# Directly Coupled Supercritical-Fluid Extraction/Capillary Supercritical-Fluid Chromatography of Polymer Additives

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## Key Words

Supercritical-fluid chromatography (SFC)
Supercritical-fluid extraction (SFE)
Trapping technique
Polymer additives

## Summary

The direct coupling of supercritical-fluid extraction (SFE) to capillary, supercritical-fluid chromatography (SFC) is described. The SFE/SFC system has a flame ionization detector and a direct injection system. The interface consists of a developed restrictor unit and a trapping tube. The fluid extract is decompressed through a restrictor into the trap where the solutes are precipitated and concentrated. The solutes are transferred from the trap to the capillary column by valve switching. The efficiency of various traps has been evaluated using n-paraffin standards. The effect of extraction temperature and pressure on the extraction efficiency is discussed for polymer additives. The applicability of the SFE/SFC system is demonstrated using several polypropylene samples.

## Introduction

Recently, there have been a number of publications demonstrating the utility of supercritical-fluid extraction directly coupled with supercritical-fluid chromatography (SFE/SFC) for analysis of a wide variety of analytes in complex matrices [1–8]. There are several trapping techniques for coupled SFE/SFC; cryotrapping has become the most commonly used method [1–5]. This requires extremely low temperatures because volatile analytes are partially or completely lost, especially when long extraction times are used [3, 6]. Too low a temperature may cause plugging of the restrictor from the extraction cell, which results in lower extraction efficiency [7, 8]. The alternative to cryotrapping is a technique using a sorbent [6, 9, 10]. The use of sorbents can improve the trapping efficiency even for volatile analytes but has the drawback that the desorption rates of polar solutes from adsorptive materials are relatively slow. The peak width therefore becomes broader compared to the cryotrapping method [6, 9]. Although this problem can be solved by using a modifier [10], the use of modifiers make the use of an FID impossible.

Among SFE/SFC applications is the analysis of polymer additives [2, 9] which have a wide range of relative molecular mass, polarity and hence volatility. Therefore, SFE coupled with gas chromatography (SFE/GC) has limitations, although the technique is well documented [7, 8].

This work describes the development of coupled SFE/capillary SFC and its application to the analysis of polymer additives. Various traps with or without stationary phase, including a packed trap, were used. The effect of temperature and extraction time on trapping efficiency was examined. The effect of temperature on extraction efficiency was also studied for polymer additives.

## Experimental

### Apparatus

Figure 1 shows a schematic diagram of the SFE/SFC system which consisted of three sections; extraction, collection and separation. Since the system is also equipped with an ordinary injector, liquid sample can be injected without changing the plumbing. Liquefied carbon dioxide was delivered with a model LC-6A pump (Shimadzu, Kyoto, Japan) equipped with a home-made pressure controller.

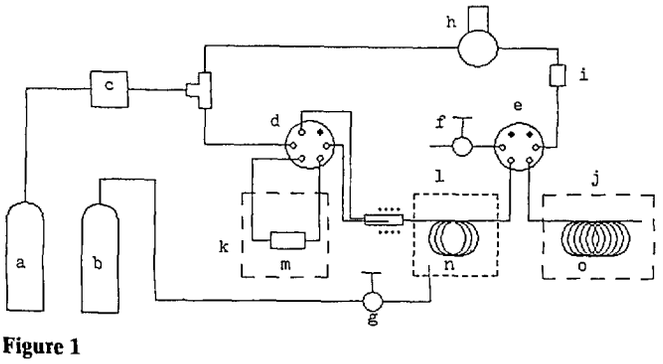


**Figure 1**
Schematic diagram SFE/SFC system.
(a) $CO_2$ for SFE and SFC, (b) $CO_2$ for cooling, (c) pump, (d) and (e) six-way valve, (f) and (g) stop valve, (h) injector, (i) mixing chamber, (j) and (k) oven, (l) cooling bath, (m) extraction chamber, (n) trapping tube, (o) analytical column.



0009-5893/91/12 0549-06 $ 03.00/0

The pump head was cooled with a MC-28T microcooler (Netsudenshi Kogyo, Tokyo, Japan). Carbon dioxide used as the extracting solvent and as the mobile phase was of food additive grade (99.99 % purity). The GC-6A gas chromatograph oven (Shimadzu) was used to control column temperature and the FID from a gas chromatograph was used for SFC detection. The column outlet restrictor was inserted into the FID nozzle. A Rheodyne 7520 injector (Cotati, California, USA) was equipped with a 0.5 µl rotor. The outlet of the injector was connected to the mixing chamber as described previously [11]. The six-way valve and stop valve were a Rheodyne 7000 and a SSI valve from Alltech (Deerfield, Illinois, USA), respectively.

As the fluid passes through the cell, sample is extracted with supercritical $CO_2$ at controlled pressure and temperature. The $CO_2$ was decompressed at the end of the restrictor and vented through the capillary trapping tube, the six-way valve and the stop valve to atmosphere. If necessary, the separation column can be cleaned with $CO_2$ at the same pressure as for extraction. After the desired extraction time, the restrictor heater was switched off and the system pump pressure reduced from the extraction pressure to the starting pressure for chromatography. Two six-way valves were rotated to the positions for SFC separation and a pressure program started.

Details of the extraction chamber are shown in Figure 2. The extraction chamber was constructed from PTFE tubing (20 mm×2 mm i.d.). Quartz wool was placed in the chamber when introducing a liquid sample. The chamber was connected to a stainless steel capillary inside the stainless steel tubing (12 cm×4.6 mm i.d.). The stainless steel capillary was directly connected to a six-way valve through a 1/16″ T. A stop valve connected to a remaining port of the T was used to depressurize or clean the extraction chamber which was heated during extraction.

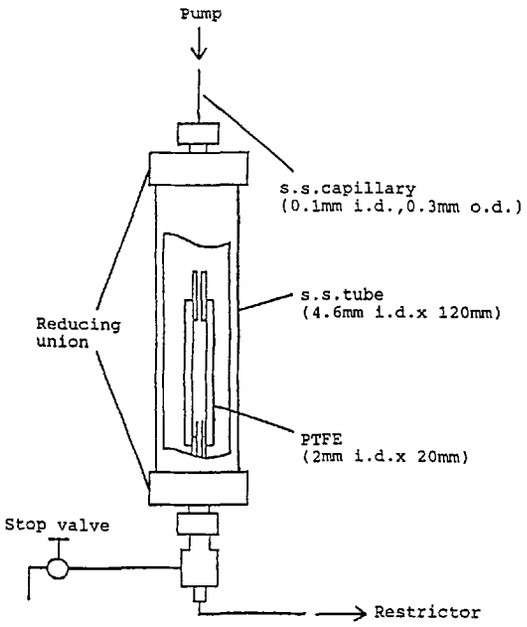


**Figure 2**
Detail of extraction chamber.

A detailed schematic diagram of the SFE/SFC interface is given in Figure 3. Both extraction line and mobile phase line (0.1 mm i.d., 0.3 mm o.d.) were soldered into a stainless steel tube (0.6 mm i.d., 1.0 mm o.d.). The mobile phase line was cut at the base, while the end of the extraction line was pinched to serve as a restrictor. The other end of each line was also soldered into a 1/16″ stainless steel tube to minimize dead volume within the six-way valve. The restrictor was placed in a stainless steel tube (50 mm × 0.6 mm i.d.), the volume of which was about 14 µl. During extraction, the restrictor was heated at 120 °C to maintain a constant flow rate. The gas flow rate used for extraction was about 10 ml $min^{-1}$ at 300 atm.

Four different types of traps were used; silylated fused silica (3 m × 0.1 mm i.d.), fused silica (3 m × 0.1 mm i.d.) coated with OV-1 0.1 or 0.25 µm thickness and fused silica (20 mm × 0.25 mm i.d.) packed with Kaseisorb ODS-300-5 (Tokyo Kasei, Tokyo, Japan). The packed trap was connected to the end of the uncoated fused-silica trap. Trapping tubes except for the packed trap were cooled when necessary.

The separation column was a fused silica capillary (10 m × 0.1 mm i.d.) with octyl phase 0.5 µm thickness (Lee Scientific, Salt Lake City, Utah, USA). The column pressure was kept at 100 atm for the first 10 min, then increased at 5 atm $min^{-1}$. The column and FID temperatures were kept at 90 °C and 250 °C, respectively.

## Samples

Two standard solutions were prepared in methylene chloride. One contained n-paraffins ($C_{12}$–$C_{20}$) 100 ppm of each. The other contained four polymer additives, BHT(2,6-di-tert-butyl-4-methylphenol), Tinuvin 326 (2-(5-chloro-2-benzotriazoyl)-6-tert-butyl-p-cresol), Seenox DM (3,3'-thiodipropionic acid dimyristyl ester), and Irganox 1010 (pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]), 100 ppm each. Polymer samples used were various commercially available, polypropylenes, which were frozen with liquid nitrogen and ground. About 1 g powdered polymer was soaked in 2 ml methylene chloride for one week. The solution was used for the comparative study of SFE/SFC and solvent extraction.

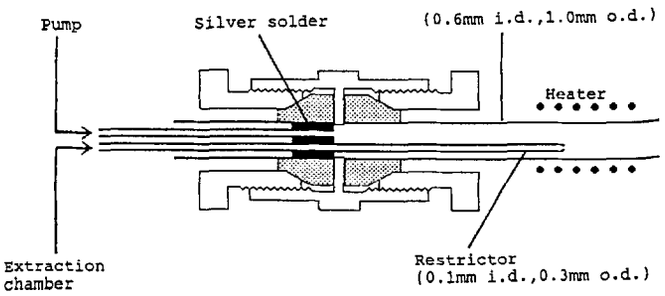


**Figure 3**
Detail of interface.

## Results and Discussion

### Efficiency of Various Traps

Generally, the success of analytical SFE/SFC largely depends on the trapping techniques to recover the extracted solutes from the expanded gas flow after depressurization, particularly when the analytes are volatile. The primary object of this research is to evaluate the efficiency of various traps and to optimize the SFE conditions for polymer additives.

First, we examined the efficiency of four types of traps using n-paraffins ($C_{12}$–$C_{20}$) as a standard sample (Figure 4). A chromatogram obtained by direct injection is also shown. The 0.5 µl standard solution was loaded in the empty extraction chamber. Extraction was at 300 atm and room temperature (about 30 °C) for 30 min. The trapping tube was also at room temperature. Although there are some variations in peak height due to the poor reproducibility of syringe injection, the result clearly indicates that the trapping efficiency is improved with increasing film thickness of the stationary phase. In spite of its short length, the efficiency of the packed trap (Figure 4-E) is comparable to that of a capillary with 0.25 µm film. Recently, Hirata et al. reported the efficient recovery of polymer additives in off-line SFE/LC using a trap packed with silica gel [12]. However, polar solutes can not be desorbed from silica gel with $CO_2$. Although ODS-silica used in this work is relatively innert [13], some of polymer additives were difficult to desorb. In the following experiment, therefore, the capillary with 0.25 µm film was used as a trapping tube.

### Effect of Temperature and Extraction Time on Trapping Efficiency

The trapping tube was cooled to each temperature during the extraction period (30 min) as shown in Figure 5. The extracts were dissolved in liquid $CO_2$ at room temperature and transferred to the analytical column. It can be seen that the most volatile solute, $C_{12}$, was trapped at 0 °C.

Figure 6 shows the effect of extraction time on trapping efficiency. The temperature of the trapping tube was 30 °C. The result indicates that volatile solutes were eluted from the trapping tube with $CO_2$ gas after longer extraction time.

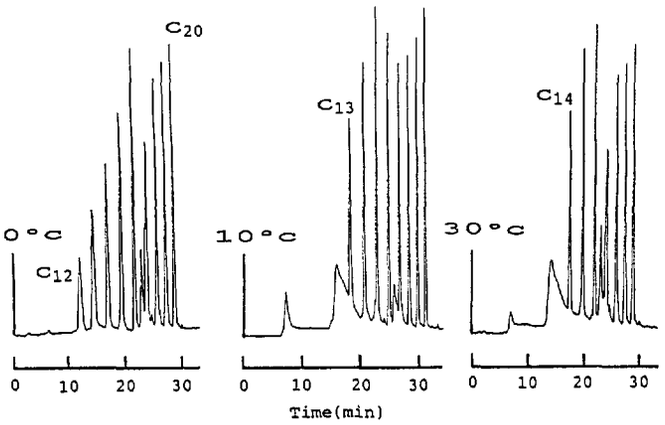


**Figure 5**
Effect of cooling on efficiency. Trap: Capillary 0.25 µm film. Other conditions as Figure 4.

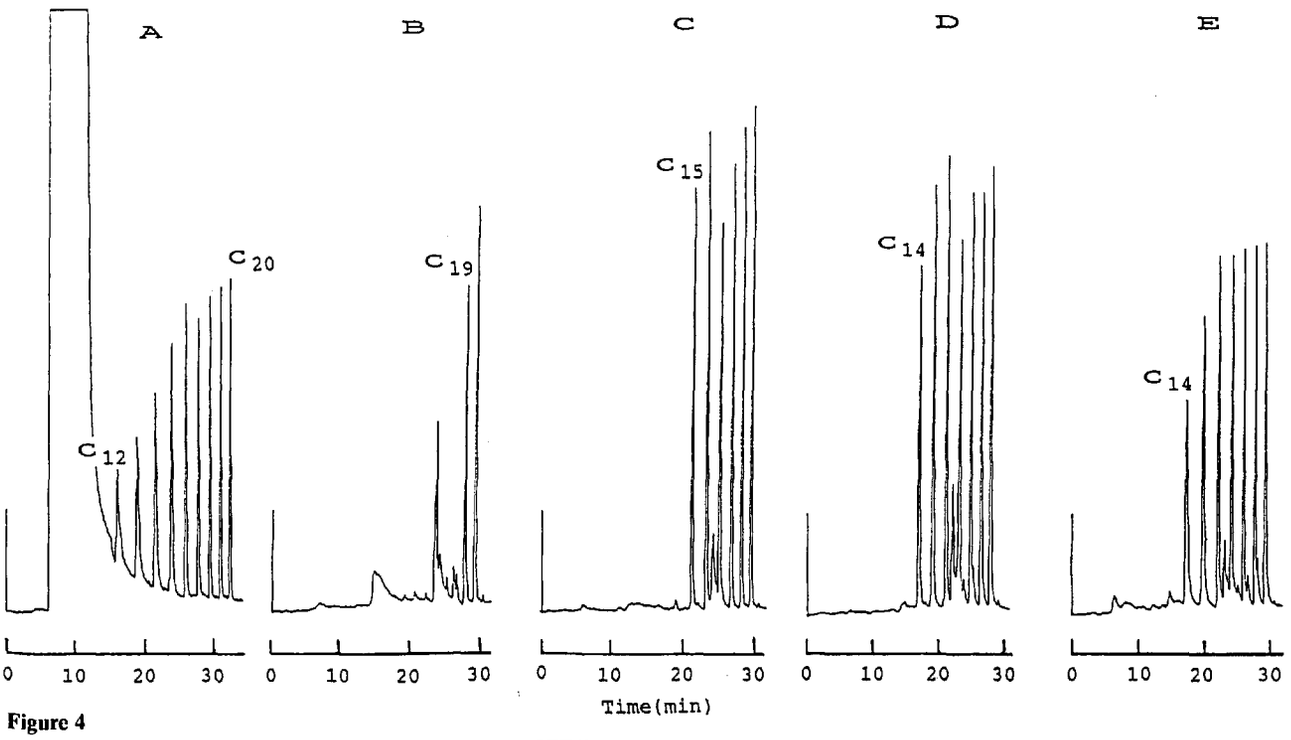


**Figure 4**
Comparison of sample recoveries using various traps in SFE/SFC systems.
Chromatogram A obtained by direct injection. Traps: uncoated capillary (B), capillary with 0.1 µm film (C), capillary with 0.25 µm film (D), uncoated capillary plus packed capillary (E), Sample: n-paraffins ($C_{12}$–$C_{20}$), 0.5 µl 100 ppm solution extracted at 300 atm for 30 min with liquid $CO_2$; trapped at room temperature. Flow rate: 10 ml $min^{-1}$ as gas. Column: 10 m × 0.1 mm id, octyl, 0.5 µm film. Column temperature: 90 °C. Column pressure: 80 atm for A and 100 atm for others for 10 min, then programmed at 5 atm $min^{-1}$. Detection: FID.

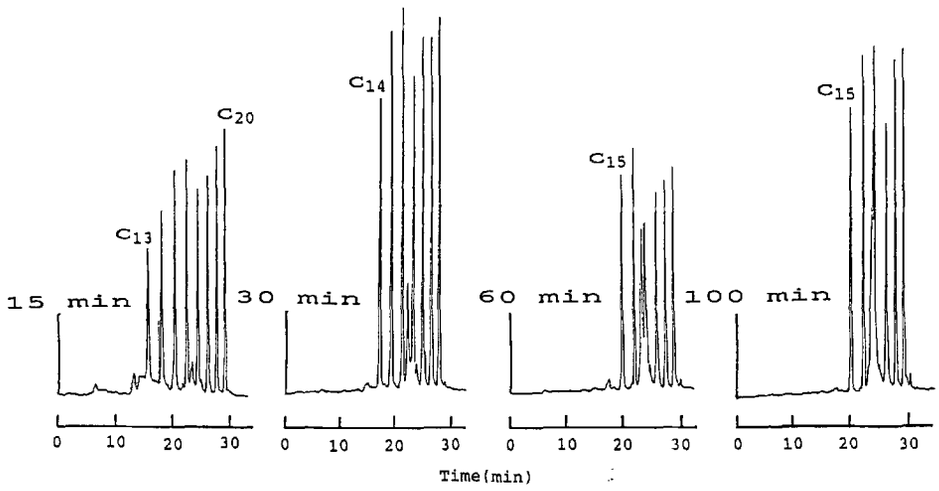


**Figure 6**
Effect of extraction time on efficiency. Trap: Capillary 0.25 µm film. Other conditions as Figure 4.

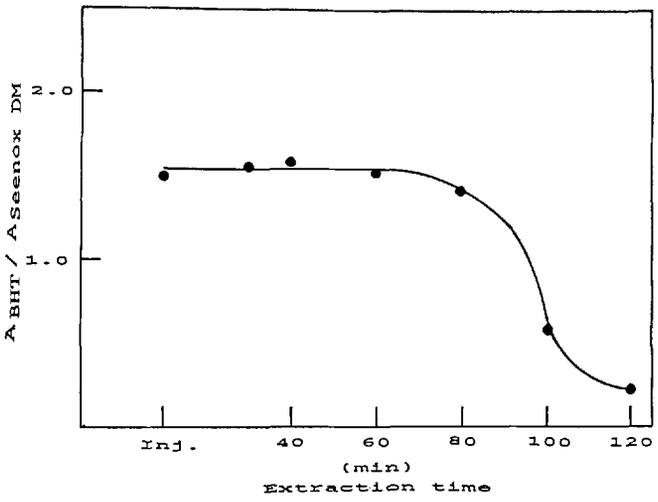


**Figure 7**
Effect of extraction time on efficiency for BHT. Extracted at 30 °C and 300 atm. Trap: capillary 0.25 µm film. Other conditions as Figure 4. Inj. = SFC direct injection.

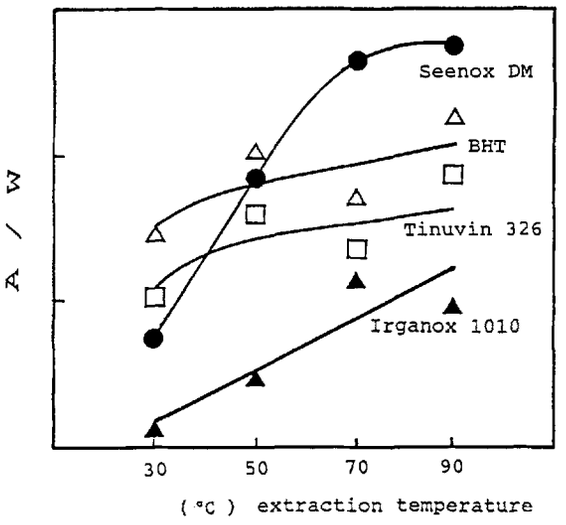


**Figure 8**
Effect of temperature on efficiency. Extracted at 300 atm 30 min. Sample: polypropylene (0.25–0.30 mg). Other conditions as Figure 4.

Cooling the trapping tube during extraction would improve the efficiency.

Figure 7 also shows the effect of extraction time on trapping efficiency for BHT. The standard solution of polymer additives was injected into the extraction chamber and then extracted under the same operating conditions as in Figure 6. Less volatile solute, Seenox DM, could be trapped without loss for a long extraction time. In order to correct the poor reproducibility of syringe injection, the ratio of peak area of BHT to that of Seenox DM is plotted against the extraction time in Figure 7. For comparison, the value obtained by direct injection is also plotted. It can be seen that BHT is retained in the trapping tube at room temperature for up to 60 min. The corresponding volume of $CO_2$ – breakthrough volume – is about 600 ml. BHT is one of most volatile solutes among polymer additives, which can therefore, be trapped quantitively without cooling the trapping tube. This is advantageous for routine work with SFE/SFC.

## Effect of Temperature on Extraction Efficiency

Figure 8 shows the effect of extraction temperature on extraction efficiency. About 0.3 mg polypropylene was extracted at 300 atm for 30 min, the temperature was varied from 30 to 90 °C. The peak area of each extract divided by sample weight is plotted. Under these conditions, all solutes can be quantitatively trapped as discussed above. Extraction efficiency increased with increasing temperature for all solutes. Extraction efficiency increased more rapidly for larger molecules. For example, extraction efficiency for Irganox 1010, which is the largest molecule (RMM = 1176), increased about ten times over this temperature range. Increase in temperature acts on solvating power in two different ways. As the density decreases with temperature at constant pressure, solvating power may decrease.

However, solvating power increases with temperature at constant density. The results obtained at constant pressure in Figure 8 imply that increase in temperature is favorable.

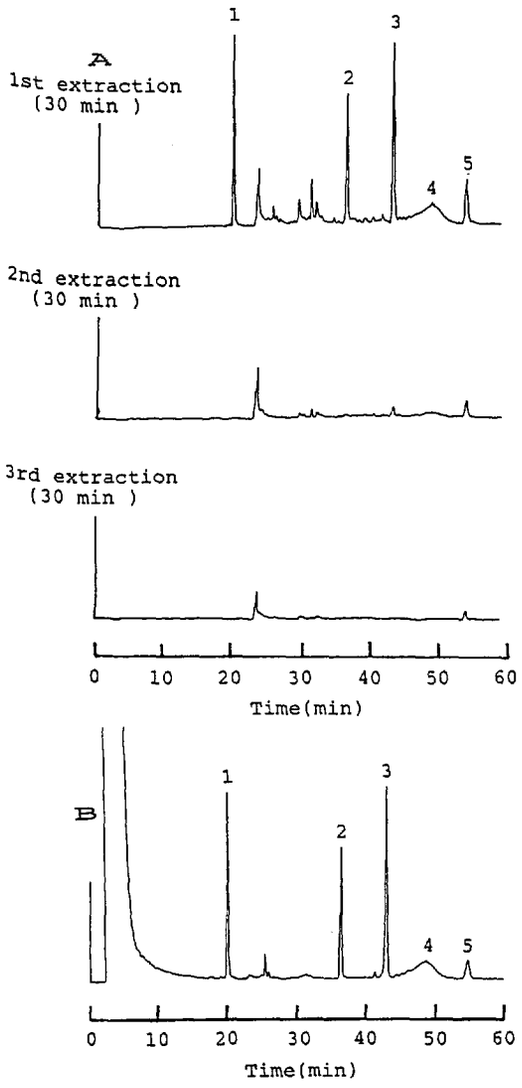


**Figure 9**

Comparison: SFE/SFC (A) and SFC direct injection (B).
(A) Sample: 0.276 mg polypropylene. Extracted at 90 °C, 300 atm. (B) Sample: methylene chloride extracts, corresponding to 0.25 mg polymer. Peaks: **1** = BHT, **2** = Tinuvin 326, **3** = Seenox DM, **4** = Tri(mono/dinonylphenyl)phosphite, **5** = Irganox 1010. Other conditions as Figure 4.

The volatility change of the solutes is an important factor in solubility. However, a more important factor in this experiment may be the increased diffusivities of $CO_2$ and/or additives in the polymer matrix.

## SFE/SFC and Direct Injection SFC

Figure 9 shows a comparison of SFE/SFC and direct injection SFC. In Figure 9-A, polypropylene (0.276 mg) was extracted at 90 °C and 300 atm for 30 min. The use of the powdered sample will reduce an inhomogeneous distribution of additives due to the small amount of sample. The third 30 min extraction was performed on the same sample to demonstrate its completeness. The absence of a significant peak after the third extraction indicates that 60 min was sufficient to extract quantitatively the additives from the polypropylene except for Irganox 1010. The chromatograms also provided data on the recovery level of the analytes of interest. At the first extraction this was greater than 95 % except for the last peak. A peak eluting at 23 min was observed in each chromatogram. This may be from contaminants extracted from the six-way valve. These chromatograms can be compared with those from direct injection SFC. In Figure 9-B, methylene chloride extract was injected directly onto the column through the injector. The sample size corresponds to 0.25 mg polypropylene. In both cases, the peak width is almost the same, and retention times are in agreement. As discussed above, moreover, all additives can be collected quantitatively under these conditions. Hence this method is suitable for identifying and determining extracted components. It is also possible to handle a very small amount of sample with this system.

Figure 10 shows the SFE/SFC analyses of various polypropylene samples. All the additives except for Irganox 1010 were completely extracted in the first 30 min. Therefore total analysis time is less than 2 h, which is much shorter than the traditional method using solvent extraction.

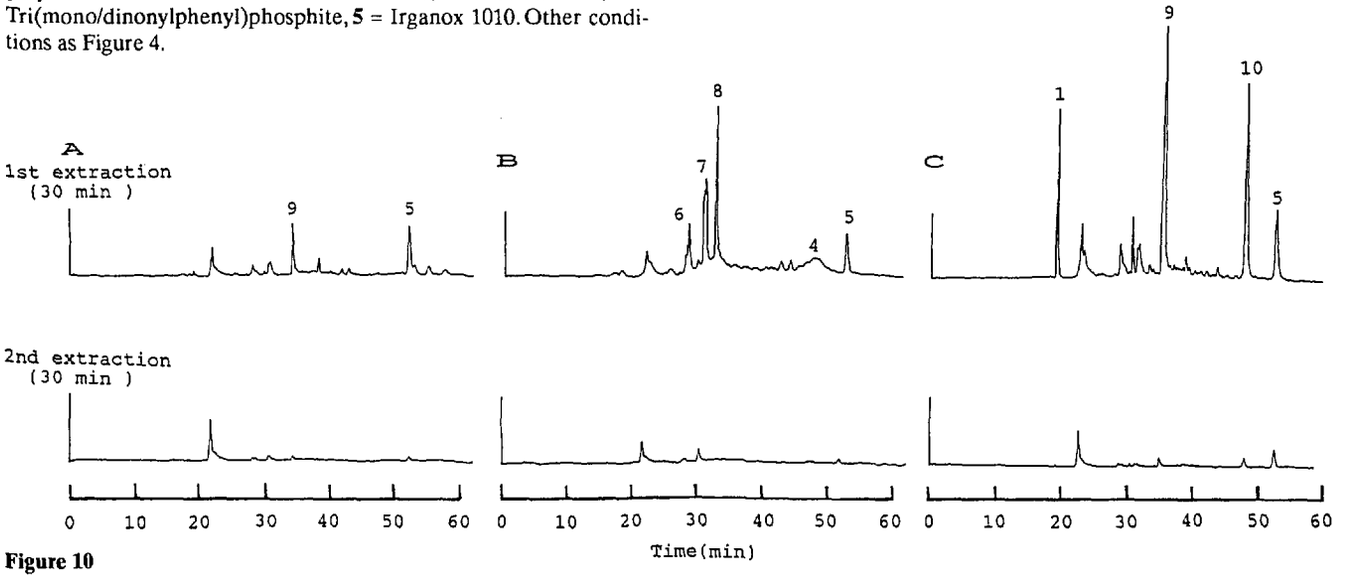


**Figure 10**

Application of SFE/SFC for various polypropylene samples. Peaks: **1** = BHT, **4** = Tri(mono/dinonylphenyl)phosphite, **5** = Irganox 1010, **6** = Glyceryl monostearate, **7** = Stearamide, **8** = 1,3,2,4-Di-p-methyl-benzylidene-sorbitol, **9** = Erucamide, **10** = Di-stearyl-thio-di-propionate. Sample: (A) 0.250 mg, (B) 0.264 mg, (C) 0.318 mg. Conditions as Figure 4.

## Selective Extraction

The same polypropylene sample as used in Figure 9 was extracted at 90 °C for 30 min at three progressively increasing pressures. The chromatograms obtained at each extraction pressure are shown in Figure 11-A. When the extraction was conducted at 100 atm, BHT was extracted almost completely. Tinuvin 326 and Seenox DM were extracted more efficiently at 200 atm together with a small amount of Irganox 1010. Increasing the pressure to 300 atm allowed the remaining Irganox 1010 to be extracted. In this way, selective extraction can be performed by changing pressures, although the selectivity is not high. The results in Figure 8 suggested that selectivity may vary with temperature. Therefore, both pressure and temperature were simultaneously changed to obtain better selectivities as shown in Figure 11-B. When the first extraction was performed at 30 °C and 80 atm, essentially only BHT was extracted. At the next extraction level of 60 °C and 150 atm, Tinuvin 326 was the major component to be extracted, although a low level of Seenox DM was also obtained. At 90 °C and 300 atm where much higher solvating conditions are obtained, the residual additives were extracted. The results imply that much better selectivity could be obtained by optimizing conditions.

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Received: July 22, 1991
Revised manuscript received: Sep. 9, 1991
Accepted: Sep. 25, 1991


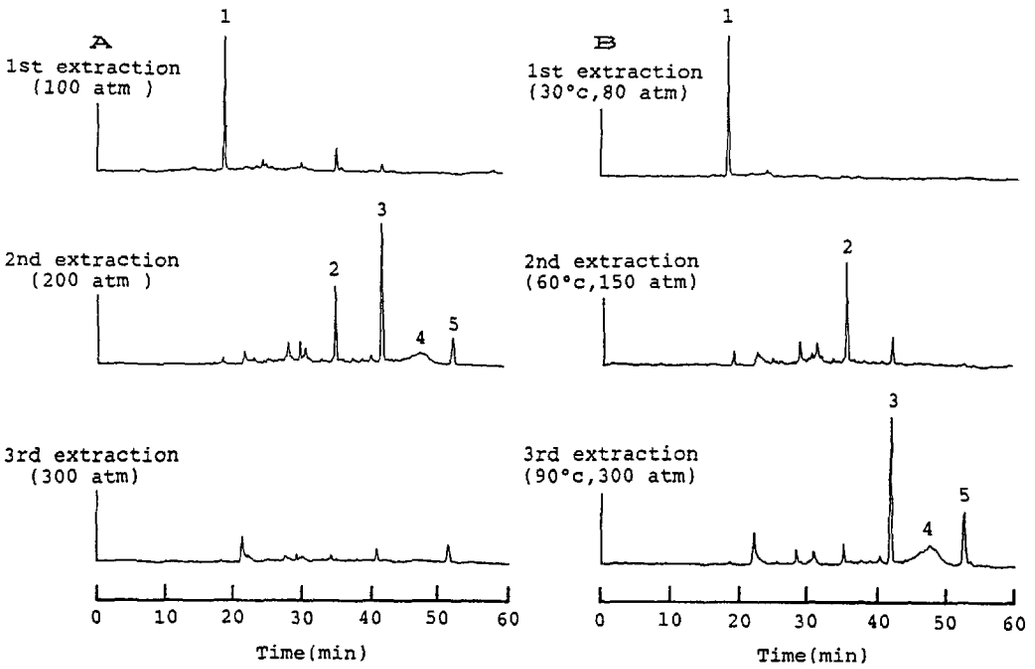


**Figure 11**

Selective extraction of polymer additives by (A) changing pressure, and (B) both temperature and pressure. (A) Extracted at 90 °C 30 min. Sample: 0.216 mg polypropylene. (B) Extracted 30 min. Sample: 0.272 mg polypropylene. Other conditions as Figure 4.