HPLC Separation with Solvent Elimination FTIR Detection of Polymer Additives

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Abstract

A mobile phase elimination interface (e.g., LC-Transform) is used in conjunction with Fourier transform infrared spectrometry to assay standard mixtures of polymer additives. Methanol and water mixtures are used as the mobile phase, along with an analytical scale octadecylsilica packed column. Infrared, ultraviolet, and light-scattering detection are applied to the nine-additive mix. Although there is a loss in resolution when the LC-Transform interface is used, each of the nine peaks can be easily discerned in order to generate clean infrared spectra. It is shown that changes in nebulizer flow have little effect on the intensity of the deposited peak. The data indicate that detection limits for these polymer additives fall in the low- to mid-nanogram range.

Introduction

Polyolefins are subject to thermal and oxidative degradation and cannot be used in practical applications unless they are protected with efficient antioxidants. Other additives are introduced to polymers to enhance resistance to static charge buildup and to afford greater ultraviolet stability, for example. The practical applicability of a polymer is determined by the amount and chemical structure of each component in the additive mixture. The analytical procedures used in polymer additives determination have been reviewed by both Wheeler (1) and Crompton (2). Analysis may be conducted in situ on the intact polymer or after separation of the additives from the polymer. Difficulties in identifying and determining additives arise from three factors according to Wheeler (1): (*a*) high reactivity and low stability of certain additives, (*b*) low additive concentration (0.1–1.0%) within the polymer, and (*c*) relatively insoluble polymer matrix.

Drushel and Sommers (3) have indicated that in situ spectroscopic techniques are not likely to be of value in the analysis of samples of unknown (or changing) composition. The wide variety of additives that are commercially available would further complicate the interpretation of data. In view of these limitations, a preliminary separation of additives from the polymer matrix is usually necessary in most cases.

Howard (4) has shown how useful gel permeation chromatography (GPC) can be for polymer additive systems. Nine 4-ft columns packed with a styrene–divinylbenzene gel and tetrahydrofuran as the eluent were used. GPC has also been employed (5) to determine the antioxidants in commercial polypropylene and automobile molded parts. Prior to performance of GPC, the additives were extracted from the polymer with methylene chloride.

Later, the determination of butylated hydroxytoluene (BHT), Irganox 1076, and Irganox 1010 additives in polyethylene by high-performance liquid chromatography (HPLC) was reported (6). After extracting the additives from the polymer with decalin at 110°C followed by cooling to precipitate the polymer, the concentration of additives present was established by normal-phase liquid chromatography (NPLC) with a variable ultraviolet (UV) wavelength detector. The stationary phase was μ-Porasil, and the mobile phase was a heptane to methylene chloride gradient. Methods were also developed by the same laboratory (7) for the determination of (*a*) mono- and diglycerides, (*b*) tertiary C_{12}–C_{16} alkyldiethanolamines, and (*c*) alkyldithiopropionates. Soxhlet extracts with chloroform of both polyethylene and polypropylene were subjected to NPHPLC on μ-Porasil.

More recently, Cortes et al. (8) have quantitatively determined polymer additives in a polycarbonate homopolymer and an acrylonitrile–butadiene–styrene terpolymer. A multidimensional system consisting of microcolumn size-exclusion chromatography was coupled on-line to either capillary gas chromatography or a conventional LC system. Results obtained for the two polymer systems indicated losses of certain additives when using the conventional precipitation approach. The lower volumetric dispersion given by the microcolumn allowed introduction of the complete additive fraction without detrimental effect on the peak shape and resolution.

It is therefore apparent that many of the current polymer and polymer additive analysis methods involve the use of LC separations. Due to the large number of additives (especially

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antioxidants and UV stabilizers) used in such polymers, identification based on retention time can be difficult. Also, many of the additives are not pure, and it is sometimes necessary to differentiate the additive itself from these impurities. Because LC methods for additives are very prevalent, it would be ideal if a spectroscopic interface could be used for identification with no modification of the chromatographic method. Kalasinsky et al. (9) reported in 1985 on an interface which allows one to obtain the infrared spectrum of components separated using NP- or HPLC. The liquid eluent was deposited onto a KCl substrate, and the diffuse reflectance infrared spectrum of each component was collected after evaporation of the mobile phase. Subsequent to this work, a number of reports have appeared on the solvent elimination approach; to our knowledge, however, none have addressed solely polymer additives (10). In 1990, a hyphenated technique consisting of a thermospray and a moving belt system in combination with diffuse reflectance optics for on-line LC with Fourier transform infrared (FTIR) spectrometry was described (11). Applications included gel permeation chromatography of polymers. The detection limits were stated to be in the 100-ng range.

The solvent elimination FTIR interface has been perfected (12) by having the chromatographic effluent pass into a nozzle which sprays the mobile phase as a tightly focused jet onto the surface of a continuously rotated sample collection disk. The disk, which is made from monocrystalline germanium, is then located in the sample compartment of the FTIR bench on a motor-driven rotating stage. The sample collection disk is aluminized so that the infrared beam passes through the deposited chromatographic peak, through the germanium, and is reflected by the aluminum interface. The result is a two-pass transmission spectrum of the deposit. The interface design is based on the work of Gagel and Biemann (13) and has been commercialized by Lab Connections, Inc. This interface has been employed (12) to analyze for additives in a polypropylene (hexane–methylene chloride, 1:1) extract. A UV detector indicated two components, but visual inspection of the collection disk showed that three components were present. Two of the components were identified as Irgaphos 168 and Irganox 1010. The third component was a low molecular weight oligomer of polypropylene that was not detected by UV (285 nm). In another study (14), quantitative analysis of polymer composition distribution was investigated using the solvent evaporation interface. The effects of the location and distribution of the deposited films as well as the morphology of the deposit was examined. Both polystyrene and poly(methylmethacrylate) were used.

Table I. Commonly Used Polymer Additives That Have Been Deposited Using the LC–FTIR-Transform Mobile Phase Elimination Interface

Polymer additive	Empirical formula	Molecular weight
Irganox 1098	$C_{40}H_{62}O_4N_2$	637
Irganox 259	$C_{40}H_{62}O_6$	639
Irganox 245	$C_{34}H_{48}O_8$	584
Irganox 3114	$C_{48}H_{69}O_5N_3$	767
Irganox 1010	$C_{73}H_{108}O_{12}$	1178
Irganox 1076	$C_{35}H_{62}O_3$	531
Irgaphos 168	$C_{42}H_{63}PO_3$	646
Tinuvin 234	$C_{30}H_{30}ON_3$	448
Tinuvin 327	$C_{20}H_{26}OClN_3$	360
Tinuvin 328	$C_{22}H_{31}N_3O$	353
Tinuvin 350	$C_{20}H_{26}ON_3$	474
Santowhite powder	$C_{22}H_{33}O_2$	377
Lowinox	$C_{23}H_{23}O_2$	340
Ethanox 330	$C_{53}H_{78}O_3$	762
Kemamide U	$C_{18}H_{35}ON$	281
Naugard	$C_{30}H_{31}O$	405
BHT	$C_{15}H_{24}O$	220
Ultranox 626	$C_{33}H_{50}P_2O_6$	604
Cyasorb 2908	$C_{31}H_{54}O_3$	474
Cyasorb 531	$C_{21}H_{26}O_3$	326

We reported the optimization and use of the LC-Transform interface for the analysis of a larger selection of polymer additives. The main goals of the study were threefold: (*a*) to determine the feasibility of depositing commonly used additives, (*b*) to determine the sensitivity of the interface to changes in gas flow and temperature, and (*c*) to determine the necessary chromatographic resolution for adequate Gram–Schmidt peak discrimination or differentiation. We were also interested in the chromatographic integrity of the infrared interface relative to UV and light-scattering detection.

Experimental

The chromatography for these experiments was run on a Waters (Milford, MA) 600-MS liquid chromatograph. Methanol (EM Science, Gibbstown, NJ) and water (Mallinckrodt Chemical, Paris, KT) mixtures were used as the mobile phase. Injections of individual polymer additives dissolved in 100% methanol were made using a Valco (Houston, TX) six-port injection valve with external sample loops from Supelco (Bellefonte, PA). The mobile phase was delivered at 1 mL/min through a 250- × 4.6-mm Spherisorb ODS-2 column (5-µm particles) purchased form Phenomenex (Torrance, CA). A UV detector at 280 nm was placed between the column and solvent elimination interface. An evaporative light-scattering detector (ELSD) (Alltech-Varex, Deerfield, IL), which was used because some additives had no significant UV chromophore, was connected to the secondary outlet of the interface splitter mechanism. This secondary detector received approximately ten times the material that was directed towards the IR interface. The FTIR was a Nicolet (Madison, WI) Magna 550 equipped with a deuterated triglycine sulfate (DTGS) detector.

The additives were collected primarily from manufacturers of polypropylene and polyethylene. All solutions of additives were made by first "wetting" the solid with a small amount of methylene chloride and diluting to volume with methanol. If this procedure was not used, several of the additives were found to be not fully soluble.

A library of FTIR spectra of additives was created in our laboratory using the following methodology. Twenty microliters of each additive solution was injected onto the column. The

interface conditions included a 65:1000 split ratio, 52°C sheath temperature, 4 L/min sheath flow, 42 mL/min nebulizer flow, 7-mm nozzle height above the disk, and a 10°/min disk rotation rate. Filtered house air was used to supply the sheath and nebulizer flows. Several deposits of each additive were collected on the germanium disk. For this and all subsequent runs, the IR data were collected in chromatogram format using 8-cm^{-1} resolution and 16 scans per spectrum. The bench was purged for 20 min after the disk was inserted into the sample compartment. Background scans (256) were collected on a blank portion of the disk. Upon generation of the Gram–Schmidt reconstruction (GSR), a spectrum was generated from the maximum of each of the peaks that was baseline corrected and inserted into a spectral library.

Conditions for optimization of the solvent elimination interface were as follows. Solutions were made up using 6.5–6.6 mg of each of three additives in 0.25 mL of methylene chloride and 10 mL of methanol. The injection volume was 50 µL. The mobile phase was a 94:6 methanol–water mixture. Interface conditions included a 67:1000 split ratio (approximately 2 µg of each additive deposited), 10°/min disk rotation rate, and 7-mm nozzle height. The parameters that varied were sheath temperature (60, 70, and 90°C), sheath flow (4.0, 5.5, and 8.5 L/min), and nebulizer flow (25, 48 and 70 mL/min).

Results and Discussion

Individual additives were first injected onto the HPLC column to generate computer library spectra of samples deposited on the germanium disk of the solvent elimination interface. This process was also used as a means to verify the feasibility of depositing polymer additives in a well-defined spot. The additives are listed in Table I along with their molecular weight and formula because molecular weight is one of the primary factors influencing the additives' ability to be deposited. Only two additives could not be successfully collected on disk: BHT and Ultranox 626. The molecular weight of BHT is thought to be too low for optimal deposition. However, the molecular weight of Ultranox 626 is sufficiently high to be deposited. One possible explanation for our failure to observe Ultranox 626 could be that the peak observed in the UV detector and assigned to 626 was not Ultranox 626, but a contaminant or decomposition product with a low molecular weight.

A mixture of nine additives was separated using a mobile phase gradient of 94:6 methanol–water for 8 min, after which the mobile phase composition was immediately changed to 100% methanol. After 7 min, the temperature of the sheath gas was changed, as a test, to 80, 70, 60, 50, and 40°C from the original 90°C. At 90 and 80°C, good FTIR spectra could not be consistently obtained with the solvent elimination interface because the conditions were too dry. This meant that the analytes precipitated at the exit of the nozzle, formed at plug, and were not deposited on disk. When 50°C was used, the last six polymer additive deposits were not confined to a small concentric deposit. Below 50°C, it was obvious from the aerosol spray that the conditions were too wet, because each analyte

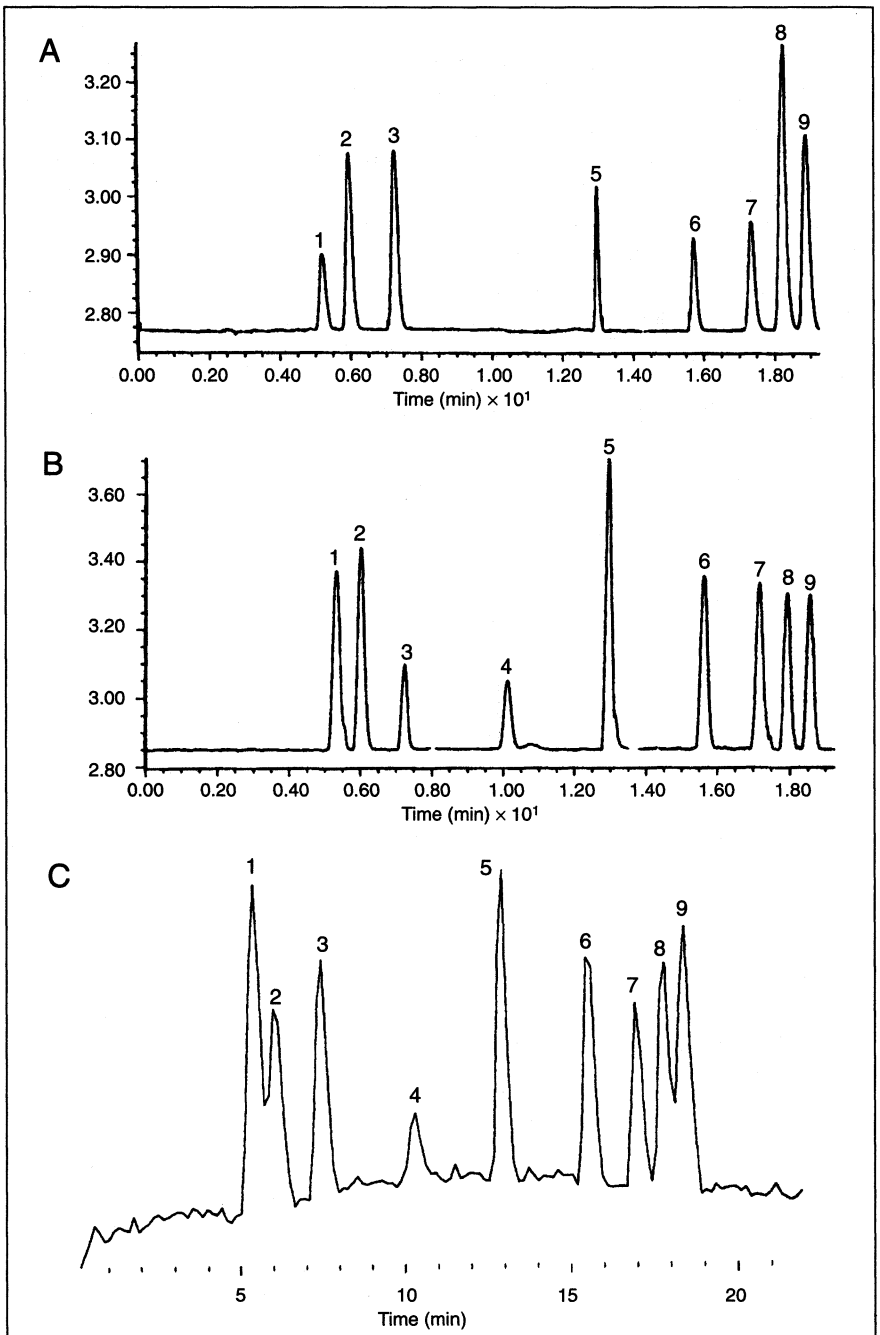

Figure 1. Chromatograms for the separation of nine polymer additives: (A) UV at 280 nm, (B) ELSD, and (C) GSR. Peaks: 1, Irganox 1098; 2, Santowhite; 3, Lowinox; 4, Kemamide; 5, Irganox 259; 6, Irganox 1010; 7, Ethanox 330; 8, Tinuvin 328; 9, Tinuvin 327.

visually interfered with the neighboring deposits. It is important to note that, under the interface conditions used for this temperature study, there was no significant increase in GSR peak intensity at higher temperatures for any of the six additives eluted with a 100% methanol mobile phase. For the three eluting components with 6% water, this was not the case. In other words, peak intensity increased at the higher temperatures.

The GSR, UV, and ELSD chromatograms for the nine-additive mix are shown in Figure 1. A direct comparison between the ELSD and GSR clearly shows a loss in resolution when the LC-Transform interface was used. Nevertheless, the nine additive peaks can still be easily discerned to generate clean IR spectra.

Chromatographic resolution versus GSR discrimination

As stated previously, one of the goals of this project was to determine the necessary chromatographic resolution for adequate GSR peak discrimination. There is virtually no reason that would necessitate complete baseline resolution in a GSR other than to maintain the ability to ascertain that different species are present. For example, subtraction routines can be used to enhance spectral individuality for significantly overlapping peaks. A general idea of the chromatographic resolution that yields a certain degree of GSR peak discrimination, however, can be helpful when standard LC methods are being developed.

To accomplish this goal, the first three analytes in the additive separation were used. The light-scattering detector was used to determine chromatographic resolution parameters. The equation used to calculate resolution (R) was:

$$R = \frac{\Delta T}{(W_1 + W_2)(0.5)}$$

where ΔT is the retention time of peak 2 minus the retention time of peak 1, and W is the portion of the baseline intersected by tangents drawn to the peaks. The following methanol–water mobile phase compositions were used: 1, 100:0; 2, 97:3; 3, 95:5; 4, 94:6; and 5, 91:9. At the same time, three solvent elimination interface disk rotation rates were used to correlate with chromatographic resolution because the rate at which the disk rotates affects GSR peak characteristics as well as the retention distance between the peaks.

Figures 2–4 are representative of these data. Chromatographic resolution factors of 2.5–3.0 resulted in GSR peaks that were resolved enough for peak identification in most cases, regardless of disk rotation rate. At the 97:3 mobile phase chromatographic conditions, a resolution factor of 3.2 resulted in adequate separation at all rotations except 5°/min. At the slower rotation rate, components were less separated because the disk was traveling slowly, allowing only a short distance between separated peaks. Also, at slower disk rotation rates, the flow was focused above the deposited film for a longer period of time, which can spread the already-laid deposit or cause a residual thin track of analyte between deposits, especially at high sheath flows. Although the 100:0 methanol–water data showed that peaks that were efficiently resolved on the ELSD

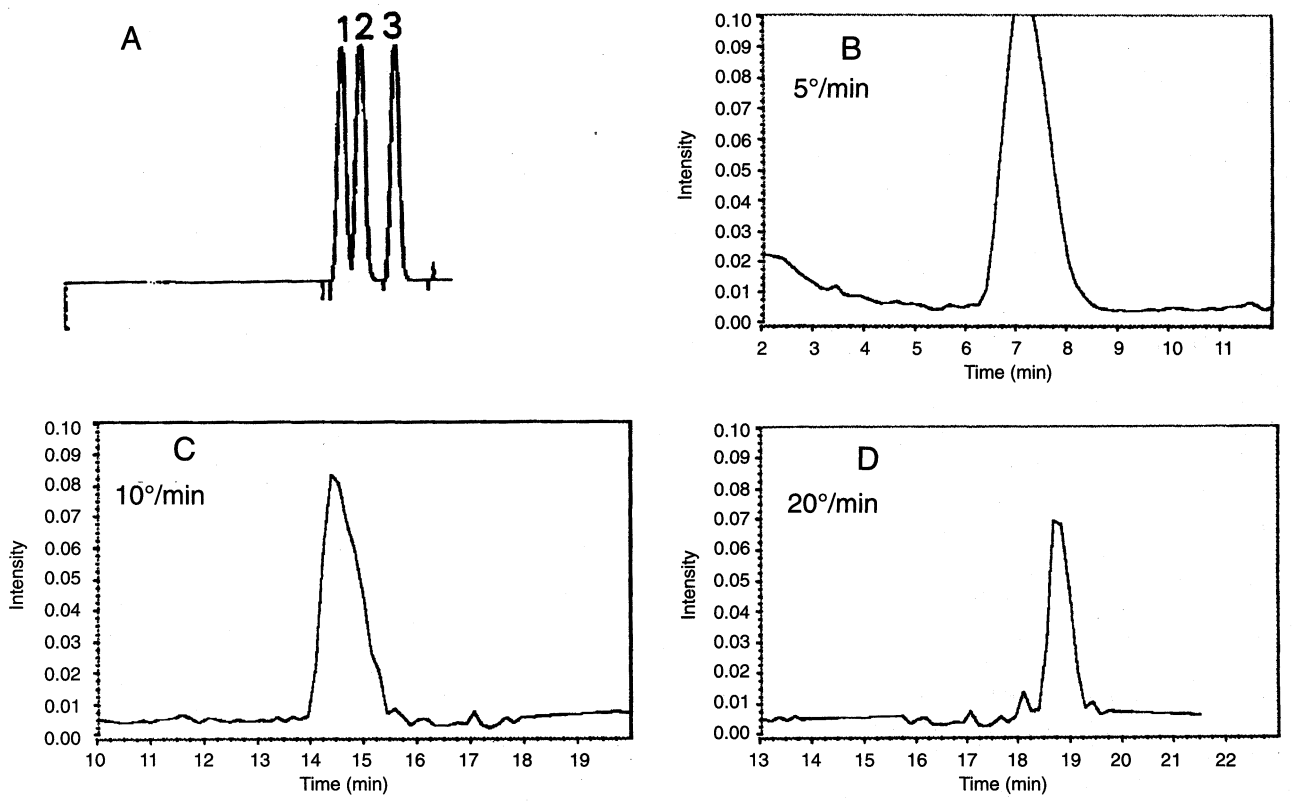

Figure 2. Chromatographic peak resolution (ELSD detection): 100:0 methanol–water. R = 1.1 for peaks 1 and 2; R = 2.0 for peaks 2 and 3. A represents the ELSD chromatogram; B, C, and D are the IR reconstructions.

(baseline resolution is $R = 1.5$) were not sufficiently resolved to be identified as multiple peaks on the GSR, several spectra may be taken throughout a single GSR peak to determine if more than one component is present.

Reproducibility

Several other factors that could affect the nature of the disk deposit or GSR trace were explored. Among these was the reproducibility of depositing a series of analytes several times on the same disk followed by FTIR analysis in one continuous run. Peaks deposited first in a long chromatogram can sometimes be characteristically smaller than peaks that are deposited last. Also, if several shorter chromatographic runs are collected on the same disk, the peaks in the first run are often smaller than those in the last chromatogram. This phenomenon is represented in Figure 5, in which a separation of three components was performed in triplicate; each peak was deposited on the same disk. The earliest deposition gave rise to the lowest IR signal. The relative standard deviations (RSDs) for peak heights from additives 1, 2, and 3 in the reconstruction were 10, 8, and 10%, respectively. Factors related to deposit lifetime, stability, and consistency need to be considered when peak heights are being used for quantitative purposes or low levels of analytes are being investigated.

It is important to take into account the number of scans taken per spectrum, especially when peaks with low chromatographic resolution are being deposited. If the number of scans simultaneously added into a file spectrum is reduced (thereby increasing the number of data files), the shape of the peak is enhanced and, therefore, so is the separation between neighboring peaks. With this resolution advantage, the disadvantage of increased baseline noise must be taken into account as well as the increase in data storage space that must be allocated because a much larger number of spectral files will be collected for any given run.

Limit of Identification

Absolute limits of identification and detection were not calculated for these additives. However, an estimate was made by using the following procedure. Sample infrared spectra taken from a GSR derived from the injection, chromatography, and deposition of three additives are given in Figure 6. A 5-µL injection which approximated to 0.21-µg deposited was made with a 5°/min disk rotation. Peak-to-peak noise for several regions of an IR spectrum corresponding to a 0.21-µg deposit was determined by taking the difference between the peaks with the lowest and highest noise in a selected spectral region. Before calculating the noise, the IR software corrected any baseline tilt using a least-squares correction method. The averages of these readings were then used in the estimation of detection limit (e.g., three times the peak-to-peak noise). Apparent detection limits are given for each of the three additives in Table II. Table II also lists the absorbances for several peaks in each of the spectra. In only two cases (Irganox peaks 1 and 3) did the peak intensity of the 0.21-µg spectrum fall below three times the peak-to-peak noise. As one can see,

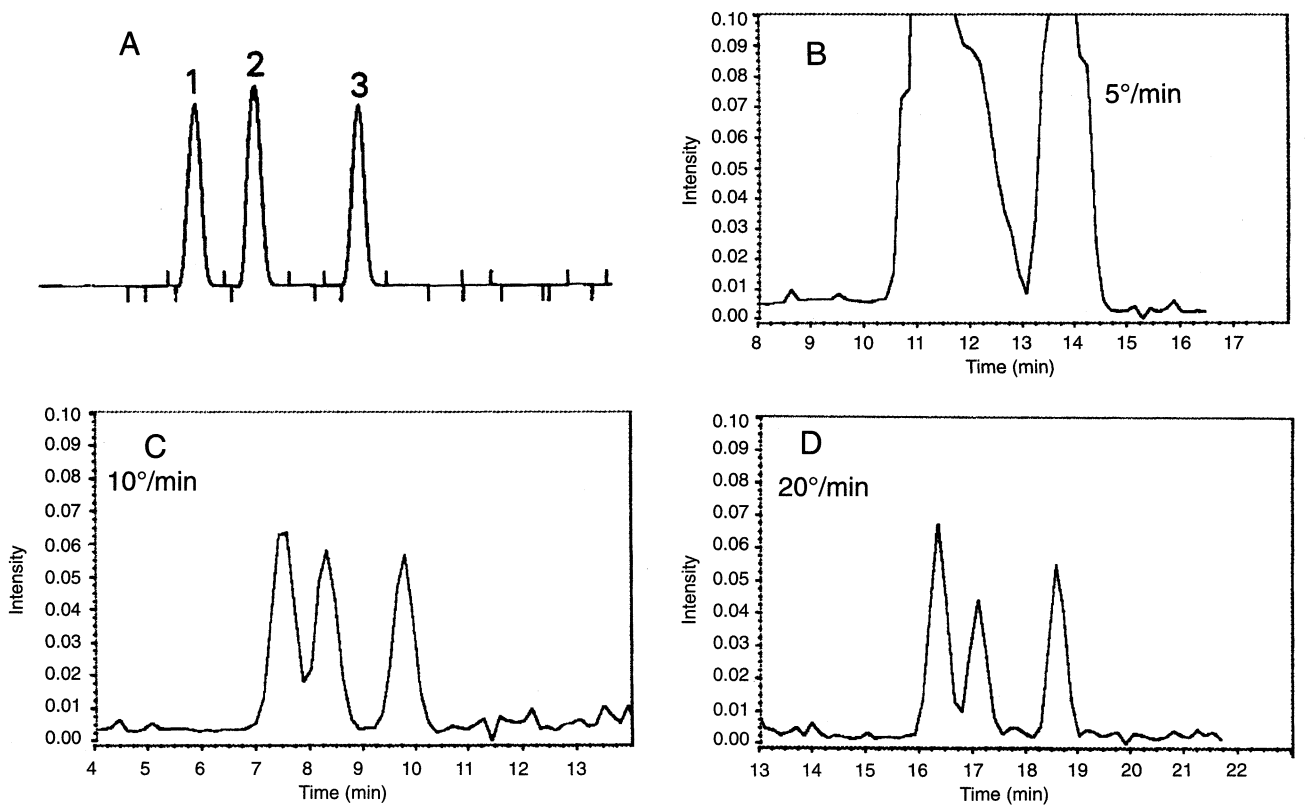

Figure 3. Chromatographic peak resolution (ELSD detection); 95:5 methanol–water; $R = 2.5$ for peaks 1 and 2; $R = 4.2$ for peaks 2 and 3; A represents the ELSD chromatogram; B, C, and D are the IR reconstructions.

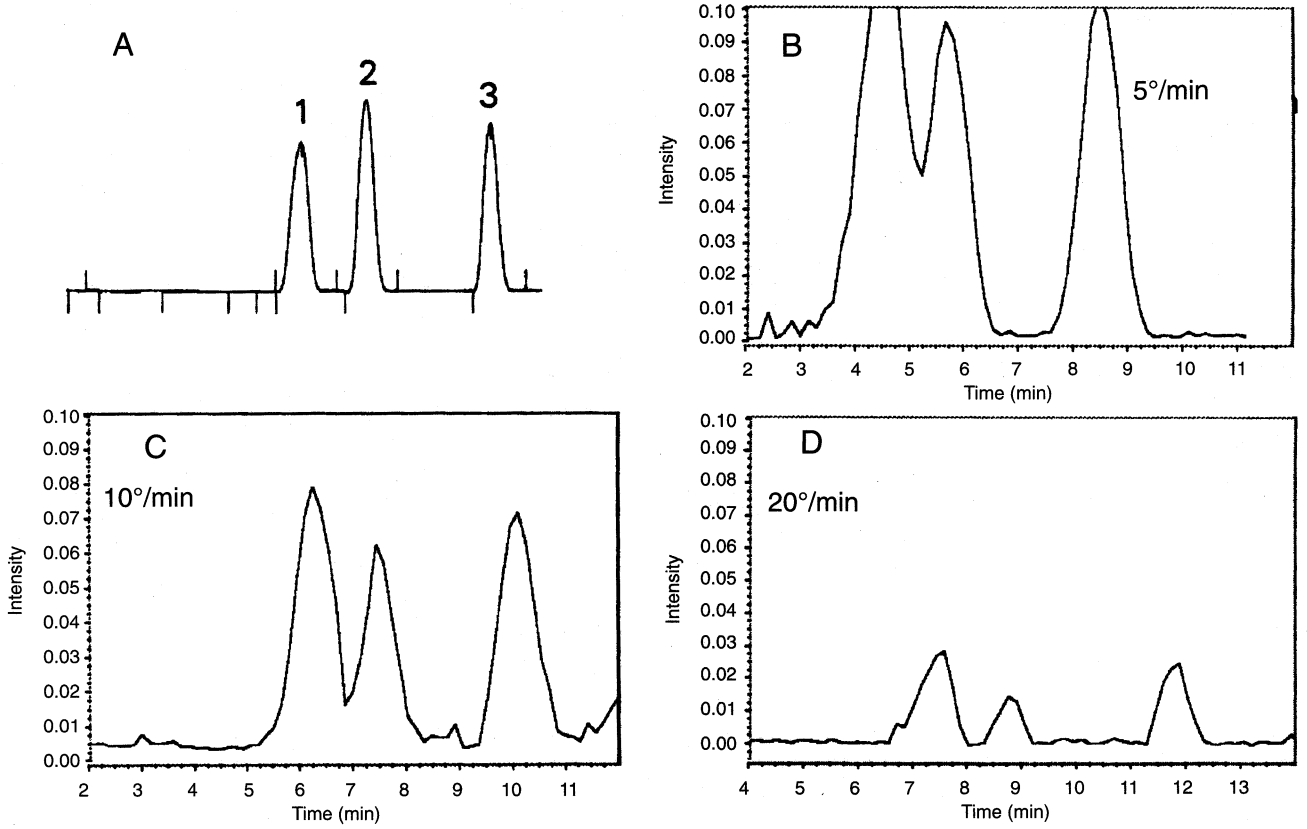

Figure 4. Chromatographic peak resolution (ELSD detection); 91:9 methanol–water; $R = 2.1$ for peaks 1 and 2; $R = 4.3$ for peaks 2 and 3; A represents the ELSD chromatogram; B, C, and D are the IR reconstructions.

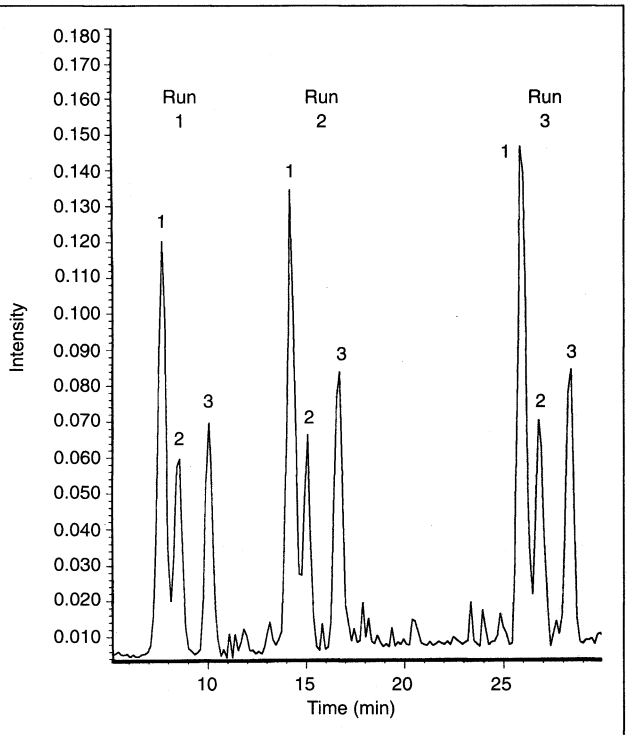

Figure 5. Reproducibility in the deposition of three analytes in three runs on a single disk. Peaks: 1, Irganox 1098; 2, Santowhite powder; 3, Lowinox.

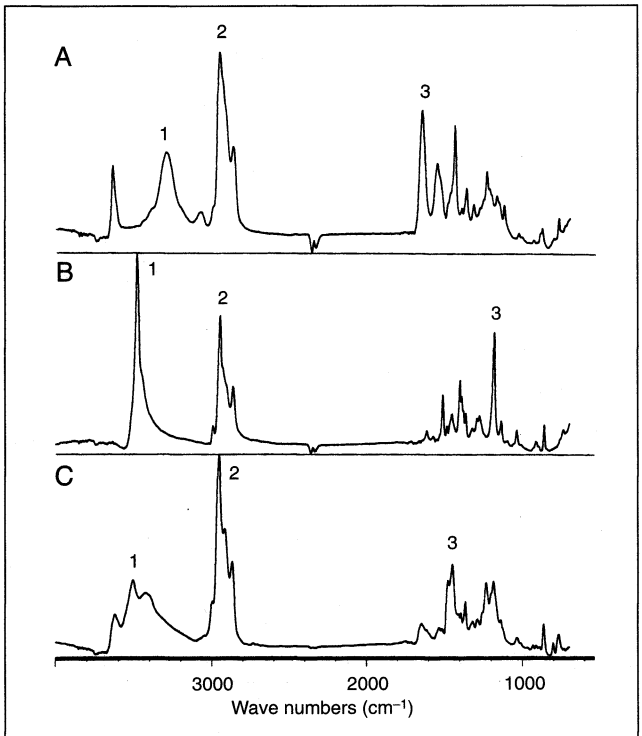

Figure 6. Spectra for (A) Irganox 1098, (B) Santowhite powder, and (C) Lowinox obtained by LC–mobile phase elimination FTIR (16 scans per spectrum).

Table II. Peak-to-Peak Noise, Detection Limits, and Peak Absorbancies for 0.21-µg Irganox, Santowhite, and Lowinox Deposited via LC–FTIR*

	Peak 1 Irganox 1098	Peak 2 Santowhite Powder	Peak 3 Lowinox
Peak-to-peak noise	0.00016	0.00014	0.00013
Necessary peak intensity for detection	0.00048	0.00052	0.00039
Absorbance	3297 cm^{-1}	3492 cm^{-1}	3507 cm^{-1}
Spectral peak intensity	0.00021	0.00113	0.00075
Absorbance	2965 cm^{-1}	2960 cm^{-1}	2965 cm^{-1}
Spectral peak intensity	0.00158	0.00128	0.00208
Absorbance	1642 cm^{-1}	1182 cm^{-1}	1447 cm^{-1}
Spectral peak intensity	8.0 e -05	0.00069	0.00042

*All values given in spectral absorbance units.

detection will vary significantly depending on the particular absorbance region of interest. For identification of a spectrum, the highest intensity carbon–hydrogen region in each of these cases was not particularly important. It was the lower intensity fingerprint regions that gave the spectra their uniqueness; therefore, identification limits are expected to be considerably higher. From these data, it is perceived that the minimum quantity of additives one would want to deposit in order to be able to accurately and spectrometrically identify a component would fall in the 0.5–1.0 µg range. Again, this estimation is highly dependent on the specific absorbance region that is used in the calculations.

Conclusion

This study demonstrates the usefulness of LC–FTIR interface for polymer additive analysis. Further interface parameter optimization might allow for significantly lower amounts of additives to be detected. Lower limits of detection would be especially important for those additives which appear at less than 1% of the polymer by weight. It was also shown that, with respect to the sheath flow, changes in the nebulizer flow had little effect on the intensity of the deposition peak. The data indicate that the detection limits for polymer additives, which are virtually ideal analytes because of their high molecular weight and powdered form, fall in the low- to mid-nanogram range.

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References

1. D.A. Wheeler. Determination of antioxidants in polymeric materials. *Talanta* **15:** 1315–34 (1968).
2. T.R. Crompton. Identification of additives in polyolefins and polystyrenes. *Euro. Polym. J.* **4:** 473–96 (1968).
3. H.V. Drushel and A.L. Sommers. Direct determination of inhibitors in polymers by luminescence techniques. *Anal. Chem.* **36:** 836 (1964).
4. J.M. Howard. Gel permeation chromatography and polymer additive systems. *J. Chromatogr.* **55:** 15-24 (1971).
5. A.M. Wims and S.J. Swarin. Determination of antioxidants in polypropylene by liquid chromatography. *J. Appl. Polym. Sci.* **19:** 1243–56 (1975).
6. J.F. Schabron and L.E. Frenska. Determination of BHT, Irganox 1076, and Irganox 1010 antioxidant additives in polyethylene by high-performance liquid chromatography. *Anal. Chem.* **52:** 1411–15 (1980).
7. J.F. Schabron. Determination of polyolefin additives by normal phase high-performance liquid chromatography following soxhlet extraction. *J. Liq. Chromatogr.* **5:** 1269–76 (1982).
8. H.J. Cortes, R.M. Campbell, R.P. Himes, and C.D. Pfeiffer. *J. Microcol. Sep.* **4:** 239–44 (1992).
9. K.S. Kalasinsky, J.A.S. Smith, and V.F. Kalasinsky. Microbore high-performance liquid chromatography/FT–IR interface for normal or reversed-phase liquid chromatography. *Anal. Chem.* **57:** 1969–74 (1985).
10. C. Fujimoto and K. Jinno. Chromatography/FT-IR spectrometry approaches to analysis. *Anal. Chem.* **64:** 476A–481A (1992).
11. J.A. Jansen. On-line liquid chromatography–FTIR spectroscopy for the analysis of polymers and additives. *Fresenius J. Anal. Chem.* **337:** 398–402 (1990).
12. J. Dwyer. Analysis of Polymers by Combined Liquid Chromatography and Infrared Spectroscopy. *Amer. Lab.* 22–26 (1994).
13. J.J. Gagel and K. Bieman. Continuous infrared spectroscopic analysis of isocratic and gradient elution reversed-phase liquid chromatography separations. *Anal. Chem.* **59:** 1266–72 (1987).
14. T.C. Schunk, S.T. Balke, and P. Cheung. Quantitative polymer composition characterization with a liquid chromatography–Fourier transform infrared spectrometry–solvent evaporation interface. *J. Chromatogr.* **661:** 227–38 (1994).

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