Optimization of Experimental Parameters for the Quantification of Polymer Additives Using SFE/HPLC

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ABSTRACT: Analysis of low concentration additives; for example, antioxidants, in polymeric materials remains a difficult task. In the usual analytical methods, additives are extracted using large quantities of solvents first followed by concentrating the resulting solution for making possible the analysis. The supercritical fluid extraction (SFE) technique eliminates the use of large quantities of solvents and simplifies the analytical procedure. This work has been done with the goal of extracting the antioxidants Irganox 1010 and Irgafos 168 from a polypropylene matrix by using the SFE technique and by subsequent analysis using high-performance liquid chromatography (HPLC). The experimental parameters; that is, temperatures, pressure, and modifiers have been varied to find the best extraction conditions. The optimum temperature and pressure for extraction of above-mentioned polymer additives were found to be 120°C and 384 bar, with methanol as the modifier. The quantitative extractions are significantly faster than those reported earlier in the literature. The results point out that the technique used in these experiments—SFE combined with HPLC—is a reliable and environmentally friendly alternative to the commonly used liquid extraction and analytical methods. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 938–946, 2000

Key words: supercritical fluid extraction technique; polypropylene; antioxidants; high performance liquid chromatography

INTRODUCTION

Polyolefines, such as polypropylene and polyethylene, are readily subjected to thermal and oxidative degradation.[1] Polypropylene is sensitive to thermal oxidation, as it contains one hydrogen at a tertiary carbon atom in each repeating unit. Hydrogen atoms at tertiary carbons have a lower bond dissociation energy than other hydrogen atoms in the polymer and, therefore, are easier to extract by propagating radicals. To ensure nondegradative processing and long-term stability, polypropylene is stabilized by antioxidants mainly composed of sterically hindered phenols in combination with phosphites.[2] These additives are not chemically bonded to the polymer chains, but rather are physically dispersed within the polymer matrix.[3,4] Failures in polymeric materials can often be attributed to the leaching of antioxidants from the polymer[5] or the chemical transformation of certain additives. Some of the stabilizers added to polymers during primary processing may still be present after long usage, their amounts being dependent on the service history of the products. There is a need to develop reliable methods capable of identifying and quantifying antioxidants present in used plastic products.

Analysis of antioxidants in commercial polymeric materials is not simple. The difficulty arises from three factors; namely, high reactivity and low stability of antioxidants, very low concentrations (0.03–0.3%)[6] at which they are present, and insoluble polymer matrix. The criteria for an ideal method for extracting antioxidants from

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        ┌─────────────────┐
        │   Liquid CO₂    │
        └─────────────────┘
                 │
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        │  High pressure  │
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        │ Sample chamber  │
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Rinse solvent  ┌───────────────┐  Gaseous CO₂
   ─────────▶  │ Analyte trap  │  ─────────▶
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        │  Fraction vial  │
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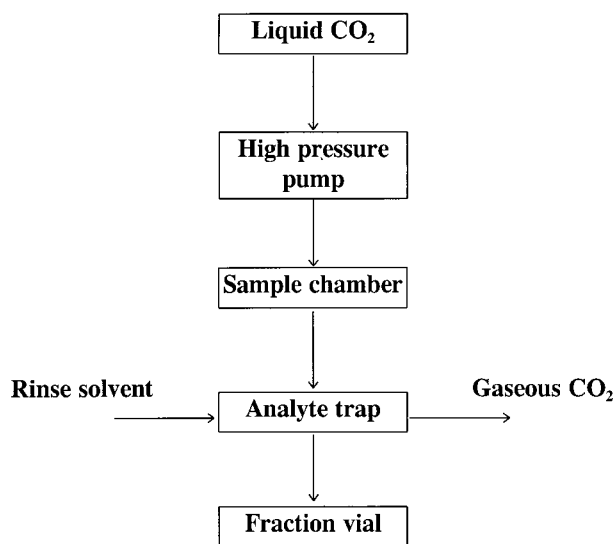
Figure 1 The most important steps in the SFE analytical procedure. CO_2 is stored in liquid form before it is heated and pressurized and then flows through the sample chamber. In the chamber, are the additives extracted from the polymer matrix, and when the pressure is released, the supercritical fluid evaporates and leaves the additives in the analyte trap. Finally, a solvent rinses the trap and collects the additive.

polymers are as follows. It should be rapid, simple, and inexpensive to perform. It should yield large quantities without loss or degradation. It should yield a sample for further analysis without additional concentration needed. Finally, it should not generate additional laboratory wastes. The SFE-technique fulfills all these criteria. The extraction process consists of four steps, as illustrated in Figure 1. The sample chamber is initially heated and pressurized. The first stage is a static phase wherein the polymer is allowed to swell in the supercritical fluid. The second stage is where the additive is extracted from the sample as the result of the supercritical fluid flow through the chamber. In stage 3, the supercritical fluid evaporates, leaving the additives in the analyte trap. In the last stage, a solvent rinses the trap and collects the additives. The resulting solution is then collected in a test vial and transferred for analysis. The rinse step is repeated to clean the trap for the next extraction.

Two factors may influence the rate of extraction: (1) the solubility of the extracted material in the supercritical fluid; and (2) the rate of mass transfer out of the matrix by the analyte. For example, CO_2 by itself may not be able to extract the analytes from the matrix. To overcome this

problem, CO_2 is often used with a modifier.[7–10] Poor analyte recoveries are often attributed to poor extraction efficiencies, although in some cases, they are caused by incomplete analyte collection after the extraction.[11] The aim of this article is to develop an efficient, rapid method for the quantitative analysis of antioxidants in polypropylene. Although earlier studies[12–16] on the extraction of antioxidants from a polypropylene matrix show promising results, there is a lack of results showing quantitative recovery using short extraction times.

Good results from the use of on-line SFE/SFC[12,13] and also off-line SFE in combination with SFC[14] for extraction of antioxidants from a polypropylene matrix have been reported. Cotton et al.[13] used the relative peak areas to confirm quantitative results; they claimed that because the relative peak areas for all antioxidants corresponded well with actual concentrations, they had reached quantitative recovery. High recoveries have also been reported by Cotton et al.[14] in a later study, but for reaching almost 100% recovery, the extraction time needed was 5 hours.

Properties of Supercritical Fluids

The supercritical fluid takes the best physical properties from liquid and gas and combines them into a fluid with unique physical properties. The solute diffusion coefficients in supercritical fluids are intermediate between those in gases and in liquids, and the solvent power is high because of its high density. The influence of density on the solvent strength of the supercritical fluid can be described through the following well-known equation:[17]

$$\delta = 1.25 P_c^{0.5}[\rho/\rho_1] \qquad (1)$$

where δ is the Hildebrand solubility parameter, P_c is the critical pressure of the fluid, ρ is the density of the supercritical fluid, and ρ_1 is the density of the liquid gas under standard conditions. The solubility parameter, which measures roughly the power of the solvent to dissolve various substances, can vary from zero at low pressures up to liquid-like values at ultra-high pressures. The solubility parameter of a supercritical fluid can be varied by changing the density of the fluid by means of temperature and pressure variations. Raising the pressure increases the density of the supercritical fluid and causes it to become

more liquid-like; whereas, raising the temperature causes the density of the supercritical fluid to decrease, and the phase approaches the gaseous state. The surface tension of a supercritical fluid is very low, almost zero; this means that it can penetrate through small capillaries of almost any material, and it will solvate such nonpolar compounds as polypropylene.

CO_2 is the most commonly used supercritical fluid, because it has modest critical conditions, can readily be separated from solutes, poses no environmental problems, and is nonflammable and inexpensive.[18] CO_2 as the supercritical fluid in SFE has been used for extraction of a wide range of substances. As mentioned, earlier studies have been carried out on the extraction of antioxidants from polypropylene.[12–16]

EXPERIMENTAL

A nonstabilized polypropylene polymer from Borealis Company was selected for use in this work, and in the optimization part, the stabilizer system was added to the polymer resin by using a Brabender DSK 42/7 double screw extruder with five heating zones. The mixing was done at temperatures of 180, 190, 200, 220, 220°C.

In the second part of the study, the nonstabilized polypropylene polymers were compounded in a Brabender plasticorder AEV 330 for about 5 min at 200°C and 40 rpm. The antioxidants were added to the polymer resin in a very controlled way to ensure no loss of antioxidants because of the compounding.

A Hewlett-Packard (HP) supercritical fluid extractor, SFE model 7680A, was used for the extraction of additives from the polymer. The polymer samples used weight approximately 50 mg, the thimble capacity being 7 mL. The rest of the thimble was filled with glass beads to prevent the samples from sticking to the thimble walls. The glass beads were 2-mm in diameter. All extractions were carried out at 10-min static mode followed by 50-min dynamic mode. The extracts were accumulated in a column which was packed with C18 silica. Vials with 2-mL sample capacity were used, and two rinse steps were performed; however, all antioxidants were always found in the first vial. A modifier pump of HPLC-type was used for incorporating the modifier into CO_2. It should, however, be mentioned that, because of the lack of phase diagrams for mixtures of carbon dioxide with different types of modifier, it is not

always clear whether the extraction is performed strictly under supercritical conditions. The critical parameters of the mixtures used in this investigation were calculated according to eqs. (2) and (3) to ensure that the extractions were performed under supercritical conditions.

$$T_c = X_{CO_2}T_{c(CO_2)} + X_m T_{c(m)} \tag{2}$$

$$P_c = X_{CO_2}P_{c(CO_2)} + X_m P_{c(m)} \tag{3}$$

where X_{CO_2} and X_m are the mole fractions of CO_2 and modifier, respectively.[11]

The chromatography of the extracted antioxidants was carried out on HP 1050 reverse-phase HPLC system. The column used was 200 × 4.6 mm and contained LiChrosorb RP-18 5 μm. Detection was by UV absorbency detector at 280 nm. 20 μL of the extract was injected, and the antioxidants were eluted using a gradient from H_2O/methanol (95/5) to methanol (100) within 17 min at a constant flow rate of 1.5 mL/min. Peak areas were measured, and the additive concentrations were calculated from standard graphs obtained by analyzing pure antioxidant samples.

SFE Experimental Design

As mentioned earlier, the supercritical fluid extraction process involves two different and independent steps. The first is extraction of the interesting analytes from the matrix, and the second is collection of these analytes from the supercritical fluid stream. Both steps are closely related to each other, but each is controlled by separate variables. For this reason, the joint optimization of the two steps is difficult to perform, and they must be studied independently. Therefore, the experiments are based on two sets of trials, where the parameters have been varied according to Table I using a factorial design method. Further experiments were then carried out to investigate how to achieve 100% recovery of antioxidants.

Test Materials

Nonstabilized polypropylene from Borealis Company was selected for use in this work. Polypropylene samples with known amounts of antioxidants were prepared by mixing the polymer and the additive. The amount of antioxidants was 0.25% by weight of each in the optimization experiments and 0.25–2.0% in the second part of the study. The selected antioxidants were Irganox

Table I   Parameters Varied in Optimization Experiments

Parameters	Experimental Plan 1	Experimental Plan 2
Chamber and nozzle temperature during extraction	65–120°C	120°C
Chamber pressure	90–384 bar	384 bar
Supercritical fluid flow	0,5–4 mL/min	4 mL/min
Modifier	acetone or methanol	methanol
Amount of modifier	2–10%	2–8%
Analyte trap temperature during absorption	70°C	20–100°C
Analyte trap temperature during rinse	40°C	15–45°C
Nozzle temperature during rinse	40°C	15–45°C

1010 and Irgafos 168 from Ciba-Geigy, Ltd. and their structures are as follows:
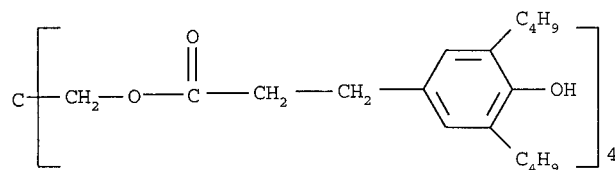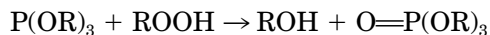

Irganox 1010
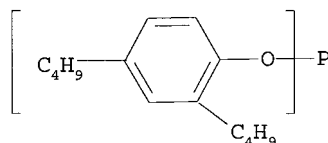
Irgafos 168

The combination of these antioxidants has an synergistic effect[19,20] and are, therefore, often used together. Irgafos 168 is an phosphite, and it is less polar than Irganox 1010. Irgafos 168 reacts with hydroperoxides and produces phosphates according to the following reaction.[21]

$$P(OR)_3 + ROOH \rightarrow ROH + O{=}P(OR)_3$$

Irgafos 168 is a short-term antioxidant designed to provide protection during processing or fabrication to finished product. Antioxidants intended to provide protection during processing must be capable of migrating freely throughout the polymer mass to reach the large number of initiation sites generated at elevated temperatures, and the short-term antioxidants are, therefore, often small molecules. Short-term antioxidants, as the term implies, are not intended to give protection during extended use and are often consumed in used plastic products.

Irganox 1010, on the other hand, is an antioxidant designed to give long-term protection and is, therefore, larger in size and has less mobility through the polymer. Irganox 1010 has four sterically hindered phenolic groups, all of which function as antioxidants, and partly oxidized Irganox 1010 is still active as antioxidant. The mechanistic action of phenolic antioxidants have been reviewed by Pospisil.[22]

RESULTS AND DISCUSSION

Initially, in this study, calibration of the HPLC equipment for the selected antioxidants were performed. A typical HPLC chromatogram for the SFE extract of polypropylene is shown in Figure 2. The peaks at 7 and 15 min originate from Irganox 1010 and Irgafos 168.

Optimization of Extraction Efficiency

In the first part of the investigation, the extraction efficiency was optimized. Modifiers were used, because organic solvents added to the CO_2 can bring about softening or swelling of the polymer matrix, thus allowing easier penetration of the extraction fluid. During all experiments, the parameters of the second part of the equipment were kept constant, and the values were selected based on the experience gained in IFPs laboratory.

The results from the first stage of the optimization were found to be similar for both types of antioxidants. The highest levels of recovery were achieved at 120°C and a pressure of 384 bar. The most effective modifier was found to be methanol, and the optimum concentration of modifier was
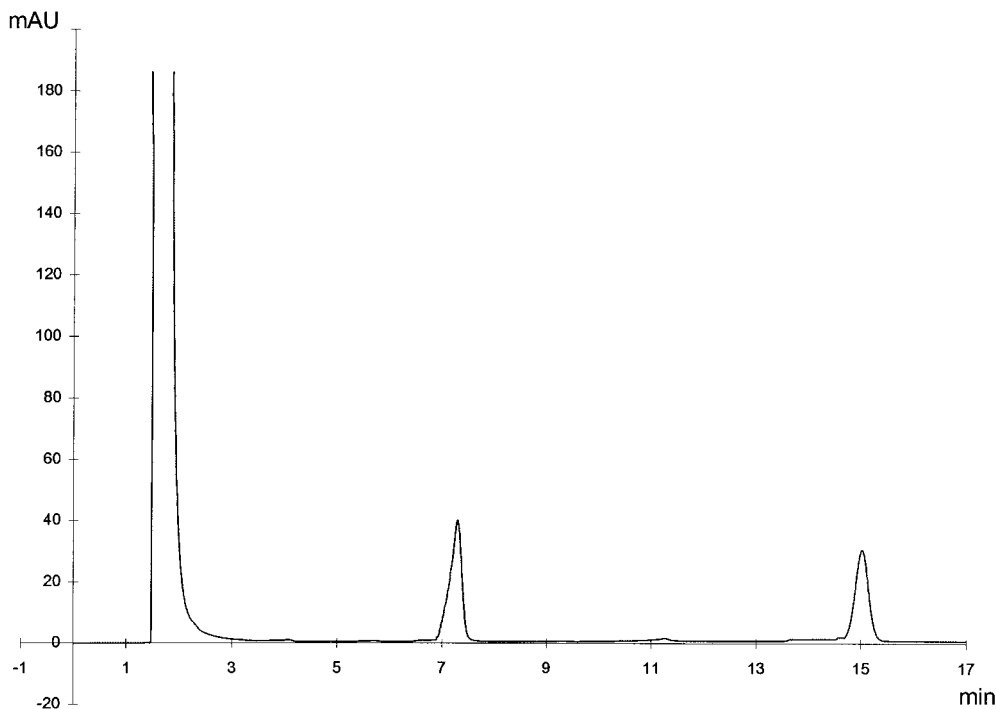
Figure 2   A typical HPLC chromatogram for the SFE extract of polypropylene. The peaks at 7 min and 15 min originate from Irganox 1010 and Irgafos 168.

2%. The highest levels of recovery were received when the flow of supercritical fluid was 4 mL/min.

In Figure 3, the recoveries of Irganox 1010 are shown as a function of pressure and temperature. The modifier is 2% methanol, and the flow of CO_2 is 4 mL/min. The recoveries of Irgafos 168 at similar experimental conditions are shown in Figure 4. As can be seen from the figures, the amount of extracted antioxidant is greater at higher temperatures, despite the fact that the density, and consequently, the solvating power of the super-
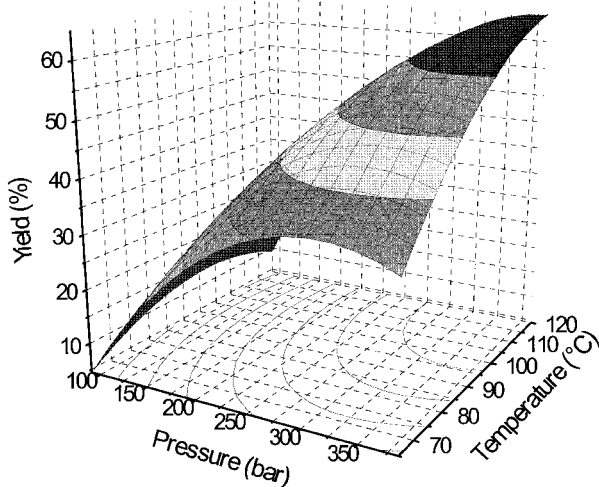

Figure 3   Recoveries of Irganox 1010 as a function of pressure and temperature. The modifier is 2% methanol and the flow of CO_2 is 4 ml/min.
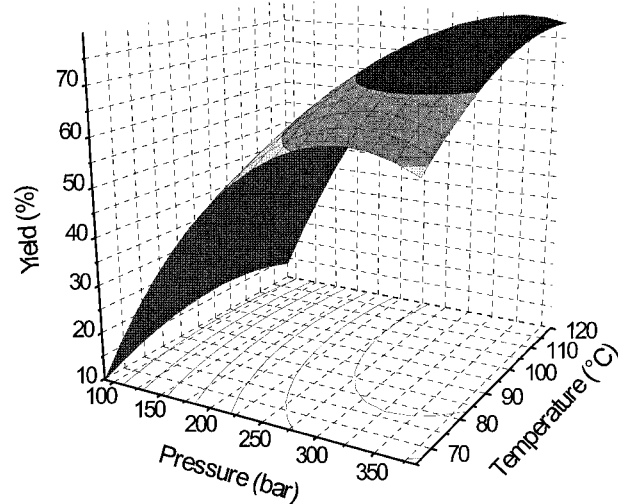

Figure 4   Recoveries of Irgafos 168 as a function of pressure and temperature. The conditions are similar to those in Figure 3; e.g., the modifier is 2% methanol and the CO_2-flow is 4 mL/min.
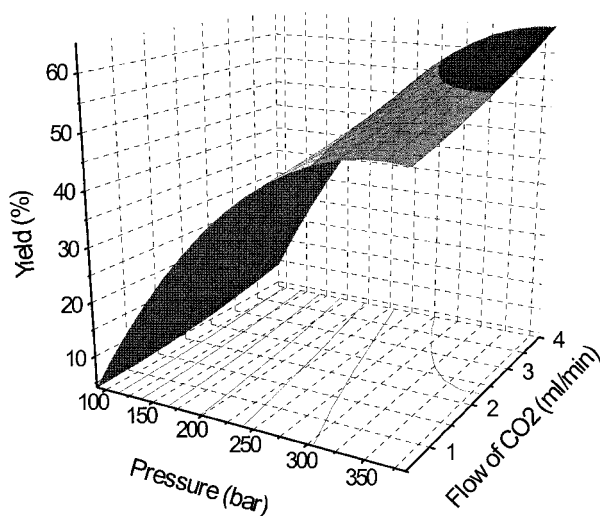
Figure 5 The effect of the flow of the supercritical fluid on the recoveries of Irganox 1010. The temperature is 120°C, and the modifier is 2% methanol.

critical fluid decreases with increasing temperature. This indicates that the solubility parameter of the fluid is not the most important factor for achieving high recoveries. The increased diffusivities of CO_2 and antioxidants in the polymer matrix at higher temperatures may be a more important contributing factor.

Moreover, the mechanism could involve the effect of pressure based on two opposite factors. On one hand, the higher the pressure, the greater is the density increase and the increase in the solubility parameter, according to eq. (1). On the other hand, an increase in pressure would lead to a decrease in the diffusion capacity of the supercritical fluid and, consequently, to a lower accessibility of the analytes. The importance of solubility factor relative to accessibility allows the pressure to have either a positive or a negative effect on the extraction efficiency, as shown in Figures 3 and 4. There are differences between the effect of the pressure at high versus low temperature. As seen in Figures 3 and 4, the effect of low solubility at low pressures is more pronounced at 65°C as compared with 120°C. Figures 5 and 6 show the recovery as influenced by the supercritical fluid flow. At 120°C and for 2% methanol as the modifier, it is advantageous to use high levels of supercritical fluid flow and pressure.

Optimization of the Collection Efficiency

The second part of the optimization work was aimed at optimizing the collection efficiency. For antioxidants extracted from polymers, no work has been found in the literature on the collection efficiency as a function of trapping and rinsing conditions. It was, therefore, decided to investigate the performance of the trap with various modifier concentrations and trap temperatures. In this part, the pressure was 384 bar, the temperature was 120°C and the CO_2-flow was 4 mL/min with methanol as modifier according to the optimization work concerning the first part of the equipment. The trapping was carried out at temperatures above and below the boiling point of the modifier. The boiling point of methanol is 64.7°C at 1 atm. If the trap is maintained above the boiling point of the modifier, the modifier should vaporize upon contact with the trap and vent to waste. However, the analytes of interest may not effectively trap at the temperatures required to vaporize the modifier. On the other hand, if the trap temperature is maintained at temperatures below the boiling point of the modifier, the modifier may condense in the trap and influence the trapping efficiency. Because of these facts, it is important to optimize the temperature of the trap to get as effective trapping as possible. As mentioned earlier, no work has been published on the collection efficiency concerning antioxidants extracted from polymers, but the work of Mulcahey and Taylor[9] indicates that cryogenic trapping is an important component in trapping of volatile compounds. The optimum conditions for trapping and rinsing in the present study were found to be
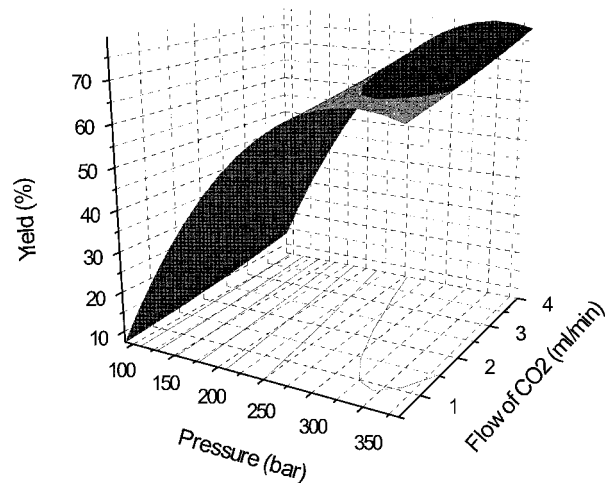

Figure 6 The effect of the flow of the supercritical fluid on the recoveries of Irgafos 168. The conditions are similar to those in Figure 5; e.g., the temperature is 120°C, and the modifier is 2% methanol.

Table II   Recoveries from the Optimizations

	Recovery (ppm)	Recovery (%)	SD (%)
Irganox 1010 (optimization 1)	1570	62.6	2.8
Irgafos 168 (optimization 1)	1850	74.1	2.0
Irganox 1010 (optimization 2)	1450	57.2	5.0
Irgafos 168 (optimization 2)	1720	68.7	2.9

Results are from four replicate tests.

as follows; trap temperature during extraction 100°C, nozzle temperature during rinse 45°C, and trap temperature during rinse 15°C. The modifier concentration should be 2%. As seen in Table II, the recoveries are slightly less than those received in the first optimization stage.

Investigation of the Reasons for Low Recovery

As is obvious, it has not been possible to recover completely the amount of antioxidants that were initially mixed into the polymer resin. The deviation of recovered antioxidants may be attributable to several factors, including evaporation during mixing of the components, transformation of antioxidants during the mixing period, and the uniformity of distribution of antioxidants in the matrix. The antioxidant may also react during the extraction and analysis, and the reaction products are difficult to quantify.

To rule out the matrix effects from the extraction and investigate only the solubility and trapping, the antioxidants were extracted from two different inert supports (cotton pads and standard filter paper) at the optimum conditions found in the optimization experiments. The antioxidants were dissolved in acetone before they were applied to the inert supports. Different amounts of antioxidants were applied to the inert supports, and the results are shown in Figure 7,
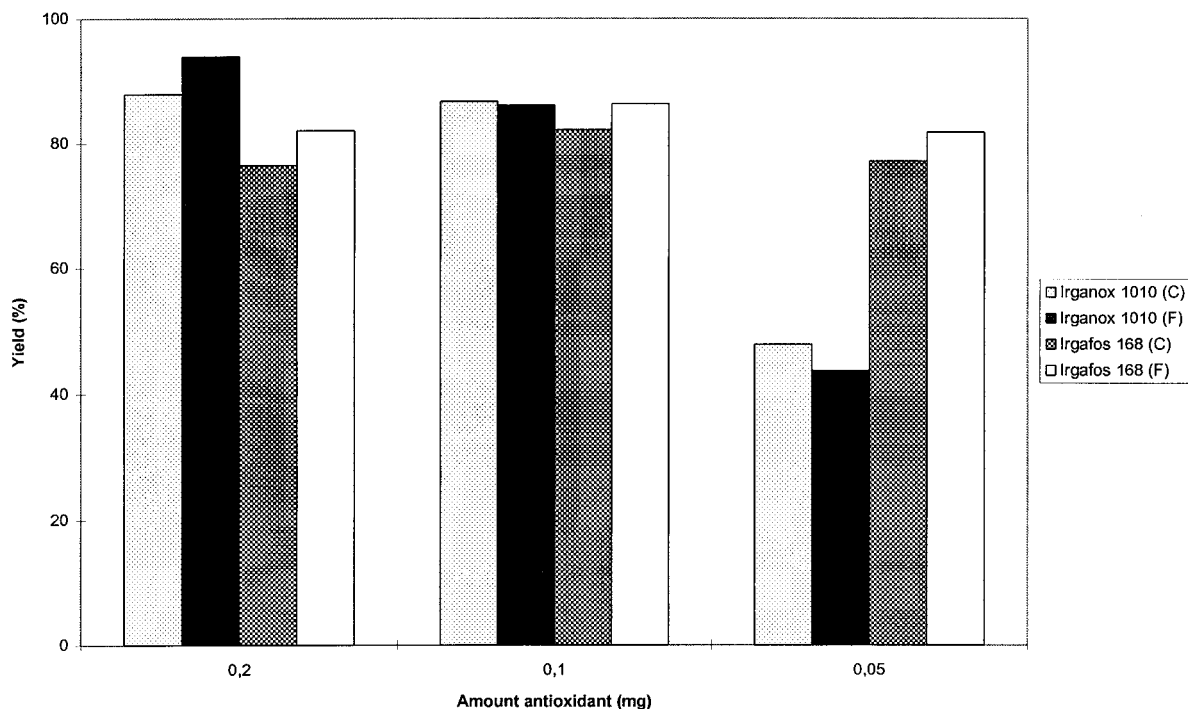

Figure 7   Recoveries of Irganox 1010 and Irgafos 168 from two inert supports, (C) cotton pads and (F) standard filter paper. The extractions were performed at the optimal conditions found in the optimization experiment.

Table III   Recoveries from Cotton Pads and Standard Filter Paper

Amount (mg)	Cotton Pads				Filter Paper			
	Irgafos 168 (%)	SD (%)	Irganox 1010 (%)	SD (%)	Irgafos 168 (%)	SD (%)	Irganox 1010 (%)	SD (%)
0.2	76.5	16.1	87.9	12.1	82.0	2.6	94.0	3.2
0.1	82.2	13.8	86.7	8.5	86.4	0.7	86.1	2.9
0.05	77.2	10.8	47.9	10.3	81.9	9.9	43.7	3.5

The results are from four replicate tests.

the recoveries, including standard deviations, are shown also in Table III. When the inert supports were used at relatively high concentrations of antioxidants, the recoveries were approximately 90%. The recoveries from inert support are higher than that from the polymer matrix. This shows that the reason for not having a 100% recovery may not only be attributable to the transport of antioxidants out of the polymer matrix. It may also be attributable to the solubility of the antioxidants in the CO_2 and the trapping of antioxidants in the analyte trap. Rinsing of the trap, however, was always complete, and this was confirmed by the fact that no antioxidants were obtained from a second rinse of the trap.

The difference between levels of recovery from a polymer matrix and a inert support may also be attributable to losses of antioxidants during the compounding process. To investigate this aspect, a new compounding was made in a very controlled manner. The compounding was done with 40 g polymer in each batch. The antioxidants were carefully added during the compounding, and no visual losses were recognized. The aim of the first part of this study was to optimize the recoveries, and the second part was to investigate the reliability of the method. The concentrations of the antioxidants in this second part were 250–2000 mg/g polymer (0.25–2%). As shown in Figure 8, recoveries for both antioxidants are quantitative at the concentrations used in commercial polymers; for example, concentrations lower than 500 mg/g. This indicates that the deviations from expected yields in our experiments reported earlier was probably attributable to problems associated with the compounding process and not to uncertainties in the extraction and analytical method. The recoveries are lower at higher concentrations of antioxidants, and this could be attributed to the low solubility of the antioxidants in the polymer matrix.[4] The low solubility of the antioxi-

dants in the polymer matrix leads to losses of antioxidants during handling, this effect being larger at higher concentrations.

CONCLUSIONS

The effect of experimental variables was investigated to develop a rapid, reliable, and quantitative SFE method for extraction of antioxidants from a polypropylene matrix. It is shown that the temperature and pressure are the most important parameters for obtaining effective extraction. The optimum condition for extraction of the antioxidants Irganox 1010 and Irgafos 168 were found to be at a temperature of 120°C and at a pressure of 384 bar; these are the maximum allowable levels. The other extraction parameters do not have any significant effect on the results.

The optimum conditions for the trapping and rinsing were found to be: trap temperature during extraction 100°C; nozzle temperature during rinse 45°C; and trap temperature during rinse 15°C. The modifier concentration should be 2% or lower. The optimum recoveries are 74% for Irgafos 168 and 63% for Irganox 1010. Because the highest extraction temperature gives the best results, it can be concluded that high solubility is not the only reason for high extraction efficiency. The results indicate that, in the temperature and pressure range used, the mobility of the antioxidants in the polymer matrix is a much more important factor than the solvating power for achieving an effective extraction. It is also shown that the trapping and rinsing parameters are very important for optimizing high recoveries.

The results also show that it is very important to control the compounding procedure, because there could be significant losses of antioxidants during the mixing of polymer and antioxidant. It was demonstrated that, with very controlled compounding,
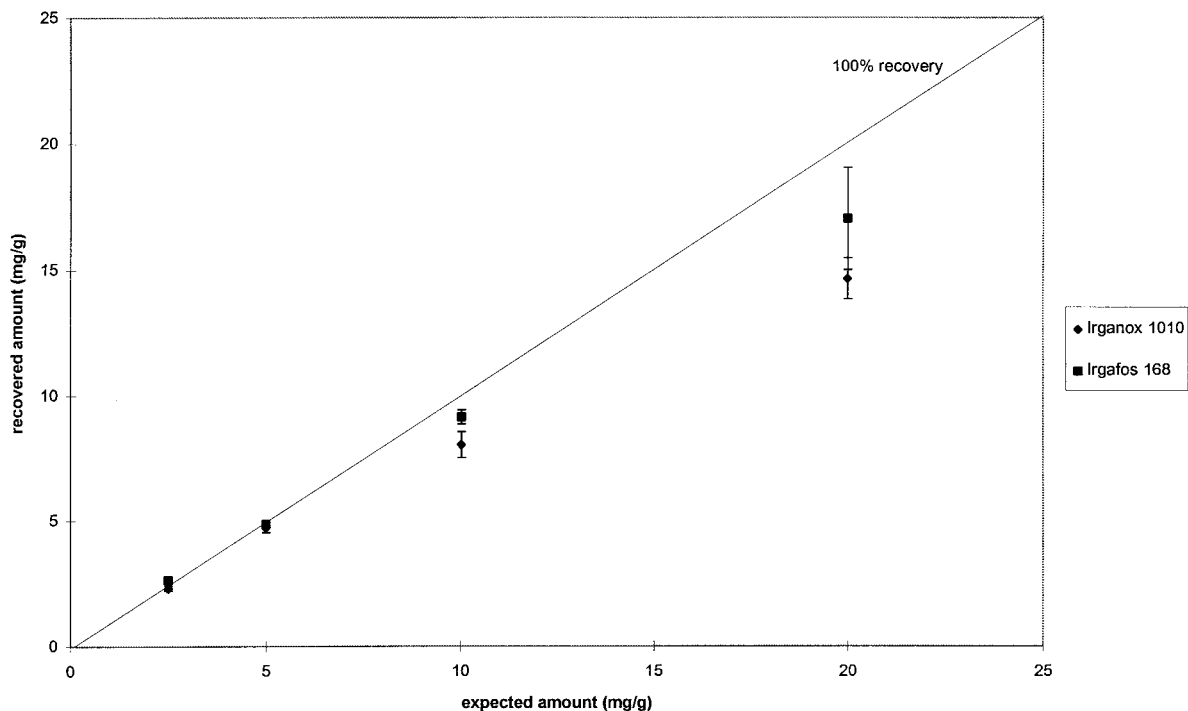
Figure 8 Recoveries of Irganox 1010 and Irgafos 168 from polymer samples where the antioxidants were added to the resin in a very controlled way. The extraction were performed at the optimal conditions found in the optimization experiment.

the recoveries at the optimized extraction conditions reached a level of approximately 100%.

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