

ACQUITY UPLC with PDA and ELS Detection - Polymer Additives

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Abstract

This application note describes a two and a half minute analysis of a blend of 10 polymer

additives using the Waters ACQUITY UPLC System with PDA and ELS detection and Waters Empower 2 Software. With the built-in advanced mathematical algorithms, the polymer additives were quantitatively identified in a single run. The analysis is fast and reproducible. The ability to quickly and unambiguously analyze for polymer additives can facilitate workflow in quality control, new product development, deformation of competitive polymer products, and product troubleshooting in the manufacturing of polymer additives as well as polymer and plastic products.

Benefits

Enables rapid, sensitive, baseline resolved separations, and information rich data for a blend of polymer additives

Introduction

Polymer additives protect and enhance the performance of polymer and plastic products throughout the cycle of manufacturing, processing, storage and final applications. Products used every day such as fibers, textiles, furniture, sports equipment, packaging, wire and cable, consumer electronics, telecommunication equipment, automobiles, and airplanes are all made entirely or partially of polymers and plastics. Their widespread use results not only from the development of new polymer chemistry and resins but also from the advancement of polymer additives. A variety of additives are used in polymer resin processing to generate products with specific processing characteristics and functional properties (color, shape, mechanical strength) as well as resistance to heat, flame, oxidation, aging, and light degradation.¹⁻²

In manufacturing, a synergistic blend of polymer additives is incorporated into polymer and plastic products; small differences in the mixture can dramatically affect the characteristics of the products. To ensure that the intended amount of additive is in the polymer solution, accurate, reliable, and robust analytical methods are needed in QC and Central Analytical labs. Chromatographic techniques are the most widely used methods for the analysis of polymer additives. The typical separation time using conventional HPLC is approximately 20 to 40 minutes.²⁻⁶

This application note describes a two and a half minute analysis of a blend of 10 polymer additives using the Waters ACQUITY UPLC System with PDA and ELS detection and Waters Empower 2 Software. With the built-in advanced mathematical algorithms, the polymer additives were quantitatively identified in a single run. The analysis is fast and reproducible. The ability to quickly and unambiguously analyze for polymer additives can

facilitate workflow in quality control, new product development, deformation of competitive polymer products, and product troubleshooting in the manufacturing of polymer additives as well as polymer and plastic products.

Experimental

Analytes are Lowilite 20 (1), [131-57-7]; Lowinox TBM6 (2), [96-69-5]; Chimassorb 81 (3), [1843-05-6]; Irganox 1035 (4), [41484-35-9]; Tinuvin 326 (5), [3896-11-5]; Erucamide (6), [112-84-5]; Lowilite 27 (7), [3864-99-1]; Vitamin E (8), [10191-41-0]; Irganox PS 800 (9), [123-28-4]; and Lowilite 36 (10), [103597-45-1]. 1-4, and 8 were dissolved in CH₃CN to make 2 mg/mL stock solution. 5 and 7 were dissolved in CH₃CN/DMSO (1:1 by volume) to make 1 mg/mL stock solution. 6 was dissolved in acetone/DMSO (1:1 by volume) to make 1 mg/mL stock solution. 9 was dissolved in acetone to make 2 mg/mL stock solution. 10 was dissolved in CHCl₃ to make 2 mg/mL stock solution. The stock solutions were mixed and diluted with CH₃CN to give a working solution with 125 ppm of 1-10. Seven levels of calibration standards having 10, 15, 20, 25, 30, 35, and 40 ppm of 1-10 were prepared by dilution of the 125 ppm working solution with CH₃CN.

UPLC System and Operation Conditions

System:	ACQUITY UPLC w/PDA and ELS detectors
Software:	Empower 2
Weak wash:	CH ₃ CN (600 µL)
Strong wash:	CH ₃ CN (600 µL)
Seal wash:	90:10 Water: CH ₃ CN (5 min)
Column temp.:	50 °C
Flow rate:	1.0 mL/min
Injection:	2 µL (full loop)

Detection:	PDA 210 to 500 nm
Sampling rate:	20 pts/s
Filter response:	0.1 s
Column:	ACQUITY UPLC BEH C ₁₈ 2.1x 50 mm
Mobile phase A:	0.05 v% of TFA in H ₂ O
Mobile phase B:	0.05 v% of TFA in CH ₃ CN
Linear Gradient:	50% to 100% B in 1.4 minutes, hold for 1.1 minutes at 100% B

Note: Column equilibrated with 50%B for 2.5 min before each injection.

ELSD Parameters

Gain:	500
N ₂ Gas pressure:	40 psi
Drift tube temp.:	57 °C
Nebulizer:	Cooler
Date rate:	20 pt/s
Time constant:	0.1

Results and Discussion

Figure 1 shows the chemical structures of polymer additives (1-10): light stabilizers and UV absorbers (1, 3, 5, 7, and 10), antioxidants and heat stabilizers (2, 4, 8, and 9), slip and mold release agent (6). They are commonly used to improve the performance of polymer and plastic products based on the following resins: ABS, PC, PE, PP, PVC, Acrylics, Polyacetal, Polyamides, Polyesters, Polystyrene, Polyurethanes, Elastomers, and Rubbers.

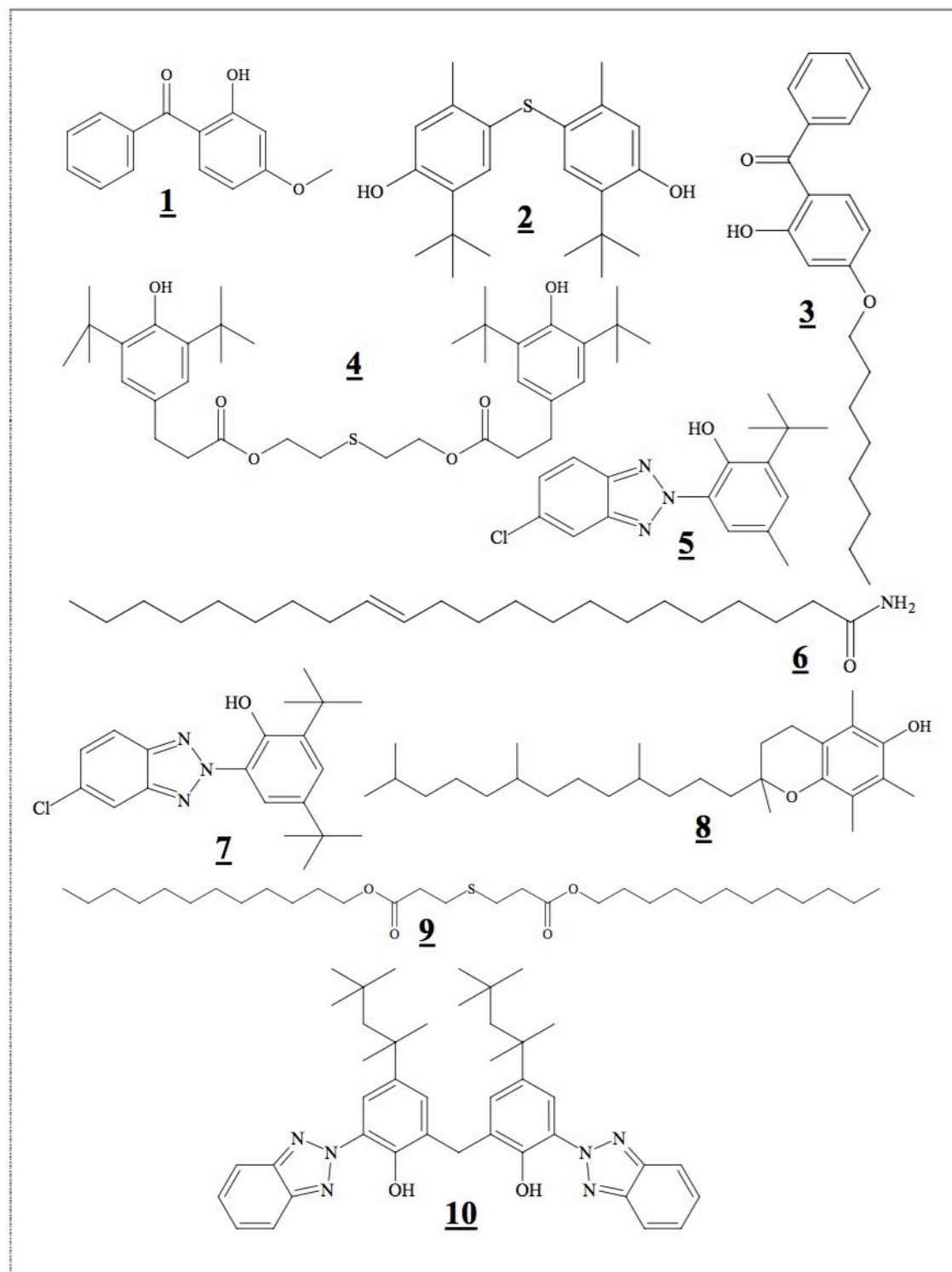


Figure 1.

Chemical structures of polymer additives. Chemical names are in reference 10.

A blend of the polymer additives (1–10) was separated in 2.5 minutes using the Waters ACQUITY UPLC System with a linear gradient method.

Figure 2 is an overlay of 7 replicate injections of PDA timed wavelength chromatograms. Visual examination shows the overall reproducibility is excellent. The chromatograms show that eight polymer additives are well-resolved by the gradient method. The additives Erucamide and Irganox PS 800 (6 and 9) don't have a strong UV chromophore and weren't observed. An unknown impurity in the Vitamin E (8) sample was found. Tables 1 and 2 show the retention times and peak area of each polymer additive observed in the 7 replicate injections with statistical analysis results generated by Empower. The excellent %RSD results are good indicators of the robustness and suitability of UPLC with BEH column chemistry for the analysis of polymer additives.

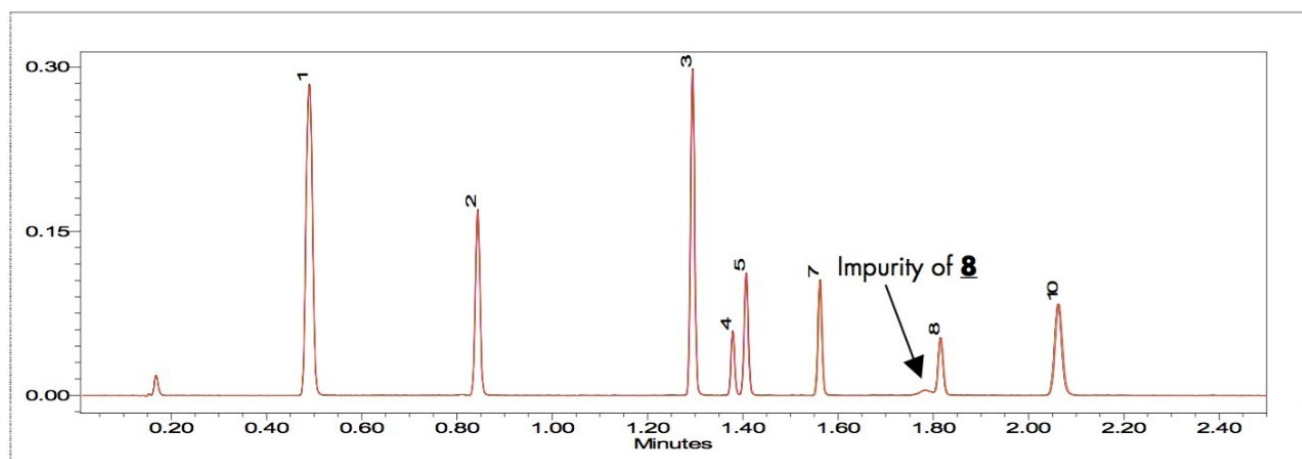


Figure 2. Overlay PDA timed wavelength chromatograms, retention time and peak area tables of 7 replicate injections of a blend of polymer additives sample containing 40 ppm of 1-10: (0.00 min, 320 nm; 0.6 min, 275 nm).

	1 (min)	2 (min)	3 (min)	4 (min)	5 (min)	7 (min)	8 (min)	10 (min)
1	0.490	0.843	1.295	1.379	1.408	1.561	1.815	2.063
2	0.490	0.843	1.294	1.378	1.406	1.562	1.814	2.061
3	0.490	0.844	1.295	1.380	1.408	1.561	1.815	2.062
4	0.490	0.843	1.294	1.379	1.407	1.562	1.815	2.062
5	0.490	0.844	1.295	1.379	1.408	1.561	1.815	2.062
6	0.490	0.844	1.295	1.379	1.407	1.561	1.815	2.062
7	0.490	0.844	1.295	1.380	1.408	1.563	1.816	2.064
Mean	0.490	0.843	1.295	1.379	1.407	1.562	1.815	2.062
Std. Dev.	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001
% RSD	0.07	0.05	0.04	0.04	0.04	0.05	0.04	0.05

Table 1. Component summary for retention time.

	1	2	3	4	5	7	8	10
1	267836	115147	176434	31584	68465	60975	39276	89901
2	268385	115152	176419	31765	68629	60937	38960	90615
3	268179	115335	176468	31478	68294	61050	39159	90031
4	267946	115169	176208	31460	68318	61092	38741	89953
5	268062	115090	176213	31482	68239	60838	38936	89671
6	268178	115058	176268	30975	67542	60974	38958	89741
7	268383	115191	176518	31568	68415	61157	38747	90225
Mean	268139	115163	176361	31473	68272	61003	38968	90020
Std. Dev.	207	88	128	243	347	106	197	320
% RSD	0.1	0.1	0.1	0.8	0.5	0.2	0.5	0.4

Table 2. Component summary for area.

Seven levels of calibration standards (10 to 40 ppm) were analyzed. With Empower's built-in advanced mathematical features, calibration curves were created from the standards and the quantities of analyte in each sample were calculated automatically. Figure 3 shows the calibration plots generated by Empower, using the peak areas vs the concentration. The linearity of the calibration curves was excellent with the R^2 values (residual sum of squares) above 0.9995. Table 3 shows a typical analysis results for peak identification and quantification using a blend of polymer additives as a sample. The last column shows all the results matching well with actual value (10 ppm). The data suggest that the UPLC system is well suited for the quantitative analysis of polymer additives in sub-ppm.

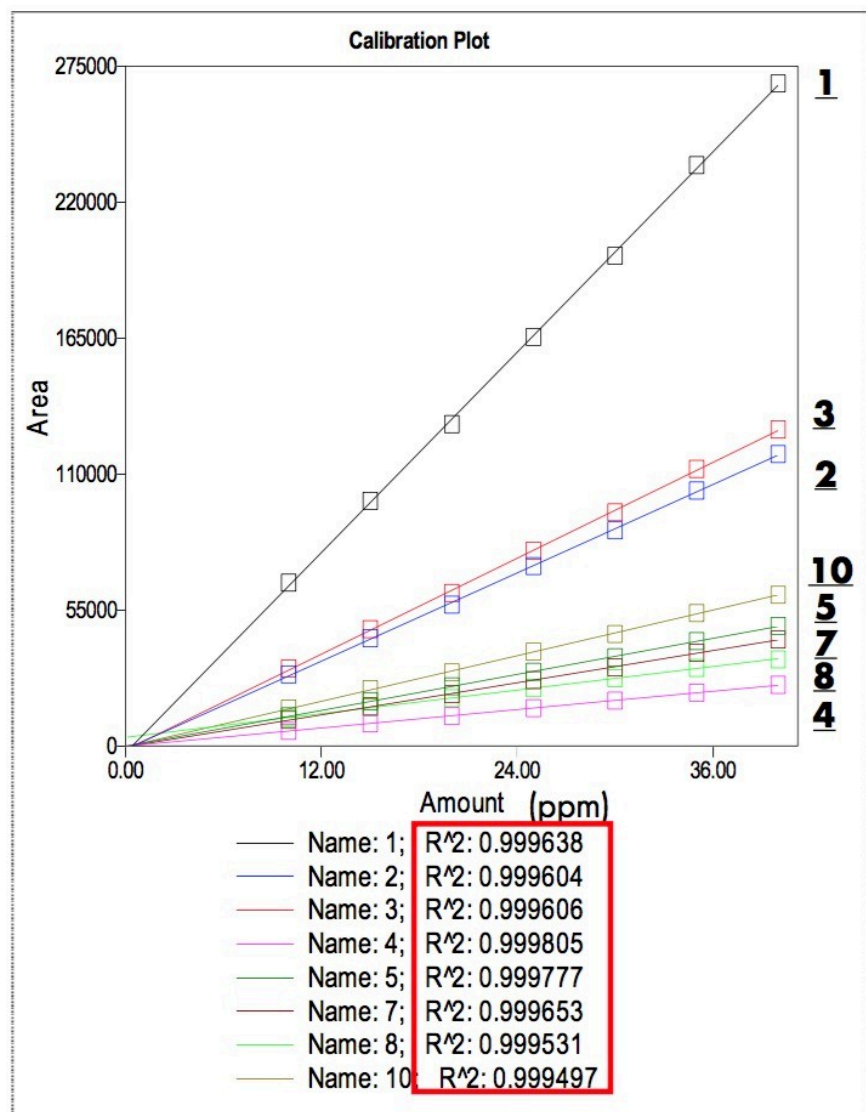


Figure 3. Calibration curves for polymer additives.

UV photodiode array (PDA) detection combined with Empower 2 Software enables a powerful range of detection and identity confirmation possibilities for chromatographic separations. Empower 2 provides the capability of creating a PDA library from pure component peaks in user chromatograms. The library matching and peak purity features can be used to confirm peak identities and to give added confidence that spectrally distinct peaks are not-coeluting. Using Spectral Contrast theory, Empower 2 quantitatively compares the shapes of UV spectra during library matching and Peak Purity analysis.⁷⁻⁹ Figure 4 shows UV spectra, extracted from PDA chromatograms of polymer additive standards, that were used to create a library with names and retention times.

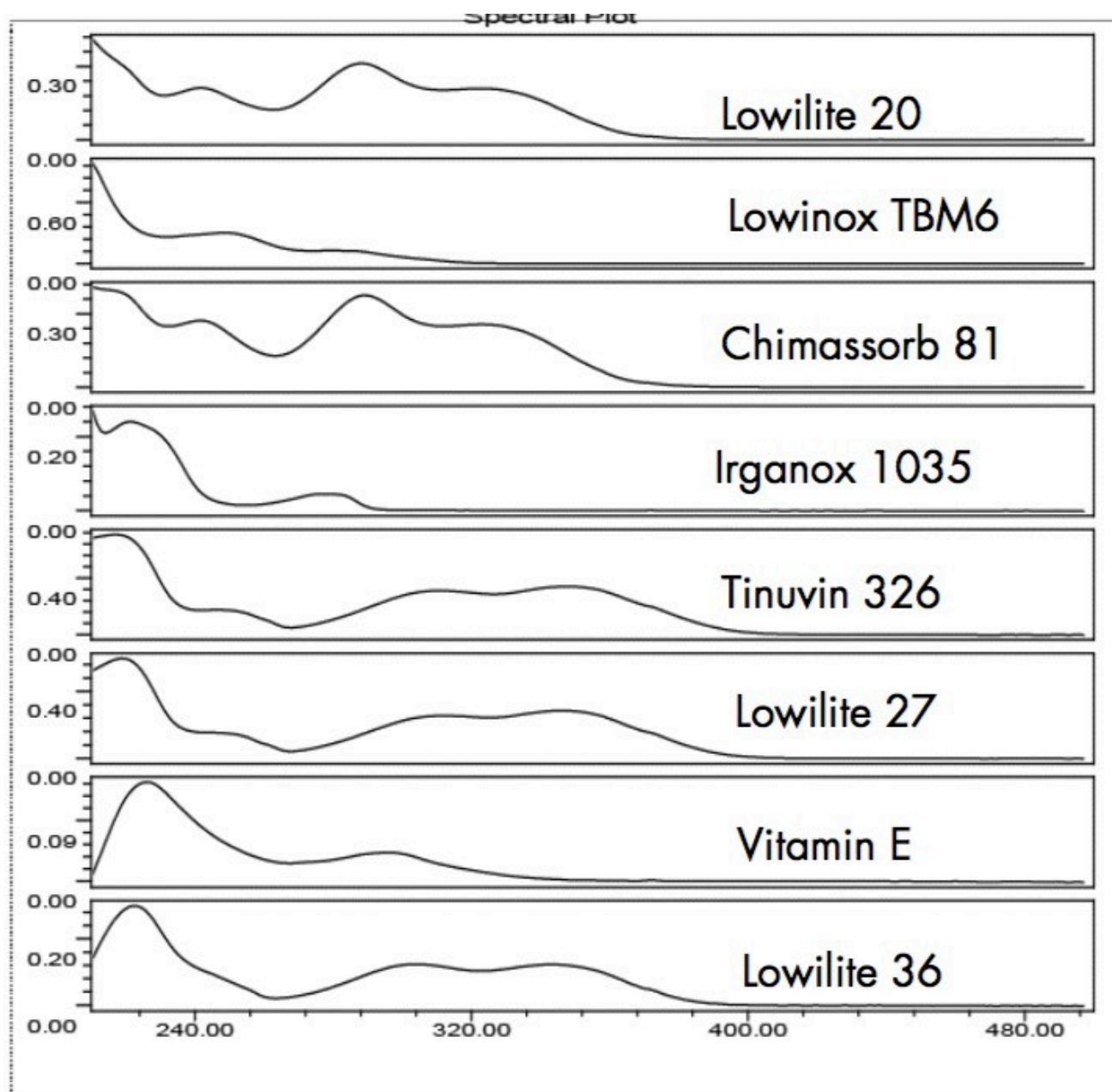


Figure 4. UV spectra of additives extracted from PDA data.

Table 3 is an example of a default Empower Report table with PDA library matching and Peak Purity results. In general, if the value of Match Angle is smaller than Match Threshold and the value of Purity Angle is smaller than Purity Threshold, the results indicate that the analyte is well separated and well matched with the PDA library standard.

	Component	Match1 Spect. Name	Match1 Angle	Match1 Threshold	Purity1 Angle	Purity1 Threshold	Amount (ppm)
1	1	Lowilite 20	0.058	1.084	0.121	0.352	10.10
2	2	Lowinox TBM6	0.268	1.192	0.134	0.416	10.24
3	3	Chimassorb 81	0.054	1.072	0.110	0.349	10.22
4	4	Ingranox 1035	1.215	1.969	0.769	1.104	10.13
5	5	Tinuvin 326	0.054	1.066	0.088	0.344	10.01
6	7	Lowilite 27	0.076	1.067	0.156	0.364	10.22
7	8	Vitamine E	4.054	1.382	0.811	0.768	9.95
8	10	Lowilite 36	0.083	1.113	0.197	0.435	10.07

Table 3. Peak identification and quantification.

The data in Table 3 indicate that all the UV absorbing polymer additives except 8 were well separated and matched with PDA libraries. The values obtained from Empower indicate that peak 8 is not spectrally pure, perhaps suggesting coeluting components. As indicated earlier in Figure 2 there is an overlap between the peaks of 8 and its impurity. Empower indicated this by returning a Purity1Angle greater than a Purity1Threshold.

To further characterize the impurity of 8, a longer BEH C₁₈ column (2.1 x 100 mm) might be used to optimize the separation and a mass spectrometer added as a detector. These experiments are outside the scope of this application note.

Figure 5 is an evaporative light scattering (ELS) chromatogram of a sample containing 40 ppm each of the additives (1-10). The chromatogram shows that nine (2-10) of the ten additives have significant response under the ELS detection conditions; the two non-UV absorbing additives (6 & 9) are well separated from the others. The low ELS response of 1 is could be related to its volatility.

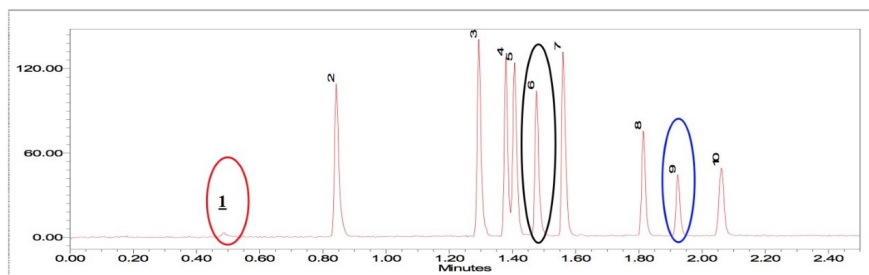


Figure 5. ELS chromatogram of polymer additives (40 ppm each of 1-10.).

The ELS data fit well with quadratic equations. Figure 6 shows the typical quadratic calibration plots generated by Empower, using the peak areas vs the concentration of analyte. The R² values (residual sum of squares) for 6 and 9 are 0.998 and 0.997, respectively.

These results demonstrate the utility of combined PDA and ELS detectors with an ACQUITY UPLC System for analyzing polymer additives. With a single chromatographic run, all the UV and non-UV absorbing polymer

additives can be analyzed simultaneously. Since many polymer additives lack a UV chromophore, an ELS detector, in conjunction with a PDA detector, is well suited for this type of analysis.

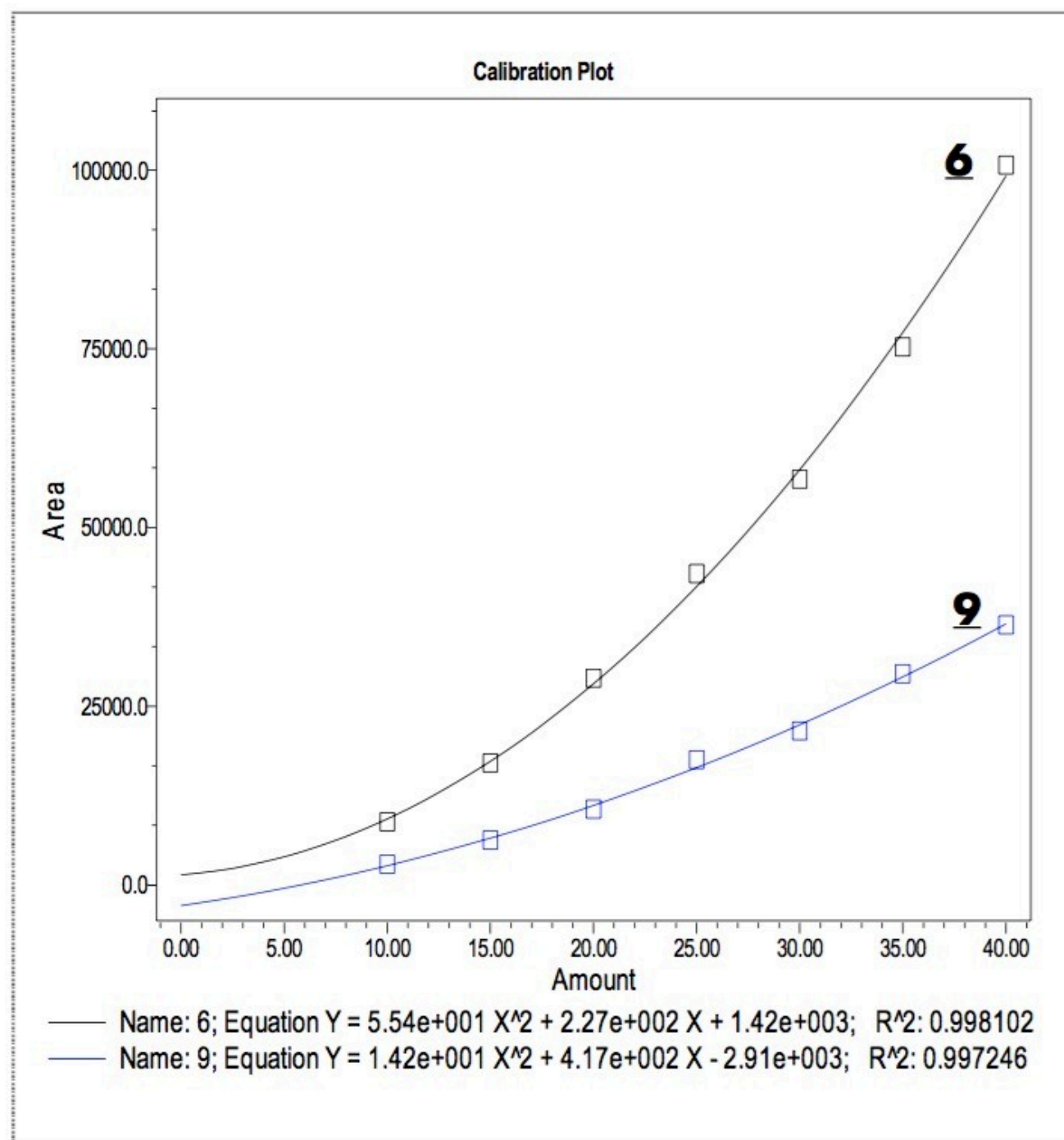


Figure 6. Calibration curves (Quadratic fit) for ELS detector responses of 6 and 9.

Conclusion

The Waters ACQUITY UPLC with PDA and ELS detectors is an ideal system for the analysis of polymer additives. It enables rapid, sensitive, baseline resolved separations, and information rich data for a blend of polymer additives. All analytes cannot be detected using a single detection technique. By employing complementary detectors, more information per chromatographic run can be obtained, thus dramatically increasing productivity. With Empower, the data obtained from both PDA and ELS detectors can be analyzed simultaneously for polymer additive quantification. The PDA library matching and peak purity functions can be automated to add confidence in peak identification for UV absorbing analytes. The easy to employ experimental conditions are suitable for R&D, analytical and service laboratories involved in polymer/plastics development and production. Additional applications of this methodology may include the evaluation of food and medicine contamination by polymer additives that migrate from packaging, medical tubing, and medical devices.

References

1. M. Boutin, *et al.*, *J. Am Soc Mass Spectrom*, 15, 1315–1319, 2004.
2. L. Coulier, *et al.*, *J. Chromatogr. A*, 1062, 227–238, 2005.
3. D. Munteanu, *et al.*, *Chromatographia*, 23, 7–14, 1987.
4. M. Ashraf-khorassani, *et al.*, *J. Chromatogr. A*, 995, 227–232, 2003.
5. J-M Plankeele, *et al.*, The Utility of Evaporative Light Scattering technique in Polymer Additive Detection, Waters Corporation, Application Note 72000959EN, 2004.
6. S. Bullock, LC-GC, The Application Notebook, February, 51, 2006.
7. M. V. Gorenstein, *et al.*, LC-GC, 12, 768–772, 1994.
8. Peak Identification with Waters 996 Photodiode Detector: Library Matching, Waters Corporation, WPP12, Library No. 960405.
9. Empower\Help\Interpreting PDA Peak Purity Results.

10.

Peak No.	Trade Name	CAS No.	Chemical Name
1	Lowilite 20	[131-57-7]	2-hydroxy-4-methoxy-benzophenone
2	Lowinox TBM6	[96-69-5]	4,4' Thiobis (6-tert-butyl-m-cresol)
3	Chimassorb 81	1843-05-6	2-hydroxy-4-n-octoxybenzophenone (oxybenzone)
4	Irganox 1035	41484-35-9	Thiodiethylene bis[3-(3,5 -di-tert-butyl-4hydroxyphenyl)propionate]
5	Tinuvin 326	3896-11-5	2-(3,5-Di-tert-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole
6	Erucamide	112-84-5	Ethoxylated tetramethyldecyldiol
7	Lowilite 27	3864-99-1	2- (2'-hydroxy-3',5'-di- <i>t</i> -pentylphenyl) benzotriazole
8	Vitamin E	10191-41-0	DL-alpha-Tocopherol
9	Irganox PS 800	123-28-4	Dilauryl 3,3'-thiodipropionate
10	Lowilite 36	103597-45-1	Methylenbis[6-(2H-benzotriazol-2-yl) -4-(1,1,3,3-tetramethylbutyl) phenol]

Featured Products

- [ACQUITY UPLC System <https://www.waters.com/1000396>](https://www.waters.com/1000396)
- [ACQUITY UPLC PDA Detector <https://www.waters.com/514225>](https://www.waters.com/514225)
- [ACQUITY UPLC ELS Detector <https://www.waters.com/514219>](https://www.waters.com/514219)

720001881, September 2006



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