Pyrolytic analysis of complex stabilizers in polypropylene

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SUMMARY

Pyrolysis gas chromatography was used to determine high-molecular-weight stabilizers in polypropylene. Chimassorb 944®, Tinuvin 622® and Sandostab P-EPQ® were pyrolyzed and characteristic fragments were separated on a non-polar capillary column. After the retention times of characteristic fragments had been determined, polypropylene extract was analyzed to identify the limitations of using a single characteristic peak and retention time data for quantitative determination of stabilizers. The use of nitrogen–phosphorus detection decreases interference from fragments that do not contain nitrogen or phosphorus. There is no significant interference from the extraction solvent or the polymer matrix.

INTRODUCTION

Quantitative and qualitative determination of complex stabilizers in polypropylene has been the focus of interest[1–22]. Successful separation of complex stabilizers requires a well balanced compromise between resolution, separation temperature and analysis time. Thus, a large amount of effort has gone into the characterization of each of these variables.

Stabilizers are added to polymers to protect the resin from a variety of degradation processes. Antioxidants are used to prevent degradation caused by atmospheric oxygen[3]. UV absorbers are added to polymers to decrease photodegradation induced by sunlight or other UV-rich light source[4]. A large number of antioxidants and UV absorbers of different chemical compositions are available to meet these special requirements. Since these additives are present in the polymer matrix at low concentrations, the analysis of polymer extracts has been used commonly[5].

Polymer additives may be classified by their functional group. Accordingly, hindered amines, phosphites, quenchers, hindered phenols, benzotriazoles and benzophenones[3–8] may be mentioned. The typical molecular weight for these stabilizers may be in the range of 200–2000 and >2000 for polymeric additives. In most cases high-molecular-weight stabilizers produce longer outdoor life for most polymers[4].

The qualitative and quantitative analysis of additives can be achieved by chromatographic methods. Supercritical fluid chromatography (SFC)[2], gas chromatography (GC) or liquid chromatography are frequently used. SFC is a sensitive method, however, it is limited by the high molecular weight. A high-resolution SFC technique was reported recently[2] for the analysis of additives of molecular mass up to 1178. Universal or sensitive selective detect ion methods, *e.g.* flame ionization detection (FID) or nitrogen–phosphorus detection (NPD) make GC techniques particularly attractive. However, thermal instability may limit the analysis of high-molecular-weight stabilizers. Typically, GC techniques are not feasible for molecules with a molecular weight larger than 800. Although high-performance liquid chromatography (HPLC) does not have the molecular weight limitation, it lacks a detection system comparable to that of GC techniques[2,19–21]. Nevertheless, GC is a frequently used method, in spite of its limitations by the high molecular weight and thermal instability of many complex stabilizers[6]. This thermal instability may be utilized when pyrolysis (Py) is employed to generate characteristic fragments.

Unfortunately, to date, such applications have been substantially hindered by the lack of suitable analytical methodology. The concentration of characteristic fragments is too low at lower pyrolytic temperature, while at higher temperature, the fragmentation would produce too many peaks for a universal detection method. The application of selective GC detectors can improve pyrolytic determination of polymeric stabilizers. We have recently begun to apply Py–GC techniques for the analysis of complex stabilizers in polypropylene. The pyrolysis is performed at relatively low temperature to achieve characteristic fragmentation.

Characteristic fragments containing nitrogen and phosphorus are detected by NPD. Chimassorb 944®, Tinuvin 622® and Sandostab P-EPQ® were chosen for the development of this method. To illustrate typical chemical structures of polymeric stabilizers, two structures are depicted in Fig. 1.
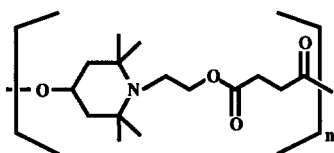
TINUVIN 622
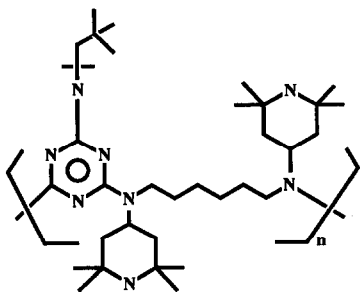
CHIMASSORB 944

Fig. 1. Typical chemical structures of complex stabilizers[6].

Determination of these stabilizers is especially difficult because of their polymeric structure. Sandostab P-EPQ was analyzed by SFC–Fourier transform infrared spectroscopy (FT-IR) using microscopic accessories and solvent eliminator interface[2]. However, this method may not be feasible for Tinuvin 622 and Chimassorb 944. Examples in which Py–GC has been used to achieve analysis of complex stabilizers in polymers are limited in the literature. A Py–GC method using packed columns was described previously[1] for the analysis of Tinuvin 622 and Chimassorb 944. Complicated sample preparation, high retention times, overlapping characteristic peaks and low recovery (72–94%) limited the practicality of this method.

Presently, we wish to report the results of our research in which the sample preparation consists of only a one-step extraction and the recovery rate was 89.9–99.4%. The pyrolysis temperature was optimized to produce nitrogen- or phosphorus-containing characteristic fragments, which were separated on a capillary column and detected by NPD.

EXPERIMENTAL

Chemicals

The antioxidant Sandostab P-EPQ was manufactured by Sandostab and the UV stabilizers Chimassorb 944 and Tinuvin 622 were obtained from Ciba-Geigy. Polypropylene was used as a polymeric matrix. The solvents toluene and methylene chloride were purchased from Fisher Scientific in analytical grade.

Apparatus

The chromatographic system consisted of a Hewlett-Packard Model 5890A with FID and NPD while a Quadrex capillary aluminum clad column was used for separation (25 m × 1.7 μm I.D.). The pyrolysis unit was a Scientific Glass Engineering Pyrojector. The operation conditions of GC were: detector temperature 260°C, oven temperature, initial 70°C, rate 5°C/min, final 130°C, splitless injector temperature 240°C. The pyrojector temperature was set at 800°C. Helium was used as the carrier gas for the pyrojector. The flow-rates were set as follows: column 2.43 ml/min, injector purge 6 ml/min, pyrojector purge 1.5 ml/min. Data were analyzed using Turbochrom software. Data were stored on hard disk and were recalled for data analysis.

Sample preparation

An appropriate sample size (0.2–2.0 g) was obtained from the polymer and was then transferred into 50 ml of toluene. The solvent was refluxed for 5 min and the polymer was then precipitated by adding methylene chloride. The solution was filtered to remove the precipitated polymer. Most of the solvent was then evaporated to concentrate the stabilizer solution using dry nitrogen purging.

Calibration solutions

Several dilutions of Tinuvin 622, Chimassorb 944 and Sandostan P-EPQ solutions were prepared in toluene. These solutions were injected in the same way as the polymer extracts into the pyrojector-GC system.

TABLE I

RETENTION TIME OF CHARACTERISTIC STABILIZER PEAKS

Stabilizer	Retention time (min)
Chimassorb 944	1.26 ± 0.02
Tinuvin 622	1.10 ± 0.02
Sandostab P-EPQ	2.36 ± 0.02

RESULTS AND DISCUSSION

　　Initially, toluene solutions of the additives in Table I were injected into the pyrojector to determine the retention times of the fragments. As mentioned previously, NPD and FID were used to detect the separated fragments. The FID chromatograms obtained showed very complex fragmentation (Fig. 2). The fragments were not well resolved and different additives had fragments of similar retention times. The large solvent peak also limited the usefulness of the chromatogram. Using NPD, on the other hand, decreased the number of peaks considerably. Typical pyrograms of Tinuvin 622, Chimassorb 944 and Sandostab P-EPQ are shown in Figs. 3, 4 and 5, respectively. All the fragments are well resolved and demonstrate the capability of capillary Py–GC–NPD for analysis of complex polymer additives within a few minutes. Peak retention times were found to be very reproducible for identification purposes. This may be attributed to proper temperature control of the pyrojector and column. No cross interference was found when all three additives were injected simultaneously.

　　After careful examination of the chromatograms, one characteristic peak was chosen for each stabilizer (Table I). The area of these peaks was found to be proportional to the amount of stabilizers. Calibration curves were obtained for each stabilizer by using the peak with 1.28 ± 0.02 min retention time for Chimassorb 944, 1.10 ±
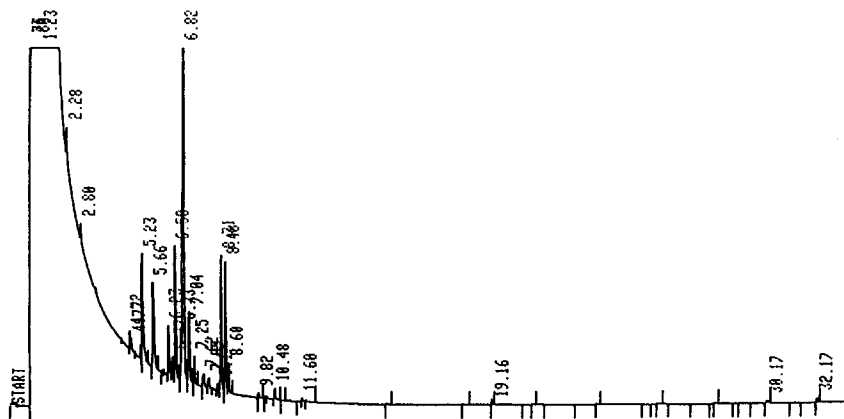

Fig. 2. Typical chromatogram of complex fragmentation of Chimassorb 944 detected by FID. 800°C.
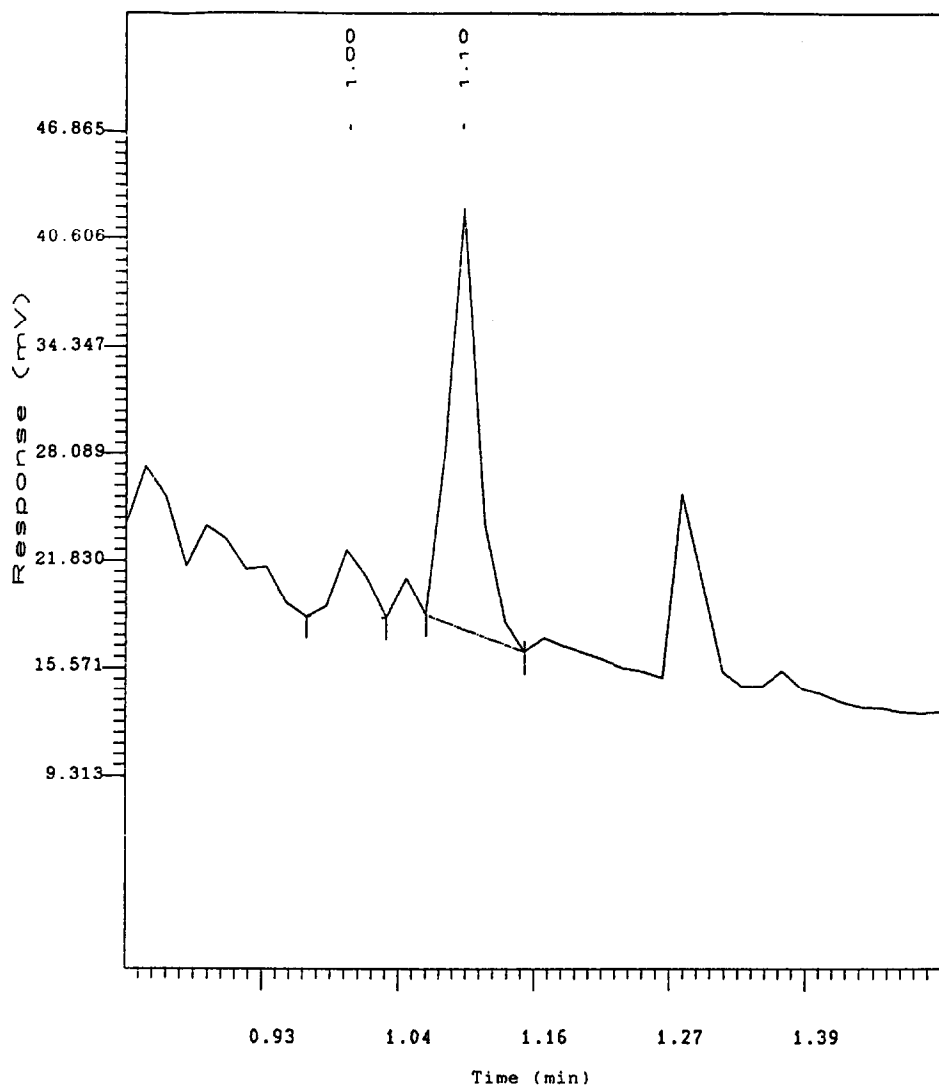
Fig. 3. Typical pyrogram of Tinuvin 662.

0.02 min for Tinuvin 622 and 2.36 ± 0.02 min for Sandostab P-EPQ. The relatively short retention times of these characteristic peaks permitted fast analysis and decreased interference.

Calibration solutions were injected into the pyrojector–GC system and calibration curves were obtained for each stabilizer by plotting concentration *versus* peak area of the characteristic peak. Solutions in toluene were made to obtain concentrations of 50–10 000 ppm. The calibration curves for Chimassorb 944, Tinuvin 622 and Sandostab P-EPQ are depicted in Fig. 6, 7 and 8, respectively.
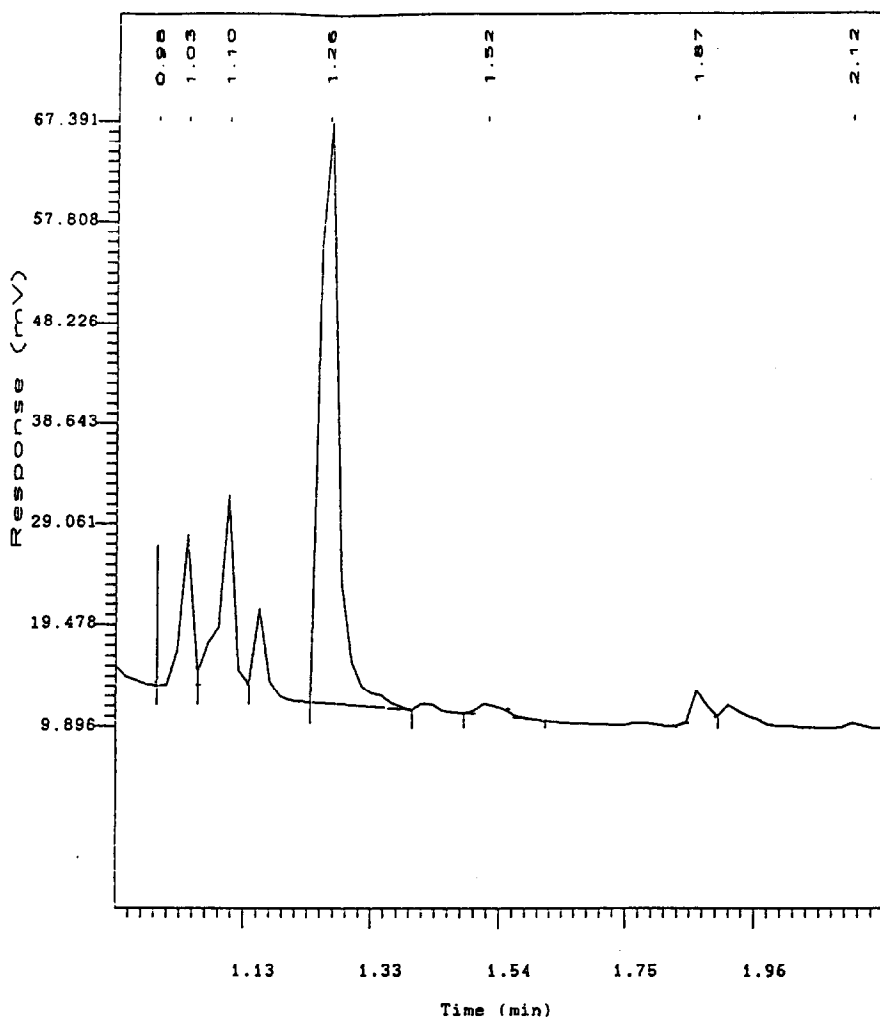
Fig. 4. Typical pyrogram of Chimassorb 944.

The polymer extraction samples, prepared as described in the Experimental section, were quantitized by the standard addition method. The results obtained for different amounts of samples are shown in Tables II, III and IV. Detection limits less than 50 ppm were achieved with this method. The method resulted in a wide dynamic range with no significant deviation observed from linearity up to 10 000 ppm. For concentrations higher than 10 000 ppm, dilutions of the final extract should be made to preserve the linearity.

The preliminary results reported here demonstrate the analytical power of combining capillary Py–GC with the selectivity of NPD for the quantitative and qualitative analysis of complex high-molecular-weight and polymeric stabilizers. This method has been successfully used for the analysis of unknown concentrations of
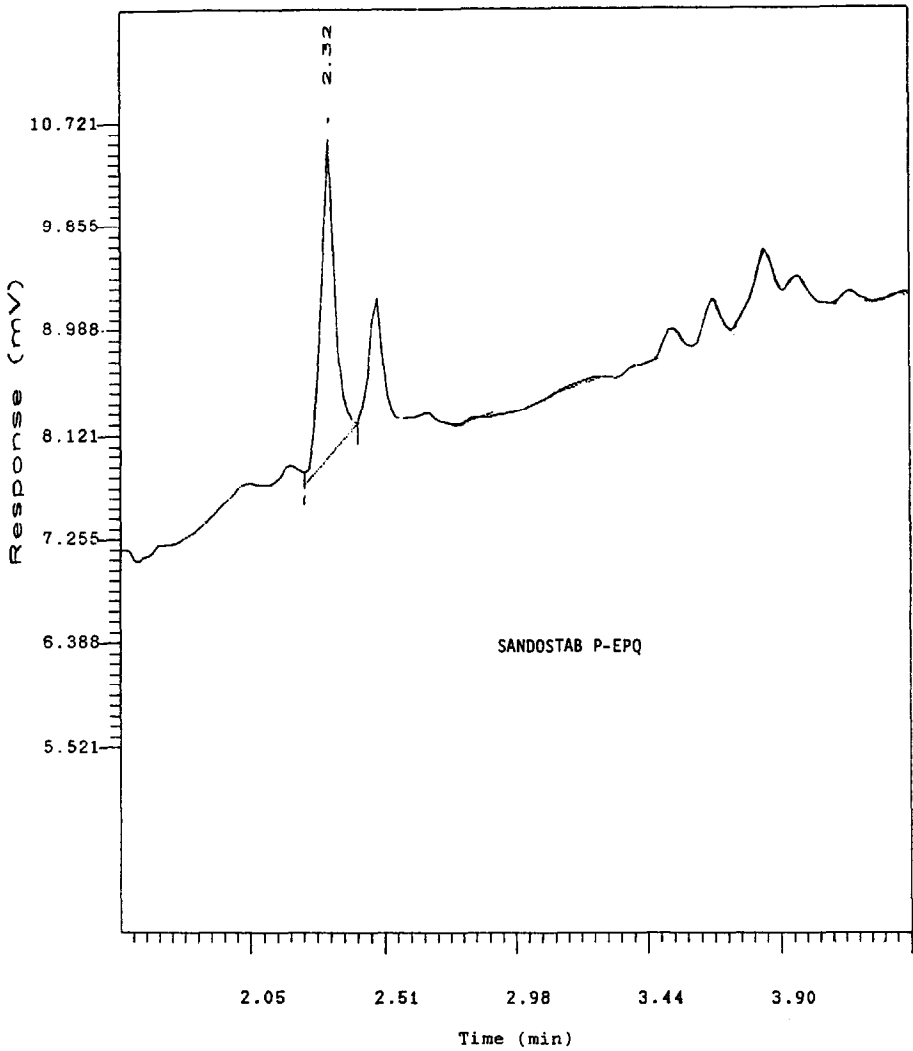
Fig. 5. Typical pyrogram of Sandostab P-EPQ.

TABLE II

RECOVERY OF TINUVIN 622 FROM POLYPROPYLENE

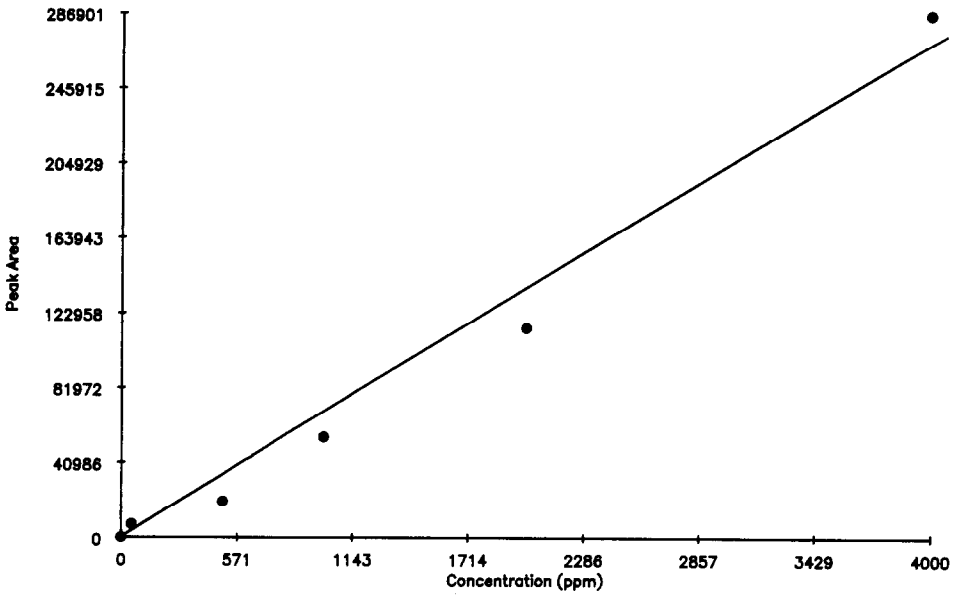| Target (ppm)	Concentration found (ppm)	Recovery (%)
10 230	8790	86.0
7350	7189	97.8
5500	5323	96.7
218	210	96.3

Fig. 6. Calibration curve for Chimassorb 944.

complex polymeric additives in polypropylene samples. This method should create significant industrial interest because of the simplified sample preparation requirements, the short analysis time and the good recovery rate. Further studies are necessary to determine the extent of interference of other complex stabilizers.
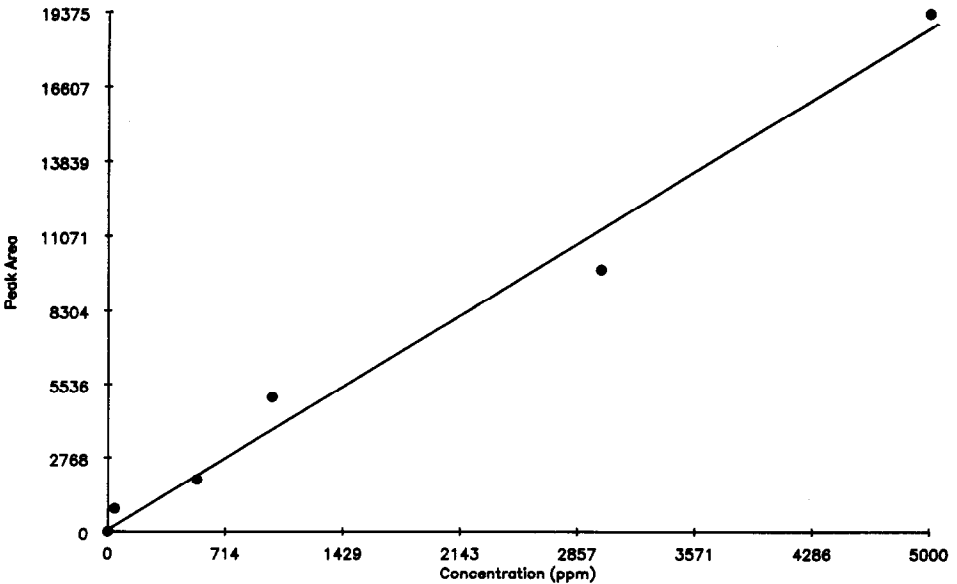

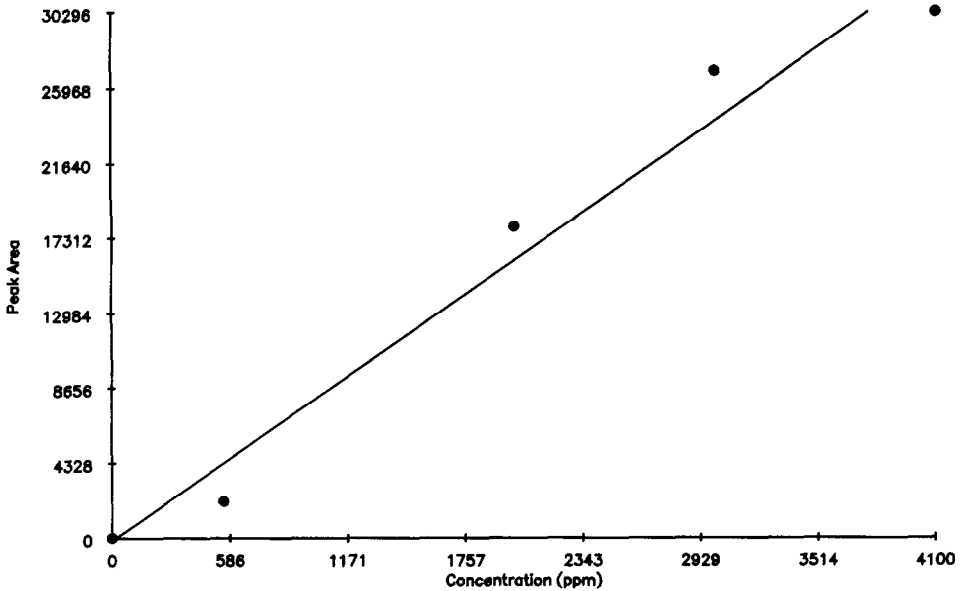Fig. 7. Calibration curve for Tinuvin 622.

Fig. 8. Calibration curve for Sandostab P-EPQ.

TABLE III

RECOVERY OF CHIMASSORB 944 FROM POLYPROPYLENE

Different dilutions of 8000 and 550 ppm were analyzed.

Target (ppm)	Concentration found (ppm)	Recovery (%)
8000	7947	99.9
8000	8214	102.7
550	530	96.4
550	528	96.0
50	46	92.0

TABLE IV

RECOVERY OF SANDOSTAB P-EPQ® FROM POLYPROPYLENE

Target (ppm)	Concentration found (ppm)	Recovery (%)
10 280	9230	89.8
9030	8831	97.9
1300	1298	99.8
1180	1122	95.0

REFERENCES

1 P. Orme and P. Perlstein, *J. Chromatogr.*, 325 (1985) 87–93.
2 M. W. Raynor, K. Bartle, I. Davies, A. Williams, A. Clifford, J. Chalmers and B. Cook, *Anal. Chem.*, 60 (1988) 427–433.
3 M. Dexter, in H. F. Maek (Editor), *Encyclopedia of Polymer Science and Engineering*, Vol. 2, Wiley, New York, 1985, pp. 371–420.
4 G. R. Lappin, *Encyclopedia of Polymer Science and Technology*, Vol. 14, Interscience, New York, 1971, pp. 125–147.
5 B. N. Norbert (Editor), *Encyclopedia of Polymer Science and Technology*, Vol. 12, Interscience, New York, 1970, 725–737.
6 *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 23, 1983, Wiley, New York, 615–627.
7 A. Hoff and S. Jacobsson, *J. Appl. Polym. Sci.*, 29 (1984) 465–480.
8 R. Juvet, J. Smith and K. Li, *Anal. Chem.*, 44 (1971) 49–56.
9 W. Blum and L. Damascemol, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 472–476.
10 M. Krull, A. Kogerman, O. Kirret, J. Plogan, A. V. Yudin and A. S. Schevchenk, *Eesti NSV Tead. Akad. Toim. Recm.* 27 (3) (1978) 171–175.
11 C. Vogt and S. Kapila, *J. Chromatogr. Sci.* 17 (1979) 546–550.
12 Y. Gurvich, E. L. Styskin and A. A. Grinberg, *Kauch. Rezina*, 30 (1971) 53–54.
13 P. Perlstein, *Anal. Chim. Acta*, (1983) 155–173.
14 R. Basher, K. Chakbraborty and G. Scott *Polym. Degradation Stab.*, 4 (1982) 1.
15 N. S. Allen and A. Parkinson, *Polym. Degradation Stab.*, 4 (1982) 161.
16 N. S. Allen, A. Parkinson J. L. Gardet and J. Lemaire, *Polym. Degradation Stab.*, 5 (1983) 35.
17 W. Freitag, *Anal. Chem.*, 316 (1983) 495–501.
18 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 300 (1984) 303–355.
19 D. Munteanu, A. IsFan, C. IsFan and I. Tincul, *Chromatographia*, 23 (1987) 7–14.
20 M. A. Holney and W. A. Dark, *J. Chromatogr. Sci.*, 18 (1980) 655–659.
21 F. Sevini and B. Marcato, *J. Chromatogr. Sci.*, 260 (1983) 507–512.
22 Santyo, *Brit. Pat.*, 1 196 224 (Jap. priority 22.61967).