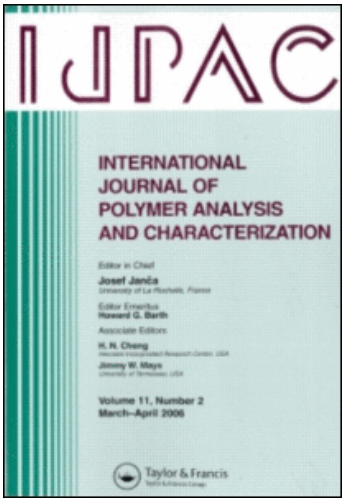

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HPLC Quantification of Thioether Antioxidants in Polyethylene after Dissolution of the Polymer under Pressure in an Aliphatic Solvent

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A new method is described for the quantitative determination of some sulfur-containing antioxidants in polyethylene (PE). The polymer matrix is dissolved in hot n-heptane/isopropyl alcohol, 97/3 v/v at 160°C under elevated pressure (0.33 MPa) and precipitated by cooling. The solution is injected directly into a normal-phase silica gel column flushed with the same solvent as used for the dissolution of the polymer. This method gave high recovery of the antioxidants, good repeatibility of the analysis (σ = 2.6%) and a low detection limit of 0.011 mg 4,4′-thiobis(3-methyl-6-*tert*-butylphenol) (Santonox R) /1 g PE; 0.074 mg ditetradecyl-β,β′-thiodipropionate (Chimox 14) / 1 g PE; and 0.125 mg dioctadecyl-β,β′-thiodipropionate (Irganox PS 802) /1 g PE.

Keywords: Polyethylene, antioxidants, HPLC

INTRODUCTION

Most plastics contain antioxidants, UV stabilizers, pigments, fillers, etc. Some of them, for example antioxidants, are present in very low concentration and the amount may change with time due to their migration out off

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the material, their decomposition and/or their chemical reactions with other substances. A decrease in concentration may negatively influence the physical properties of polymer materials. Therefore, knowledge of the amount of the antioxidants being present is of great value both for practical applications and in research on stabilization of polymers.

The determination of low concentrations of antioxidants within a polymer material is a difficult task, especially in the case of partially crystalline polyolefins. Conventional Soxhlet extraction is carried out with solvents, for example, chloroform, tetrahydrofuran, and acetonitrile, which do not dissolve the crystalline fraction; therefore, it can be expected that a small part of the antioxidant remains occluded in amorphous regions which are densely enclosed by crystalline materials. In practice, the extraction usually does give 100% recovery of the additive. Furthermore, conventional extraction requires a long time, and the solvent used for the extraction has to be evaporated and the residue containing the additive has to be redissolved in another solvent, which is more suitable for subsequent HPLC analysis.

It is known that hot n-heptane is a solvent for polyethylene [1]. Because the boiling point of n-heptane at atmospheric pressure is 99°C, dissolution of polyethylene in n-heptane requires the use of elevated pressure to keep heptane in liquid state at 160°C. Accordingly, the required pressure is only 0.45 MPa at 160°C [2].

As we have recently shown [3], the use of a pressure vessel enables the dissolution of polyethylene also in the mixture n-heptane/isopropyl alcohol, 100/0.5 vol. The solution obtained may then be directly injected into an HPLC column flushed with the same solvent. In this way, quantitative analysis of an antioxidant is substantially simplified—no additional evaporation, preconcentration, redissolution, etc. are necessary.

Recently we have used a new autoclave for dissolution of the polymer, which enables us to obtain more precise and reproducible results, and we have applied the improved procedure to the quantitative determination of one thiophenolic and two thioester antioxidants in polyethylene (Table I and Fig. 1).

The application of the above antioxidants is broad—they are used for stabilization of polyethylene, polypropylene, polystyrene, poly(vinyl chloride), polyamide and terpolymer acrylonitrile-butadiene-styrene [4].

Table II summarizes the HPLC systems for the analysis of 4,4′-thiobis(3-methyl-6-*tert*-butylphenol) and dioctadecyl-β,β′-thiodipropionate described in the literature. For ditetradecyl-β,β′-thiodipropionate, no literature reference could be found.

TABLE I Trade names and producers of thioether antioxidants given in Figure 1

Chemical Name *Trade Name*	*Producer*
4,4'-thiobis(3-methyl-6-tert-butylphenol)	
Santonox R	Monsanto, Brussels, Belgium
Antigene WX	Sumitomo Chem. Co., Ltd., Osaka, Japan
AO-736	Ethyl Corp., New York, N.Y., USA
Irganox 415	Ciba-Geigy A.G., Basel, Switzerland
Nocrac 300	Ouchi Shinko Chem. Ind. Co., Ltd., Tokio, Japan.
Seenox BCS	Shipro Kasei, Shiraishi, Japan
Antioxidant TMB6	Borg-Warner Chemicals, Washington, D.C., USA
Yoshinox SR	Yoshitami, Pharmaceutical Ind., Ltd., Tokio, Japan
ditetradecyl-β,β'-thiodipropionate	
Chimox 14	Chimosa- Chimica Organica, Bologna, Italy
Irganox PS 801	Ciba-Geigy, Basel, Switzerland
Carstab DMTDP	Cincinnati Milacron, Ohio, USA
dioctadecyl-β,β'-thiodipropionate	
Irganox PS 802	Ciba-Geigy, Basel, Switzerland
Antigene TPS	Sumimoto Chem. Co., Ltd., Osaka, Japan
Carstab DSTDP	Cincinnati Milacron, Ohio, USA
Negonox DSTDP	Imperial Chem. Ind., Ltd., London, England
Plastanox DSTDP	Cyanamid, GmbH, Frankfurt/M., Germany
Seenox DS	Shipro Kasei, Shiraishi, Japan
Sandostab 4020	Sandoz A.G., Basel, Switzerland
Chimox 18	Chimosa-Chimica Organica, Bologna, Italy
Hostanox VPSE-2	Hoechst A.G., Frankfurt/M., Germany

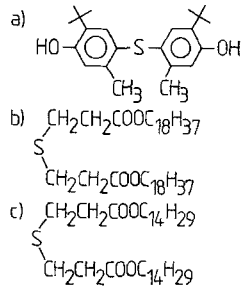

FIGURE 1 Structures of the antioxidants: a) 4,4'-thiobis(3-methyl-6-*tert*-butylphenol); b) dioctadecyl-β,β'-thiodipropionate; c) ditetradecyl-β,β'-thiodipropionate.

TABLE II LC systems for the separation of 4,4'-thiobis(3-methyl-6-tert-butylphenol) and dioctadecyl-β, β'-thiodipropionate described in the literature

Columm Packing	*Method*	*Eluent*	*Ref.*
4,4'-thiobis(3-methyl-6-tert-butylphenol)			
alumina	LSC	methanol/water	5
silica gel	LSC	benzene	6
		isooctane/ethylacetate/dichloromethane	7
		hexane/isopropanol	8
		heptane/isopropanol	10
		heptane/dichloromethane/isopropanol	10
		heptane/di-isopropylether/isopropanol	10
		heptane to dichloromethane, gradient	11,12
		hexane to dichloromethane gradient	13
reversed phase		methanol/water/butanol	10
		ACN; ACN/water	14
		methanol/water	15
PS/DVB	GPC	chloroform	16
		THF	17
		THF	18
dioctadecyl-β, β'-thiodpropionate			
PS/DVB	GPC	THF	9
		THF	18
		chloroform	16
reversed phase		ACN/THF/water, gradient	19,20
		ACN/THF/acetic acid	21
		acetone	22

As shown in Table II, n-heptane (or n-hexane) plus a polar modifier in combination with silica gel sorbent is a suitable system for LC identification of 4,4′-thiobis(3-methyl-6-*tert*-butylphenol) [8-13]. Therefore, after dissolution of a polymer sample in n-heptane/isopropyl alcohol a direct injection of a solution into an HPLC column appeared to be feasible for all additives shown in Figure 1.

EXPERIMENTAL

Instruments

The HPLC assembly consisted of an LC pump (model 510, Waters, Milford, MA), an injection valve with a 20-μL sample loop, a stainless-steel column 25 × 0.4 cm i.d. (Knauer, Berlin, Germany) packed with 13-μm particles of silica gel Silpearl (Glass Works Kavalier, Votice, Czech

Republic), an UV/visible detector (model 975, Jasco Co., Tokyo, Japan), and a recorder (model 540, Kontron, Basel, Switzerland). The detector also measured the UV spectrum of the analyzed components. The data from the detector were digitalized and integrated with a computer program.

The sample solutions were filtered during transfer into the syringe used for injection through a glass-fiber filter with pore size of about 3 μm (Tessek, Prague, Czech Republic).

For the dissolution of polymer samples, an autoclave (Model II, 300 mL/100 bar, Roth, Karlsruhe, Germany) with an autoclave vessel volume of 300 mL was used (Fig. 2). The autoclave was equipped with a pressure gauge and thermostat, and could be used to purge the contents of the vessel with an inert gas and to mix the contents. Original seals of the autoclave are made from polytetrafluoroethylene and could not be used repeatedly; they were replaced by Viton^R seals produced by Rottner, St. Michael, Austria.

For quantitative measurements the autoclave was used without the pressure gauge, since condensation of the solvent within this device changed the concentration of the components in the solution.

Chemicals

Solvents used were n-heptane (for synthesis) and isopropyl alcohol (p.a.) (Merck, Darmstadt, Germany). Commercial Santonox R, Chimox 14, and Irganox PS 802 were used (cf. Table I and Fig. 1).

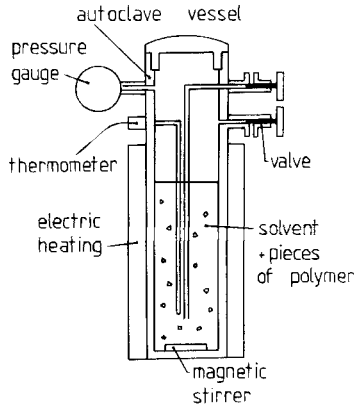

FIGURE 2 Scheme of the autoclave used for the dissolution of the polyethylene samples.

The polyethylene PE without additives and the polymer containing the antioxidants was PE-MD (density = 0.934 g/mL, M_w = 120 kg/mol) obtained from Neste Oy Chemicals, Porvoo, Finland.

Procedure

The polymer sample was cut in small pieces with dimensions 1–3 mm. One gram of the polymer and 100 mL of the mixture n-heptane/isopropyl alcohol (97/3 v/v) was added to the pressure vessel. After closing the autoclave vessel, the content of the autoclave was heated with mixing. After 15 min, the temperature of solvent reached 160°C and was kept constant for 75 min. The pressure in the vessel was about 0.33 MPa. The pressure vessel then was cooled in cold water. The autoclave was opened and the content of the vessel was poured into a glass container in which a G4 Jena glass filter was inserted. The sample solution was then aspirated from the glass filter into a glass syringe through a glass-fiber filter with 3-μm pore size and injected (at least three times) into the HPLC column. The UV absorbance of effluent at 250 nm was monitored with the detector and the height of peaks were measured manually. The areas of peaks were evaluated also by a personal computer.

The signal of the detector corresponding to the antioxidant was calibrated using a standard solution of the antioxidant in n-heptane/isopropyl alcohol, 97/3 v/v (0.016 mg/g) prepared by weighing. It was prepared by dilution of a more concentrated solution of the additive (0.16 mg/g).

The concentration of isopropyl alcohol in n-heptane controls retention in the HPLC column. A decrease of the concentration of the alcohol causes increased retention of the antioxidant.

Preparation of Model Samples

One gram of PE-MD without additives was mixed with 67 g (*i.e.*, about 100 mL) of a standard solution of Santonox R dissolved in n-heptane/isopropyl alcohol, 97/3 v/v. The advantage of this method is that the concentration of the additive is precisely known and the results are not influenced by the inhomogeneous distribution of the additive in the polymer.

Authentic Samples

All samples were taken from a tube made of PE-MD containing 0.1 wt % Santonox R. The antioxidant was added to the polymer prior to extrusion. In this case, some amount of the antioxidant may be lost due to its

migration out of the polymer or chemical degradation. Moreover, the distribution of the antioxidant within the polymer material may be inhomogeneous.

RESULTS AND DISCUSSION

For detection of Santonox R, 250 nm was chosen (Fig. 3), since at this wavelength, the UV absorption of this additive shows a maximum. This wavelength could be used also for the two other additives, analyzed in this study.

The repeatability and the recovery of the described analytical procedure was tested with a series of measurements of both the samples and authentic PE samples. We have checked two procedures of peak evaluation: Peak height measured manually and peak area determined by the computer. The base line under a peak was manually approximated with a straight edge, the computer approximated the base line with a third degree polynomial. As shown in Table III and IV, both evaluation method give almost identical results; the stability of the base line with the UV detector was very good.

Table III confirms that the described procedure of analysis yields 100% recovery of Santonox R. The small deviations are caused by the reproducibility of repeated injections into the LC system, which our system has relative standard deviation of $\varphi = \pm 0.6\%$.

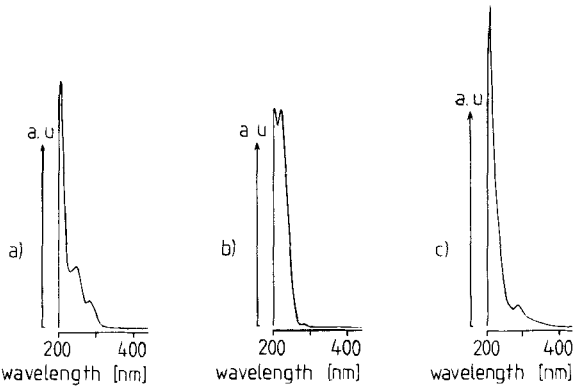

FIGURE 3 UV spectra of antioxidants: a) Santonox R; b) Chimox 14; c) Irganox PS 802.

TABLE III Mass content (wt%) of Santonox R found for the model system made of 1 g PE-MD with 1 mg of Santonox R (mass content = 0.1000 %)

Run No.	*Peak Height Measured Manually*	*Peak Area Measured with PC*
1	0.1005	0.0981
2	0.0998	0.0998
3	0.0990	0.1005
4	0.0997	0.0991
5	0.1001	0.1000
6	0.1032	0.1029
7	0.1009	0.1009
8	0.1022	0.1009
Mean	0.1008	0.1003
Relative standard deviation	±0.0014	±0.0014

During the measurements, we have observed that the height of the peaks for the standard solution of Santonox R (Fig. 4a) decreased slowly with time. However, the height of a small later elution peak (marked with an arrow in Fig. 4b), increased directly proportional with time (Fig. 5). To eliminate the influence of this effect, a new standard solution of Santonox R was prepared each day.

According to Pospíšil,[23] Santonox R may degrade in several ways and the small peak in Figure 4b may correspond to one of the degradation products. A peak with the same retention volume was observed also in the chromatograms of all real PE-MD samples (Fig. 4c), where only about 80% of the originally added Santonox R was found (Table IV). We assume that the rest of the antioxidant was decomposed (and/or migrated out) during the production and life of the tube.

TABLE IV Recovery of Santonox R from polyethylene tube made of a PE-MD formulation with 0.1 wt. % of Santonox R

Run	*Peak Height Measured Manually*	*Peak Area Measured with PC*
1	0.0752	0.0758
2	0.0771	0.0781
3	0.0798	0.0809
4	0.0776	0.0799
5	0.0806	0.0803
6	0.0783	0.0791
Mean	0.0783	0.0791
Average standard deviation	±0.0019	±0.0019
Relative standard deviation [%]	±2.6%	±2.4%

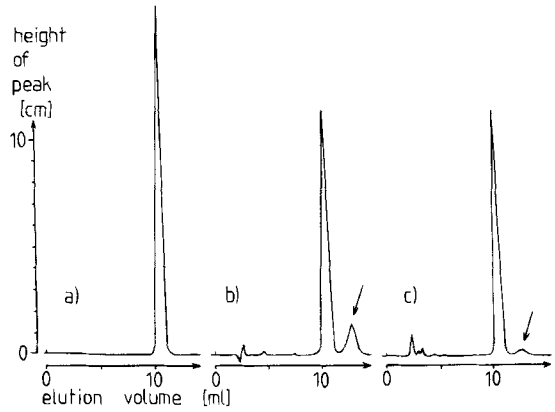

FIGURE 4 Example of chromatogram: a) standard solution Santonox R, concentration 0.016 mg/g; b) standard solution of Santonox R after three days; c) solution isolated from a PE tube containing Santonox R. The arrow shows the peak of unknown degradation product of Santonox R. Column: Silica gel Silpearl, 25 × 0.4 cm i.d.; mobile phase: n-heptane / isopropyl alcohol, 97/3 v/v; detection at 250 nm; range 0.0005×; flow rate 1.0 mL/min.

The described procedure has a detection limit (calculated from the height of a peak which is three times higher than the noise) of 0.011 mg Santonox R/1 g PE, corresponding to a concentration 0.1472 μg Santonox R in 1 gram of the eluent.

The same analytical method was applied to the analysis of Chimox 14 and Irganox PS 802. In this case, the content of isopropyl alcohol in n-heptane was lowered to 0.5 v% (Fig. 6). The estimated detection limits were:

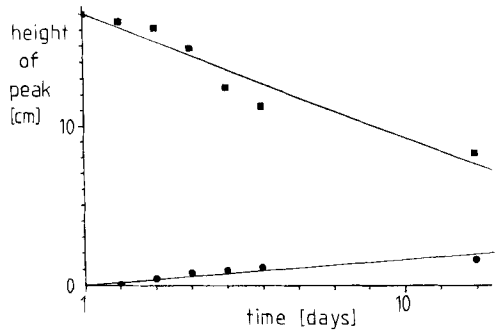

FIGURE 5 Dependence of the peak height on time of both Santonox R (■) and unknown degradation product (●) of Santonox R.

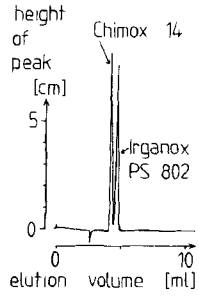

FIGURE 6 Chromatogram of the antioxidants Chimox 14, concentration 0.56 mg/1mL and Irganox PS 802, concentration 0.62 mg/mL. Column: Silica gel Silpearl, 25 × 0.4 cm i.d.; mobile phase: n-heptane / isopropyl alcohol, 100/0.5 v/v; detection at 254 nm; range 0.25×; flow rate 0.86 mL/min.

0.074 mg Chimox 14/1 g PE and 0.125 mg Irganox PS 802/1 g PE. These detection limits are lower than that one for Santonox R due to the decreased UV adsorbance of these additives at 250 nm.

CONCLUSIONS

A new procedure for the quantitative analysis of thiophenolic antioxidants polyethylene was developed. The polyolefin sample is dissolved under pressure in a hot aliphatic solvent. After cooling and precipitation of polyethylene, the supernatant containing the additive is injected directly into the chromatographic column. The mobile phase within the column contains the same solvent as used for the dissolution of the polymer. No additional manipulation with the solution (evaporation, preconcentration, dissolution, etc.) is necessary. Thus the described analytical procedure is both substantially simpler and faster than other published methods; moreover, it has good reproducibility and a low detection limit. The procedure may be applied to the analysis of not only thioether antioxidants, but also the additives in other crystallizing polymers.

Acknowledgements

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References

[1] Brandrup, J. and Immergut, E. H. (1989). (eds.); *Polymer Handbook*, (J. Wiley & Sons, New York), pp. VII/208.

[2] Riddick, J. A. and Bunger, W. B. (eds.) (1970). *Organic Solvents*, (J. Wiley & Sons, New York), pp 86.

[3] Macko, T., Siegl, R. and Lederer, K. (1995). *Angew. Makromol. Chem.*, **227**, 179.

[4] Čaučík, P., Krivošík, I. Náplava, A., Ondrejmiška, K. Špilda, I., Špirk, E. and Vöröšová, M. (1985). "*Prísady do plastov*" (*Additives for polymers*); (Alfa, Bratislava), pp 121 (in Slovak).

[5] Campell, R. H. and Wise, R. W. (1963). *J. Chromatogr.*, **12**, 178.

[6] Crompton, T. R. (1971). *Chemical Analysis of Additives in Plastics*; (Pergamon, New York), pp 295.

[7] Pasteur, A. G. (1977). *Anal. Chem.*, **49**, 363.

[8] Majors, R. E. (1974). In *Bonded Stationary Phases Chromatography*; Eli Grushka, (ed.); (Ann Arbor Sci., Ann Arbor, MI), pp 139.

[9] Wims, A. M. and Swarin, S. J. (1975). *J. Appl. Polym. Sci.*, **19**, 1243.

[10] Gross, D. and Strauss, K. (1976). *Kautsch. Gummi Kunstst.*, **29**, 741.

[11] Schabron, J. F. and Fenska, L. E. (1980). *Anal. Chem.*, **52**, 1411.

[12] Schabron, J. F., Smith, V. J. and Ware, J. L. (1982). *J. Liq. Chromatogr.*, **5**, 613.

[13] Lichtenthaler, R. G. and Ranfelt, F. (1978). *J. Chromatogr.*, **149**, 553.

[14] Munteanu, D., Isfan, A., Isfan, C. and Tincul, I. (1987). *Chromatographia*, **23**, 7.

[15] Duval, M. and Giguere, Y. (1982). *J. Liq. Chromatogr.*, **5**, 1847.

[16] Nakamura, S., Ishiguro, S., Yamada, T. and Moriizumi, S. (1973). *J. Chromatogr.*, **83**, 279.

[17] Protivová, J., Pospíšil, J. and Holčik, J. (1974). *J. Chromatogr.*, **92**, 361.

[18] Majors, R. E. and Johnson, E. J. (1978). *J. Chromatogr.*, **167**, 17.

[19] Vargo, J. D. and Olsen, K. L. (1985). *Anal. Chem.*, **57**, 672.

[20] Vargo, J. D. and Olsen, K. L. (1986). *J. Chromatogr.*, **353**, 215.

[21] Haney, M. A. and Dark, W. A. (1980). *J. Chromatogr. Sci.*, **18**, 655.

[22] Greibrokk, T., Berg, B. E., Hoffmann, S., Norli, H. R. and Ying, Q. (1990). *J. Chromatogr.*, **505**, 283.

[23] Pospíšil, J. (1990). In *Oxidation and Inhibition in Organic Materials*, J. Pospisil and P. P. Klemchuk, (eds.); vol. 1; (CRC Press, Boca Raton, FL), pp 33.