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Determination of low levels of an antioxidant in polyolefins by large-volume injection temperature-programmed packed capillary liquid chromatography

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Abstract

Sub-ambient column temperatures, promoting strong interactions between the analyte and the stationary phase material, were utilized to focus large volumes of the polyolefin antioxidant Irganox 1076 [benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester] on the column inlet, using pure acetonitrile as sample solvent and mobile phase. Injection volumes up to 100 μl were successfully employed on a 50 cm×320 μm I.D. capillary column packed with 5 μm Kromasil 100 ODS particles. Irganox 1076 was eluted after completed injection by temperature programming, using a temperature program from 7 to 90°C, in 3°C min^{-1}. UV detection, using a low-dispersion ''U''-shaped flowcell, was performed at 280 nm. The method was applied for the determination of Irganox 1076 that was extracted from low-density polyethylene (0.6 ppm, w/w). Both Soxhlet and microwave-aided solvent extractions were performed, using chloroform and acetonitrile as solvents, respectively. The microwave-aided extraction with acetonitrile was found to give approximately the same yield as the standard Soxhlet reference method. Consequently, small volumes of acetonitrile could be used both as extraction solvent, sample solvent and mobile phase, simplifying the analysis process. The mass limit of detection of the method was found to be 3.3 ng, corresponding to a concentration limit of detection of 33 ng ml^{-1}, utilizing an injection volume of 100 μl. The within and between day precision of retention times displayed relative standard deviations below 1.2%.

Keywords: Packed capillary columns; Temperature programming; Large-volume injections; Polyolefin; Antioxidants; Irganox

1. Introduction

In order to improve the physical properties and extend the lifetime of synthetic polymers, most polymeric materials contain additives, such as antioxidants, UV stabilizers, metal deactivators, slip agents, antiblock agents and antistatic agents [1]. Antioxidants are added to interrupt the oxidation degradation process [1]. The antioxidants are consumed during the polymer degradation process, and the amount of unreacted antioxidant in the polymeric material is an indicator of how far the oxidation process has come. The initial concentration of added antioxidants is in some cases low (low ppm) and

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since a considerable fraction often is consumed during the oxidation process, there is a need for sensitive analytical methods for the determination of low levels of antioxidants in polymeric materials.

Supercritical fluid chromatography (SFC) has in several studies been shown to be suitable for polymer antioxidant determination, with the advantage of utilizing sensitive gas chromatography (GC) detectors [2–6]. However, SFC has not become widely used, despite the obvious advantages offered by this technique. The relative high molecular mass and the polar functional groups of many antioxidants limit the use of GC [7]. Consequently, reversed-phase liquid chromatography (LC) has been the most commonly used technique for these applications [6–12].

Recently, packed capillary columns in LC have received increased attention. Compared to conventional LC, packed capillary LC offer several advantages, such as reduced consumption of mobile and stationary phases, increased mass sensitivity, suitability of using temperature programming for retention control and availability of longer columns to enhance the resolution of complex mixtures and overall efficiency [13].

Solvent gradient elution is the traditional way to adjust the elution strength of the mobile phase in LC during the chromatographic run. However, this technique is not simple with columns of small inner diameters, due to instrumental limitations with regard to the low flow-rates required [14]. Many polymer additives have limited solubility in aqueous solutions, which further complicates reversed-phase solvent gradient elution. Temperature-programmed packed capillary LC has successfully been utilized on packed capillary columns for separations of polyolefin antioxidants [15–18]. Packed capillary columns are especially well suited for temperature programming, due to their low thermal mass [13].

According to the theoretical downscale factor [19], a reduction of the column inner diameter (I.D.) can enhance the sensitivity by several orders of magnitude. An injection volume of 0.05 μl is typically used in packed capillary LC. However, injection volumes up to 200 μl have successfully been focused on packed capillary columns without loss in efficiency [20]. Thus, enrichment on packed capillary columns allows total sample injection and thereby providing determination of limited sample volumes of low concentrations [20–23].

When large-volume injection in LC is to be performed, the analytes are traditionally dissolved and injected in a solvent with non-eluting properties, promoting solute focusing at the column inlet [20–24]. However, the solubility of polymer antioxidants may be very low in such weak solvents. Alternatively, the antioxidants can be dissolved in a solvent of sufficient solvent strength at ambient temperature, and focused at the column inlet at sub-ambient temperatures, which provides reduced elution strength of the solvent. When the sample introduction is completed, temperature programming can elute the solutes efficiently, eliminating the use of other solvents.

The antioxidants have to be extracted from the polymer prior to chromatographic determination. Soxhlet extraction has been the most widely used technique, but is both solvent and time consuming, often utilizing strong solvents [25]. Fast and efficient extractions of the antioxidants, using the same solvent that promotes on-column focusing at sub-ambient temperatures are preferred when sub-ambient temperature enrichment large-volume injection in packed capillary LC with temperature programming is to be utilized for the determination of low levels of antioxidants in polyolefins. Both microwave-aided solvent extraction (MASE) and pressurized liquid extraction (PLE; Dionex tradename Accelerated Solvent Extraction) have such a potential [25].

The aim of this study was to develop a temperature enrichment large-volume injection temperature-programmed packed capillary LC method for the determination of low concentrations of the polyolefin antioxidant Irganox 1076 (Fig. 1) in low-density polyethylene (LDPE), utilizing the same solvent as extraction solvent, injection solvent and mobile phase.

2. Experimental

2.1. Materials and reagents

Acetonitrile and chloroform of HPLC grade were obtained from Rathburn (Walkerburn, UK). All

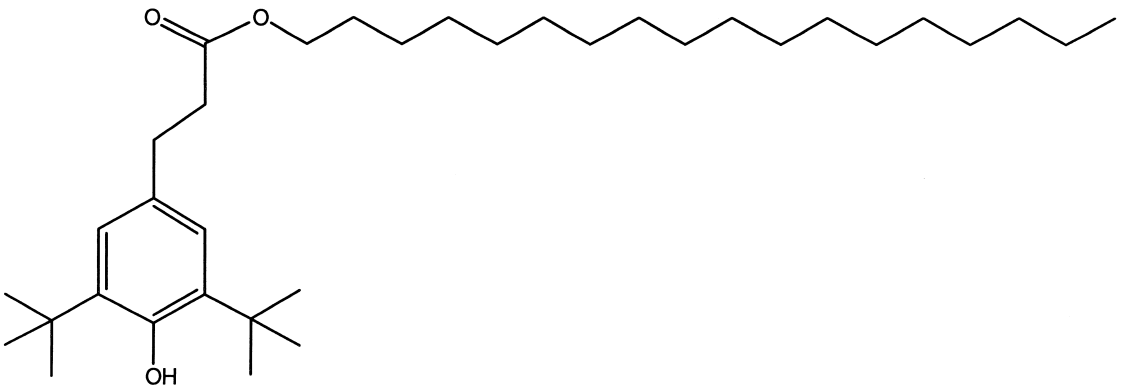

Fig. 1. Chemical structure of Irganox 1076.

fused-silica capillaries were obtained from Polymicro Technologies (Phoenix, AZ, USA). Helium and nitrogen (99.998%) were purchased from AGA (Oslo, Norway). LDPE and the Ciba-Geigy products (Basel, Switzerland) Irganox 1076 [benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester], Irganox 3114 [1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris{[3,5-bis-(1,1-dimethylethyl)-4-hydroxyphenyl]methyl}], Irganox 1010 [benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, 2,2-bis{[3-[3,5-bis(1,1-dimethylethyl) - 4 - hydroxyphenyl] - 1 - oxopropoxy]-methyl}-1,3-propanediyl ester] and Irgafos 168 [phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)] were received from Borealis (Stathelle, Norway).

2.2. Column preparation

The packed capillary columns were prepared according to a procedure previously described, using supercritical CO_2 as the slurry medium [15]. The stationary phase material was 5 μm Kromasil 100 ODS porous particles (HiChrom, Reading, UK). Valco ZU1C unions with 2 μm Valco 2SR1 steel screens served as column end fittings, and the columns were connected to the end fittings by Valco FS1.4 polyimide ferrules and steel nuts (Valco Instruments, Houston, TX, USA). The column body was of fused-silica (320 μm I.D.×450 μm O.D.) with a polyimide protection layer. The columns were prepared in lengths of 50 cm.

2.3. Instrumentation

The instrumental set-up consisted of a Merck–Hitachi L-7100 piston pump. Manual injections were performed with either a Valco Model C4 injection valve with an internal loop of 0.05 μl or a Rheodyne Model 7010 sample injection valve (Cotati, CA, USA) with various external loop volumes for large-volume injections. The sample was transferred from the loop during large-volume injection in opposite direction of that used during loading. A Mistral column oven was employed (Spark Holland, Emmen, The Netherlands). The column was connected to the injector by a fused-silica capillary of 15 cm×50 μm I.D.×375 μm O.D. The UV detector was a Model UV 2000 (Thermo Separation System, Fremont, USA), operated at 280 nm, with a capillary ''U'' shaped detector cell with 8 mm light path, UZ-LI-CAP (LC Packings, Amsterdam, The Netherlands). To prevent the mobile phase from boiling when operating at elevated temperatures, a fused-silica linear restrictor of 36 cm×20 μm I.D.×375 μm O.D. was connected to the end of the detector capillary. A C-R5A integrator was used for data sampling (Shimadzu, Kyoto, Japan). The mobile phase consisted of 100% acetonitrile, and was helium degassed for 15 min each day. The mobile phase flow-rate was 5 μl min^{-1}.

2.4. Standard solutions

A saturated standard solution of 600 μg ml^{-1}

Irganox 1076 in acetonitrile was prepared in an ultrasonic bath for 15 min. Several other concentrations down to 10 ng ml^{-1} were prepared from this stock solution by diluting with acetonitrile.

2.5. Polymer preparation

The LDPE granules were supposed to contain 17 ppm (w/w) Irganox 1076. LDPE granules with a lower content of antioxidant were obtained by mixing the LDPE granules with LDPE granules with no content of Irganox 1076 (1:29, w/w). The mixture was re-extruded five times to obtain a homogeneous distribution of Irganox 1076 (0.57 ppm, w/w). The new polymer was subsequently pelletized and ground into 1 mm particles.

2.6. Polymer extraction and sample preparation

Initially Irganox 1076 was extracted from ground LDPE using Soxhlet extraction with chloroform, according to a standard procedure [26]. A 2.45 g sample of LDPE containing 0.57 ppm (w/w) Irganox 1076 was extracted for 3 h in 125 ml chloroform at 40°C. The chloroform extract was evaporated to dryness under nitrogen and re-dissolved in 4 ml acetonitrile, using an ultrasonic bath for 5 min. The acetonitrile solution was filtrated through a 0.45 μm Gelman Acrodisc CR PTFE filter (Ann Arbor, MI, USA), and evaporated to 1.6 ml under nitrogen. Furthermore, MASE of a 2.30 g LDPE sample in 50 ml acetonitrile was performed by the use of an ETHOS 1600 Advanced Microwave Labstation (Milestone, Sorisole, Italy). The sample was extracted for 30 min at 120°C and 2.5 bar, followed by cooling for 30 min. The acetonitrile solution was filtrated through a 0.45 μm Gelman Acrodisc CR PTFE filter, and evaporated to 1.5 ml under nitrogen.

3. Results and discussion

3.1. Injection and chromatography

It is well known in LC that temperature elevation usually results in reduced retention. And vice versa, a temperature decrement will normally decrease the elution strength of the mobile phase, promoting increased retention. Consequently, solutes that elute at one temperature may be completely retarded at a lower temperature, as commonly observed in GC. This effect was exploited by Ingelse et al. to promote temperature enrichment large-volume injection of water-soluble aldehydes at 40°C, using packed capillary temperature-programmed LC–flame ionization detection (FID) with pure superheated water as the eluent [27]. However, this technique may be more useful if solutes of limited solubility in weak solvents may be dissolved in a stronger solvent at one specific temperature, prior to on-column focusing of large sample volumes at lower temperatures.

When a mobile phase of 100% acetonitrile was employed in the present chromatographic system, Irganox 1076 eluted after more than 2.5 h at ambient temperature. At 7°C, Irganox 1076 did not elute within 10 h, and was therefore injected at this initial temperature, to promote on-column focusing. Utilizing temperature programming from 7 to 90°C, at 3°C min^{-1}, after completed injection, Irganox 1076 eluted at 36 min, well separated from other polyolefin antioxidants that might be present in the sample, such as Irganox 3114, Irganox 1010 and Irgafos 168. The influence of different injection volumes on the chromatographic performance was investigated by injecting standard solutions of Irganox 1076 in acetonitrile, keeping other conditions constant. Injection volumes of 0.05, 1, 5, 10, 50 and 100 μl were evaluated. The standard solutions were in all cases prepared in such a manner that an absolute mass of 0.3 μg Irganox 1076 was injected regardless the injection volume. Fig. 2 shows a selection of the chromatograms obtained during this evaluation. The peak height and the peak width at half the peak height did not vary for injection volumes up to 10 μl. Utilizing injection volumes exceeding 10 μl, the peak width increased slightly, indicating an incomplete focusing process of the larger sample volumes. However, the slightly increased band broadening did not influence significantly on the limit of detection (LOD) or the chromatographic performance. The asymmetry factor was not influenced by the injection volume, and was constantly below 1.2. Consequently, an injection volume of 100 μl was employed for the rest of the study, to enhance the concentration LOD (cLOD) of the method. The mass LOD (mLOD) of the method

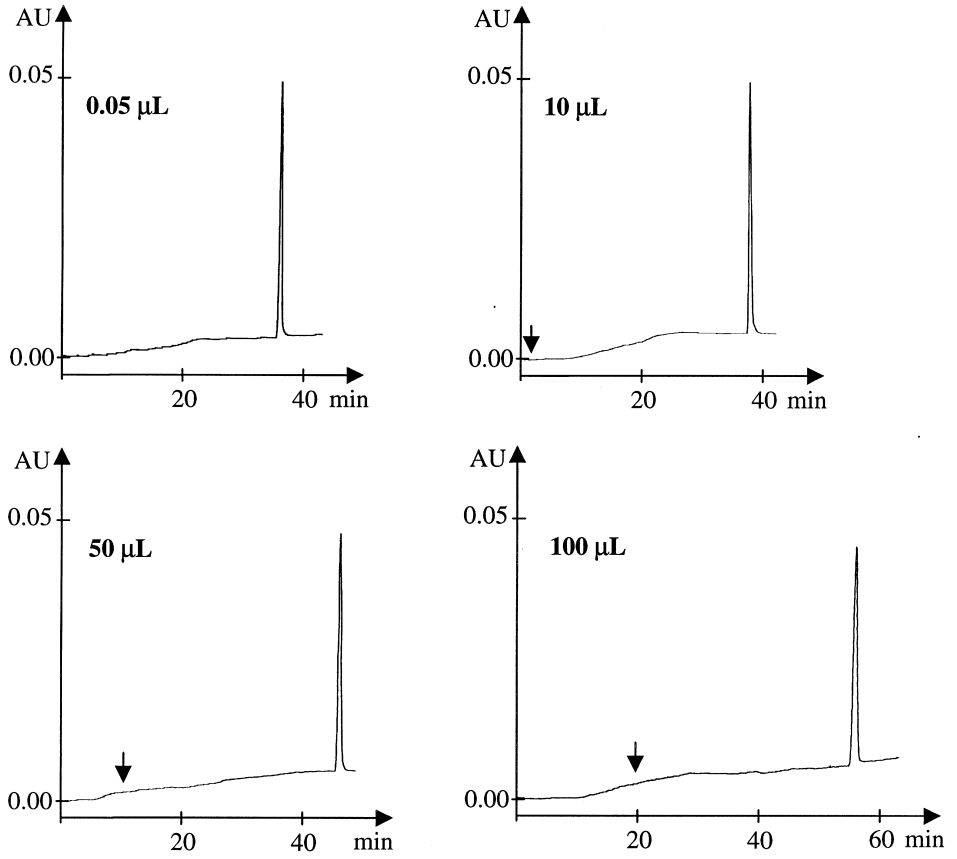

Fig. 2. The effect of injection volume on chromatographic performance of Irganox 1076 in acetonitrile. A 50 cm×320 μm I.D. column packed with 5 μm Kromasil 100 ODS particles was used with a mobile phase of 100% acetonitrile. Injection was performed at 7°C and elution with a temperature program from 7 to 90°C, at 3°C min^{-1}. The arrows indicate the start of the temperature program. An absolute amount of 0.3 μg Irganox 1076 was injected at all injection volumes.

was determined to 3.3 ng ($S/N=3$), corresponding to a cLOD of 33 ng ml^{-1}, utilizing an injection volume of 100 μl. The injection time was 20 min when the 100 μl loop was utilized, and the within- and between-day precision of retention times displayed relative standard deviations (RSDs) of 0.44 and 1.20%, respectively ($n=3$).

3.2. Analysis of polyethylene extracts

Waldeback et al. [28] γ-irradiated LDPE containing 200–460 ppm (w/w) Irganox 1076 to obtain a model for long term oxidative degradation, and found that more than 96% of the Irganox 1076 content was consumed upon this treatment. Drugs and food are often γ-irradiated to destroy bacterium cultures, strongly reducing the lifetime of any present polymeric packaging material. In the present study LDPE containing 17 ppm (w/w) Irganox 1076 was mixed with LDPE with no content of Irganox 1076 (1:29, w/w) and re-extruded, to obtain a model for long term oxidative degradation. The content of Irganox 1076 in the re-extruded polymer was subsequently approximately 0.6 ppm (w/w).

Soxhlet extraction was performed, according to a validated standard method, generally giving an extraction yield exceeding 95% [26]. Focusing of Irganox 1076 was not achieved when injecting the chloroform extract in the chromatographic system at 7°C. Consequently, the chloroform extract was evaporated to dryness under nitrogen, and re-dissolved in acetonitrile. This final solution was injected

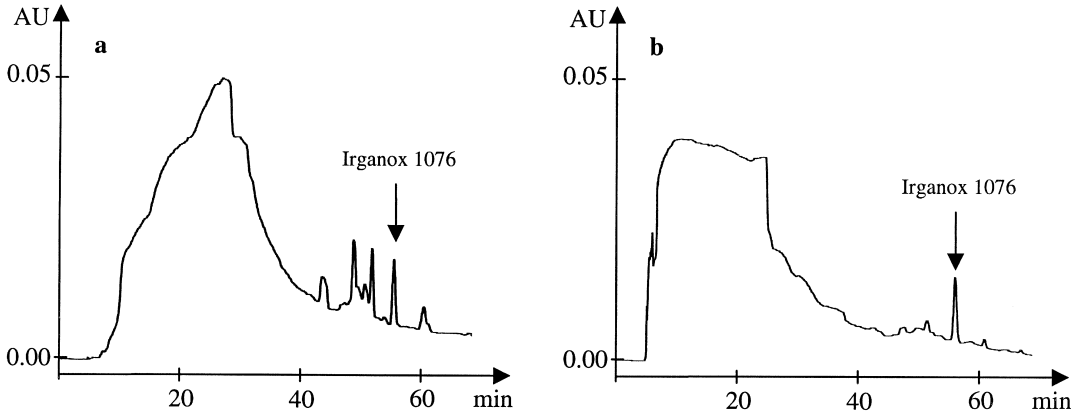

Fig. 3. Sub-ambient temperature enrichment large-volume injection temperature-programmed packed capillary liquid chromatography separation of (a) a chloroform Soxhlet extract of low-density polyethylene that has been evaporated and re-dissolved in acetonitrile and (b) an acetonitrile microwave aided extract of low-density polyethylene. All other conditions as in Fig. 2.

in the sub-ambient temperature enrichment large-volume injection temperature-programmed packed capillary LC system. As illustrated in Fig. 3a, Irganox 1076 eluted at 56 min, in accordance with the retention time of the standard, well separated from several other unidentified compounds. Spiking of the extract confirmed the identification of Irganox 1076. The extensive peak eluting in front most probably contained decomposition products of organic peroxides used to initiate the polymerization process.

One target of this study was to use small volumes of the same solvent as extraction solvent, sample solvent and mobile phase, and hence simplify the whole analysis process. Several extraction techniques utilize elevated temperatures and applied pressures to achieve more efficient and faster extractions, including PLE and MASE. Waldeback et al. utilized PLE with pure acetonitrile as solvent for the extraction of Irganox 1076 from LDPE at 100°C, and achieved competitive yields compared to other published results [28]. In the present study, MASE with pure acetonitrile was utilized for the extraction of Irganox 1076 from LDPE. After cooling to ambient temperature, the extraction solution was filtrated and evaporated to 1.5 ml under nitrogen, to achieve identical concentrations of Irganox 1076 in the solutions obtained from both extraction methods. The chromatographic analysis of the final MASE solution is shown in Fig. 3b. The peak height of Irganox 1076 is comparable to that of the Soxhlet extract, indicating almost similar extraction yields for the two methods. Assuming no degradation or loss of Irganox 1076 during extruding, extraction and further sample treatment, the theoretical concentration in the final sample solution was 0.87 $\mu g\ ml^{-1}$. By comparing the peak height of a standard solution of similar concentration to the peak heights of the extracted sample, the recovery was estimated to be approximately 90% for both methods. In addition, less additional peaks are present in Fig. 3b, supporting a theory of a slightly more selective MASE method in acetonitrile as compared to the Soxhlet method. The sub-ambient temperature enrichment large-volume injection temperature-programmed packed capillary LC method was very robust, showing similar peak performance throughout a month of extensive use. The within and between day precision of retention times throughout this period of time displayed relative standard deviations below 1.2%, displaying no differences between standard solutions and polyolefin extracts. Furthermore, similar columns have shown excellent performance and ruggedness at elevated temperatures in non-aqueous packed capillary LC systems [15].

4. Conclusions

This study has shown that simply by varying the

operating temperature during the different stages of the sample preparation and analysis process, small volumes of one single solvent may successfully be utilized throughout the whole process. When using the mobile phase as the extraction solvent, elevated temperatures enhance the extraction time and yield. After cooling and filtration, the extraction solution may be focused at the column inlet at sub-ambient temperatures, due to increased interaction with the stationary phase material. Following the completed injection, temperature programming may elute the analytes efficiently. Thus, small concentrations of compounds of limited solubility in weaker solvents may be determined.

Further method development and validation are required if the present method is to be used routinely for quantitative determinations. Nevertheless, this method has demonstrated that miniaturized LC in combination with temperature programming is a powerful technique for the determination of low levels of additives in polyolefin extracts.

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