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Application Note

ACQUITY UPLC SQD Analysis of Polymer Additives

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Abstract

This application note describes a three-minute method for identifying a mixture of 11 polymer additives using Waters UPLC with a bench top single quadrupole mass spectrometer, the ACQUITY UPLC SQD System.

Introduction

Typical polymer additives include light and heat stabilizers, UV absorbers, antioxidants, fillers, plasticizers, biocides, colorants, and mold release agents. They are used for processing polymer resins and improving the properties of polymer and plastic products. Improper uses of additives can result in product failure. To ensure product quality, accurate and reliable polymer additive analysis methods are required.[1-5]

Recent discoveries indicate that some polymer additives appear to have carcinogenic and estrogenic properties.[6-8] Due to the widespread use of polymers for food packaging and medical devices, analysis of possible polymer additive leaching into food, medicine, and environment is needed. Typical separation time using conventional HPLC is approximately 20 to 40 minutes.[9-13]

This application note describes a three-minute method for identifying a mixture of 11 polymer additives using Waters UPLC with a bench top single quadrupole mass spectrometer, the ACQUITY UPLC SQD System. ACQUITY UPLC employs high-pressure fluidic modules, novel small column particles and very low system volumes, resulting in greater separation efficiency, sensitivity, and speed. Designed to take full advantage of the UPLC technology, the ACQUITY SQD Mass Spectrometer minimizes band spread of very narrow peaks to deliver improved spectral quality for compound identification. This has the advantage of providing polymer additive profiles in unknown polymer samples and examining polymer additive migration. The ability to quickly and unambiguously analyze the content of polymer additives can also facilitate workflow for analyzing polymer additive purity and troubleshooting in QC labs.

Experimental

Sample Preparation

Analytes are Lowilite 20 1, [131-57-7]; Tinuvin P 2, [2440-22-4]; Lowinox TBM6 3, [96-69-5]; BHT 4, [128-37-0]; Chimassorb 81 5, [1843-05-6]; Irganox 1035 6, [41484-35-9]; Tinuvin 326 7, [3896-11-5]; Tinuvin 328 8, [25973-55-1]; Irganox 1330 9, [1709-70-2]; Irganox PS 800 10, [123-28-4]; and Lowilite 36 11, [103597-45-1]. 1-3, 5, and

6 were dissolved in CH_3CN to make 2 mg/mL stock solution. 4, and 7-9 were dissolved in CH_3CN/DMSO (1:1 by volume) to make 1 mg/mL stock solution. 10 was dissolved in acetone to make 2 mg/mL stock solution. 11 was dissolved in toluene to make 2 mg/mL stock solution. The stock solutions were mixed and diluted with CH_3CN to give a test solution with 20 parts per million (ppm) of 1-11.

UPLC System and Operation Conditions

System:	ACQUITY UPLC/SQD Mass Spectrometer
Software:	MassLynx v4.1
Weak & strong wash:	CH_3CN (600 µL)
Seal wash:	90:10 water:CH_3CN (5 min)
Column temp:	60 °C
Injection:	2 µL (full loop)
Column:	ACQUITY UPLC BEH C_{18} 2.1 x 50 mm
Mobile phase A:	H_2O
Mobile phase B:	CH_3OH

Gradient Method

Flow rate:	0.8 mL/min
Time (min)	%B
0	50
2	100

3	100

Inlet Pre-run Method

Flow rate:	0.8 mL/min
Time (min)	%B
0	100
0.5	50
3	50

MS Conditions

IonSABRE APCI Probe

Ionization mode:	APCI positive & APCI negative
Corona (µA):	5
Cone voltage:	+30, +50 V -30, -70
Extractor:	+3 V -3 V
Source temp:	150 ˚C
APCI Probe temp:	500 ˚C
Desolvation gas:	700 L/hr
Cone gas:	20 L/hr
Acquisition range:	100 – 780 *m/z*

Results and Discussion

Figure 1 shows the chemical structures of commonly used polymer additives (1-11). They were separated and identified in three minutes using the ACQUITY UPLC/SQD System with a 2.1 x 50 mm BEH C_{18} column. Figures 2a and 2b are the total ion chromatograms (TIC) of positive and negative atmospheric pressure chemical ionization (APCI) scans. The electronics of the ACQUITY SQD Mass Spectrometer enable rapid scanning (10,000 amu/sec) and polarity switching (20 msec) that allows detection of narrow peaks and provides mass spectra for chemical structure information in a single run. The chromatograms show that 11 polymer additives are separated with baseline resolution. Among them, seven polymer additives (1, 2, 5, 6, 8, 9, and 11) are easily detected by both positive and negative APCI, scans while polymer additives, 3, 4, and 7 have stronger peak signals with negative APCI scan. Polymer additive 10 is only observed by positive APCI mode. Acetonitrile and methanol were evaluated as the strong eluent. While 1-11 can be separated using H_2O/CH_3CN as the elution solution, H_2O/MeOH is the preferred mobile phase for obtaining better signals and spectra.

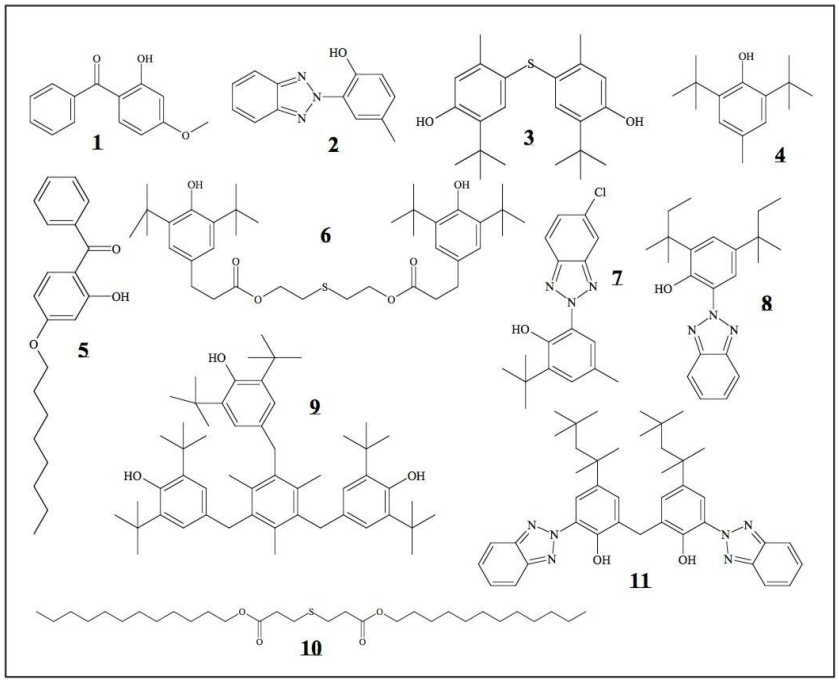
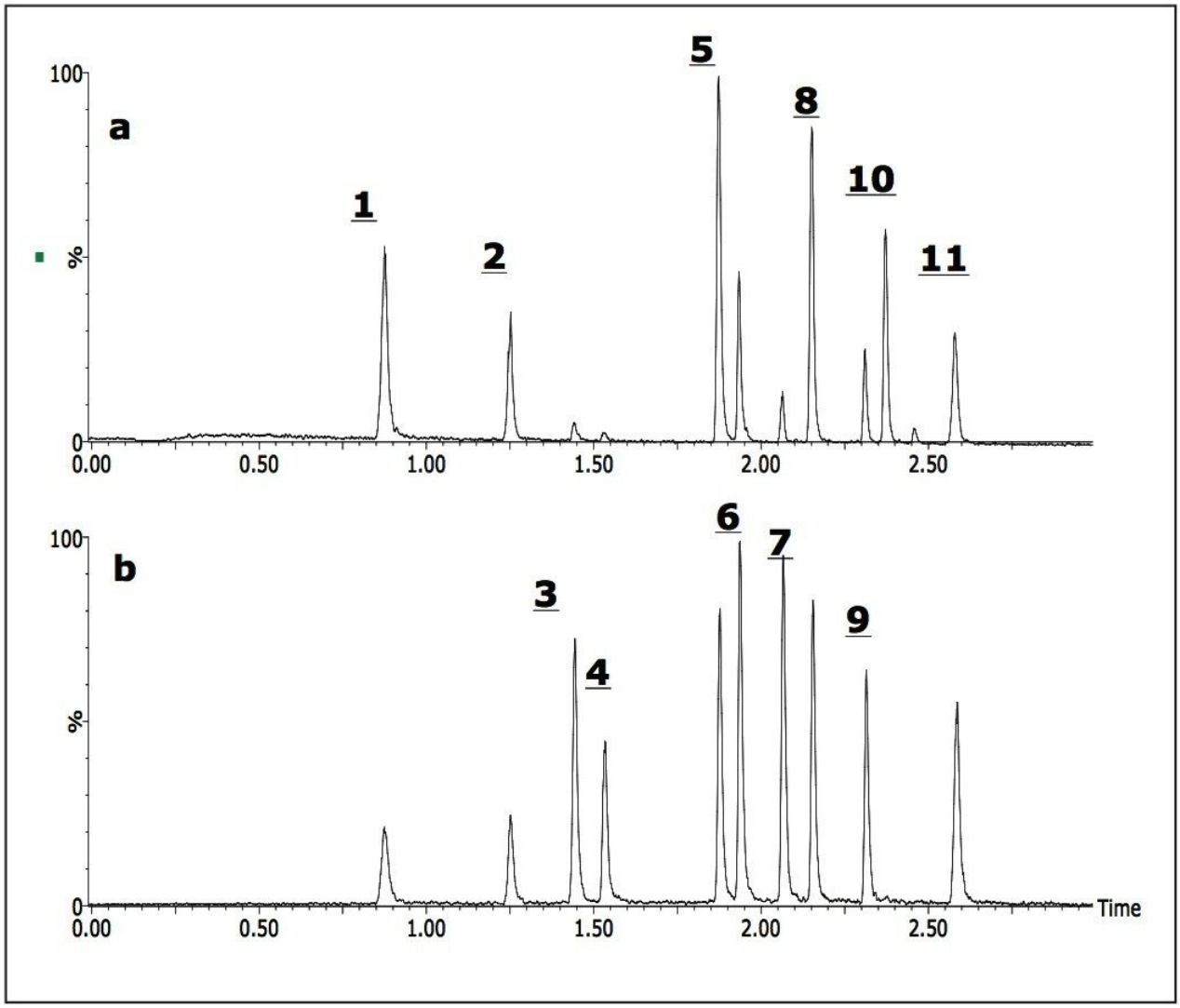


Figure 1. Chemical structures of polymer additives.



Figures 2a and b. TIC chromatograms of positive (a) and negative (b) APCI full scans at the cone voltages of +30 V and -30 V.

Figure 3 shows the extracted positive-ion mass spectra of 1, 2, 5, 8, 10, and 11. Figure 4 shows the extracted negative-ion mass spectra of 3, 4, 6, 7, and 9. The data indicate the value of APCI for the analysis of polymer additives. At a low cone voltage (30 V), the mass spectra have mostly pseudomolecular ions without notable fragmented and adduct ions. The mass spectra are easy to interpret and the observed *m/z* values match well with the theoretical intact molecular ions of additives (Table 1).

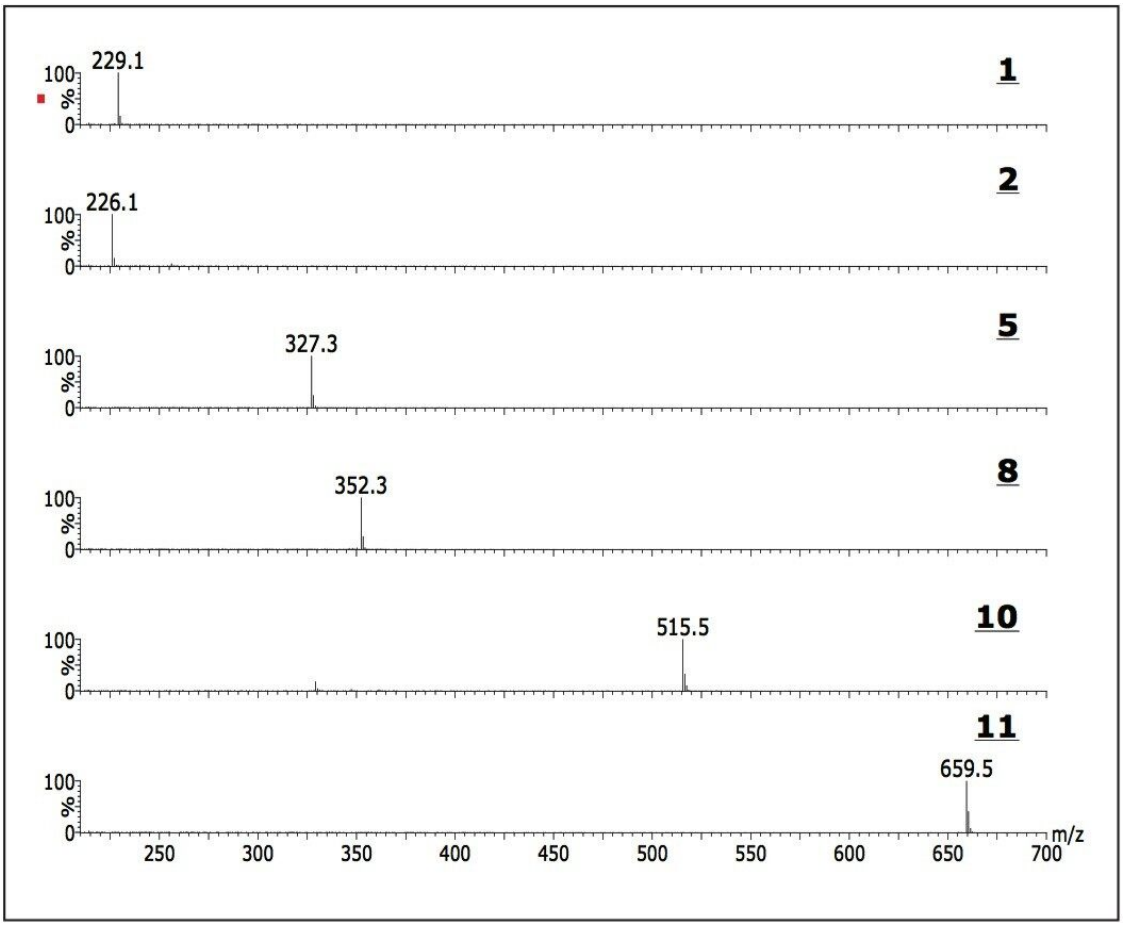


Figure 3. Positive-ion mass spectra of 1, 2, 5, 8, 10, and 11 at the cone voltage of 30 V.

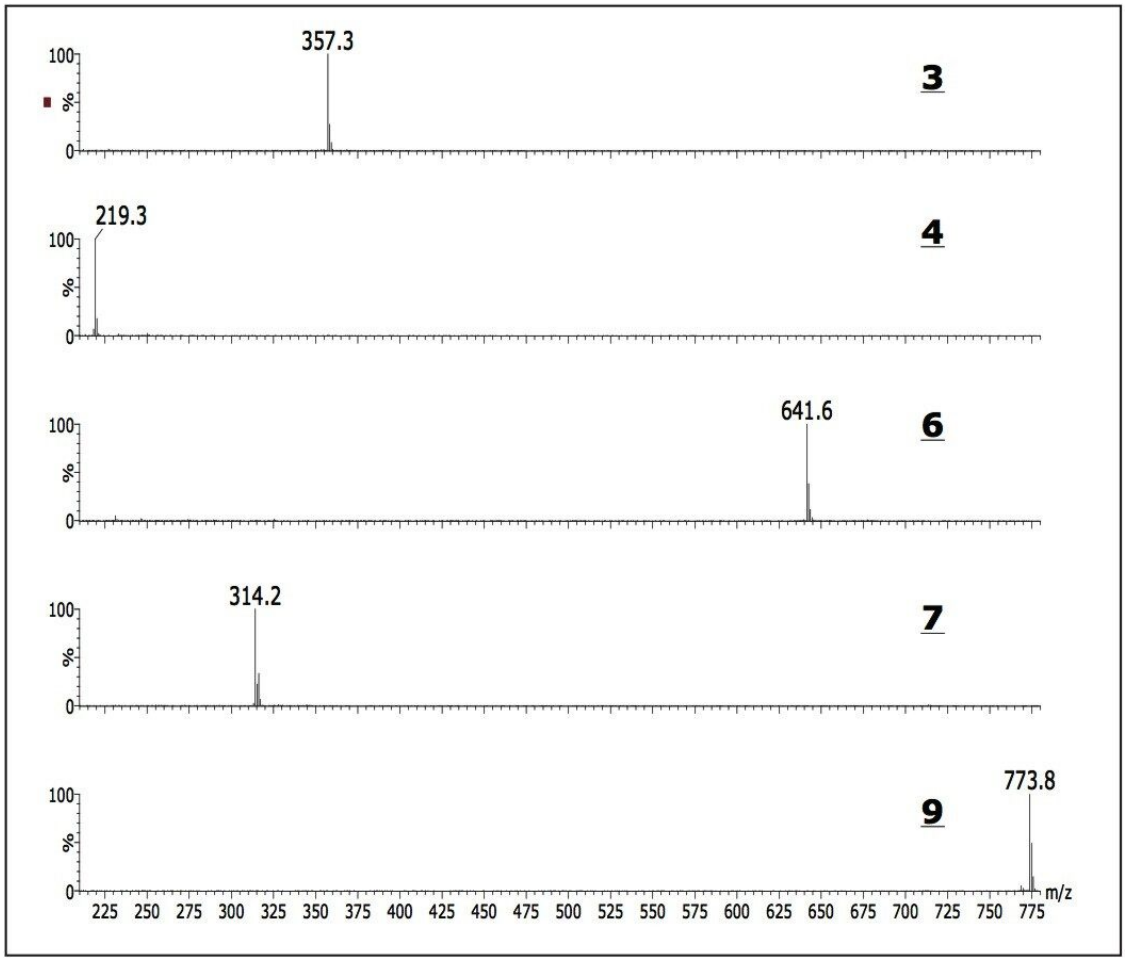
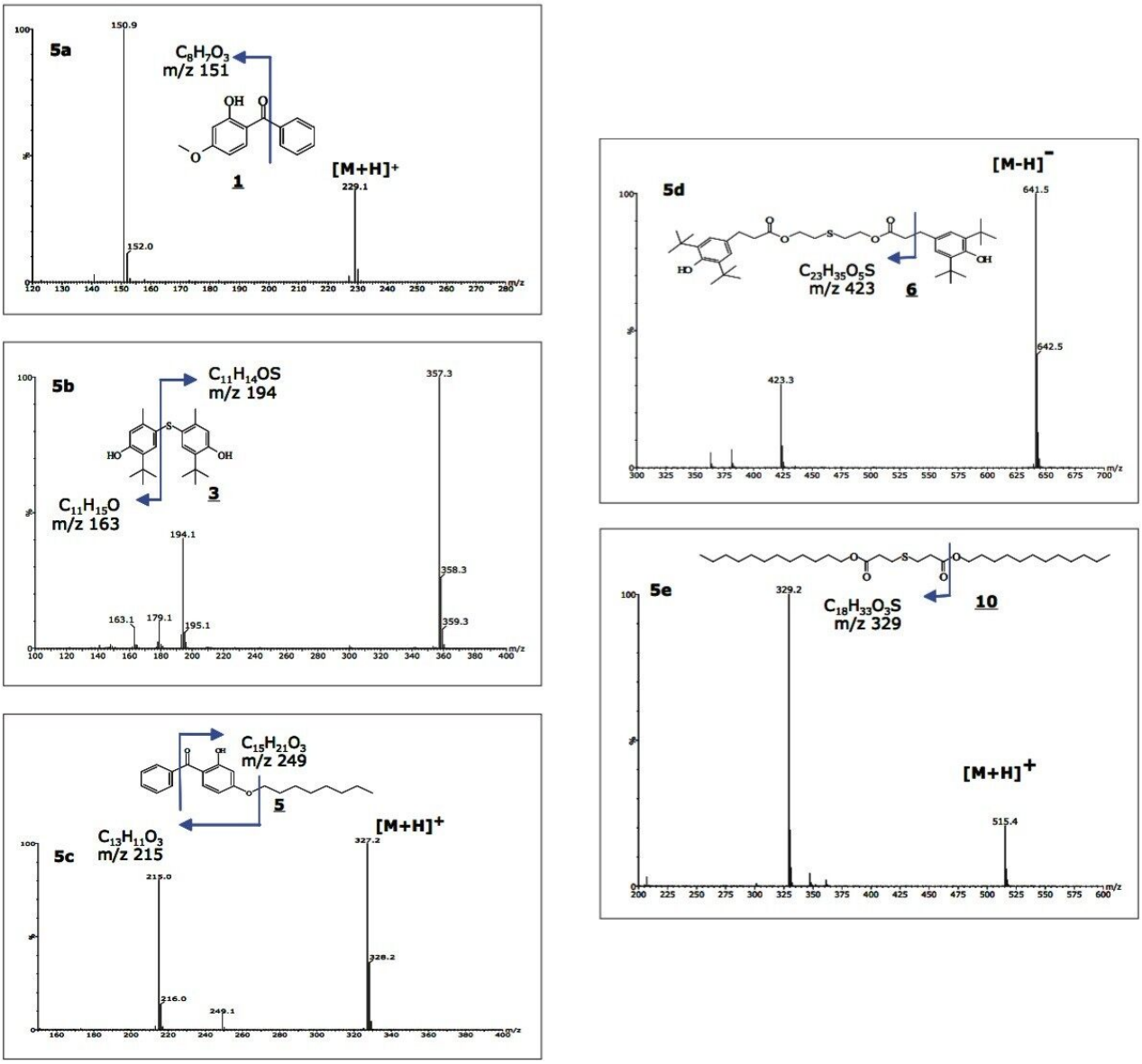


Figure 4. Negative-ion mass spectra of 3, 4, 6, 7, and 9 at the cone voltage of -30 V.

ID	Ret. Time (minute)	Compound	$[M+H]^+$	$[M-H]^-$
1	0.89	Lowilite 20	229.1	
2	1.26	Tinuvin P	226.1	
3	1.44	Lowinox TBM6		357.2
4	1.53	BHT		219.2
5	1.88	Chimassorb 81	327.2	
6	1.94	Irganox 1035		641.4
7	2.07	Tinuvin 326		314.1
8	2.16	Tinuvin 328	352.2	
9	2.31	Irganox 1330		773.6
10	2.38	Irganox PS 800	515.4	
11	2.59	Lowilite 36	659.4	

Table 1. Retention times and m/z of polymer additives.

At higher cone voltages, the pseudomolecular ions of polymer additives can be fragmented to yield product ions and provide additional structure information. Figures 5 a-e are examples of extracted positive-ion and negative-ion spectra at cone voltages of +50 V and -70 V, respectively. The fragmented ions can be used to confirm the structures of polymer additives in unknown samples to prevent false identification.



Figures 5a-e. Extracted mass spectra of 1, 5, and 10 at cone voltage of 50 V; 3, and 6 at the cone voltage of -70 V.

Conclusion

The Waters ACQUITY UPLC with SQD Mass Spectrometer is an ideal system for the analysis of polymer additives. It provides a sensitive, baseline resolved separation of 11 polymer additives in three minutes. This

high performance mass spectrometer with positive/negative switching enables optimal detection and confirms analyte identity in a single run. The system is seven times faster and consumes nine times less solvent than HPLC systems. This robust technology has broad applications in contract analytical labs, polymer product manufactures, government agencies, medical device manufacturers, and manufacturers of food plastics, wherever it is important to know the content of polymer additives and if those additives are leaching into products and the environment.

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