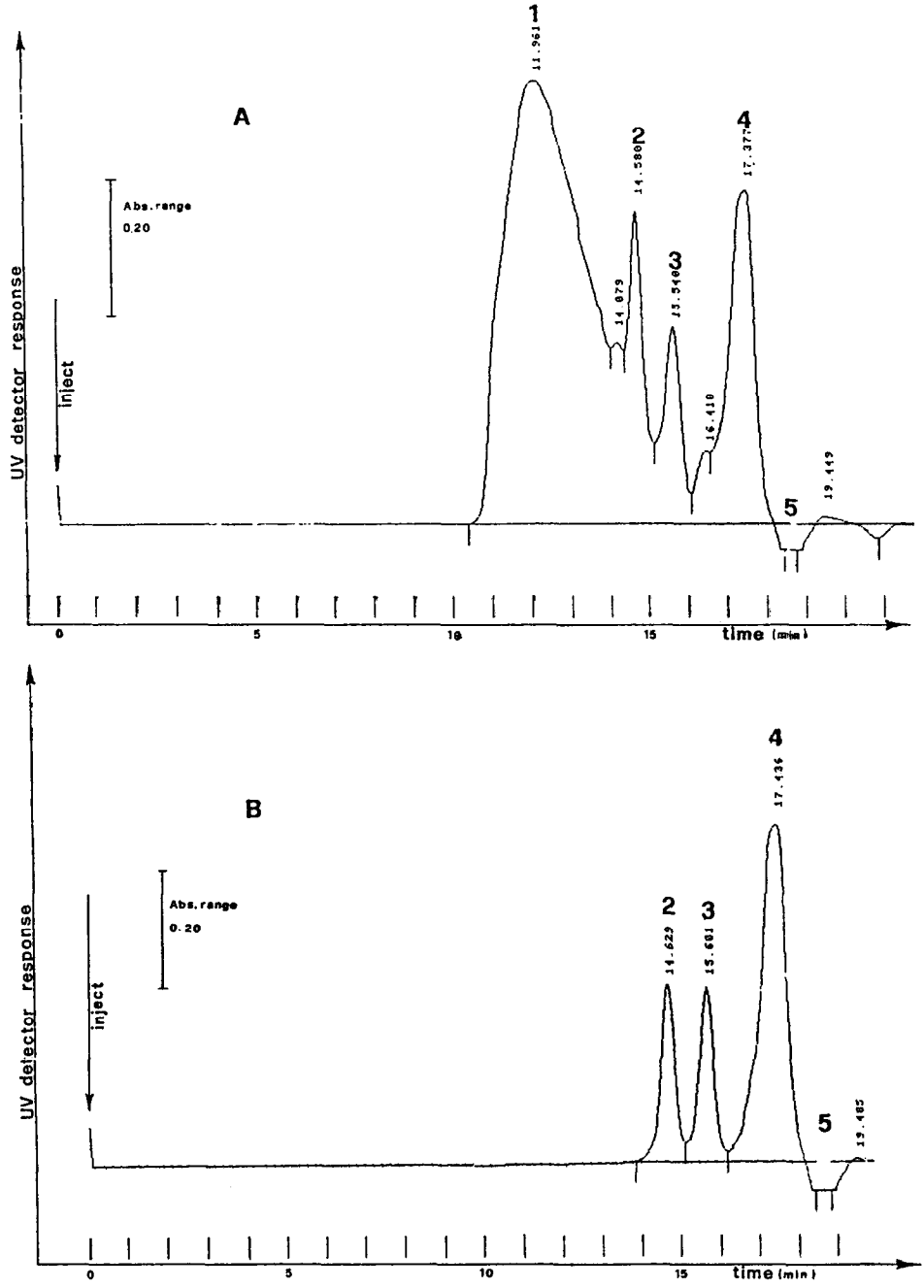

Fig. 2. (A) HPLC trace of a polymer sample extract (direct injection). (B) HPLC trace of a polymer sample extract (injection after pre-treatment on silica gel cartridge). Peaks: 1 = Chimassorb 944 commercial product A (125 μg); 2 = Irganox 1010 (75 μg); 3 = Irganox 1076 (135 μg); 4 = BHT (tetrahydrofuran stabilizer); 5 = THF solvent (negative peak).

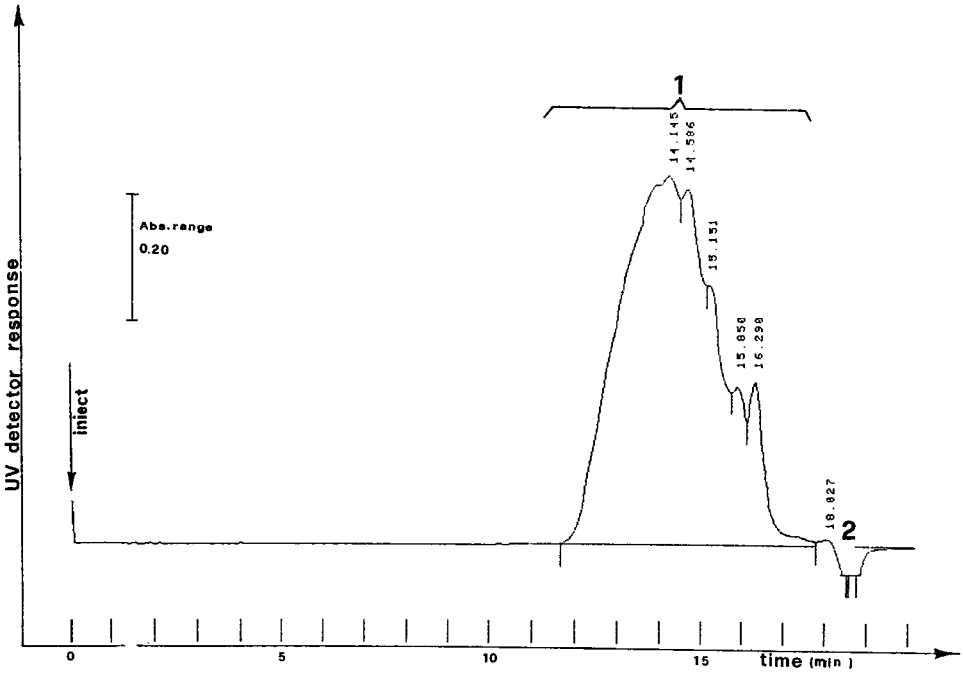

Fig. 3. Chromatogram of Cyasorb UV 3346. Peaks: 1 = telomers of Cyasorb UV 3346 (62 μg); 2 = THF solvent (negative peak).

quantitative evaluation of Cyasorb UV 3346 polymeric HALS of similar structure (Fig. 3).

The chromatograms in Figs. 1 and 3 provide useful qualitative information on the molecular mass distribution profile of the above HALS, with a better selectivity towards the medium–low molecular masses.

Fig. 4 shows the chromatogram of Chimassorb 944 and a mixture of Tinuvin 770 and Chimassorb 905 monomeric HALSs as reference compounds with known molecular masses of 427 and 2174, respectively.

Finally, a comparison of Figs. 1 and 2 demonstrates that Chimassorb 944 extracted from the polymer in the present conditions (Fig. 2) shows a similar, unchanged molecular mass distribution profile when compared to the original additive (Fig. 1).

The extraction procedure and the chromatographic conditions described in the present study seem to be adequate, with relevant adjustments, for the analysis of other polymeric HALS —even those which are not detected by UV (*e.g.*, Tinuvin 622, Ciba-Geigy), provided that, in this instance, the UV detector is replaced by a refractive index detector.

Additional work is in progress in our laboratory now, aimed at extending the present analytical conditions, and at developing proper methods to determine Tinuvin 622 and other interesting polymeric HALSs in polyolefins.

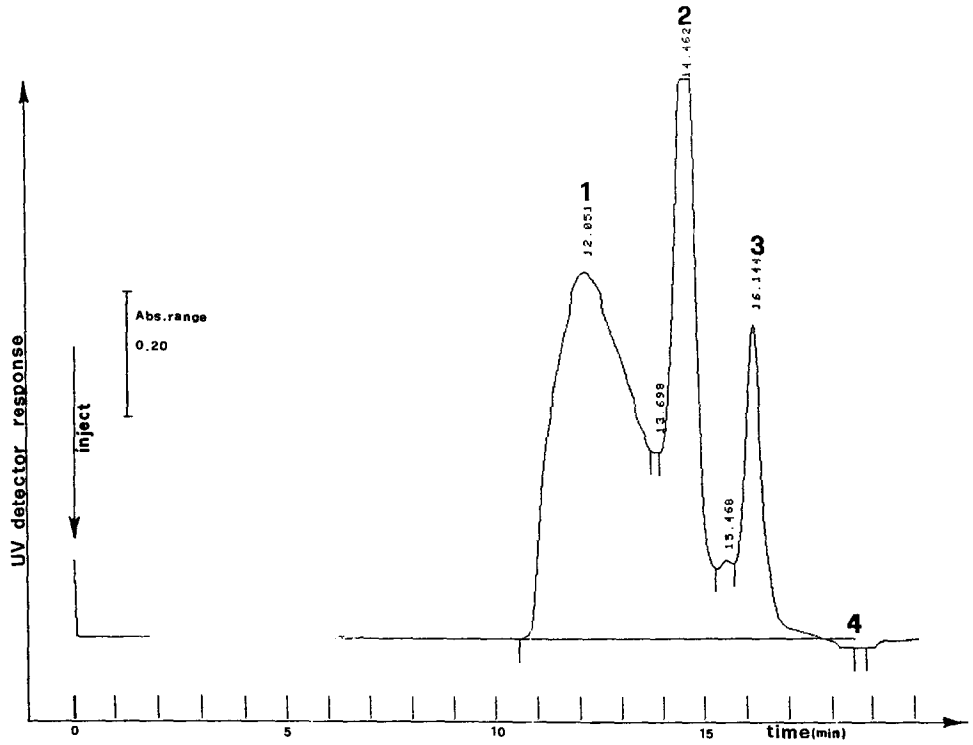

Fig. 4. Chromatogram of a mixture of Chimassorb 944, Chimassorb 905 and Tinuvin 770. Peaks: 1 = Chimassorb 944 (commercial product A) (100 μg); 2 = Chimassorb 905, molecular mass 2174 (25 μg); 3 = Tinuvin 770, molecular mass 427 (1250 μg); 4 = THF solvent (negative peak).

Accuracy

The accuracy of the present method appears satisfactory, as shown by the average concentrations of Chimassorb 944 determined by HPLC in comparison with those evaluated by nitrogen analysis [13,14] on polypropylene samples at 0.025% and 0.15% of additive: the recovery ranges from 90 to 100% (Table I). Moreover, nitrogen analysis carried out on polymers after extraction shows that the extraction procedure is efficient as no residual additive is detected.

TABLE I

RECOVERY TESTS ON POLYPROPYLENE PELLETS BY THE HPLC METHOD

Sample	Chimassorb 944 by nitrogen analysis (%, w/w)	Chimassorb 944 by this HPLC method (%, w/w)	Recovery (%)
A	0.027	0.025	92
B	0.145	0.0150	103
C	0.138	0.140	101

Interference

As outlined above, interference from the usual antioxidants and UV stabilizers is avoided. However, each monomeric and polymeric HALS may interfere to some extent, depending on its chemical structure. For instance, Tinuvin 770 interferes with Chimassorb 944 determination at weight ratios Tinuvin 770:Chimassorb 944 $\geqslant 8$.

Detection limits

An effectively low detection limit can be achieved for either stabilizer, *i.e.*, 1.0 μg for Chimassorb 944 and 0.5 μg for Cyasorb 3346, corresponding to a concentration of 10 and 5 ppm in the polymer sample, respectively.

Precision

The repeatability of the HPLC method was evaluated on the basis of several independent runs of the same polypropylene sample, containing 0.17% of Chimassorb 944. The following results were obtained: average value (%, w/w): $\bar{X} = 0.167$. Relative standard deviation: $s/\bar{X} = 0.030$. Confidence limits (95% probability) for a single analysis (%, w/w): ± 0.012 ($\pm 7\%$).

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