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Identification of Antioxidant and Ultraviolet Light Stabilizing Additives in Plastics by Liquid Chromatography/Mass Spectrometry

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The information obtained by absorbance detection when coupled with liquid chromatography is usually not specific enough to allow the qualitative identification of compounds present in complex samples with any degree of certainty. With the use of mass spectrometric detection (LC/MS), characteristic mass spectral data can be obtained which greatly aid in elucidating the identity of unknown compounds. In this paper, mass spectrometric detection is used in series with absorbance detection to identify or characterize antioxidants and UV light stabilizing additives in plastic materials which were separated by liquid chromatography. The two detectors were operated in series without any significant loss of chromatographic resolution. Nanogram quantities of additives could be detected by LC/MS. Lower detection limits were achieved by reconstructing mass chromatograms for selected ions. These studies demonstrate the feasibility of using LC/MS to characterize additives in plastic materials.

Chemical additives are frequently used to enhance the useful lifetime of polymeric materials. Antioxidants and ultraviolet (UV) light stabilizers are added to minimize potential polymer degradation by oxidative (*1–3*) or photochemical processes (*3, 4*). Identification and quantitation of these compounds are necessary for polymer degradation studies and for quality-assurance tests.

Due to the low concentration of additives in the polymer matrix (typically less than 1%), a sensitive method of analysis must be employed. The high molecular weight and polarity of many antioxidants and UV light stabilizers often precludes the use of gas chromatography. High-performance liquid chromatography has been used to effectively separate these compounds (*2, 5–9*). Identification of compounds present in real samples is based on comparison of the peaks' retention times or capacity factors (k') with those of known standards. Identification by this method not only is tedious and time-consuming but also requires one to have all of the suspected compounds on hand so that tentative identifications can be made. Even so, erroneous identifications can often be made due to the relatively poor separating ability of HPLC (compared to capillary gas chromatography) and the chemical similarity of many compounds.

The combination of liquid chromatography with mass spectrometric detection (LC/MS) can circumvent many of these problems. Many compounds, such as distearyl thiodipropionate (DSTDP), which do not absorb ultraviolet light at standard UV detection wavelengths (254 nm and 280 nm) will not be detected with a conventional UV absorbance detector. The mass spectrometer is a more universal detector. The information yielded by LC/MS greatly aids in elucidating the structure of unknown compounds.

In our laboratory, ultraviolet absorbance and mass spectrometric detection were used in series to provide unique qualitative and quantitative information on plastic additives separated by liquid chromatography. Additional peak broadening introduced by this detection arrangement was minimal. The system was used to characterize the additives present in several polymeric samples.

EXPERIMENTAL SECTION

Standards and Extracts. Antioxidant standards were obtained from Chem Service, Inc., West Chester, PA. The ultraviolet stabilizers, Cyasorb UV 5411 and UV 531, were purchased from American Cyanamid Co., Wayne, NJ. Trade names and chemical names for the additives are listed in Table I. Standard stock solutions were made up in acetonitrile with enough tetrahydrofuran (THF) added to dissolve the compounds.

Plastic samples were cut into small shavings with a drill bit prior to extraction. Approximately 1 g of the plastic shavings was extracted overnight with 5 mL of acetonitrile. The extraction was performed at ambient temperature in a sealed amber vial with constant stirring. The additives of interest were sufficiently soluble in the acetonitrile extracting solvent due to the small amounts of analyte present. The extract solutions were filtered prior to analysis. Future experiments will evaluate the efficiency of various solvents for the extraction of additives in plastic materials.

Liquid Chromatography. Liquid chromatographic separations were achieved with a dual pump–gradient system (Model 6000A pumps, Model 680 LC gradient controller, Waters Associates, Milford, MA). Ultraviolet absorbance detection was accomplished with a Kratos Model 773 variable wavelength detector equipped with a 0.5-μL flow cell (Kratos Analytical Instruments, Westwood, NJ). All absorbance detection was done at 280 nm. Chemical separations were achieved on a $^1/_8$ in. o.d. × 2.1 mm i.d. × 25 cm long column packed with 5-μm diameter ODS particles (Alltech Associates, Inc., Deerfield, IL). Sample injections were made with a Valco injection valve (Valco, Houston, TX) equipped with a 10-μL loop. A precolumn filter was used to remove particulate material from the injection sample (Upchurch Scientific, Oak Harbor, WA).

The gradient elution scheme shown in Table II was used for the LC separations. The acetonitrile used was HPLC grade. THF was freshly distilled in the laboratory. The gradient controller was set for a flow rate of 0.2 mL/min. At this flow rate, it takes approximately 10 min for the mobile phase in the solvent mixing chamber to reach the column inlet. Therefore, injections were not made until the gradient controller was 7.0 min into the gradient elution program. This reduced the amount of computer time and disk space required to record an LC/MS chromatogram.

Mass Spectrometry. Mass spectrometric detection was achieved with a Finnigan-MAT Model 4615 quadrupole mass spectrometer which was equipped with a moving belt LC/MS interface (Finnigan-MAT, San Jose, CA). Methane chemical ionization (CI) was used for most of the experiments. The ion source was pressurized to 0.3 torr with methane reagent gas, which was ionized with 70-eV electrons. Typically, solutes were desorbed from the polyimide LC/MS interface belt at 230 °C. The ion source temperature was 120 °C. Chemical ionization spectra from m/z 200 to 1200 were recorded repetitively at 3 s/scan. Electron ionization spectra were recorded from m/z 50 to 800 at 3 s/scan.

The LC/MS moving belt interface was modified so that the column effluent was deposited on the belt in a fine spray. The design of the nebulizer was similar to the one described by Karger et al. (*10*). With this system, the LC/MS interface was capable of efficient operation with the mobile phases used at flow rates up to 0.2 mL/min. There was no significant loss of resolution

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Table I. Trade Names, Chemical Names, and Mass Spectral Data for Antioxidant and UV-Stabilizer Additives

trade name	chemical name	characteristic ions in methane chemical ionization mass spectrum: most intense ion, m/z	predominant molecular ion species[d]: m/z	rel int[c]
BHT[a]	2,6-di-*tert*-butyl-4-methylphenol	220	220	100
Santowhite Powder	4,4′-butylidenebis(3-methyl-6-*tert*-butylphenol)	219	383[b]	18
Topanol CA	1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane	381	544	71
UV 5411	2-(2-hydroxy-5-octylphenyl)benzotriazole	324	324[b]	100
UV 531	2-hydroxy-4-(*n*-octyloxy)benzophenone	327	327[b]	100
Irganox 1010	pentaerythritol tetra-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	221	1176	nd[e]
Ionox 330	1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene	219	774	4
Irganox 1076	octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	475	530	37
DSTDP	distearyl thiodipropionate	325	683[b]	9

[a] Many other trade names. [b] Protonated molecular ion. [c] Intensity relative to the most intense ion in the spectrum. [d] Molecular ions and protonated molecular ions were observed in the mass spectra. [e] nd, not detected.

Table II. Gradient Elution Scheme

time, min	% solvent A[a]	% solvent B[b]
0	100	0
10	60	40
20	0	100
30	0	100
32	100	0

[a] Solvent A, 75% acetonitrile and 25% water. [b] Solvent B = 50% THF and 50% acetonitrile.

Table III. Comparison of LC Column Efficiencies Determined by Absorbance Detection and LC/MS[a]

test compd	column efficiency (N): abs, detection	LC/MS
phenol	6900	7000
o-cresol	7900	7400
3,5-dimethylphenol	7700	7100

[a] Isocratic elution with 50% CH_3CN/H_2O.

or efficiency in going from the absorbance detector to the mass spectrometer when the two detectors were used in series. When the absorbance detector and mass spectrometer were operated in series, a 20-cm length of 0.01 in. i.d. stainless steel tubing was used to connect the absorbance detector outlet to the LC/MS interface.

RESULTS AND DISCUSSION

Evaluation of the LC/MS Interface. Extracolumn broadening of the chromatographic peaks was found to be minimal for mass spectrometric detection with our system. In a preliminary experiment, the observed column efficiency (N) for a mixture of three phenolic compounds was compared for absorbance detection and mass spectrometric detection (Table III). The observed values of N are very similar for both detection systems. These data indicate that the LC/MS connective tubing, interface, and mass spectrometer itself do not contribute significant peak broadening when the system is optimized.

LC/MS of Antioxidants and UV Light Stabilizers. A complex mixture of nine commonly used antioxidants and UV light stabilizers (Table I) was used to develop a general gradient elution scheme and to optimize the LC/MS parameters. The separation of these compounds with near base line resolution is presented in Figure 1. Detection was achieved with the absorbance and mass spectrometric detectors in series. The resolution between adjacent chromatographic peaks (i.e., peaks 4 and 5) was not significantly affected by our dual

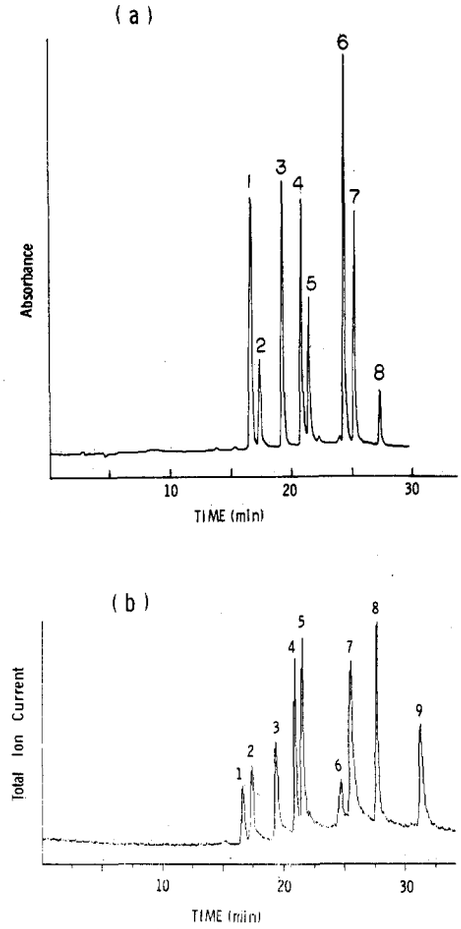

Figure 1. Absorbance chromatogram at 280 nm (a) and total ion current chromatogram (b) of antioxidants and ultraviolet light stabilizers: (1) BHT, 3.1 μg; (2) Santowhite, 0.9 μg; (3) Topanol CA, 2.7 μg; (4) UV 531, 0.66 μg; (5) UV 5411, 0.68 μg; (6) Irganox 1010, 4.5 μg; (7) Ionox 330, 2.4 μg; (8) Irganox 1076, 1.2 μg; (9) DSTDP, 1.7 μg. DSTDP was not detected with absorbance detector at 280 nm.

detection arrangement. Compounds which may not sufficiently absorb light at the monitored absorbance wavelength can often be detected by the mass spectrometer, as was the case for DSTDP (peak 9).

Limits of Detection. The limits of detection ($S/N = 3$) were experimentally determined with a three-component mixture consisting of Santowhite, UV 5411, and Ionox 330. The compounds were detected by both absorbance and mass spectrometric detection. Mass spectrometric detection limits

Table IV. Limits of Detection

	detection limit, ng		
	Santowhite	UV 5411	Ionox 330
abs at 280 nm	3	2	5
total ion current	80	60	150
selected ion current $S/N = 3$	4[a]	2[b]	30[c]

[a] $m/z = 219$. [b] $m/z = 324$. [c] $m/z = 219$.

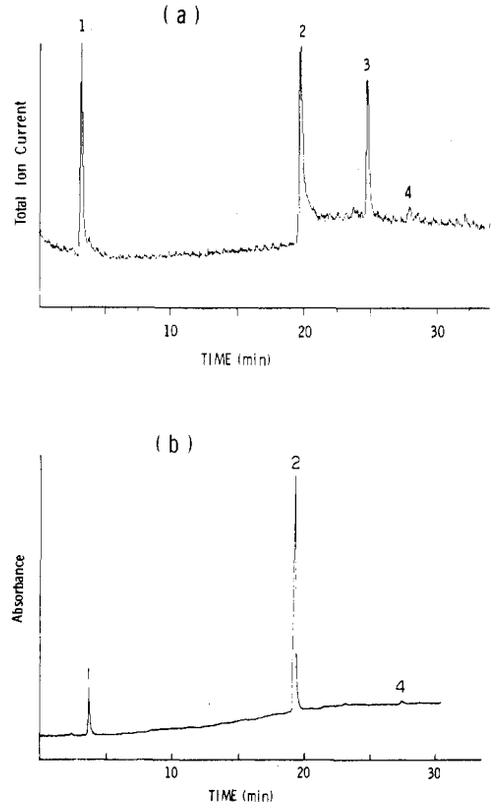

Figure 2. Total ion current chromatogram (a) and absorbance chromatogram at 280 nm (b) of extract from polypropylene beads: (1) unidentified mixture, (2) Topanol CA, (3) octadecanol, (4) Irganox 1076.

were determined from total ion current chromatograms (m/z 200 to 1200) and from reconstructed mass chromatograms of selected ions. Molecular ions or protonated molecular ions and characteristic fragment ions were selected for the reconstructed mass chromatograms (Table I). The limits of detection for the discussed modes are presented in Table IV. Reconstructed mass chromatograms significantly improved the mass spectrometric detection limits because of the relatively intense total ion current background associated with LC/MS. Presumably, even lower detection limits could be obtained with selected ion monitoring.

Characterization of Additives in Plastics. The leachable additives in the extracts from two plastic samples were separated and characterized by liquid chromatography with both absorbance and mass spectrometric detection in series. Some of the additives were identified and quantitated by standard addition with absorbance detection.

Figure 2 shows the chromatogram obtained by both detectors for the separation of additives in the extract from polypropylene beads. Topanol CA and a small amount of Irganox 1076 were present. Octadecanol was also determined to be present in the extract by mass spectrometric detection. By standard addition and absorbance detection, the concentration of Topanol CA in the original sample was determined to be 0.95 mg/g.

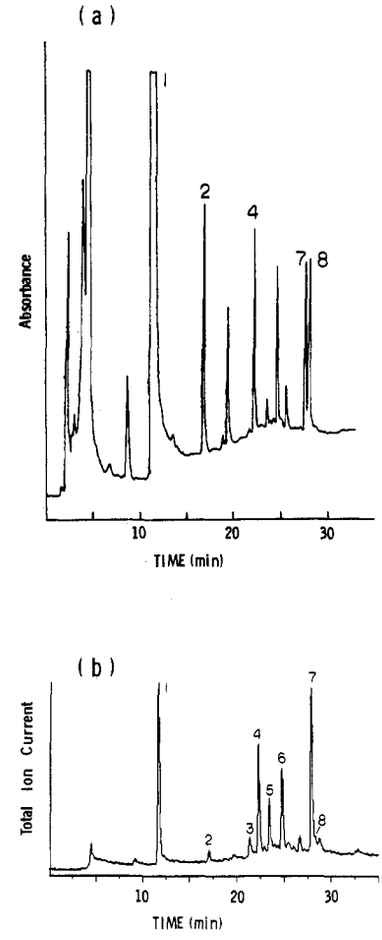

Figure 3. Absorbance chromatogram at 280 nm (a) and total ion current chromatogram (b) of an extract from a molded polypropylene part: (1) unidentified, mol wt 240; (2) BHT; (3) palmitic acid; (4) dioctyl phthalate plasticizer; (5) stearic acid; (6) octadecanol; (7) unidentified, mol wt 390; (8) Irganox 1076.

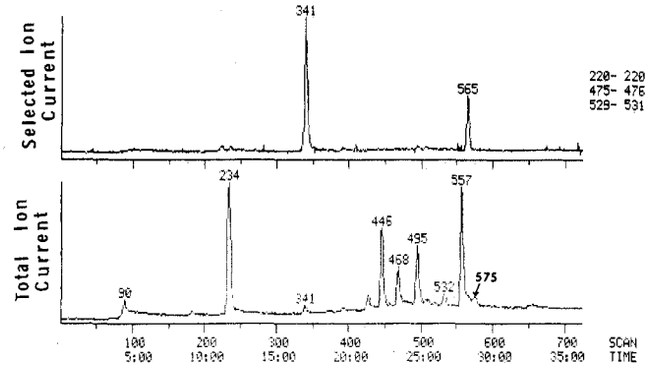

Figure 4. Identification of antioxidants in the extract from a molded polypropylene part by plotting selected ion current profiles. The numbers above peaks correspond to the computer scan number (3 s/scan). Scan number 341 is BHT while scan number 565 corresponds to Irganox 1076.

The additives in an automotive component molded from polypropylene were separated and identified (Figure 3). BHT and Irganox 1076 were identified in the extract. By standard addition and absorbance detection, the amounts of BHT and Irganox 1076 in the original sample were determined to be 0.25 mg/g and 0.072 mg/g, respectively. In addition, several other additives were identified. Identification of these additional additives was simplified by the availability of both electron ionization and chemical ionization mass spectra. Unidentified compounds, which presumably have large molar absorptivities at 280 nm, were detected by the absorbance

detector but not by the mass spectrometer. Those compounds account for the four unidentified peaks appearing between 15 and 30 min in the absorbance chromatogram (Figure 3).

The utility of reconstructed mass chromatograms is evident in Figure 4. BHT and Irganox 1076 are easily detected in the reconstructed mass chromatogram, but in the total ion current chromatogram, Irganox 1076 is obscured by the peak at scan 557.

LITERATURE CITED

(1) Wheeler, D. A. *Talanta* **1968**, *15*, 1315.
(2) Wims, A. M.; Swarin, S. J. *J. Appl. Polym. Sci.* **1975**, *19*, 1243.
(3) Rodriguez, F. "Principles of Polymer Systems", 2nd ed.; McGraw-Hill: New York, 1982; pp 277-302.
(4) "Cyasorb UV 531 Light Absorber"; Technical Bulletin D-42, American Cyanimid Co.: Wayne, NJ, 1982.
(5) Lichtenthaler, R. G.; Ranfelt, F. *J. Chromatogr.* **1978**, *149*, 553.
(6) Schabron, J. F.; Fenska, L. E. *Anal. Chem.* **1980**, *52*, 1411.
(7) Pasteur, G. A. *Anal. Chem.* **1977**, *49*, 363.
(8) Perlstein, P. *Anal. Chim. Acta.* **1983**, *149*, 21.
(9) Hanley, M. A.; Dark, W. A. *J. Chromatogr. Sci.* **1980**, *18*, 655.
(10) Hayes, M. J.; Lankmayer, E. P.; Vouros, P.; Karger, B. L.; McGuire, J. M. *Anal. Chem.* **1983**, *55*, 1745.

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Electrospray Interface for Liquid Chromatographs and Mass Spectrometers

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Electrospraying LC effluent into a dry bath gas creates a dispersion of charged droplets which rapidly evaporate. As the droplets grow smaller the increase in surface charge density and the decrease in radius of curvature result in electric fields strong enough to desorb solute ions. Part of the resulting dispersion of ions in bath gas passes through a small orifice or channel into an evacuated region to form a supersonic free jet. The core of this jet passes through a conical skimmer orifice and transports the ions to the inlet of a mass analyzer. The reported results suggest that from the standpoints of flexibility, convenience, sensitivity, cleanliness, and ease of maintenance, this ESPI source may comprise an effective and practical LC-MS interface.

The successful union of gas chromatography with mass spectrometry spawned a revolution in chemical analysis. An important impediment to the marriage was a basic incompatibility between vital features of each partner's mode of operation. The lifeblood of a gas chromatograph is the flow of carrier gas in which the species of analytical concern are usually present in only trace amounts. To the mass spectrometer, which is happy only under high vacuum, the prospective flood of carrier gas diluent was anathema. Clearly needed to overcome this impediment was a means of removing and discarding a large fraction of the carrier gas before the stream to be analyzed entered the mass spectrometer. One of the early and most successful devices for accomplishing this removal was the so-called jet separator first described by Ryhage and still widely used in one form or another (*1*). This device derived from the research of E. W. Becker and his colleagues who were exploring the use of supersonic free jets expanding into vacuum for molecular beam sources as had been proposed by Kantrowitz and Grey (*2*). Surprisingly large species separation effects were observed when the free jet gas comprised a mixture of heavy and light molecules (*3*, *4*). Originally attributed to pressure diffusion during the expansion, this separation was subsequently shown to stem from preferential inertial penetration of heavier species into the stagnation zone behind the bow shock wave on the sampling probe immersed in the supersonic flow (*5*, *6*).

More recently the rapid and highly successful development of high-performance liquid chromatography (HPLC) has reached the stage where its practitioners have for some time also been contemplating the advantages of mass spectrometric detection. As was the case in GC-MS there is an impediment to the union of LC with MS that is similar but even more formidable. To be successful an LC-MS interface must not only divert a large fraction of the mobile phase from the mass spectrometer inlet but it must also make possible the transformation of nonvolatile and fragile species from solutes in a liquid to ions in a vacuum ready for mass analysis. To accomplish the latter step has been an exceedingly refractory problem to which until recently there have been no really satisfactory solutions even when the sample is static and there are no harsh constraints on the time available for preparation.

In the last few years there has emerged a new breed of ion sources that to a much greater extent than their predecessors seem at once to be effective, easy to use, and compatible with both partners of the LC-MS union. Similar in some sense to the field ionization (FI) and field desorption (FD) sources introduced by Beckey and his collaborators, the newcomers apparently share a common mechanism: field ion desorption from liquids (FIDL) (*7*). Their membership includes the electrohydrodynamic (EHD) source of Evans and co-workers, the atmospheric pressure ion evaporation (APIE) source of Iribarne and Thomson, and the Thermospray (TS) source of Vestal and his colleagues (*8-18*). Along with other techniques for the ionization of nonvolatile molecules, these FIDL sources have recently been reviewed by Vestal (*19*).

In this paper we report some experience and results with another variation on the FIDL theme, an electrospray ion (ESPI) source that has its roots in some experiments performed 15 years ago by Malcolm Dole and his collaborators. They attempted to produce beams of charged macromolecules by electrospraying a solution of polystyrene molecules into a bath gas to form a dispersion of macroions that was ex-

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