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Quantitative analysis of additives in polymers using coupled supercritical fluid extraction–supercritical fluid chromatography

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SUMMARY

A procedure is described for the quantitative analysis of additives in polymers by a coupled supercritical fluid extraction (SFE)–supercritical fluid chromatography (SFC) system. Various polyethylene and polypropylene samples from several manufacturers were extracted by SFE and the extracts analyzed by SFC. Successful extractions and analyses were performed on ten different additives ranging from butylhydroxytoluene (218 a.m.u.) to Irganox 1010 {pentaerythritol tetrakis[3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propionate], 1178 a.m.u.}. Extraction efficiencies are generally greater then 92%. This technique provides a rapid and accurate alternative for investigators who may normally use a traditional solvent extraction method followed by chromatography or spectroscopy.

INTRODUCTION

Analysis of polymer additives is important in both research and quality control for manufacturers and users of various polymers including polyolefins, synthetic rubbers, polystyrene, etc. Raw materials and finished products are analyzed for these additives. The compounds have a wide variety of physical (*i.e.* volatility and molecular weight) and chemical (*i.e.* amides, esters) characteristics. Consequently, a number of different chromatographic methods have been used for analysis of polymer additives. Gas chromatography (GC) is limited to the separation of low-molecular-weight, volatile, thermally-stable compounds[1,2], although some compounds with a molecular weight greater than 1000 daltons have been analyzed using high-temperature GC[3]. The most widely used method of analysis for these compounds, high-performance liquid chromatography (HPLC), lacks a simple sensitive universal detector that is compatible with all liquid mobile phases[4–7].

More recently, supercritical fluid chromatography (SFC) using flame-ionization detection (FID) and Fourier-transform infrared (FT-IR) detection has been applied to the analysis of polymer additives[8,9]. Its was shown in these reports and it has been our experience that many of the more common polymer additives can be analyzed by SFC using a single mobile phase (CO_2), column type and chromatographic parameters.

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Off-line liquid phase extraction before analysis of these compounds in polymer samples generally involves many time consuming steps, including Soxhlet extraction, concentration, clean-up, reconcentration and reconstitution of the sample in an appropriate solvent for analysis by GC, LC or SFC. Hirata and Okamoto[10] have successfully used supercritical fluid extraction (SFE) as a single rapid method to collect additives for subsequent analysis by micro-LC. There have been a number of publications demonstrating the utility of SFE directly coupled with GC[11–15], LC[16,17] ad SFC[18–27] for facile analysis of a wide variety of analytes in complex matrixes.

In this work, we describe a method for the direct SFE–SFC analysis of additives in polymers. Analysis of polymer additives using a coupled SFE–SFC system is an effective alternative method. Additives are typically extracted under relatively mild conditions. Oligomers are also extracted, but at much higher pressures. This enables the investigator to selectively extract either oligomers or additives. When necessary, ultraviolet and flame ionization can be used in series as detectors for SFC, a single high-pressure extraction analysis can be employed to provide the concentration of a chromophoric additive against an oligomer fingerprint. Extraction–analysis times are generally under 1 h.

The coupled system was used because of the high degree of automation. When the SFE–SFC system is automated, sample handling is reduced to loading the extraction vessel with the sample. This aids in eliminating variations in quantitative results.

Using the coupled SFE–SFC system, the objective was to extract various additives from several commercial polymer samples and to quantitate the level of additives in the sample. In defining the analytical methods, the key questions addressed were: (1) Is the analysis reproducible? (2) Is the analysis quantitative? (3) Is the quantitation linear over the range of concentrations expected for the analysis? (4) What is the recovery level of the analytes of interest? (5) Will chromatographic efficiency degrade for the SFE–SFC analysis of a sample relative to direct injection SFC analysis of the standard?

EXPERIMENTAL

Materials

The equipment used (Fig. 1) was a Model 311B extractor/accumulator, a Model 10000 SFC–GC system, and a Model 747DS data system (all by Computer Chemical

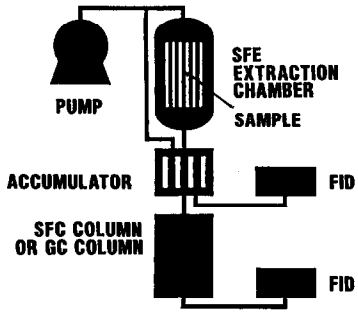


Fig. 1. Schematic of a coupled SFE–SFC system.

Systems, Avondale, PA, U.S.A.). The CCS Model 311B was equipped with a 0.5-ml volume extraction chamber and a 100 × 2 mm accumulation column containing 5-μm Nucleosil Cyano packing. The Model 10000 SFC–GC system was equipped with a post-column crimped stainless-steel restrictor calibrated to an expanded gas flow-rate of 20 ml/min at 2000 p.s.i. to 100 ml/min at 6000 p.s.i. (column oven temperature 150°C). The FID system was maintained at 350°C. UV detection was via a Linear™ UVIS 204 fitted with a high-pressure detector cell (Linear Instruments, Reno, NV, U.S.A.). Separations were achieved using a 250 × 1 mm Deltabond™ 300 Octyl column (Keystone Scientific, State College, PA, U.S.A.). Baker-analyzed HPLC-grade dichloromethane used to dissolve standards of the additives was purchased from VWR Scientific (Philadelphia, PA, U.S.A.). The supercritical fluid used for extraction and analysis was SFC grade from Scott Specialty Gases (Plumsteadville, PA, U.S.A.).

Creation of calibration curves for additives

Standards of the additives were prepared in dichloromethane. Concentrations varied according to additive concentrations in the polymer samples to be analyzed. A solution volume containing a known amount of the additive standard(s) was then applied via a microsyringe to a bed of quartz wool in the extraction vessel. The additives were extracted using supercritical CO_2 for 10 min at 50°C and 6000 p.s.i. The extract was accumulated by cryofocussing on the accumulator column at 10°C. When extraction was complete, the sample was desorbed at 50°C from the accumulator onto the analytical column for analysis. A second extraction–analysis was performed to determine whether all the additive standard(s) had been extracted from the quartz wool bed. In no case was residual additive detected.

Several differing amounts of the additives were extracted. These data points were plotted to provide a curve, the slope of which was an area response factor (μg additive/area counts) and could be compared directly to area counts observed in

TABLE I

RESULTS OF DUPLICATE SUPERCRITICAL FLUID EXTRACTIONS AND CHROMATOGRAPHY ON ERUCAMIDE STANDARDS OVER THE RANGE 12.5–100 μg

Linear regression: standard deviation = $2.6 \cdot 10^2$; slope = $1.4 \cdot 10^4 \pm 2.8 \cdot 10^2$ counts/μg; y-intercept = $4.2 \pm 1.6 \cdot 10^4$; correlation coefficient = 0.9

Aliquot (μ)	*Concentration (μg/μl)*	*μg*	*Area counts (10^5)*	*Percent difference*
2.5	5	12.5	1.9	0
2.5	5	12.5	1.9	
5.0	5	25.0	4.4	1.4
5.0	5	25.0	4.3	
5.0	10	50.0	7.6	0.9
5.0	10	50.0	7.6	
10.0	10	100.0	14.6	1.0
10.0	10	100.0	14.8	

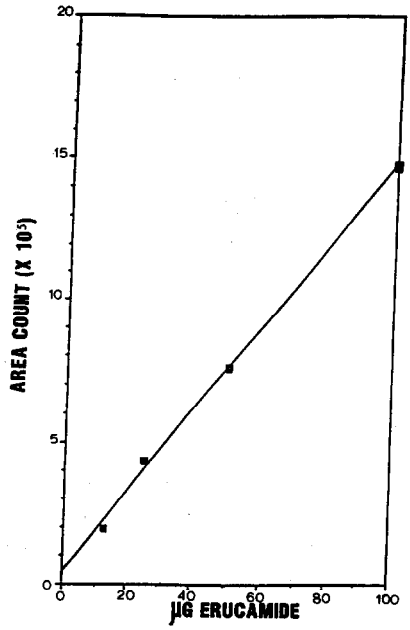


Fig. 2. Calibration curve of the data for the erucamide standards obtained from Table I. $y = 0.4 + 0.1\,x$; correlation coefficient = 0.9.

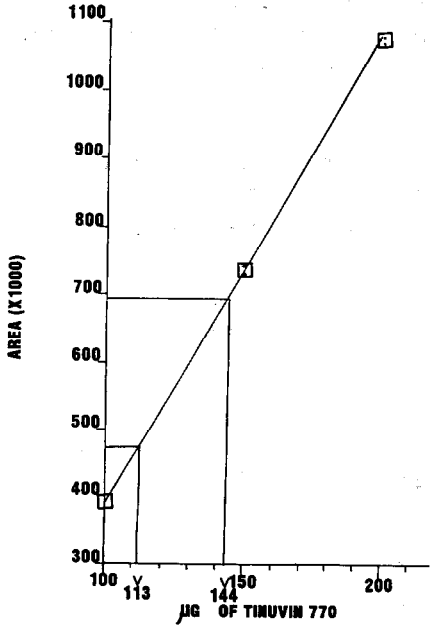


Fig. 3. Calibration curve for Tinuvin 770 over the range of 100–200 μg.

actual polymer samples. Table I shows the results of duplicate supercritical fluid extractions and chromatography on erucamide standards over the range of 12.5 μg to 100.0 μg. Fig. 2 is the calibration curve of the data for the erucamide standards obtained from Table I. Fig. 3 is a calibration curve for Tinuvin 770 over the range of 100–200 μg. Fig. 4 shows the calibration curve for Irgafos 168 and Irganox 1010 over the range of 10–60 μg.

SFE of polymer samples

When calibration curves were complete, ground samples of polymer (40–80 mesh) were placed in the extraction vessel. Extraction conditions varied from sample to sample, but generally fell into two categories: low-pressure and high-pressure extractions. Low-pressure extractions were carried our at 2000 p.s.i. for a duration of 30 min (expanded gas flow at the extractor restrictor was 80–100 ml/min). High-pressure extractions were performed at 6000 p.s.i. for 15 min (expanded gas flow at the extractor restrictor was 300–400 ml/min). In both cases, extraction temperature (50°C), accumulation temperature (10°C) and desorption temperature (50°C) remained constant.

RESULTS AND DISCUSSION

The first concern was reproducibility of the analysis. Fig. 5 shows the comparison of two extraction–analyses performed on the same polyethylene sample. Because

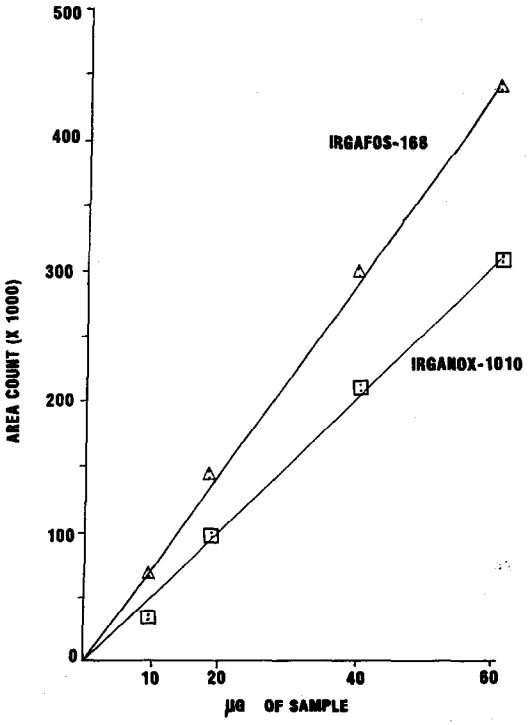


Fig. 4. Calibration curve for Irgafos 168 and Irganox 1010 over the range of 10–60μg.

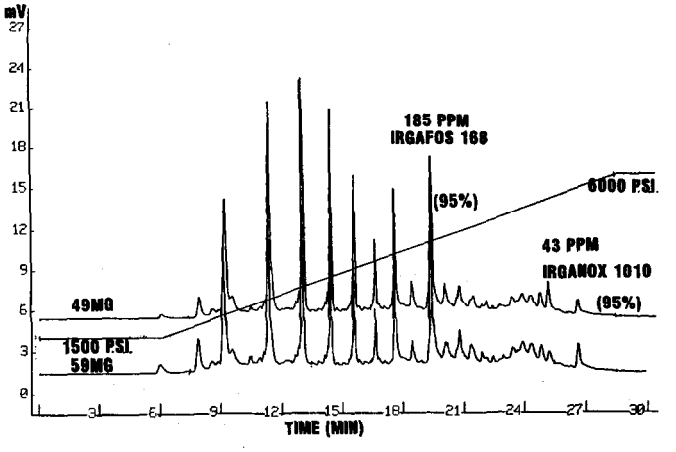


Fig. 5. Comparison of two extraction–analyses performed on the same polyethylene sample. Extraction parameters: 6000 p.s.i. for 15 min. at 50°C, desorption temperature 50°C. SFC parameters: 1500 p.s.i. starting pressure held for 6 min, then 200 p.s.i./min to 6000 p.s.i. Column: 250 × 1 mm Deltabond 300 Octyl, FID 350°C, oven temperature 150°C.

an area response factor is being used for quantitation and the response is linear over a wide range, it is not necessary to keep sample weight constant. In this case a 49 mg sample and a 59 mg sample were extracted. Using the area response factor, the concentrations of Irgafos 168 and Irganox 1010 determined experimentally were within 5% of concentration supplied by the manufacturer.

The next concern was the ability to achieve quantitative results. In addition to the results obtained in Fig. 5, Fig. 6 is a comparison of one 50-μg standard of erucamide to an extraction of a commercial polyethylene sample also containing 50 μg of

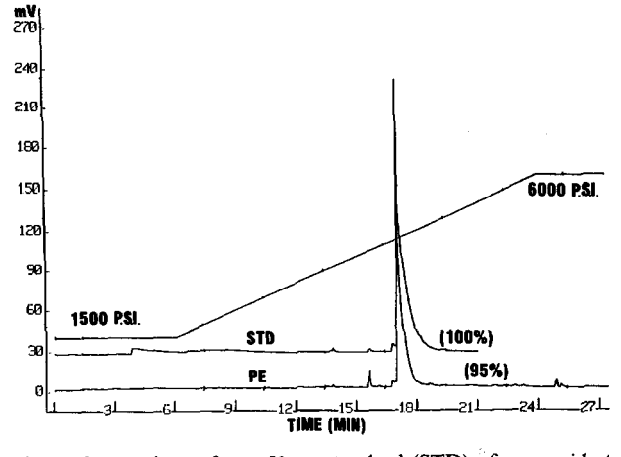


Fig. 6. Comparison of one 50-μg standard (STD) of erucamide to an extraction of a commercial polyethylene (PE) sample also containing 50 μg of erucamide. Extraction duration 10 min, other conditions as in Fig. 5.

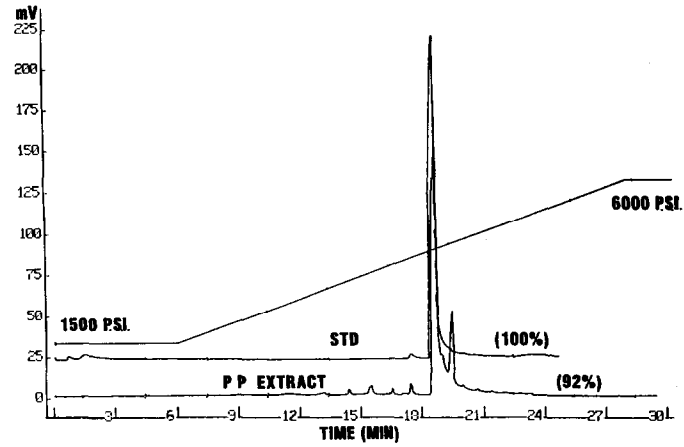
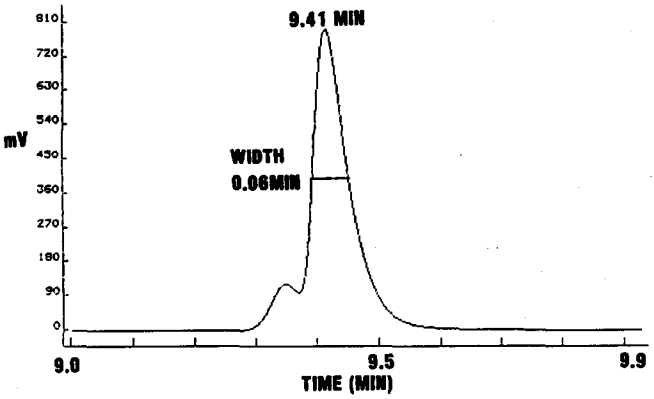


Fig. 7. Comparison of one 150-μg standard of Tinuvin 770 to an extraction of a commercial polypropylene (PP) sample also containing 150 μg Tinuvin 770. Conditions as in Fig. 6.



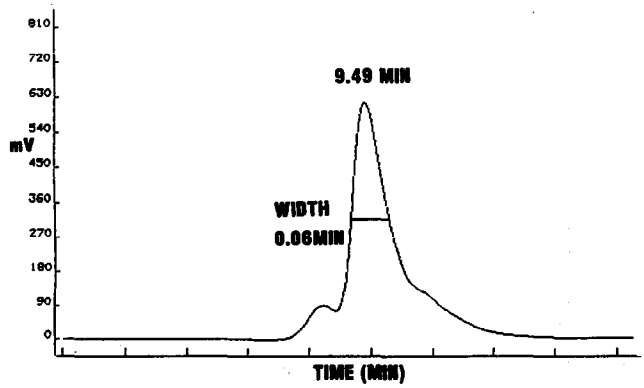


Fig. 8. Comparison of a direct injection SFC analysis (top) to a coupled SFE–SFC analysis (bottom) of Irgacure 651. SFC parameters as in Fig. 5, SFE parameters as in Fig. 6. Theoretical column plate count: SFC: 136 389; SFE–SFC: 134 207.

erucamide. The amount of erucamide in the polyethylene sample was 95% of that in the erucamide standard. Fig. 7 shows the analysis of Tinuvin 770 in polypropylene employing the same SFE–SFC method. In this case, recovery was 92% of the expected result, although no additional Tinuvin 770 was noticed in a subsequent extraction–analysis.

Linearity of the calibration is very important. When the calibration curve is linear and passes through the origin, an area response factor can be calculated using a single-point calibration. The examples in Figs. 2, 3 and 4 indicate that the quantitation is linear.

Figs. 5, 6 and 7 also provide data on the recovery level of the analytes of interest. The lowest recovery level was 92%, with higher values more common. All analyses were followed by second extractions in order to determine if an incomplete extraction had occurred. In the polymer samples, an additional 5–8% of the additives were observed in the second extraction. This is in agreement with an extraction efficiency of 92% or greater for the initial extraction.

Chromatographic efficiency of the coupled SFE–SFC system is comparable to that achieved by direct injection SFC. Fig. 8 is a comparison of an SFC injection to an SFE–SFC analysis of Irgacure 651. In both cases, the peak width at half-height remained 0.06 min, while the apparent theoretical column plate count of the SFE–SFC analysis was 98.4% of that achieved with the direct injection analysis. The difference observed in the retention time of 0.08 minutes between the SFC and SFE–SFC analyses is due to a slightly longer sample path when using the extractor. To compensate for this difference standards are generally run by spiking the extraction vessel as was done in this study.

Fig. 9 is a typical example an extraction–analysis of polyethylene using the coupled SFE–SFC system. In this case, three additives were succesfully extracted from the polymer matrix using a low-pressure extraction. Quantitation of these re-

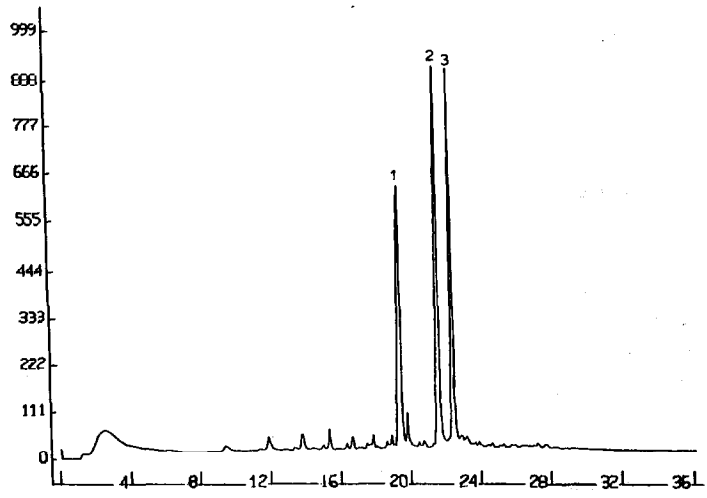


Fig. 9. Typical extraction analysis of three additives from a polyethylene sample. Extraction pressure: 2000 p.s.i., duration 30 min. All other parameters as in Fig. 5. Peaks: 1 = Tinuvin 326 (601 ppm); 2 = Irgafos 168 (737 ppm); 3 = Irganox 1076 (543 ppm).

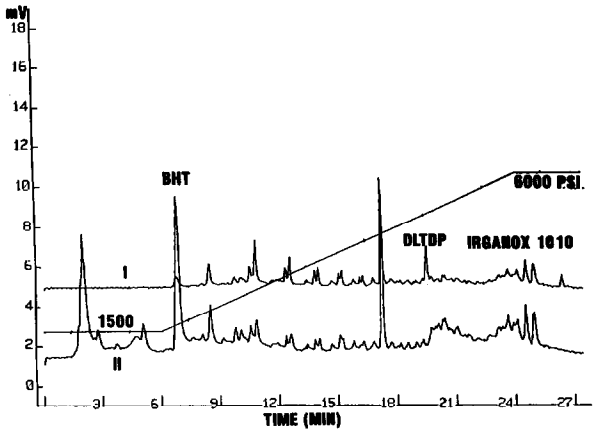


Fig. 10. Analysis of two polyethylene samples from the same manufacturer each containing different additives. Sample I contains dilaurylthiodiproprionate (DLTDP) and Irganox 1010, sample II contains butylhydroxytoluene (BHT). Conditions as in Fig. 6.

sults indicated that the concentration of the additives in the polyethylene were within 8% of the manufacturers formulation.

Fig. 10 is an analysis of two polyethylene samples from the same manufacturer, but containing different additives. Sample I contained dilaurylthiodipropionate and Irganox 1010 while Sample II contained butylhydroxytoluene. Note the similarities in the oligomer fingerprint, and also the presence of the large peak at *ca.* 18 min which could be an unidentified additive.

Fig. 11 is an example of the utility of a UV detector when the oligomers interfere with additive identification/quantitation. This is an atypical polyethylene sample containing an oxidative colorant which causes rapid degradation of the polymer. Usually the oligomer fingerprint is not as pronounced *versus* the additive peaks.

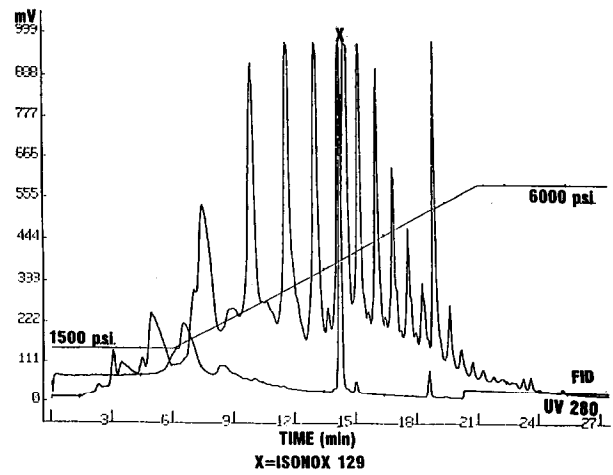


Fig. 11. The utility of a UV detector when oligomers interfere with additive identification/quantitation. Partially oxidized polyethylene. Conditions as in Fig. 9.

CONCLUSION

Successful on-line extraction and chromatographic analysis of additives in polymers was performed using coupled SFE–SFC. Accurate quantitation was achieved along with high extraction efficiency. This technique should prove a viable alternative to traditional off-line liquid-phase extraction and analysis methods. Continuing efforts are being focused on optimization of the procedure in order to allow investigators to further reduce method development time while maintaining high efficiency.

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