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應用手冊

Sample Profiling of Pesticide Formulations Using UV and MS Detection for Component Identification

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Abstract

In this application note, optical and mass detection were combined to provide a thorough profile of a commercially available pesticide formulation concentrate.

Benefits

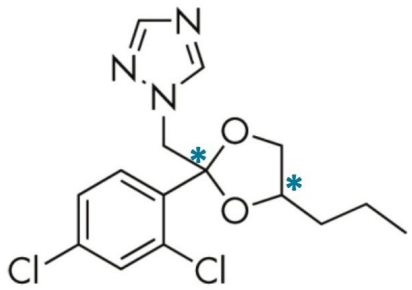
- Improved sensitivity over UV for low-level components present in the pesticide formulation
- Increased confidence in peak identification when mass detection is used with PDA detection
- Structural similarities between the active ingredient and the low-level components identified in a single analysis

Introduction

Agricultural chemicals decrease crop damage, resulting in a food supply that is both plentiful and of high quality.[1] For the agricultural chemicals industry, the analytical quality control of pesticide products ensures that a consistent and effective product reaches the farm.[2] More specifically, the detection, characterization, and quantitation of the active ingredient(s) as well as all other components in the formulation, including impurities and degradation products, is necessary to support product development, quality control, and product registration. The addition of a mass detector in conjunction with UV detection can increase the specificity and selectivity of methods used during analytical testing to provide additional information about a sample during a single analysis.

Waters ACQUITY QDa Detector is a novel mass detector that can be integrated into existing liquid chromatography configurations in order to complement the results obtained by UV detectors and increase the detection selectivity. The enhanced selectivity is ideal for the detection and initial identification of low-concentration components present in samples. When MS data is combined with the UV response, it allows the analyst to determine a wider range of analytes in one analytical run with an increased level of confidence.

In this application note, optical and mass detection were combined to provide a thorough profile of a commercially available pesticide formulation concentrate. The formulated product contained the triazole fungicide propiconazole, which contains two chiral centers in its chemical structure, as shown in Figure 1. The triazole fungicides are a commonly used group of pesticides due to their potent activity against a broad spectrum of crop diseases.[3]



Propiconazole

Figure 1. Structure of propiconazole. The asterisks denote the stereogenic centers.

Experimental

UPLC conditions

LC system:	ACQUITY UPLC H-Class
Column:	ACQUITY UPLC BEH C_{18} 2.1 x 150 mm, 1.7 µm
Column temp.:	50 °C
Injection volume:	3 µL
Flow rate:	0.60 mL/min
Mobile phase A:	10 mM ammonium formate in water
Mobile phase B:	Acetonitrile

Gradient table:

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.60	70	30	6
10.0	0.60	30	70	6
11.0	0.60	10	90	6
12.0	0.60	10	90	6
12.1	0.60	70	30	1

Table 1. UPLC gradient method for analysis of the formulation.

MS conditions

MS system:	ACQUITY QDa Detector
Ionization mode:	ESI+
Capillary voltage:	0.8 kV
Desolvation temp.:	500 °C
Source temp.:	150 °C
Cone voltage:	7 V
Sampling rate:	5 Hz
MS scan range:	100 to 1000 *m/z*

PDA conditions

Detector:	ACQUITY UPLC PDA
Wavelength range:	210 to 400 nm
Sampling rate:	20 Hz

Empower 3 Software Feature Release 2 was used for chromatographic data processing.

Sample preparation

1 gram (g) of the commercially available pesticide formulation was weighed, 9 mL of 50:50 (v/v) acetonitrile/water was added. The resulting mixture was sonicated for 10 minutes, and the sample was syringe filtered into an autosampler vial using a 0.2-µm PVDF filter in preparation for sample analysis. Authentic propiconazole standard was made up in 50:50 (v/v) acetonitrile/water.

Results and Discussion

A UPLC UV chromatogram at 220 nm comparing the standard propiconazole and the propiconazole present in the formulation is shown in Figure 2. The ACQUITY UPLC H-Class System's separation of propiconazole resulted in two peaks at retention times (t_R) of 7.45 min (peak 3) and 7.54 min (peak 4). The observed peaks likely originated from the propiconazole diastereomers. The t_R's of the propiconazole standard match those in the formulation. Two minor components (peak 1 and peak 2) at t_R 6.23 min and t_R 6.43 min, respectively, were noted in the UV chromatogram of the formulation. When measured in the UV, the area% contributions from peak 1 and peak 2 were 1.20% and 0.80%, respectively.

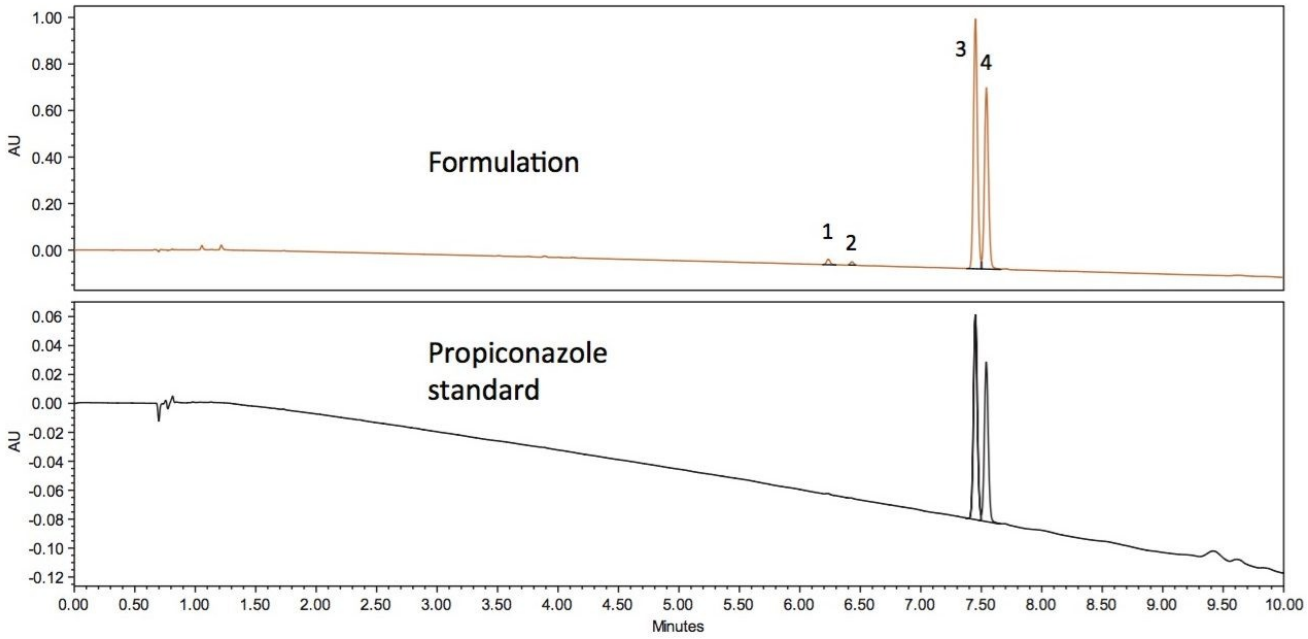


Figure 2. The ACQUITY UPLC PDA Detector's UV chromatogram of the propiconazole present in the formulation and propiconazole standard at 220 nm.

The total ion chromatogram (TIC) from the ACQUITY QDa Detector that was acquired simultaneously with the UV detector is shown in Figure 3. A protonated molecular ion, $[M+H]^+$ that corresponds to a mass-to-charge (*m/z*) ratio of 342 was observed for the propiconazole diastereomers.

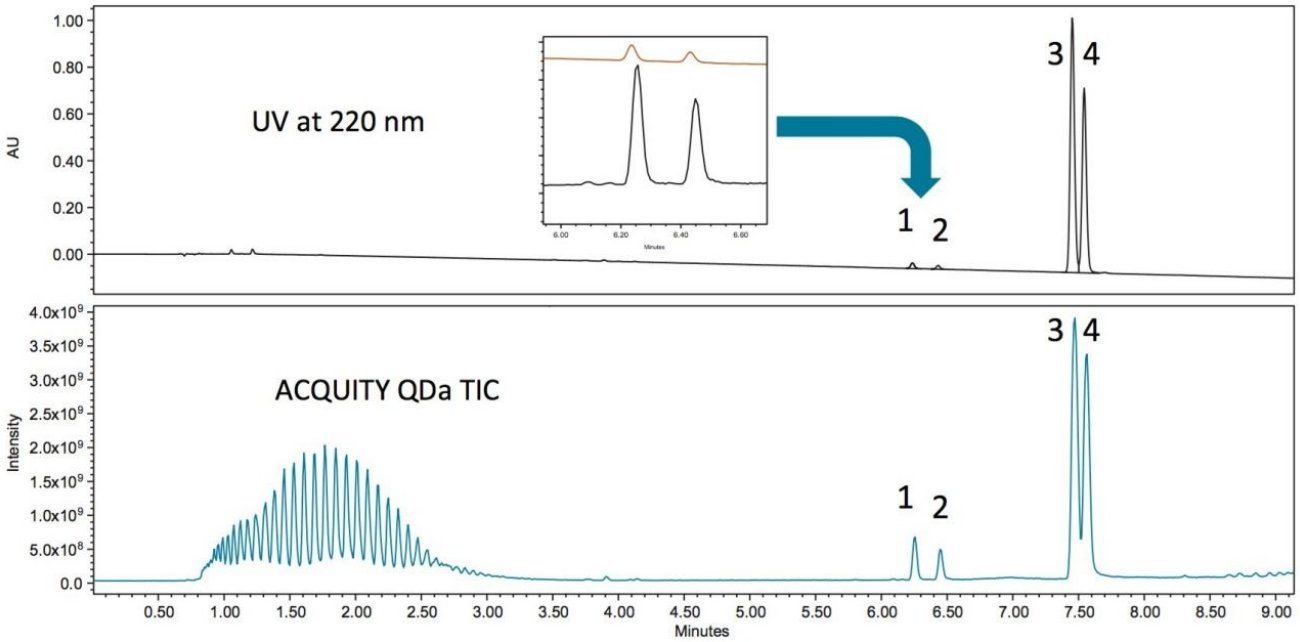


Figure 3. The ACQUITY UPLC PDA Detector's UV chromatogram of the formulation at 220 nm with the ACQUITY QDa Detector's mass chromatogram.

The signal response of all components improved in the mass chromatogram when compared with the UV chromatogram, illustrating the improved likelihood of detecting low-level components using the mass detector (inset Figure 3). The detection limits can be further improved by extracting ions of interest from the TIC to give an extracted ion chromatogram (XIC), shown in Figure 4. This enhances the confidence in compound identification. Other formulation components that could not be seen in the UV were clearly observed in the mass chromatogram, demonstrating that mass spectrometry combined with UV detection can give a more comprehensive sample profile. A series of peaks eluting between 0.80 and 3.0 min, with the *m/z* increasing by 44 amu with respect to the elution order, was observed in the mass chromatogram. The masses are consistent with a polymeric component, which is likely a surfactant present in the formulation that is used to aid in the application of the active ingredient.

Empower 3 Software's mass analysis window provides a single location to associate chromatographic peaks from all detectors used in the analysis with their corresponding spectra. The spectra from the detected peaks are time-aligned and displayed in a window above the chromatograms. The mass analysis window is shown in Figure 4.

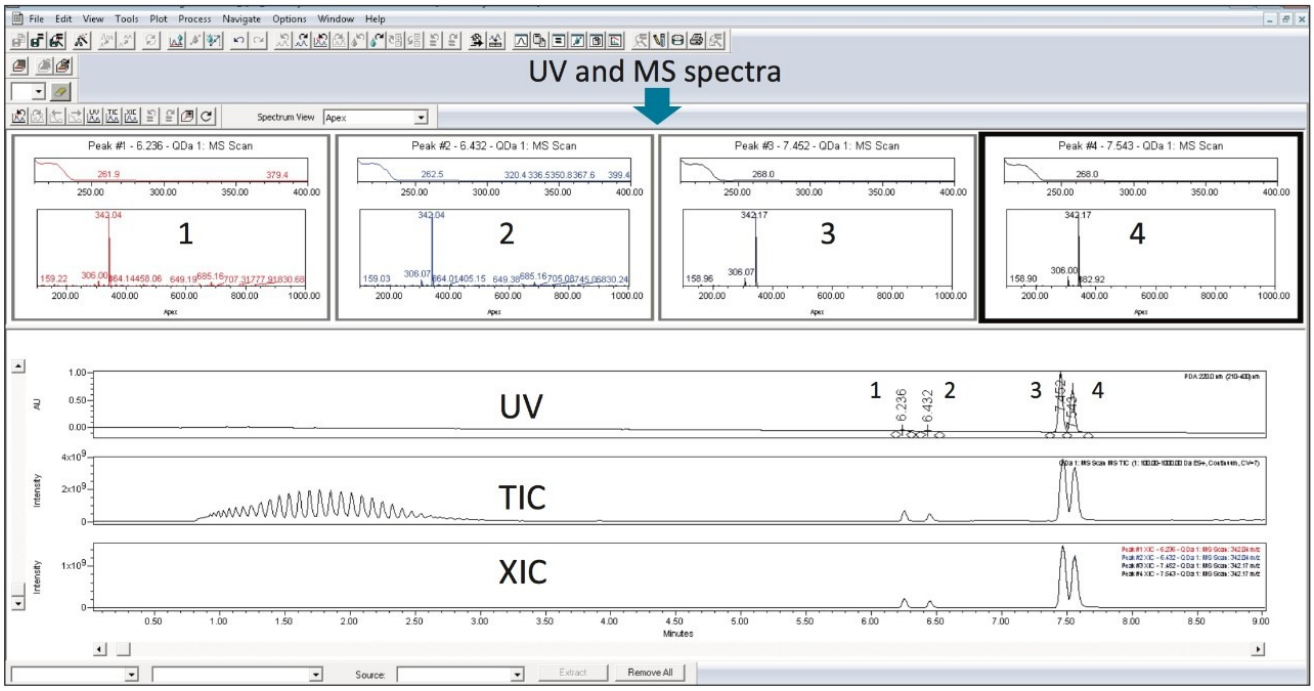


Figure 4. Empower Software's mass analysis window. UV and MS spectra, along with UV and mass chromatograms and extracted ion chromatograms (XIC), can be viewed in a single window.

Interrogation of the data in the mass analysis window indicated relationships between peak 1 and peak 2 with the active ingredient, propiconazole. The UV spectra showed the same maxima at 220 nm with an apparent shift

noted in the second absorbance maxima of both peak 1 and peak 2, when compared to the spectra of the propiconazole. The mass spectra show that peak 1 and peak 2 have an *m/z* of 342 which is the same as the active ingredient. In addition, the isotopic pattern is typical of a dichlorinated compound and is identical to that of propiconazole. In a single analytical run, the unknown components were identified as having the same mass and isotopic pattern as the active ingredient. The presence of the mass detector provided additional structural information and increased the confidence in the detection and identification of the compound. The UV and mass spectra for peak 1 and peak 2 and the propiconazole diastereomers are shown in Figure 5.

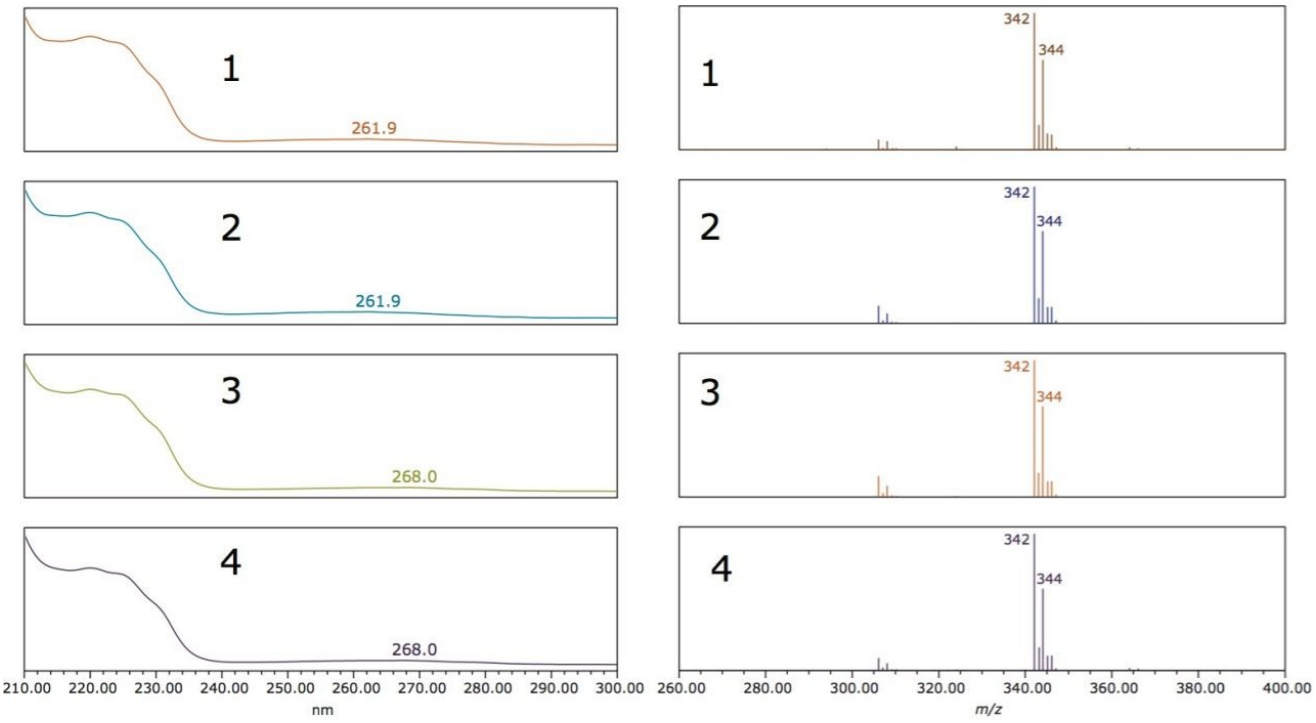


Figure 5. UV and mass spectra for peaks 1 and 2, and the propiconazole diastereomers, peaks 3 and 4, in the formulation.

Conclusion

The ACQUITY QDa Detector, in combination with PDA detection, allows for low-level components to be detected with increased confidence in pesticide formulations. The components were identified as having similar optical and structural properties to propiconazole, the active ingredient present in the formulation. Inert formulation components not seen in the UV were readily detected by the ACQUITY QDa Detector.

The Empower mass analysis window provides a single place to associate the chromatograms and spectra from

all detectors used in the analysis. The consolidation of this information in one place makes data review and interpretation easy.

The addition of mass detection as a complementary analytical detection technique enhances confidence in compound detection and identification. Using the familiarity of a PDA detector, the ACQUITY QDa Detector provides a cost-effective means to make mass detection part of the routine analysis in laboratories that have previously relied on less selective detectors.

References

1. E M Ulrich, C N Morrison, M R Goldsmith, W T Foreman. Chiral Pesticides: Identification, Description and Environmental Implications. *Reviews of Environmental Contamination and Toxicology*. (2012) 217: 1-74.
2. Quality Control of Pesticide Products. Prepared by the Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture. (2009) http://wwwpub.iaea. org/MTCD/publications/PDF/te_1612_web.pdf
3. L Toribo, M J del Noza, J L Bernal, J J Jimenez, C Alonso. Chiral separation of some triazole pesticides by supercritical fluid chromatography. *J Chrom A*. (2004) 1046: 249-253.

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- ACQUITY UPLC H-Class PLUS System <https://www.waters.com/10138533>
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- Empower 3 CDS Software <https://www.waters.com/10190669>

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