High speed polarity switching MS/MS applied to polymer additives analysis

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Introduction

Polymer additives include those materials used to make and modify polymers and are used in a highly diverse range of applications such as plastics, synthetic fibers, elastomers, adhesives, polyols, polyurethanes and lubricating oils and greases. As innovation expands polymer types and uses, formulations become increasingly complex and as a result identifying additives in polymer formulations is critical to product formulation for performance, health, safety and cost of manufacture. It also allows for analysis of competitive products and investigation of alternative technologies.

A fast polarity switching method with high speed data acquisition has been developed for MS/MS analysis to identify unknown additives in polymer formulations.

Materials and Methods

A mixture of representative polymer additives (a standard sample):

A sample solution was prepared by mixing the following polymer additives' standard in methanol; Irganox 245, Irganox MD 1024, Irganox 1098, Tinuvin P, Cyanox 2246, Cyanox 425, Irganox 1035, Tinuvin 120, Tinuvin 328, Irganox 1330, Irganox 565, Irganox 1076.

A sample of plastic laminates preparation:

Polymer additives were extracted from 100mg sample material of plastic laminates using 1mL of tetrahydrofuran (THF) with ultra-sonication for 1 minute. The THF supernatant was then transferred to a clean vial and 5mM ammonium acetate (1mL) was added and resulted supernatant was collected, and filtered with 0.45um filter. These samples were applied to LC-MS/MS to screen additives by multi-polarity simultaneous scanning (survey scan) and automatic product ion scanning (dependent scan).

LC-MS/MS:

Samples were analyzed using a Nexera UHPLC system coupled to a LCMS-8030 triple quadrupole mass spectrometer (Shimadzu Corporation, Japan). Polymer additives were separated using a Shim-pack XR-ODS Ⅱ (2.0 mmI.D. x 75 mm, 2.2um) using a gradient elution with formic acid and methanol.

Key features of Nexera UHPLC system

- pressure range up to 130 MPa
- high-speed injection, overlap injection
- highly-efficient gradient mixing
- precise solvent delivery, excellent reproducibility
- near-zero carryover

Key features of LCMS-8030 triple quadrupole mass spectrometer

- ultra fast polarity switching of 15msec & ultra fast scan speed of up to 15,000 u/sec
- UFsweeper® technology dramatically minimizes cross talk
- excellent linearity with wide dynamic range

Fig. 1 Nexera UHPLC system & LCMS-8030 triple quadrupole mass spectrometer

Experimental & Results

LC-MS/MS screening method

Identifying additives in polymer formulations is a critical step for both molecular ion and fragment ion formulation. In this study, sample acquisitions were performed using auto MS/MS Synchronized Survey Scan function on the following condition;

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Analytical Conditions

HPLC (Nexera UHPLC system)

Column: Shim-pack XR-ODS (75 x 2.0 mmI.D., 2.2um)
Mobile phase A: 0.1% formic acid
Mobile phase B: Methanol
Gradient program: 25%B (0 min) - 100%B (2.5-7.5min) - 25%B (7.51-10min)
Flow rate: 0.5 mL/min
Column temperature: 40 °C

Mass (LCMS-8030 triple quadrupole mass spectrometry)

Ionization: ESI
Polarity: positive & negative
Scan mode:

#	type	polarity	range (*m/z*)	CE
1	Q3 scan	+	200-800	-
2	I- Product ion scan	+	100-800	20 V
3	I- Product ion scan	+	100-800	40 V
4	Q3 scan	-	200-800	-
5	I- Product ion scan	-	100-800	20 V
6	I- Product ion scan	-	100-800	40 V

Synchronized Survey Scanning refers to the execution of MS/MS scanning triggered by survey scan signals (in this case, Q3 scan). Thus, during the elution of a peak in Q3 scan analysis, a full product ion mass spectrum can also be obtained. By applying both fast polarity switching (15msec switching speed) and high speed data acquisition (15,000u/sec) resulted in high information product ion spectra. This approach generated a sequence of 6 scan modes in less than 400msec. The sequence included 3 positive ion acquisitions scanning, #1 Q3 scan mode; #2 product ion scan mode at a low collision energy (20V) and #3 at a high collision energy (40V); this sequence was then repeated in negative ion mode to complete a cycle of 6 full scan modes in less than 400msecs.

Analysis of polymer additives samples

At first, a mixture of representative polymer additives (a standard sample) was acquired. All of the 12 polymer additives standard in the sample were clearly detected in Q3 scan and dependent product ion scan (spectra data of all compounds at two collision energies) at positive and/or negative polarity.

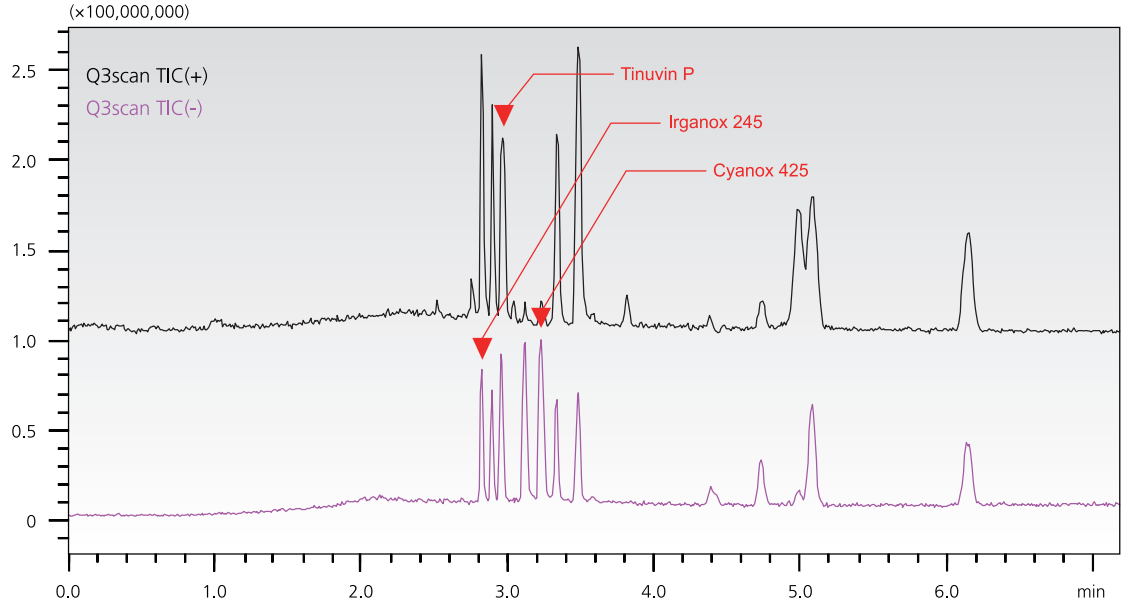

Fig. 2 Q3 scan (positive and negative) TIC of polymer additives standard

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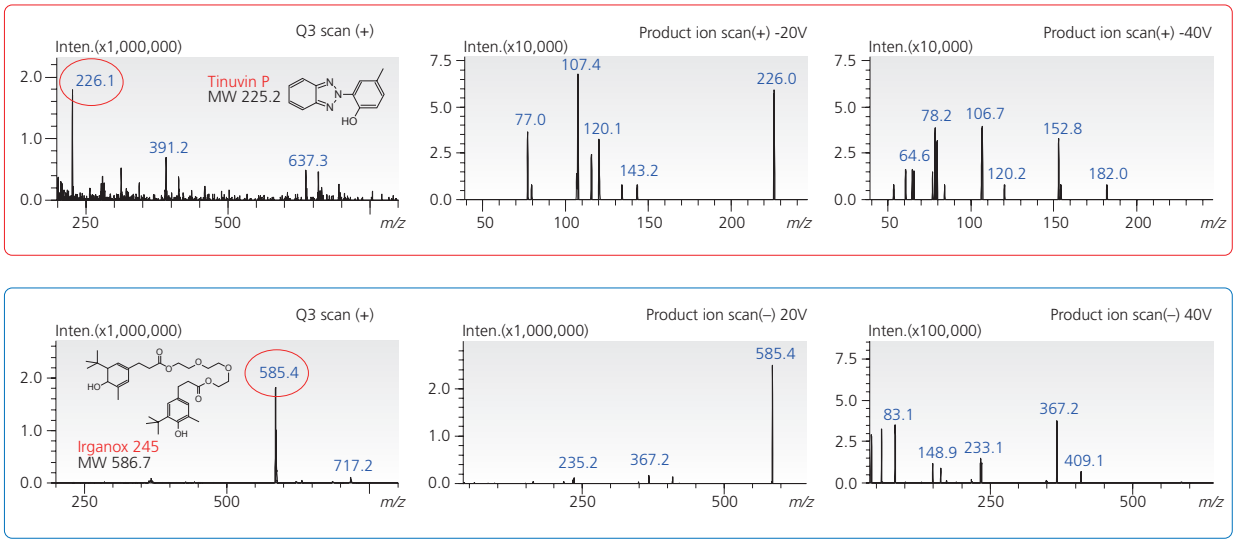

Fig. 3 Q3 scan spectra and Product ion scan spectra of polyme additives standard (a) Tinuvin P and (b) Irganox 245

Next, a sample of plastic laminates was acquired. The polymer additives in the sample were clearly identified using polarity and Q3 scan and product ion spectra data at differing collision energies. Confirming the presence of 12 known additives in a commercial product, three of them were detected, Tinuvin P, Irganox 245, Cyanox 425. Several peaks except for the 12 kinds of additive standard had been detected, so the existence of other additives was suggested.

As a consequence of the high speed of data acquisition this method can be applied to a diverse range of polymer additive analysis with a high degree of confidence in component identification.

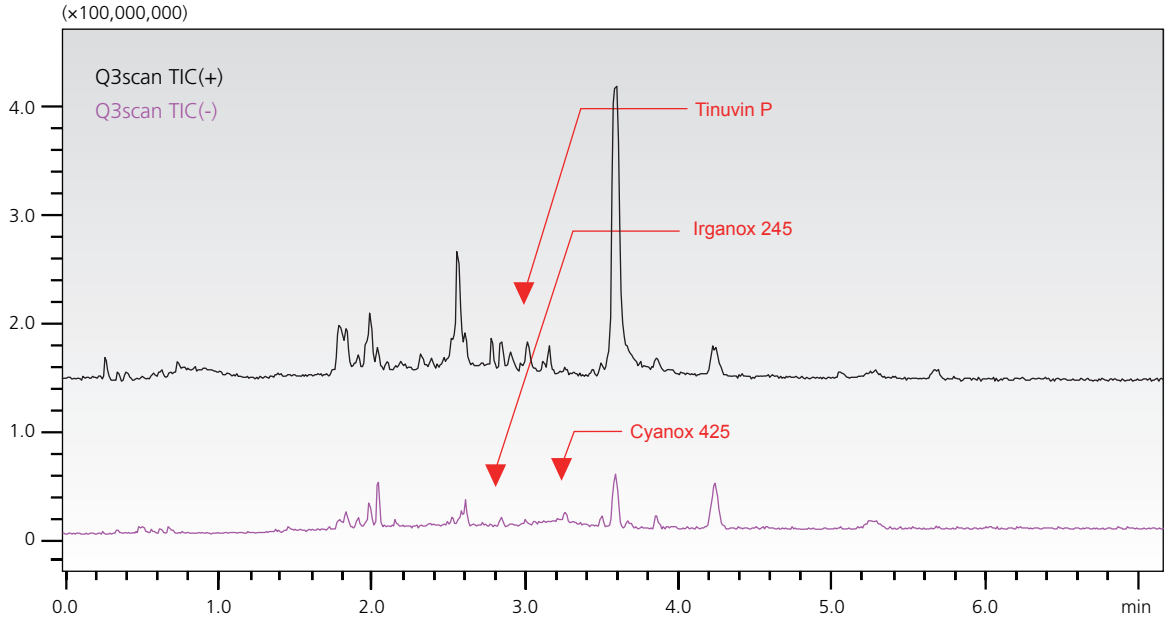

Fig. 4 Q3 scan (positive and negative) TIC of plastic laminate sample

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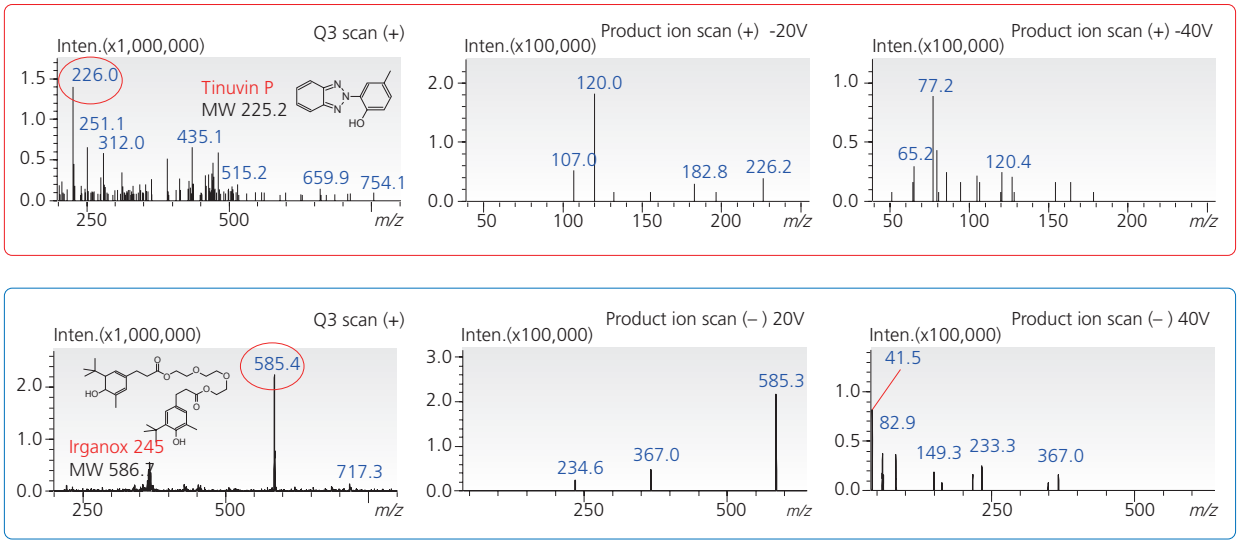

Fig. 5 Q3 scan spectra and Product ion scan spectra of plastic laminate sample (a) Tinuvin P and (b) Irganox 245

Table 1 Screening results of polymer additives

#	Polymer additives	Standard			Plastic laminate	
		R.T.	Detection		R.T.	Detection
1	Irganox 245	2.82	O	–	2.81	O
2	IrganoxMD 1024	2.89	O	–	–	X
3	Irganox1098	2.96	O	+/–	–	X
4	Tinuvin P	2.98	O	+	2.98	O
5	Cyanox 2246	3.12	O	–	–	X
6	Cyanox 425	3.23	O	–	3.25	O
7	Irganox 1035	3.33	O	–	–	X
8	Tinuvin 120	3.48	O	+/–	–	X
9	Tinuvin 328	4.40	O	+	–	X
10	Irganox 1330	4.73	O	–	–	X
11	Irganox 565	5.07	O	+/–	–	X
12	Irganox 1076	6.15	O	–	–	X

Conclusion

- Data acquisition using Synchronized Survey Scan function with ultra fast polarity switching & ultra fast scan speed enabled to detect all MS and MS/MS spectra of the 12 kinds of polymer additives standard at one run.
- It was confirmed that at least three kinds of polymer additives were contained in plastic laminates by this screening method.
- Lots of qualitative information was obtained from MS spectra and MS/MS spectra in two collision energies at multi polarity acquired by ultra fast polarity switching & ultra high speed scanning function.

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