

COMPARISON OF HPLC AND UHPLC ANALYSIS OF POLYMER ADDITIVES WITH ELUCIDATION OF MASS DETECTION

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INTRODUCTION

Polymer manufacturers rely on their timely analytical and quality control services for the characterization of their raw materials. One aspect of polymer analysis is the qualification and quantification of polymer additives such as Irganox 1010.¹ Legacy instrumentation methods lead to long analysis times and tell only part of the story. However, transferring legacy high performance liquid chromatography (HPLC) methods to an ultra high pressure liquid chromatography (UHPLC) system method, with photodiode array (PDA) and added mass detection, can provide the information in one quarter of the time with an assigned mass to charge ratio for unique peak and impurity identification.² The addition of mass detection can identify Irganox 1010 and its unknown components in order to see subtle changes that may affect product quality, yet enable control charts and monitoring specification limits.



Figure 1. Waters Alliance HPLC and ACQUITY Arc systems with post column flow to the Waters 2998 PDA and ACQUITY QDa Mass Detector.

OVERVIEW

- Explore adding the Waters® ACQUITY® QDa® Mass Detector to the HPLC and UHPLC chromatographic instrument stack.
- Easily transfer methods from Waters Alliance HPLC to the Waters ACQUITY Arc™ UHPLC using Waters' columns and column calculator tool.
- Assess the additional benefits of higher sensitivity detection that the ACQUITY QDa brings to polymer additive characterization.

METHODS

Conditions for demonstration measurements

For the HPLC and UHPLC sample analyses, polymer additives were dissolved in isopropanol. A mobile phase consisting of 10 mM ammonium formate in water [A] and in acetonitrile [B] was used with a Waters XBridge phenyl Column, 4.6 x 150 mm, 5.0 μm (HPLC) and 4.6 x 75 mm, 2.5 μm (UHPLC). The column temperature was maintained at 40 °C. PDA was collected at 254nm wavelength and mass detection with default settings were used.

Chromatographic System Control

Empower® 3 FR3 Software for instrument control, data acquisition and chromatographic data processing.

The screenshot shows the Column Calculator tool interface. It is divided into 'From...' (original method) and 'To...' (target method) sections. Both sections have input fields for Column (Diameter, Length, Particle Size, L/dp), System (Dwell volume, High pressure limit), and Method (Injection volume, Temperature, Run time). Below these are two tables showing chromatographic data for the original and target methods. The 'To...' section also includes a 'Flow rate' section with radio buttons for 'Scaled' and 'Custom'.

Time (min)	Flow Rate (mL/min)	%A Water	%B Acetonitrile	Column Volumes
1 0.00	0.500	50.0	50.0	0.00
2 12.00	0.500	50.0	50.0	3.65
3 40.00	0.500	1.0	99.0	8.51
4 40.10	0.500	1.0	99.0	0.03

Time (min)	Flow Rate (mL/min)	%A Water	%B Acetonitrile	Column Volumes
1 0.00	1.000	50.0	50.0	0.00
2 3.00	1.000	50.0	50.0	3.65
3 10.00	1.000	1.0	99.0	8.51
4 10.03	1.000	1.0	99.0	0.03

304 psi Maximum pressure

1,217 psi Maximum pressure 10.0 μL Injection volume 10.00 min Run time 550 μL Pre-injection volume

Figure 2. Column Calculator tool: transferring from HPLC method to UHPLC method.

RESULTS AND DISCUSSION

Using a legacy HPLC method for the analysis of the polymer additive Irganox 1010, the method is transferred from the Waters Alliance HPLC system to the Waters ACQUITY Arc UHPLC system and calculated by entering the method parameters into the column calculator tool (Figure 1 & 2). The column choices are based on keeping the ratio of column length to packing particle size (L/dp) constant between methods. The column calculator tool enables planning of the experiment, ordering columns, and consideration of system capabilities before entering the lab. System capabilities such as pressure limits and solvent consumption for waste reservoirs have an impact on safely performing analytical procedures.³

The HPLC and UHPLC chromatograms of Irganox 1010 are compared in Figure 3 with the MS spectra from the ACQUITY Arc-QDa analysis shown below. With the assigned mass-to-charge ratio (m/z) as further characterization, mass detection can be helpful in the quality control (QC) assurance of a polymer additive raw material. This mass-to-charge ratio could be quantified in a concentration series, and then control charted for internal QC gates. These chromatographic peaks can be monitored over time in order to alert the users of batch to batch changes or manufacturing plant changes.^{4,5}

The same analysis tools in use for the Irganox 1010 are applied to a polymer additive mixture. As depicted in Figure 4, one peak of the mixture is a co-elution of two Tinuvin additives. The co-elution is further elucidated by mass detection, as are all of the components in the additive mixture (Figure 5). These analysis techniques can bring value to a manufacturing environment by providing information not identified using PDA detection alone. As an example, the ACQUITY QDa identifies an unknown component in the Irgafos 168 spectra that has a m/z 16 units higher than the known value of 663: evidence of oxidation.

Once the polymer additives have passed internal QC, the additives are blended with proprietary formulations. These blends can be quickly confirmed with the ACQUITY Arc UHPLC analysis, with the assigned m/z . From the previously created concentration curves, the proprietary blends can be checked for process control of blending procedures and formulations.

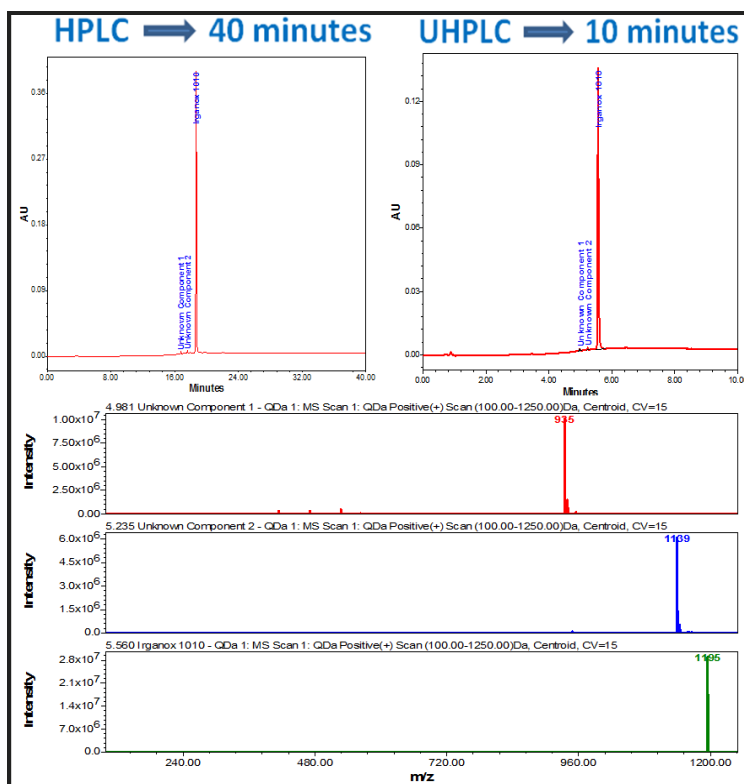


Figure 3. Irganox 1010 PDA chromatograms and ACQUITY QDa spectra.

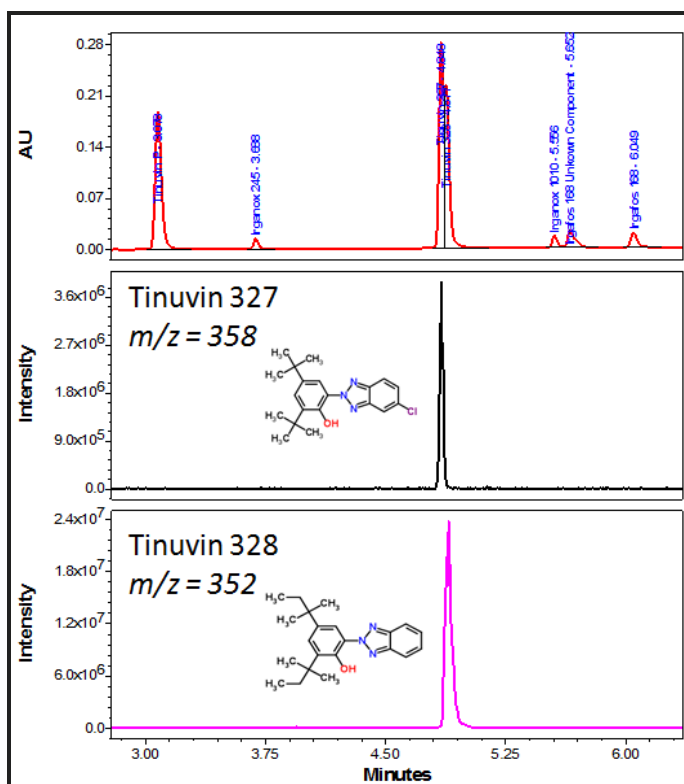


Figure 4. Polymer additive mixture: ACQUITY Arc UHPLC separation and PDA chromatogram. Co-eluting Tinuvin 327 & 328 isolated by ACQUITY QDa extracted m/z .

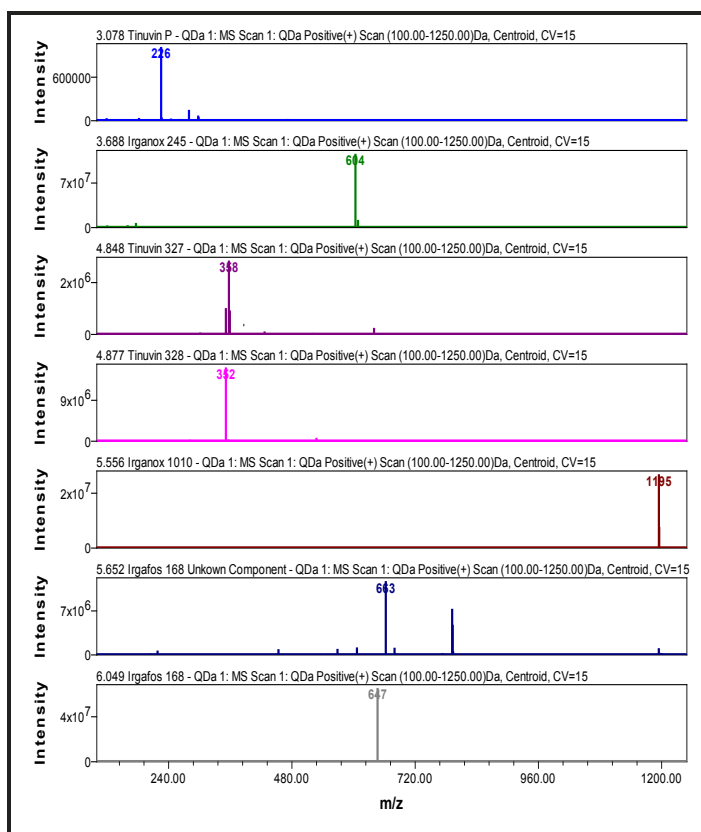


Figure 5. ACQUITY QDa positive ion scan of polymer additives: $[M + H]^+$ and some $[M + NH_4]^+$.

REFERENCES

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3. Buchberger, Wolfgang; Stiftinger, Martin (2012), "Analysis of Polymer Additives and Impurities by Liquid Chromatography/Mass Spectrometry and Capillary Electrophoresis/ Mass Spectrometry". Advanced Polymer Science 249: 39-68.
4. Acuity Arc System Operation Diagnostic and Method Transfer, <http://www.waters.com/waters/educationInstance.htm?eiid=134919269>
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CONCLUSIONS

- Transferring methods from HPLC to UHPLC can significantly shorten analysis times.
- LC method development is easily calculated and transferred to an ultra high pressure system using the family of Waters' columns and the Column Calculator tool.
- Delivering higher sensitivity to chromatographic detection by adding mass detection to these UHPLC experiments brings expanded polymer additive characterization while maintaining a robust separation, lower solvent consumption, and shorter analysis times.

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