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C146-E111

Identification of Unknown Polymer Additives by LCMS-IT-TOF

Technical Report vol.8

1. Introduction

It would be very difficult to imagine what our lifestyle would be like without plastics. We depend on plastics for just about everything. There are hundreds of polymers available for thousands of different applications. What is not so well-known is that synthetic polymers nearly always require polymer additives to achieve key performance properties. For example, when plastics are exposed to heat and light, or when they come into contact with oxygen, they require the inclusion of heat stabilizers or antioxidants to keep them from degrading in performance. There are thousands of common additives and mixtures used commercially, including ultraviolet light absorbing agents (UVA: Ultraviolet Absorbers) and stabilization agents (HALS: Hindered Amine Light Stabilizers). Even one polymer from a single manufacturer can contain different types of additives and blends of additives depending on the grade and intended use.

For this reason, identification of the additives used in the polymer material becomes important for adjusting product characteristics with respect to competiters' products, as well as for improving products within a company's product line.

This report introduces a unique method for identifying polymer additives.

2. Strategy and Pretreatment

This study was undertaken to identify the polymer additives used in a particular type of polymer. Starting with the assumption that the most likely additives were fairly common commercial materials, we recognized that if the composition formula candidates could be sufficiently narrowed, we could predict the composition based on formulae published in catalogs posted on the Internet by chemical additive manufacturers. Accurate mass measurement using MS^n with the LCMS-IT-TOF instrument can quickly narrow the composition formula candidates to just the most likely compounds. The predicted structures for the composition formulas were obtained by comparing them to known structures in different chemical databases.

Sample preparation consisted of adding one of the beads from among those provided by the customer in 1 mL THF/methanol (50/50) solution, and then extracting the additives by placing the vial in an ultrasonic bath for 30 minutes. The analysis was conducted by injecting 10 μL of the supernatant directly into the HPLC column.

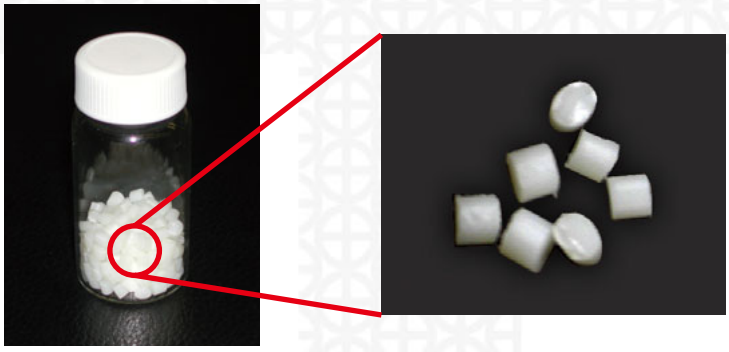

Fig. 1: Polymer Beads Used for Measurement

The 3-D ion trap-time-of-flight mass spectrometer (LCMS-IT-TOF) is used to analyze the masses of the components eluting from the HPLC column, and for structural elucidation. The design of the instrument allows for high-speed MS^n analysis because the ion acceleration method used to remove ions from the trap ballistically ejects all of the ions from the ion trap towards the TOF simultaneously. Taking advantage of the high-speed performance of this instrument, the precursor ion automatic selection measurement mode is utilized to conduct MS, MS^2 and MS^3 analysis in order of intensity during peak elution. High-speed polarity switching was used to allow analysis of different types of ions in a single run.

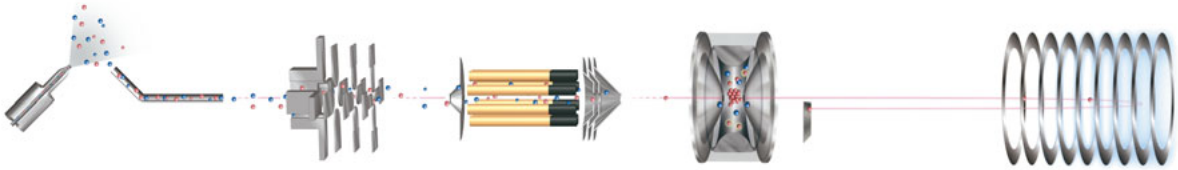

Fig. 2: LCMS-IT-TOF Ion Path

3. Analytical Conditions

Column	:	Imtakt Cadenza CD-C18 3.0 mm I.D. x 75 mm L
Mobile phase A	:	5 mM ammonium acetate - water
Mobile phase B	:	Acetonitrile
Gradient program	:	50%B (0 min)→100%B (20-40min)→50%B (40.01-50min)
Flow rate	:	0.4 mL/min
Injection volume	:	10 μL
Column temp.	:	40°C
Ionization mode	:	ESI(+) ESI(-)
Nebulizing gas	:	1.5 L/min
Drying gas pressure	:	100 kPa
Probe voltage	:	+4.5 kV -3.5 kV
CDL temperature	:	200°C
BH temperature	:	200°C

4. Results

4-1. Chromatogram and Mass Chromatograms

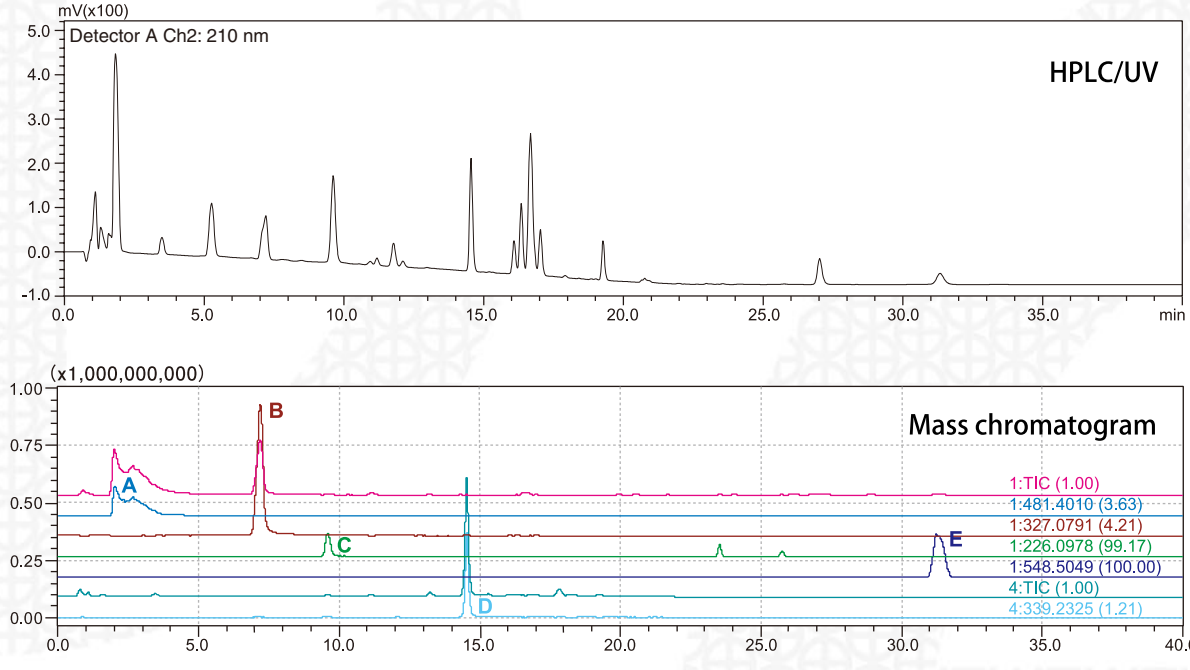

Fig. 3: UV Chromatogram and Mass Chromatogram Peaks A, B, C and E were detected by ESI+, peak D was detected by ESI-.

4-2. Analysis of Peak A

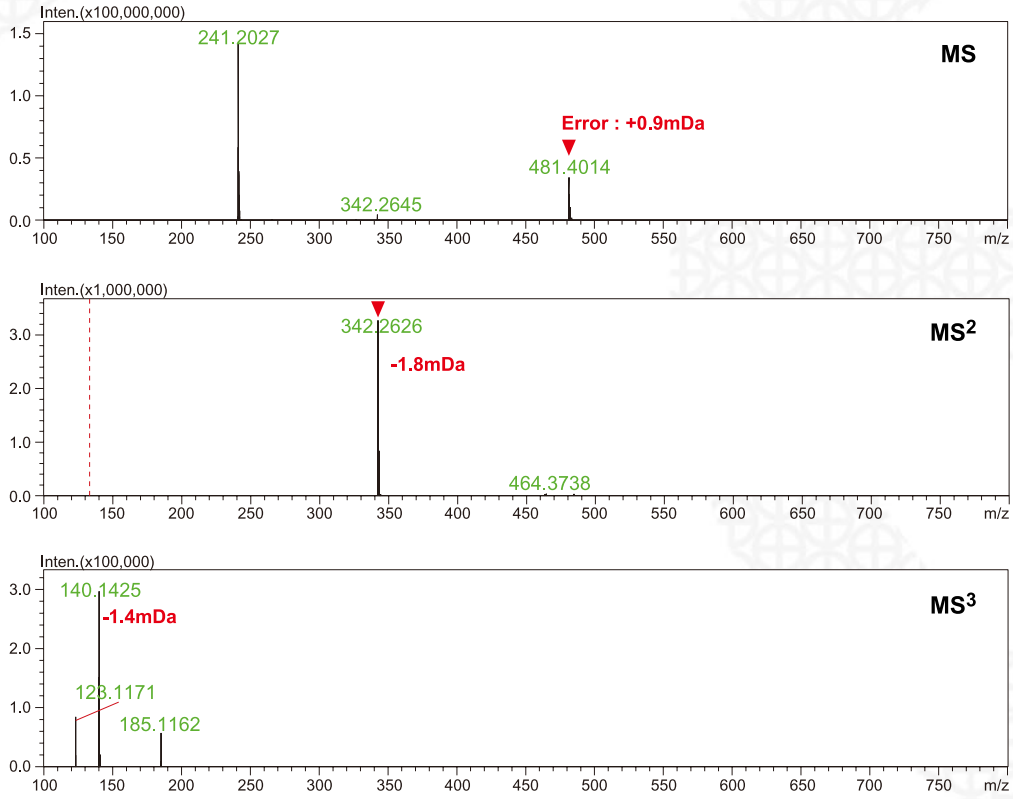

Fig. 4: MS, MS^2 and MS^3 Spectra of Peak A ▼ indicates the selected precursor ion.

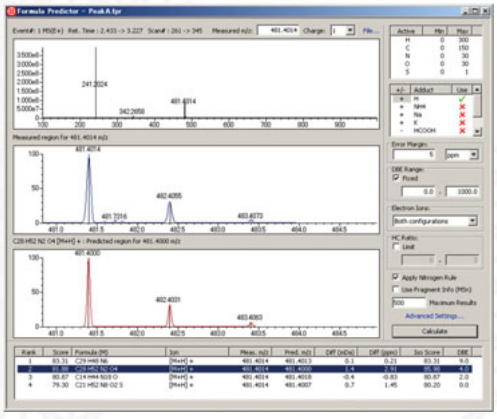

Fig. 5: Predicted Composition Results by Formula Predictor (Electron mass is not considered.)

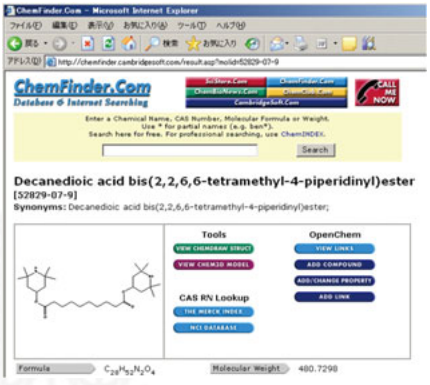

Fig. 6: Database Search Results Using ChemFinder

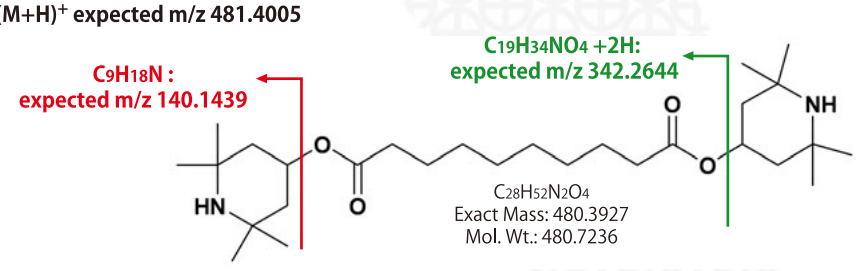

Fig. 7: Predicted Structure and MS^2, MS^3 Spectra Assignments

4-3. Identification Table

Other peaks were identified by this technique. For some of these compounds, the predicted composition formula and mass accuracy are summarized in the table below.

	Compound name	MW	Formula	Calc. $(M+H)^+$	Meas. $(M+H)^+$	ERR (ppm)	Calc. $(M-H)^-$	Meas. $(M-H)^-$	ERR (ppm)
A	Decanedoic acid bis (2,2,6,6-tetramethyl-4-piperidyl) ester	480.3927	$C_{28}H_{52}N_2O_4$	481.4005	481.4014	1.87			
B	Triphenyl Phosphate	326.0708	$C_{18}H_{15}O_4P$	327.0786	327.0788	0.61			
C	Tinuvin P	225.0902	$C_{13}H_{11}N_3O$	226.0980	226.0981	0.44			
D	2,2-Bis (3-sec-butyl-4-hydroxyphenyl) propane	340.2402	$C_{23}H_{32}O_2$				339.2324	339.2322	-0.59
	Compound name	**MW**	**Formula**	**Calc. $(M+NH_4)^+$**	**Meas. $(M+NH_4)^+$**	**ERR (ppm)**	**Calc. $(M-H)^-$**	**Meas. $(M-H)^-$**	**ERR (ppm)**
E	Irganox 1076	530.4699	$C_{35}H_{62}O_3$	548.5043	548.5067	4.38			

5. Conclusion

The technique of determining the compositional formula by MS^n along with searching a compound database using that composition formula as a keyword is a realistic method for determining polymer additive candidates. Utilization of the predicted structure obtained from the compound database compared with the MS^n spectrum obtained from the accurate mass can be considered a unique method enabled by the use of the LCMS-IT-TOF. It is the ability to conduct MS^n measurements along with accurate mass that makes identification fast and easy. This technique can be applied not only to identification of polymer additives, but also to identification of many compounds, including natural products, metabolites, impurities, and degradation products.

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