


Abstract

In this application note, we present a novel method to monitor the composition, detect impurities, contaminants, degradation and by-products present in surfactants, as well as identify potential carcinogenic or allergenic compounds. Excellent resolution for approximately 20 oligomers has been achieved using lower temperatures than GC or traditional SFC analysis, making UltraPerformance Convergence Chromatography (UPC²) more amenable for the analysis of thermally labile compounds. A significant reduction in the consumption of toxic solvents was also achieved compared to normal phase HPLC analysis.

Benefits

UPC² with either UV or MS detection for the analysis of non-ionic surfactant, offers:

- High-efficiency separation with excellent resolution for approximately 20 oligomers.
- Analysis time less than 2 min with PDA detection.
- Reduction in consumption of organic solvents.
- Analysis at lower temperatures than in GC or SFC.
- The detection of: additional minor series components; by-products; impurities; degradation products or contaminants.

Introduction

The non-ionic surfactant Triton X-100 (Figure 1), an excellent detergent and wetting agent, is readily biodegradable and achieves effective performance across a broad temperature range. It can also be used as a dispersant and emulsifier for oil in water systems. Because of these properties, Triton X-100 is used in many household and industrial cleaning products, paints and coatings, pulp and paper, oil fields, textiles, agrochemicals, cosmetics, and industrial materials.

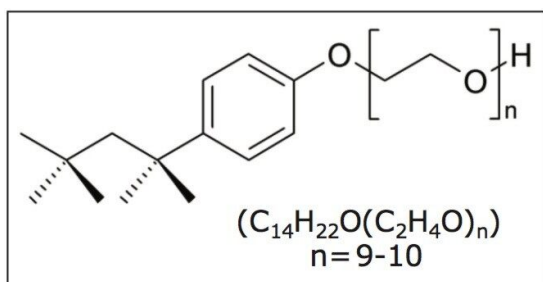


Figure 1. Triton-X-100 structure and chemical formula.

It is essential to be able to monitor the composition of the non-ionic, octylphenol ethoxylate surfactant Triton X-100, because differences in the ethoxy chain length can affect characteristics of the mixture such as viscosity, solubility, and polarity.

The ability to detect the presence of by-products, impurities, degradation products or contaminants present in surfactants is equally important. In addition to identifying potential carcinogenic or allergenic compounds, the presence of impurities can also affect the efficiency of the surfactant.

Surfactants are typically analyzed using techniques such as High Performance Liquid Chromatography (HPLC),^{1,2} Supercritical Fluid Chromatography (SFC),³ or Gas Chromatography (GC).^{4,5} Analysis by GC and HPLC can be time consuming, as these techniques may require additional derivatization stages in order to improve sensitivity, separation or resolve volatilization issues. GC or traditional SFC techniques that employ high column temperatures can also limit the analysis of thermally labile compounds. In some cases, baseline separations for oligomers using HPLC, SFC or GC analyses are not achieved.

Waters UltraPerformance Convergence Chromatography (UPC²) System, builds on the potential of normal-phase separation techniques such as SFC, while using proven Waters' easy-to-use UPLC Technology.

This application note describes the analysis Triton X-100 utilizing UPC² with PDA and MS detection. Excellent resolution for approximately 20 oligomers has been achieved using lower temperatures than GC or traditional SFC analysis, making UPC² more amenable for the analysis of thermally labile compounds. A significant reduction in the consumption of toxic solvents was also achieved compared to normal phase HPLC analysis.

Experimental

UV conditions

UV system:	ACQUITY UPC ² PDA Detector
Range:	210 to 400 nm
Resolution:	4.8 nm
UPC ² System:	ACQUITY UPC ²
Column:	ACQUITY UPC ² BEH 2.1 mm x 50 mm, 1.7 µm
Column temp.:	40 °C
Convergence column manager back pressure:	1500 psi
Injection volume:	1.0 µL
Mobile phase B:	Methanol

Mobile phase gradient for UV detection is detailed in Table 1.

Sr no.	Time(min)	Flow Rate(mL/min)	%A	%B	Curve
1	Initial	2.00	98.0	2.0	-
2	1.25	2.00	65.0	35.0	6
3	1.30	2.00	98.0	2.0	6

4	2.00	2.00	98.0	2.0	6
---	------	------	------	-----	---

Table 1. ACQUITY UPC² mobile phase gradient for UV detection.

Instrument control, data acquisition, and result processing

Empower 3 Software was used to control the ACQUITY UPC² System and ACQUITY UPC² PDA Detector, and provide data acquisition and processing.

MassLynx Software was used to control the ACQUITY UPC² System and Xevo TQD, and provide data acquisition and processing.

MS conditions

MS system:	Xevo TQD
Ionization mode:	ESI +
Capillary voltage:	3.5 kV
Source temp.:	150 °C
Desolvation temp.:	500 °C
Desolvation gas flow:	800 L/hr
Cone gas flow:	50 L/hr
Acquisition:	Full scan
UPC ² System:	ACQUITY UPC ²
Column:	ACQUITY UPC ² BEH 2.1 mm x 50 mm, 1.7 µm
Column temp.:	65 °C

CCM back pressure:	1600 psi
Injection volume:	1.0 µL
Mobile phase B:	Methanol

Mobile phase gradient for MS detection is detailed in Table 2.

Sr No.	Time(min)	Flow Rate(mL/min)	%A	%B	Curve
1	Initial	2.00	97.0	3.0	-
2	20.00	2.00	80.0	20.0	6
3	21.00	2.00	97.0	3.0	6
4	23.00	2.00	98.0	3.0	6

Table 2. ACQUITY UPC² mobile phase gradient for MS detection.

Results and Discussion

UV detection results

UPC² conditions were optimized for the separation and detection of 20 Triton X-100 oligomers. The UV chromatogram for a 10 mg/mL standard in isopropanol alcohol is shown in Figure 2.

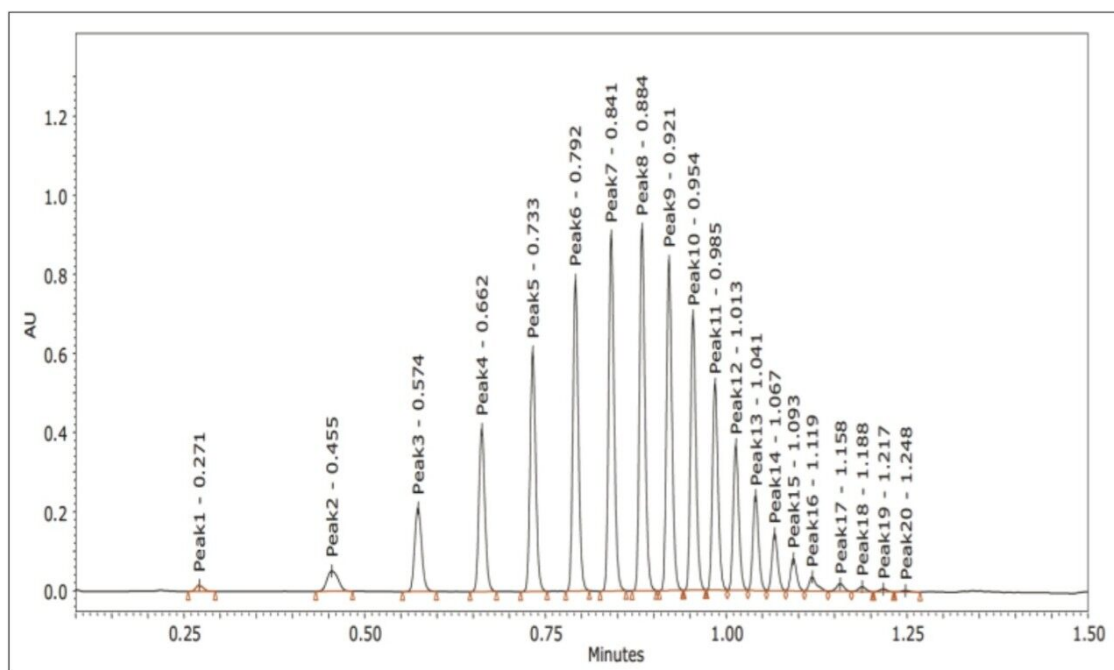


Figure 2. UV chromatogram for a 10 mg/mL Triton X-100 standard.

MS detection results

The UV method demonstrated the speed and simplicity of UPC² for the analysis of Triton X-100. With further optimization of the separation, in this example using a slower gradient, with MS detection additional characterization of the surfactant was achieved.

The chromatogram for Triton X-100 with MS detection, using the described UPC² and MS conditions, is shown in Figure 3. The oligomers detected can be further identified considering the MS spectra, shown in Figure 4 for the oligomers identified as a, b, c, and d in Figure 3.

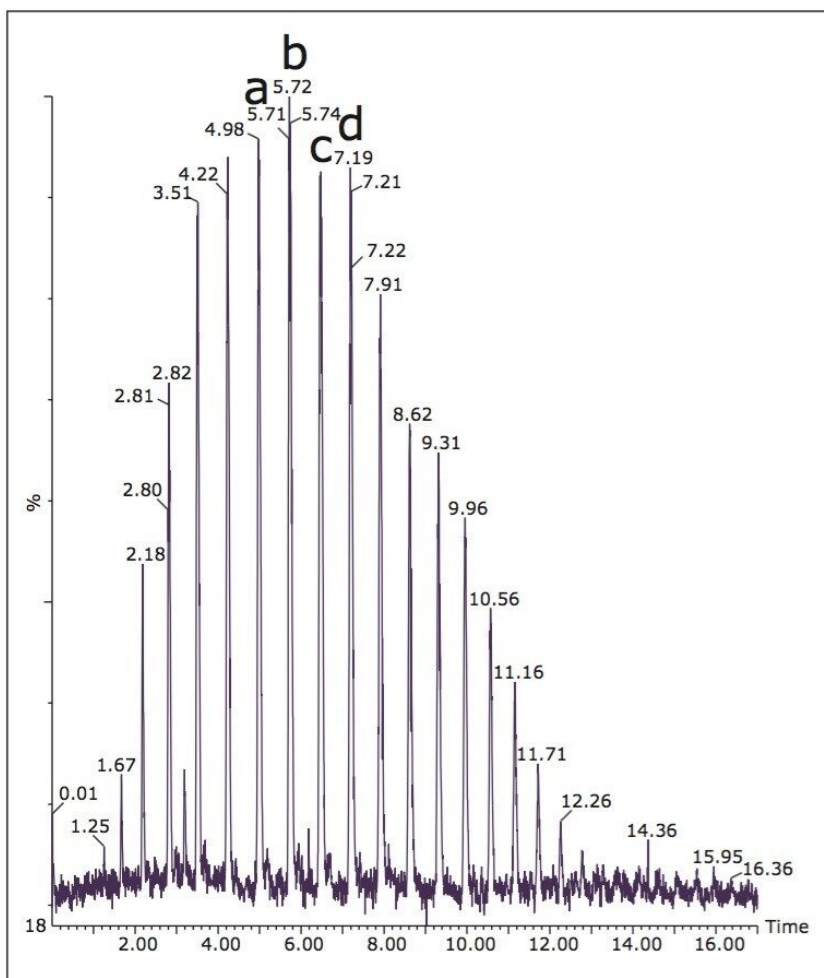


Figure 3. MS chromatogram for a Triton X-100 standard.

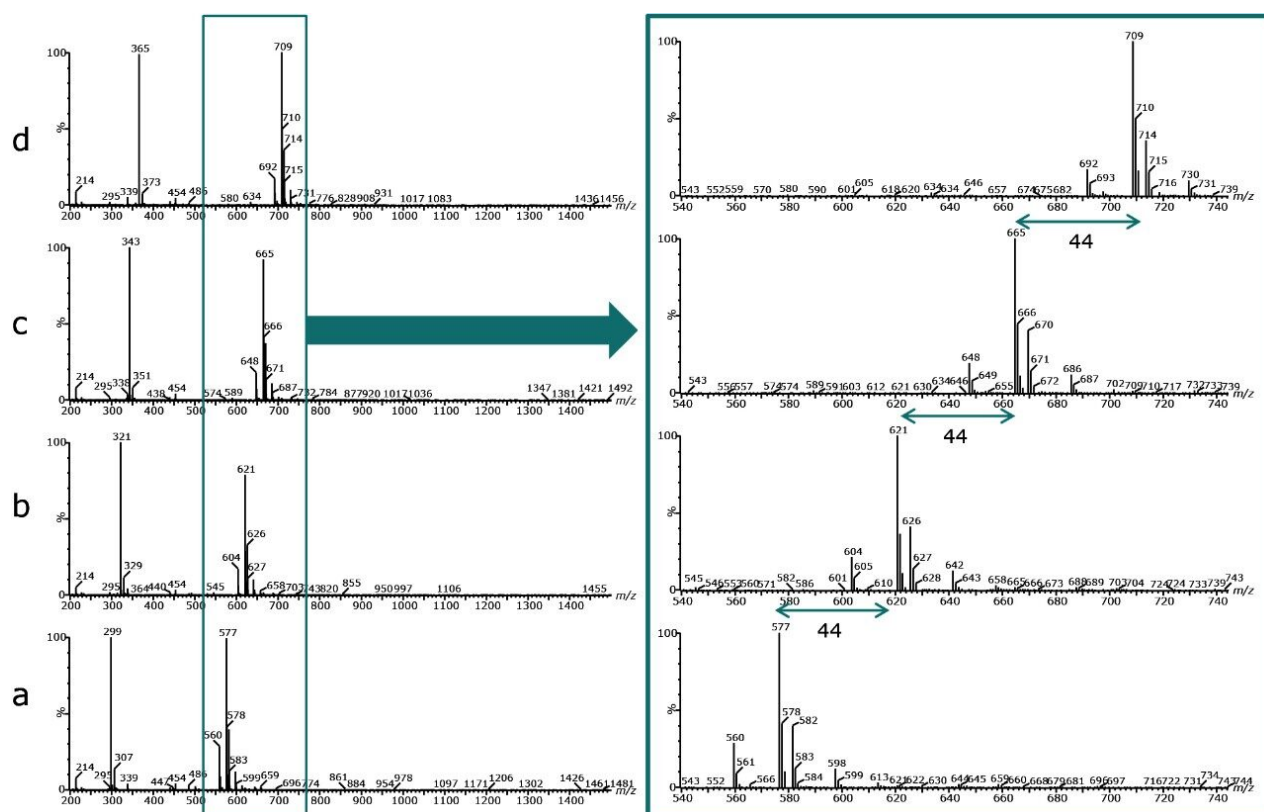


Figure 4. Mass spectra for the individual Triton-X oligomers as indicated in Figure 3.

By using a slower gradient additional details can be observed, such as the detection of: additional minor series components, by-products, impurities, degradation products, or contaminants. An additional minor series present in the analyzed sample of Triton X-100 is shown in Figure 5.

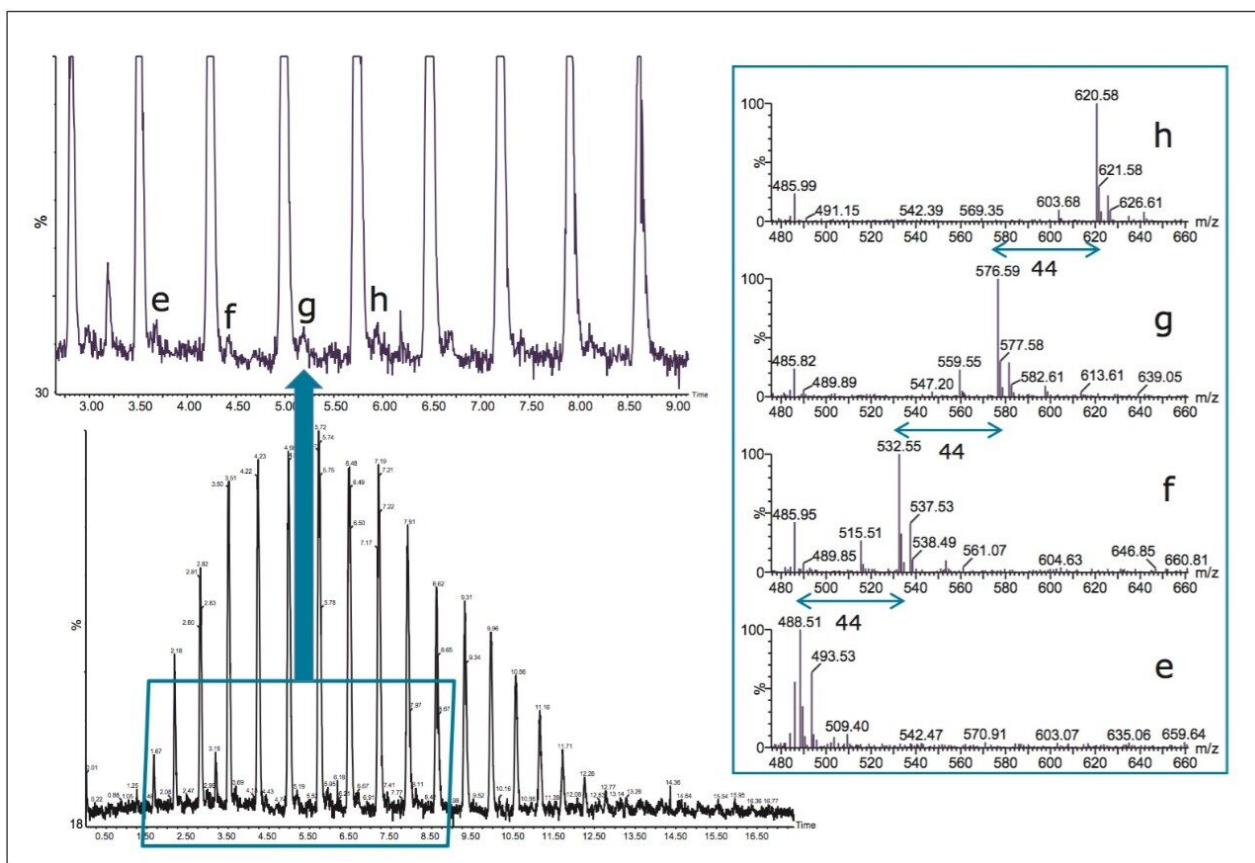


Figure 5. Additional minor series highlighted in the analyzed sample of Triton X-100, with respective mass spectra.

Conclusion

- Rapid, high efficiency separation with analysis time of less than 2 min with PDA detection.
- Excellent resolution for approximately 20 oligomers.
- Analysis occurs at lower temperature than in GC or SFC.
- Reduction in consumption of organic solvents.
- MS detection can be used to further characterize the surfactant, such as the identification of specific oligomers, detection of additional series components, by-products, impurities, degradation products of contaminants.

References

1. R A Escott, S J Brinkworth, T A Steedman. The determination of ethoxylate oligomers distribution of Non-Ionic and Anionic Surfactants by HPLC. *J Chromatography*. 282: 655–661, 1983.
2. K Nakamura, Y Morikawa, I Matsumoto. Rapid Analysis of Ionic and Non-Ionic Surfactants Homologs by HPLC. *Journal of the American Oil Chemists' Society*. 58: 72–77, 1981.
3. B J Hoffman, L T Taylor. A Study of Polyethoxylated Alkylphenols by Packed Column Supercritical Fluid Chromatography. *Journal of Chromatography*. 40: 61–68; Feb 2002.
4. C Bor Fuh, M Lai, H Y Tsai, C M Chang. Impurity analysis of 1,4-dioxane in nonionic surfactants and cosmetics using headspace solid-phase microextraction coupled with gas chromatography and gas chromatography-mass spectrometry. *Journal of Chromatography A*. 1071: 141–145; 2005.
5. J A Field, D J Miller, T M Field, S B Hawthorne, W Giger. Quantitative determination of sulfonated aliphatic and aromatic surfactants in sewage sludge by ion-pair/supercritical fluid extraction and derivatization gas chromatography/mass spectrometry. *Analytical Chemistry*. 64(24): 3161–3167; 1992.

Featured Products

[ACQUITY UPC2 System <https://www.waters.com/134658367>](https://www.waters.com/134658367)

[Xevo TQD Triple Quadrupole Mass Spectrometry <https://www.waters.com/134608730>](https://www.waters.com/134608730)

[MassLynx MS Software <https://www.waters.com/513662>](https://www.waters.com/513662)

[Empower 3 Chromatography Data Software <https://www.waters.com/10190669>](https://www.waters.com/10190669)

720005496, September 2015

©2019 Waters Corporation. All Rights Reserved.