Application Note

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Analysis of Additives in a Polymer

Using the Agilent 6120B Single Quadrupole MS and MassWorks accurate mass elemental composition determination software

Author

Hirokazu Sawada, PhD.
Agilent Technologies, Inc.

Abstract

The Agilent 6120B Single Quadrupole LC/MS System was used to analyze additives in a polypropylene (PP) film. The formulas of additive components were determined from the acquired profile mode mass spectrum using MassWorks accurate mass calibration and composition/formula search software. The presence of an additive contained in a PP film was confirmed by library search using the obtained elemental composition.

Introduction

High molecular weight materials, such as plastics, are indispensable in daily life. High molecular weight materials contain traces of additives such as antioxidants and ultraviolet-absorbing compounds. It is important to understand their impact on the polymer and its quality. High-performance liquid chromatography (HPLC) is an analytical method that is effective for the qualitative and quantitative analysis of these additives. In HPLC, UV detection is the most common detector used, but it is difficult to identify unknown components by UV, due to a lack of specificity.

A more powerful, affordable, and simple-to-operate alternative is a single quadrupole LC/MS. To provide the specificity needed and improve confidence in compound identification, mass spectrometers provide information about the molecular weight of the target component. Single quadrupole mass detectors such as the Agilent 6120B Single Quadrupole LC/MS System or the InfinityLab LC/MSD Series provide unit mass resolution data, and are accurate only to the 0.x amu level.

MassWorks software from Cerno Biosciences is a powerful and complementary post-processing tool that significantly increases the mass accuracy of data from single quad mass spectrometers. MassWorks works by applying a calibration technique that produces accurate mass data down to 0.00x amu from unit mass resolution data. The combination of Single Quadrupole MS and MassWorks software provides an affordable approach to obtaining high mass accuracy data.

Additives contained in a commercial polymer product were analyzed using the 6120B Single Quadrupole LC/MS System and MassWorks software. Data obtained by the single quadrupole mass spectrometer were calibrated to produce accurate mass spectra, facilitating the determination of the unknown elemental composition (formula) of the ion observed.

Experimental conditions

A 1.5 g amount of commercial polypropylene (PP) film, was immersed in 30 mL of tetrahydrofuran (THF) and incubated for 24 hours. Then, the solution was analyzed by LC/MS. Table 1 shows LC/MS analytical conditions.

Table 1. LC/MS analytical conditions.

LC	
System	Agilent 1260 Infinity LC
Mobile phase	A) 10 mM ammonium acetate aqueous solution B) MeOH:THF (8:2)
Gradient	0–15 minutes, 35 % to 95 %B 15–40 minutes hold at 95 %B
Column	Agilent ZORBAX Eclipse Plus C18, 2.1 mm × 150 mm, 3.5 µm (p/n 959763-902)
Injection volume	2 µL
Column temperature	40 °C
UV	235 nm
Calibration substance for MassWorks	Inject erythromycin (100 ng/µL solution) using an injector program after the end of the chromatographic separation of the sample (34 minutes after the analysis start).
MS	
System	Agilent 6120B Single Quadrupole LC/MS
Ionization	ESI
Polarity	Positive
Scanning range	200–800 *m/z*
Fragmentor voltage	130 V
Scan rate (cycle time)	0.03 minutes (0.48 sec/cycle)
Threshold	Zero
Mode	Scan (profile)
Scan data storage	Full

Results and discussion

Figure 1A shows a UV chromatogram from an analysis of the THF extract of PP film, and 1B shows a total ion chromatogram (TIC) in ESI positive mode.

Figure 2 shows the mass spectrum of unknown peak A, eluting at approximately 22.5 minutes.

For the raw profile mass spectrum data obtained, the calibration of the data measured by the single quadrupole LC/MS system into accurate mass data allows the elemental composition (formula) of the unknown peak to be determined. This calibration requires a known substance be measured under the same MS conditions. The injector program function in the autosampler of the 1260 Infinity LC system was used to inject the calibrant.

THF extraction of PP film was analyzed. The duration of the elution of all compounds in the extract was 34 minutes (Figure 1). Then, erythromycin ($C_{37}H_{68}NO_{13}^{+}$) with an *m/z* value (at 735 amu) close to unknown peak A (at 664 amu) was injected as a calibration substance in the injector program. This procedure allowed the acquisition of the calibration substance in the same data file, and under the same conditions as those of the extract.

Figure 3A shows the TIC of PP film extract solution data from the MassWorks software, and 3B shows the mass spectrum after accurate mass calibration for unknown peak A. The accurate *m/z* value of unknown peak A was found to be 663.4541. As a result of elemental composition determination based on this accurate mass and the Calibrated Lineshape Isotope Profile Search (CLIPS) algorithm, $C_{42}H_{64}O_4P^{+}$ (proton adducts) was estimated as the most likely ion formula with the highest spectral accuracy (99.5 %) (Figure 4).

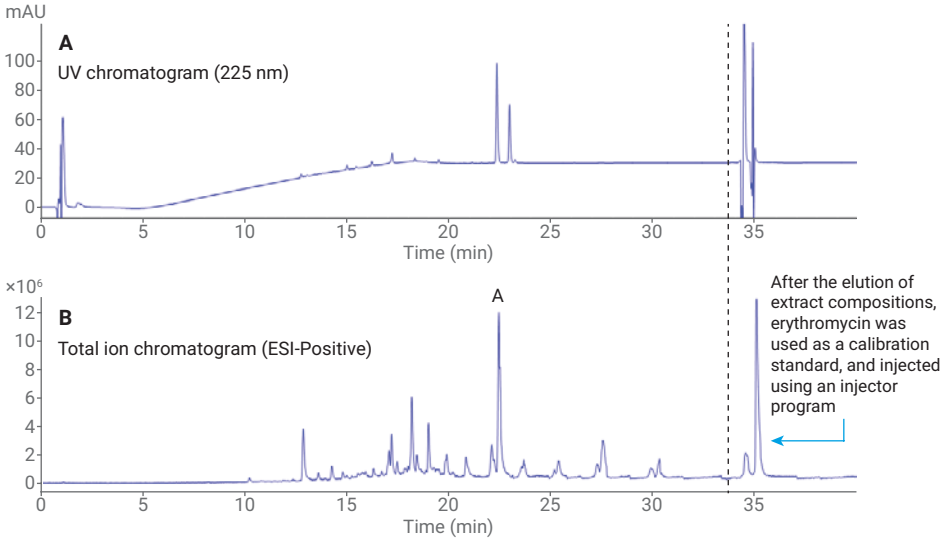

Figure 1. A) UV chromatogram and B) Total Ion Chromatogram (TIC) of PP film.

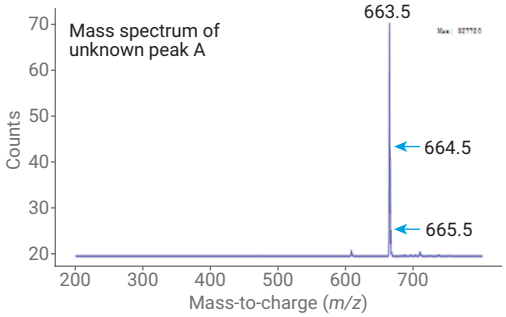

Figure 2. Mass spectrum of unknown peak A.

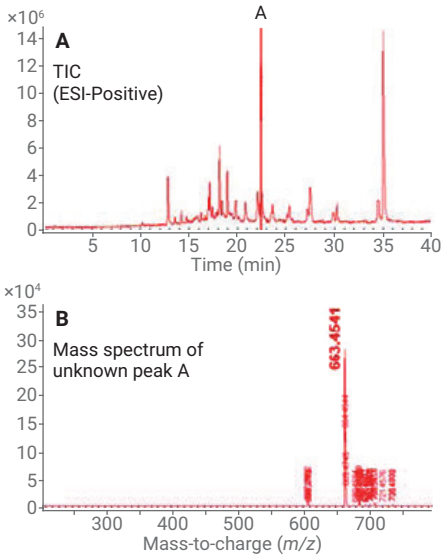

Figure 3. The TIC of the PP film and the mass spectrum for the unknown peak A after MassWorks calibration.

This combination of the single quadrupole LC/MS with MassWorks calibration and analysis software enabled the determination of elemental composition (formula) for unknown substances contained in PP film.

Various public databases can be searched for the potential structure of the compound formula obtained from the analysis. Figure 5 shows one example hit from searching ChemSpider, a chemical database. A search for the formula in the database resulted in Irgafos 168, an antioxidant used in polymer synthesis.

Conclusions

Additives in a polymer film were analyzed using the Agilent 6120B Single Quadrupole LC/MS System. MassWorks software was used to calibrate the unit-mass MS data obtained by the quadrupole mass spectrometer into an accurate mass spectrum. The accurate mass spectrum was used to determine the elemental composition (formula) of unknown components by MassWorks. The resulting formula for the additive contained in the polymer was searched against a chemical database to determine a potential structure.

This approach turns an affordable and simple to use single quadrupole MS into a powerful tool that provides accurate mass information about unknown compounds for the analysis of materials.

MassWorks is a post processing MS calibration and analysis software provided by Cerno Bioscience.

CLIPS Results for average of scans 2605 thru 2621

	Formula	Mono Isotope	Mass Error (mDa)	Mass Error (PPM)	Spectral Accuracy	RMSE	DBE
1	C42H64O4P	663.4537	0.4265	0.6429	99.4984	551	11.5
2	C42H65O2P2	663.4454	8.6692	13.0668	99.4507	603	11.5
3	C42H63O6	663.4619	-7.8162	-11.7810	99.3925	667	11.5
4	C42H66P3	663.4372	16.9119	25.4907	99.2796	791	11.5
5	C43H69OP2	663.4818	-27.7163	-41.7757	99.2645	807	10.5
6	C41H59O7	663.4255	28.5693	43.0615	98.8538	1,258	12.5
7	C45H61P2	663.4243	29.7986	44.9143	97.9009	2,304	16.5
8	C45H60O2P	663.4325	21.5559	32.4904	97.8474	2,363	16.5
9	C45H59O4	663.4408	13.3132	20.0665	97.7582	2,461	16.5
10	C39H67O8	663.4830	-28.9455	-43.6286	97.4434	2,806	6.5
11	C39H68O6P	663.4748	-20.7028	-31.2046	97.4217	2,830	6.5
12	C39H69O4P2	663.4666	-12.4601	-18.7807	97.3676	2,889	6.5
13	C39H70O2P3	663.4583	-4.2174	-6.3568	97.2833	2,982	6.5
14	C42H65P2S	663.4277	26.4278	39.8336	97.2238	3,047	11.5
15	C39H71P4	663.4501	4.0253	6.0671	97.1713	3,105	6.5
16	C46H64OP	663.4689	-14.8296	-22.3521	97.0606	3,226	15.5
17	C46H63O3	663.4772	-23.0723	-34.7760	96.9808	3,314	15.5
18	C42H64O2PS	663.4359	18.1851	27.4097	96.9356	3,363	11.5
19	C39H70P3S	663.4406	13.5411	20.4100	96.7841	3,530	6.5
20	C43H68OPS	663.4723	-18.2004	-27.4328	96.7611	3,555	10.5

Figure 4. Results of *m/z* 663.4541 accurate mass elemental composition determination by CLIPS in MassWorks software.

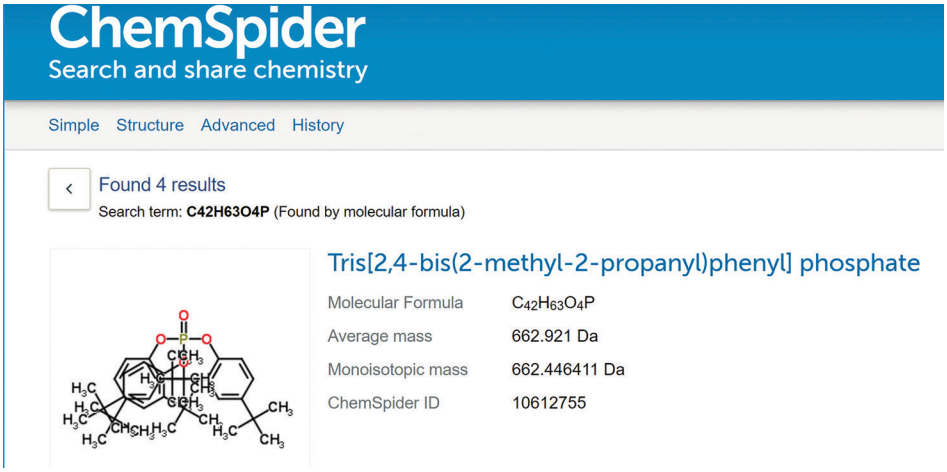

Figure 5. One example hit of ChemSpider search for $C_{42}H_{63}O_4P$.

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