

Accelerated solvent extraction of the antioxidant Irganox 1076 in linear low density polyethylene (LLDPE) granules before and after γ -irradiation

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To achieve effective and reproducible extractions of the antioxidant Irganox 1076 from linear low density polyethylene (LLDPE) components at reduced time and cost, the accelerated solvent extraction (ASE) technique was evaluated with solvent composition and temperatures as test variables. The aim was to find proper extraction conditions for the balance between high diffusion rate of the analytes *versus* solvation of the plastic material. High extraction yields and reproducible results, RSDs between 9.7–12.5%, were obtained using ethyl acetate mixed with hexane 90 : 10 (v : v) at 100 °C. The results showed that no grinding of 4 mm granules was necessary before extraction nor was concentration of the extracts needed before LC analysis. By using the established extraction method, a comparison between γ -irradiated and non-irradiated LLDPE granules showed that more than 96% of the Irganox 1076 was lost after γ -irradiation (2×25 kGy).

Keywords: Polyethylene; antioxidant; Irganox 1076; accelerated solvent extraction; γ -irradiation; food and drug packagings; optimisation; liquid chromatography

Chemical additives are frequently used to enhance the lifetime and minimise degradation of plastic materials. Analysis of polymer additives is thus important in both research and quality control for manufacturers and users of various polymers, especially for those used as packaging material for drugs and food.

The first step in an analysis involves the isolation of the additives from the polymer matrix, usually by some type of liquid–solid extraction. The most common extraction method, the Soxhlet extraction, has the drawback of being both time^{1,2} and solvent consuming. Both heating in the solvent decalin³ and supercritical fluid extraction (SFE)^{4,5} have been applied as alternative approaches to the extraction of antioxidants from polyethylene. In addition, the recently developed accelerated solvent extraction (ASE) technology has also quickly become an attractive alternative to the traditional extraction techniques⁶. By applying pressure to the extraction cell, the solvents are kept in the liquid state at temperatures above their atmospheric boiling point. The use of higher temperatures increases the rate of diffusion of the components within the polymer particles as well as their transfer rate from the particles to the extraction solvent.⁷ Moreover the solubility of most analytes in the extraction solvent is increased.

The aim of this study has been to investigate the possibility of using ASE technology to perform reproducible extractions of the antioxidant Irganox 1076 [octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] in linear low density polyethylene (LLDPE) granules. An additional aim was to use this extraction method to compare the content of Irganox 1076 in non-irradiated LLDPE granules and LLDPE granules sterilised by γ -radiation. The resulting method should be simple, accurate and fast.

Experimental

Chemicals

Acetonitrile and methanol were of LiChrosolv quality, while ethyl acetate, hexane, methylisobutylketone (MIBK), propan-2-ol and tetrahydrofuran (THF) were of *pro analysi* grade. All solvents were purchased from Merck, Darmstadt, Germany, except MilliQ-water, which was obtained from a purification system (Millipore, Watford, Herts., UK). Nitrogen, of quality 99.996% of volume, Aga, Stockholm, Sweden and the Irganox 1076 standard was from Ciba Geigy, Basel, Switzerland.

Sample

Granules and processed samples of LLDPE from several batches, containing the analyte Irganox 1076, with an original concentration according to the manufacturer in the range of 240–460 ppm (Batch A) and 200–300 ppm (Batch B), were used. The polyethylene was received from Pharmacia & Upjohn AB, Uppsala, Sweden. The approximate diameter of a sample granule was 4 mm and the weight was about 36 mg. The irradiated granules used in this study were γ -radiated by 2×25 kGy.

Instrumentation

A schematic illustration of the accelerated solvent extractor employed, ASE 200, Dionex (Sunnyvale, CA, USA) is shown in Fig. 1. The extraction cells (Dionex) were of stainless steel with a volume of 11 ml and capped with PEEK seals and stainless steel frits.

Procedure

The extraction process consisted of five steps: (i) filling and pressurising the cell with solvent at selected temperature; (ii) preheating the cell at selected temperature for equilibration at

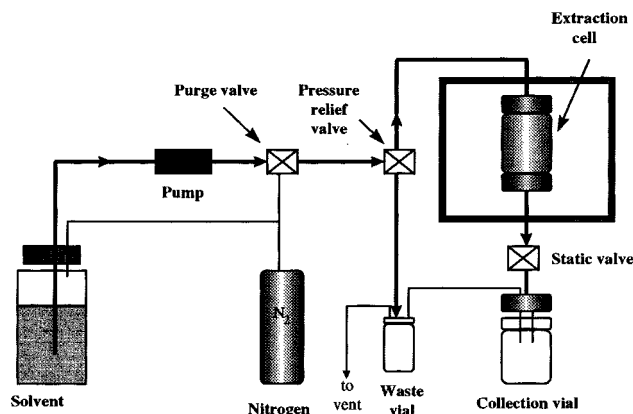


Fig. 1 Schematic illustration of the ASE system.

constant pressure for 5 min; (iii) static extraction at constant pressure and temperature over a selected period of time; (iv) flushing the cell with fresh solvent with a selected volume expressed as a percentage of the cell volume [the steps (iii) and (iv) are called a cycle, and can be repeated several times]; and (v) purging of the cell with nitrogen.

The extraction cell was filled with a cellulose filter (Dionex, 1.91 cm diameter) and with 2 g of LLDPE granules. All extractions started with preheating for 5 min at a pressure of 10.5 MPa. The effect of different temperatures and solvents was studied. Each cycle was finished by a 60% (6.6 ml) fresh solvent flush. Finally the cell was purged with an inert gas, nitrogen, for 60 s and the analytes and the solvent from the cell and the lines were collected into a vial.

The extracts were filtered by a 4 mm Millex-FH, hydrophobic PTFE-membrane with pore size 0.5 μm (Millipore). All extracts were analysed using an LC system (Waters, Stockport, UK) consisting of a pump (616), an autosampler (717), a 600 s controller and a tunable absorbance detector (486). A SYMMETRY C₈, 3.9 \times 150 mm (particle diameter 5 μm) column (Waters, Stockport, UK) was used and as a guard column a SYMMETRY C₈, 3.9 \times 20 mm precolumn was employed. The LC parameters were as follows: mobile phase, methanol–water (96 : 4), flow rate, 1.5 ml min⁻¹; injection volume, 10 μl ; and UV detection at 230 nm.

Calibration plots were made from peak area of a standard of Irganox 1076 in ethyl acetate–hexane (90 : 10). The retention times for the Irganox 1076 peak in the extract and in the standard solutions were equal within +2%. Millenium software, version 2.15.3 was used for data acquisition and processing.

Results and Discussion

The first step in an ASE method development is to select a proper solvent composition for the extraction. The solvents recommended for Soxhlet extractions have generally been the solvents of choice also in ASE.⁶ Due to the higher temperature used in an ASE extraction and the fact that the matrix in this case is a polymer, this choice might be unwise. The solvent successfully applied in Soxhlet extractions is usually also a good swelling agent for the polymer matrix,⁷ that when used at the higher temperature in an ASE extractor, may result in melting of large portions of the polymer. The risk of irreproducible results and plugging of the tubing within the instrument will therefore be high.

In an initial screening study, where the matrix consisted of a processed sample of LLDPE, cut into pieces of about 5 \times 5 mm, various conditions were tested for extraction of Irganox 1076. The extraction yield for the different combinations of solvents and temperatures is shown in Table 1. The original value of Irganox in the LLDPE from the manufacturer was said to be 200–300 ppm. The fact that the extraction yields detected always are less than 100% of the added antioxidant is probably due to losses of Irganox 1076 during the manufacturing, processing and storage of the plastic.⁸

From Table 1 it can be seen that higher temperature during the extraction generally increases the yield. These results were consistent with published data showing that an increase in temperature gives improved recovery.⁹ At temperatures above

100 °C the polymer started to melt, and this fact ruled out the use of higher temperatures. When higher temperatures were tried, the tubing of the instrument was plugged. Ethyl acetate was found to give the highest yield at the maximum temperature of 100 °C and was therefore chosen for further studies. With THF as a solvent the matrix showed traces of melting already at 75 °C, and at 100 °C the melted polymer started to plug the tubing of the ASE extractor. This excluded THF from further use although it resulted in the highest yield from all solvents tested for extractions at 75 °C.

Since the particle size is considered to be an important parameter influencing the maximum yield and the required extraction time, especially if the extraction rate is limited by diffusion within the particles,⁷ ground granules, whole granules and processed LLDPE cut into 5 \times 5 mm were extracted at different temperatures. The extraction yield was higher for the ground granules at low temperatures, but at temperatures above 80 °C these granules started to melt, while the whole granules could withstand fast extractions at 100 °C. As the grinding step, in this way, could be omitted, whole granules were used in all the subsequent experiments, which rendered a simpler and faster method according to the goal of this study. In addition the method avoided any risk of antioxidant degradation during grinding.

In order to find a proper static time for the extractions, three cycle runs of 5, 15 or 25 min were examined. When the static time was increased from 15 to 25 min no further improvement of the extraction recoveries was observed. Using 5 min static time for each cycle, a 36% lower yield was obtained. Therefore, in the following experiments a static time of 3 \times 15 min was used. The extracts required no further concentration before LC analysis. In this way losses of Irganox 1076 due to further treatment was eliminated. A typical chromatogram from the LC analysis of an extract is seen in Fig. 2.

In an effort to raise the extraction yield of the antioxidant, ethyl acetate was mixed with a swelling agent, hexane, at different concentrations and the extractions were performed at several temperatures using these mixtures. An experimental design, a full factorial design at three levels, was chosen to investigate the main variables, temperature and percentage of hexane, in ethyl acetate. The original values from the manufacturer of added Irganox 1076 in the LLDPE granules used in this study were 240–460 ppm (Batch A). The obtained results

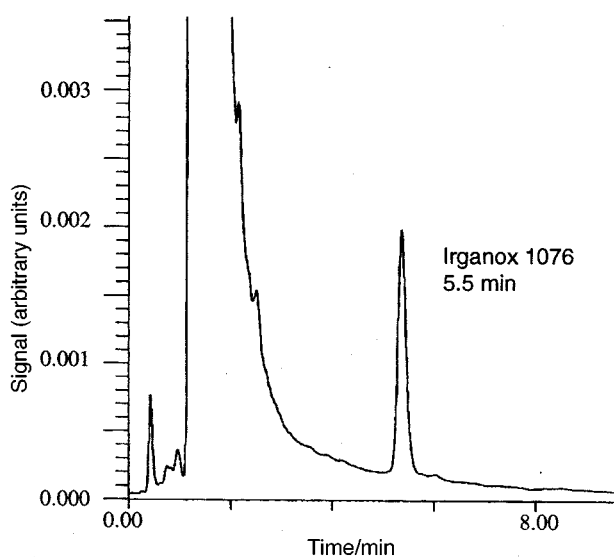


Fig. 2 A typical chromatogram from an LC analysis of an extract. Column, C₈, 5 μm particle diameter, 3.9 \times 150 mm; mobile phase, methanol–MilliQ-water (96 : 4); flow rate, 1.5 ml min⁻¹; UV detection, 230 nm; injection volume, 10 μl .

Table 1 Extraction yield in $\mu\text{g g}^{-1}$ of Irganox 1076 obtained in the screening study of processed sample of LLDPE

Temperature °C	Methanol	Aceto-nitrile	Ethyl acetate	Propan-2-ol	THF	MIBK
50	13	11	34	—	—	—
75	43	53	111	48	123	37
100	128	125	173	54	—	57

for the 11 experiments are shown in Table 2. The data was fitted to a quadratic model with multiple linear regression (MLR), and the relative standard deviation of the model was 12.8%. The significant variables were temperature and percentage hexane in the solvent used, and no significant interaction between them could be seen at 95% confidence level. From Table 2 it can be concluded that the effect of the percentage of hexane is larger at lower temperatures, *i.e.*, higher percentage of hexane gives higher yield of Irganox 1076 at lower temperatures. It is suggested that hexane works as a good swelling agent and this effect is especially important at lower temperatures. It can also be seen from Table 2 that the yield is enhanced at higher temperatures, a result which is in agreement with the results in Table 1 for every solvent composition. To show the dependence of the response as a function of temperature and percentage of hexane, a response surface plot was made with the model obtained from the data in Table 2 (see Fig. 3). From this figure it can be concluded that the temperature has a greater influence on the yield of Irganox 1076 than the concentration of hexane. Consequently, at 100 °C, the yield is high and the percentage of hexane does not seem to markedly affect the yield at this temperature.

At temperatures above 100 °C and with hexane in excess of 25% the polymer started to melt and even dissolve. Even though the melted plastic did not block the accelerated solvent extractor there was obviously a risk of plugging the tubing of the instrument. In addition, these extracts were very cloudy from dissolved plastic material, and there would be a risk that the extracted analyte Irganox 1076 could get redissolved into the co-extracted plastic material. A repeatability study was performed using the optimised parameters found in this study, where whole pellets were extracted at 100 °C with ethyl acetate–hexane 90 : 10 (v/v) as solvent and with a static time of 3×15 min. Two different batches, Batches A and B, were tested, with five replicates of each batch extracted. Reproducible results were obtained with RSD values between 9.7–12.5%, see Table 3.

Five replicates of γ -irradiated (2×25 kGy) LLDPE granules from Batch B were extracted in the same way and the average yield from the γ -irradiated granules was $4.4 \mu\text{g g}^{-1}$. The high RSD value of 33.3 results from an extreme value in sample 4, possibly caused by non-homogenous degradation of the antioxidant. More than 96% of the extractable Irganox 1076 could not be extracted after the γ -irradiation. The data are comparable

Table 2 Extraction yield in $\mu\text{g g}^{-1}$ of Irganox 1076 obtained with the experimental design from LLDPE granules, Batch A

Temperature/°C	5% Hexane	25% Hexane	45% Hexane
80	106	141	160
90	147	163, 179, 161	201
100	203	239	216

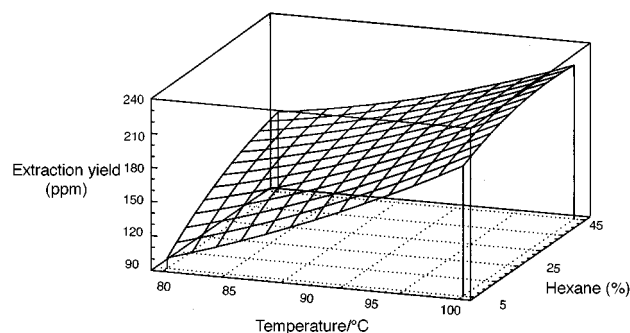


Fig. 3 Response surface plot of the extraction yield of Irganox 1076 using temperature and percentage of hexane in ethyl acetate as variables.

Table 3 Study of the reproducibility of the proposed method; extraction yield of Irganox 1076 in $\mu\text{g g}^{-1}$ in LLDPE granules from Batch A and Batch B

Sample of LLDPE	1	2	3	4	5	Average	Std.	RSD (%)
Batch A	252	218	203	198	213	217	21.2	9.7
Batch B	116	140	142	135	165	140	17.5	12.5

Table 4 Extraction yield of Irganox 1076 in $\mu\text{g g}^{-1}$ in γ -irradiated LLDPE granules

Sample of LLDPE	1	2	3	4	5	Average	Std.	RSD (%)
Batch B	4.4	3.6	3.1	6.8	3.9	4.4	1.5	33.3
γ -irradiated								

with the results obtained by Yagoubi *et al.*,¹⁰ who observed a loss of 95% in the Irganox 1076 content, after polyethylene vinyl acetate was radiotreated by 25 kGy. The difference in the Irganox 1076 yield is probably caused by scission of this molecule as pointed out by Yagoubi,¹⁰ and by the increase of crosslinking within the polymer due to the irradiation. The optimised ASE method has shown to be adequate to estimate the losses of the antioxidant Irganox when LLDPE is treated with γ -irradiation, and will be used in further experiments to determine the effect of different treatments on Irganox 1076 degradation.

This study has proved ASE to be a fast and suitable technique for a reproducible extraction of Irganox 1076 in unground samples of LLDPE (see Table 3). One sample can be extracted and analysed within less than 1 h, compared with the Soxhlet extraction where only the extraction step needs between 6 and 48 h.^{1,2} No time is needed for grinding of the LLDPE granules or to reduce the volume of the extract before LC analysis. In addition the ASE instrument used in this study could take up to 24 samples at a time for increased sample throughput.

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