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CHARACTERIZATION OF ADDITIVES IN PLASTICS BY LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

Additives in plastics, separated by liquid chromatography (LC), were characterized and identified with a tandem detection system which consisted of an ultraviolet absorbance detector and a modified LC–mass spectrometry (MS) moving belt system. The two detectors were operated in series with minimal loss of chromatographic resolution. The maximum eluent flow-rates which could be tolerated by the LC–MS system were determined for acetonitrile–water mixtures. The LC–MS system was found to operate satisfactorily as a LC detector: a linear response was observed between the integrated ion current of eluted peaks and the amount present, quantitative data were obtained with a precision of $< 10\%$ relative standard deviation, and sensitive detection limits were achieved (< 10 ng for some solutes).

INTRODUCTION

Chemical additives are incorporated in the polymer matrix of plastics to enhance their useful lifetime and physical properties. Additives are frequently used to improve optical properties, resist aging, modify bulk mechanical properties, assist in processing, or for a variety of other reasons. These additives are not chemically bonded into the polymer matrix, but are physically dispersed instead. Plastic failures can often be attributed to the leaching of additives from the polymer, the chemical transformation of certain additives, or the omission of essential additives during the formulation processes. Thus, there is a need for reliable methods which can identify and quantitate additives found in plastics.

Various methods have been developed for the determination of additives in plastics: liquid chromatography (HPLC or LC)[1–6], thin-layer chromatography (TLC)[7], gas chromatography (GC)[8–10], and mass spectrometry (MS)[11–12]. LC is the best general method. Both polar and non-volatile additives can be determined by LC, but usually not by GC. Unfortunately, conventional LC detectors are not very specific in the information that is obtained for eluted peaks. For this reason, identification must be based on a comparison of the retention time of the eluted peak with that of a known compound. This method of identification can be very time-consuming, laborious, and subject to misidentification.

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Recent advances in the design and performance of LC–mass spectrometry (MS) interfaces provide for the use of a mass spectrometer as a detector for HPLC. The spectral information provided by the mass spectrometer is unmatched by the other, more commonly used HPLC detectors. In addition, computer storage of mass spectral data allows the user to perform data operations that enhance or "clean up" the computer-generated chromatograms and plot reconstructed mass chromatograms of specific ions that are characteristic of a compound.

In our laboratory, we have constructed an HPLC system which allows both absorbance and mass spectrometric detection to be performed in series on eluted chromatographic peaks. In a previous publication[13], we utilized this detection system to identify the antioxidant and ultraviolet light stabilizing additives present in plastic materials. In this report, we describe the evaluation of this tandem detection arrangement.

EXPERIMENTAL

Standards and extracts

Antioxidant standards were obtained from Chem Service, West Chester, PA, U.S.A. The ultraviolet stabilizers, Cyasorb UV 5411 and UV 531, were purchased

TABLE I

TRADE NAMES, CHEMICAL NAMES, AND MASS SPECTRAL DATA FOR ANTIOXIDANT AND UV-STABILIZER ADDITIVES

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Trade name	*Chemical name*	*Characteristic ions in methane chemical ionization mass spectrum*		
		Most intense ion (m/z)	*Molecular ion species*	
			m/z	*Rel. int.***
BHT*	2,6-Di-*tert.*-butyl-4-methylphenol	220	220	100
Santowhite powder	4,4'-Butylidene-bis(3-methyl-6-*tert.*-butylphenol)	219	383***	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***	100
UV-531	2-Hydroxy-4-*n*-octyloxybenzophenone	327	327***	100
Irganox 1010	Pentaerythritol tetra-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propionate	221	1176	n.d.
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***	9

* Many other trade names.
** Intensity relative to the most intense ion in the spectrum.
*** Protonated molecular ion.

TABLE II

GRADIENT ELUTION SCHEME

Solvent A = acetonitrile–water (75:25); solvent B = THF–acetonitrile (50:50); reproduced with permission from ref. 13.

Time (min)	*Solvent A (%)*	*Solvent B (%)*
0	100	0
10	60	40
20	0	100
30	0	100
32	100	0

from American Cyanamid, Wayne, NJ, U.S.A. Trade names and chemical names for the additives are listed in Table I along with additional characteristic mass spectrometric information. Standard 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 extractions were performed at ambient temperature in sealed amber vials with constant stirring. The extract solutions were filtered prior to analysis.

Liquid chromatography

LC separations were achieved using a dual pump-gradient system (Model 6000A pumps, Model 680 LC gradient controller, Waters Assoc., Milford, U.S.A.). 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, U.S.A.) set at 280 nm. Chemical separations were achieved on a 25 cm × 1/8 in. O.D. × 2.1 mm I.D. column packed with 5-μm diameter ODS particles (Alltech Assoc., Deerfield, U.S.A.). Sample injections were made with a Valco injection valve (Valco, Houston, U.S.A.), equipped with a 10-μl loop. A pre-column filter was used to remove particulate material from the injected sample (Upchurch Scientific, Oak Harbor, WA, U.S.A.).

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 a LC–MS chromatogram.

Mass spectrometry

MS 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, U.S.A.). 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. Some experiments were per-

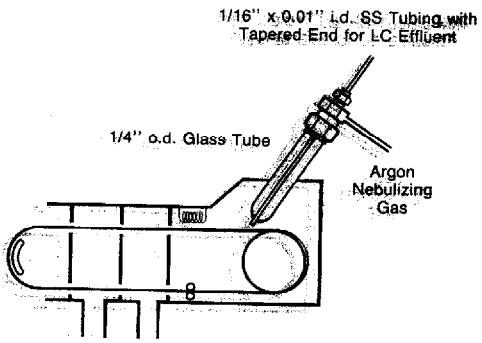

Fig. 1. Diagram of effluent nebulizer for the LC–MS interface.

formed in the electron ionization mode 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 per scan. Electron ionization spectra were recorded from *m/z* 59 to 800 at 3 s per scan.

LC–MS interface

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.*[14] (see Fig. 1). The nebulizer was connected to the end of the column or to the outlet of the absorbance flow cell (when absorbance and mass spectrometric detection were performed in series) with a 20-cm length of 0.01 in. I.D. stainless-steel tubing. A bored-through union was used to connect the interface with the connective tubing to minimize band broadening.

RESULTS AND DISCUSSION

Evaluation and optimization of the LC–MS interface

Mobile phase compositions and flow-rates could not be used for LC–MS if they caused the mass spectrometer analyzer pressure to exceeded $2 \cdot 10^{-6}$ torr. The maximum flow-rate that could be used with a given water–acetonitrile mobile phase composition was determined by measuring the mass spectrometer analyzer pressure as the flow-rate was varied (Fig. 2a). In Fig. 2b the maximum flow-rate was plotted as a function of the percentage (v/v) of water in the solvent mixture.

A mixture of nine antioxidants and ultraviolet light stabilizers was separated with absorbance and MS detection performed in series (Fig. 3). The resolution between adjacent peaks was relatively unaffected by the dual detector arrangement. DSTDP, which does not absorb light at 280 nm, could not be detected with the absorbance detector; however, it was easily detected by LC–MS. Additives which are not detected at the absorbance wavelength monitored can often be detected by MS. Conversely, sometimes additives which are not observed by MS (*i.e.*, solutes which are too volatile, too involatile, or which fragment into very small *m/z* fragments only) can be observed by absorbance detection.

Table I presents data which indicates the most intense ion in the CI mass

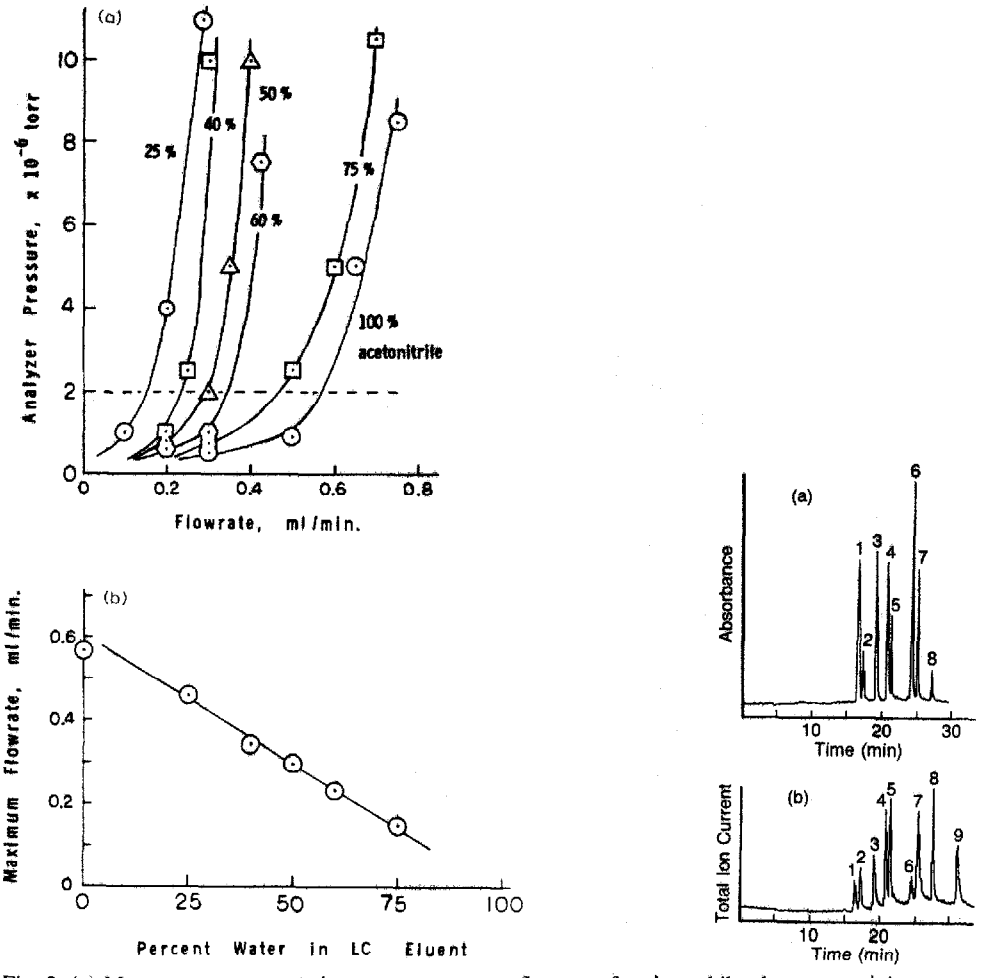

Fig. 2. (a) Mass spectrometer analyzer pressure *versus* flow-rate for six mobile phases containing water and acetonitrile. The mobile phase flowed directly onto the LC–MS interface belt. (b) Maximum flow-rate for LC–MS *versus* percent water in water–acetonitrile mobile phase.

Fig. 3. Absorbance chromatogram (a) and total ion current chromatogram (b) of antioxidants and ultraviolet stabilizers. Amount of compounds: (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 not detected with absorbance detector at 280 nm. Reproduced with permission from ref. 13.

spectra and the intensity of the molecular ion species relative to it. Some additives produced more characteristic mass spectra than others. UV 531 (Fig. 4) produced an intense protonated molecular ion, $(M + H)^+$, which made it easy to detect and observe the molecular species ion in very low amounts. However, there were virtually no characteristic fragment ions which could help determine the structure of the compound. Topanol CA (Fig. 5) is an example of an additive which produced an abundance of characteristic fragment ions in addition to the molecular ion. While it would be much easier to characterize the structure of this compound from its methane CI

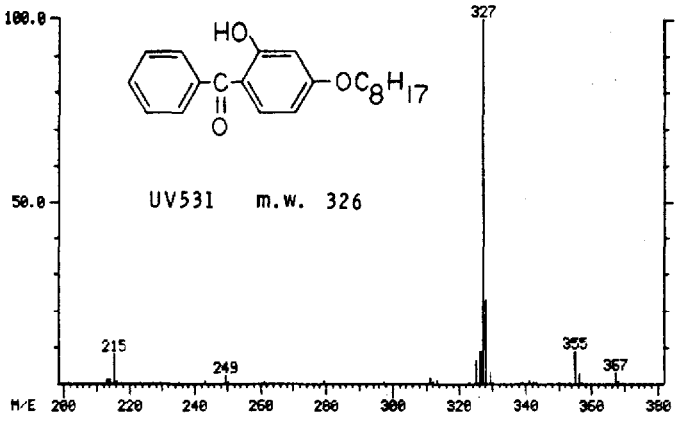

Fig. 4. Methane CI mass spectrum of UV 531.

mass spectra (in comparison to UV 531), the absolute detection limit would probably be poorer due to the distribution of the total ion current among many fragmentation ions. Irganox 1010 is an example of an undesirable situation where no molecular ion peak is observed, and the ions which are seen are very uncharacteristic and are easily obscured by a relatively intense background noise which can extend beyond *m/z* 200

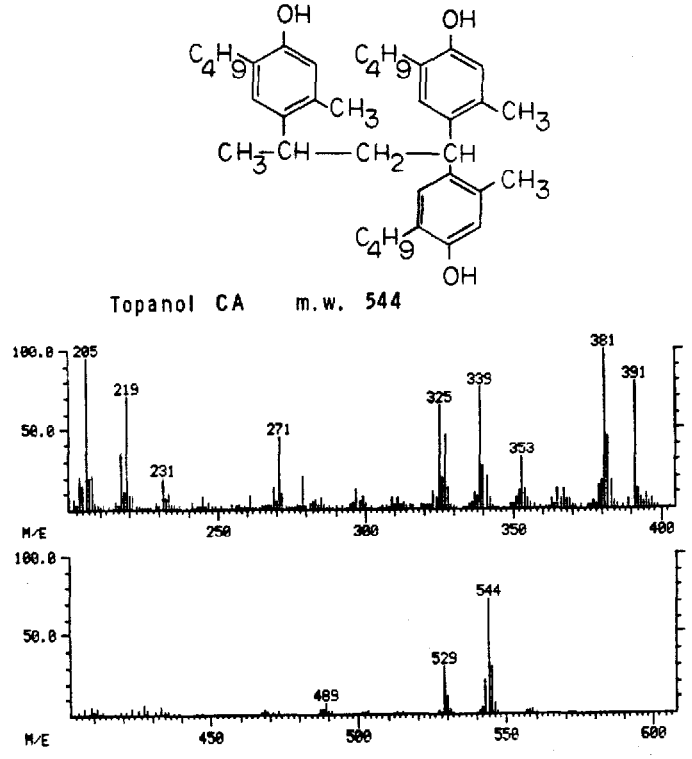

Fig. 5. Methane CI mass spectrum of Topanol CA.

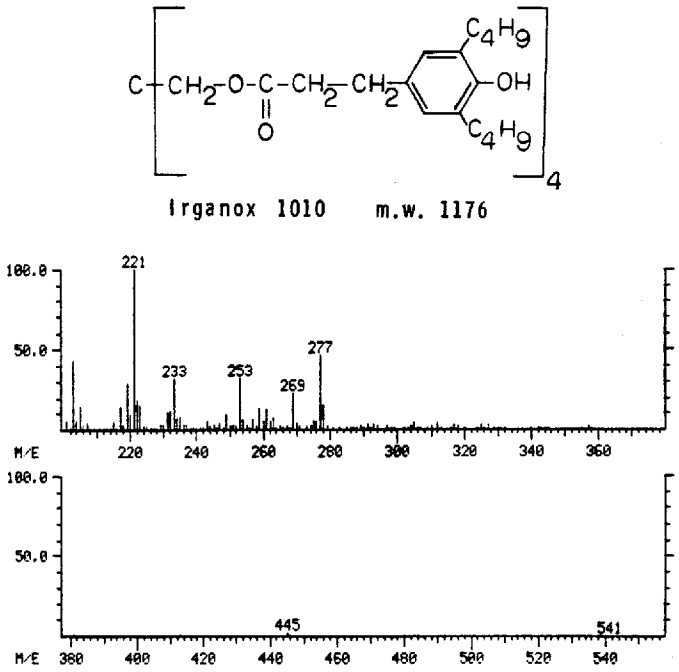

Fig. 6. Methane CI mass spectrum of Irganox 1010.

for LC–MS (Fig. 6). The net result is very poor sensitivity along with poor characterization. For this compound, identification can only be based on the chromatographic retention of the additive.

Quantitative information was obtained by measuring the peak height (absorbance detection) or the integrated peak area (LC–MS). With LC–MS detection, either the total ion current peak area or the peak area for reconstructed mass chromatograms of selected ions could be used. The precision for each quantitation method was examined for the 9-component standard mixture (Table III). A relative standard deviation (R.S.D.) of 1.6–3.7% was obtained by absorbance detection. The R.S.D. for both LC–MS methods typically exceeded the R.S.D. for absorbance detection by a factor of 2 to 3. However, the precision obtained by LC–MS is still sufficient for many applications.

A linear relation was observed between the logarithm of the LC–MS peak area and the logarithm of the amount of additive injected from 100 ng to 10 μg (Fig. 7). The limits of detection (S/N = 3) varied depending on the detection method and the particular additive (Table IV). The limits of detection obtained by measurement of the total ion current were found to be poorer (by a factor or approximately 25) than the detection limits obtained by the other two detection methods. The sensitivity provided by reconstructed chromatograms of selected ions was about the same as the sensitivity provided by absorbance detection at 280 nm. Presumably, the LC–MS detection limits could be reduced into the picogram region by monitoring and collecting data for selected ions only.

TABLE III

PRECISION STUDY FOR QUANTITATIVE DETERMINATION OF ADDITIVES

Five determinations, n = 5.

	Additive	*Percent relative standard deviation of peak height*
A. UV Detection	BHT	1.9
	Santowhite	2.5
	Topanol CA	3.5
	UV 531	2.6
	UV 5411	1.6
	Irganox 1010	3.7
	Ionox 330	2.5
	Irganox 1976	2.9
	DSTDP	Non-absorbing

	Additive	*Selected Ion (m/z)*	*Percent relative standard deviation of peak area*	
			Total ion current	*Selected ion current*
B. Mass spectrometric detection	BHT	220	3.7	3.8
	Santowhite	383	7.0	7.2
	Topanol CA	544	6.5	9.4
	UV 531	327	6.3	6.5
	UV 5411	324	3.7	0.9
	Irganox 1010		3.6	
	Ionox 330	774	8.4	10.0
	Irganox 1076	531	4.4	7.1
	DSTDP	683	6.5	3.6

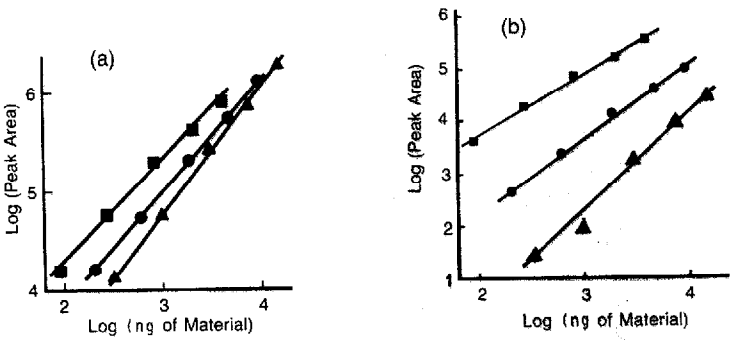

Fig. 7. LC–MS calibration curves for UV 5411 (■), Santowhite Powder (●), and Ionox 330 (▲). (a) Peak areas from total ion current chromatograms and (b) peak areas from selected ion current chromatograms: *m/z* 324 ion for UV 5411, *m/z* 383 ion for Santowhite Powder, and *m/z* 774 ion for Ionox 330.

TABLE IV

LIMITS OF DETECTION FOR SANTOWHITE, UV 5411, AND IONOX 330

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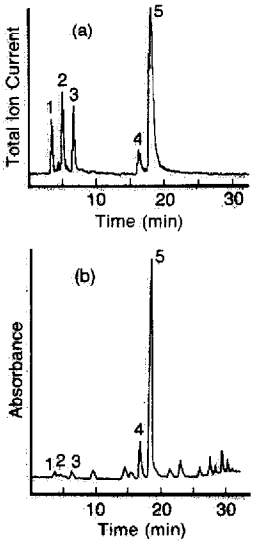
Method of detection	*Detection limit* (ng)*		
	Santowhite	*UV 5411*	*Ionox 330*
1 Absorbance at 280 nm	3	2	5
2 Total ion current measurements	80	60	150
3 Reconstructed chromatograms of selected ions.	4**	2***	30**

* Detection limit at signal-to-noise ratio (S/N) of 3.
** *m/z* 219.
*** *m/z* 324.

Characterization of additives in plastics

The additives present in several plastic samples were characterized or identified by chromatographic retention data (k') and methane CI fragmentation spectra (LC–MS). Some additives were quantitated by the standard addition method with absorbance detection.



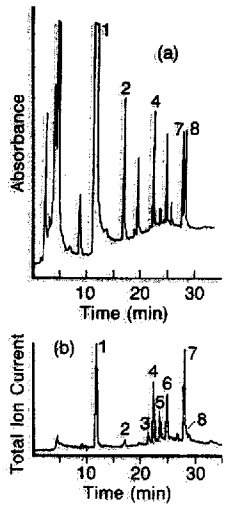


Fig. 8. Total ion current chromatogram (a) and absorbance chromatogram (b) of extract from polycarbonate window material. Identification: (1) unidentified, (2) diphenyl carbonate (tentative identification), (3) diphenyl carbonate derivative of Bisphenol A (tentative identification), (4) UV 531, (5) UV 5411.

Fig. 9. Absorbance chromatogram (a) and total ion current chromatogram (b) of an extract from a molded polypropylene part. Identification: (1) unidentified, m.w. 240, (2) BHT, (3) palmitic acid, (4) dioctyl phthalate plasticizer, (5) stearic acid, (6) octadecanol, (7) unidentified, m.w. 390, (8) Irganox 1076. Reproduced with permission from Ref. 13.

The total ion current and absorbance chromatograms are presented (Fig. 8) for the separation of additives present in the extract of a polycarbonate material. Two ultraviolet light absorbing compounds (UV 531 and UV 5411) were present in the material, presumably to prevent light-induced weathering of the clear window material. The mass spectra of peaks 2 and 3 suggest that they may be monomers or oligomeric by-products of the polycarbonate[15].

In Fig. 9, the absorbance and total ion current chromatograms are presented for an extract from a molded polypropylene part. The antioxidants BHT and Irganox 1076 were identified in the sample along with several other additives. Irganox 1076 produced a very small total ion current peak and was buried in the shoulder of peak 7. However, its identity was confirmed by reconstructing the chromatogram for its most intense ion fragments (*m/z* 475-476, 529-531). Minor components hidden in other peaks or in the baseline of total ion current chromatograms can often be found if one knows which specific ions to look for.

CONCLUSIONS

It has been demonstrated that the LC–MS interface used in our laboratory is effective for the characterization of additives in plastics. The dual detection system was found to offer complementary information without sacrificing chromatographic resolution. Quantitative analysis can be performed by LC–MS with R.S.D. $< 10\%$. Computerized data manipulations, such as background subtraction, spectrum averaging, and the construction of mass chromatograms, provide new capabilities for detecting and identifying partially resolved and minor components by LC–MS. LC–MS is now routinely used in our laboratory to characterize and identify the additives present in plastic materials.

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