Nota de aplicación

ACQUITY UPLC with ELS and MS Detection: Polyetheramines

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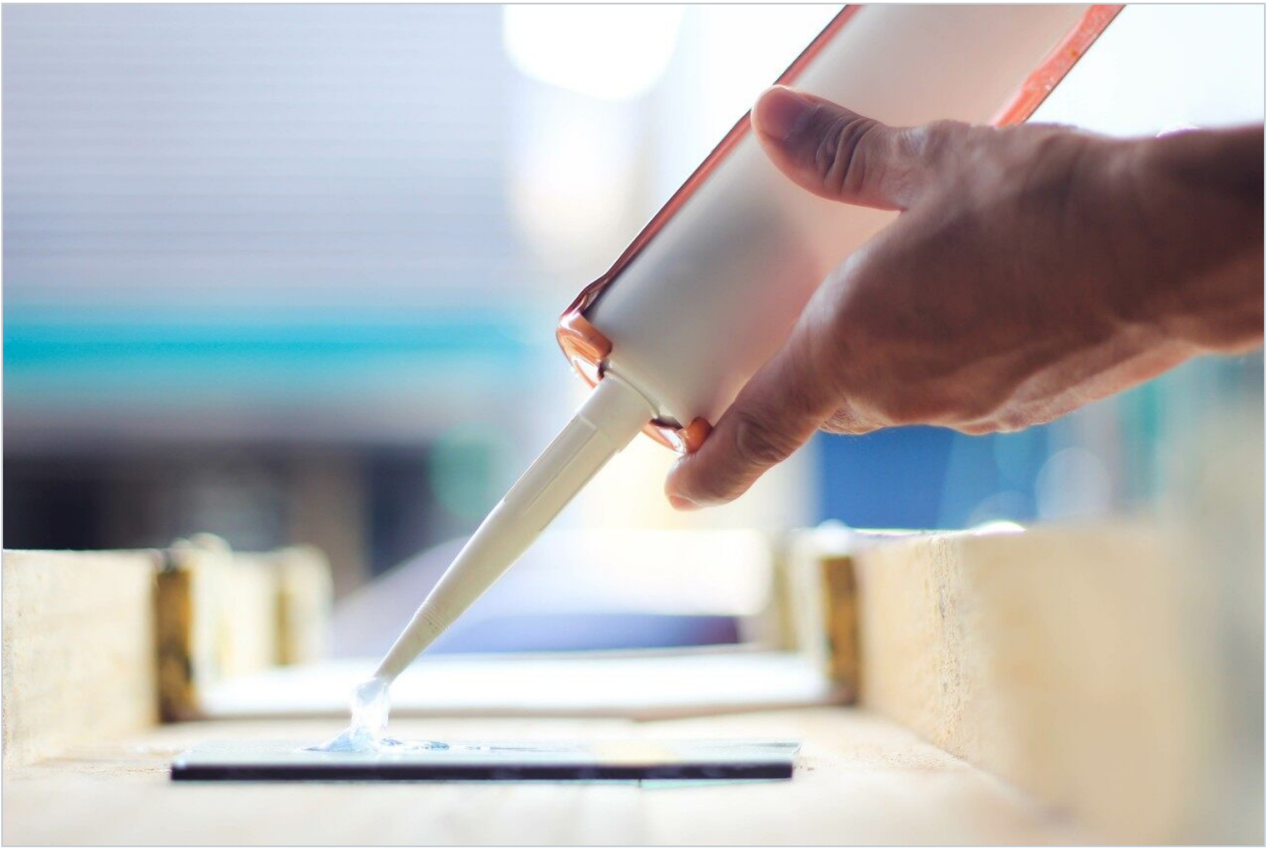

Abstract

This note describes the analysis of a series of 220–1000 average molecular weight polyetheramines using a Waters ACQUITY UltraPerformance LC (UPLC) System with an evaporative light scattering detector (ELSD), a single quadrupole MS detector and Empower Software. Polyetheramines present poor UV/VIS response because of the lack of strong chromophores. The ELSD provides an alternative detection mode to UV and the single quadrupole MS provides detailed molecular weight and structure. To compare the entire series, UPLC run time was extended to ten minutes for each product. The ability to quickly and reliably characterize polyetheramines can facilitate workflow in certifying lot-to-lot variation, quality control of raw materials, new product development, and product troubleshooting for both polyetheramine manufacturers and downstream users.

Benefits

- Provides resolution, separation speed and reproducibility
- Batch-to-batch product quality control and troubleshooting as well as monitoring the progress of new reaction products in product development

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Introduction

Polyetheramines have widespread demand in many applications including epoxy coatings, adhesives, sealants, coatings, inks and organic pigments, fuel and lubricant additives, herbicides and pesticides.[1] Commercial production of polyetheramines is based on the amination of polyols to form primary amines groups.[2,3,4] The resulting products are mixtures of varying chain lengths with amine and hydroxyl terminal groups. Conventional chromatography for this class of compounds can be poorly resolved, time consuming or lack robustness. Consequently, managers supporting manufacturing, customers and R&D rely on other analytical techniques that require higher levels of operator expertise.

This note describes the analysis of a series of 220–1000 average molecular weight polyetheramines (Figure 1) using a Waters ACQUITY UltraPerformance LC (UPLC) System with an evaporative light scattering detector (ELSD), a single quadrupole MS detector and Empower Software. Polyetheramines present poor UV/VIS response because of the lack of strong chromophores. The ELSD provides an alternative detection mode to UV and the single quadrupole MS provides detailed molecular weight and structure. To compare the entire series, UPLC run time was extended to ten minutes for each product. The ability to quickly and reliably characterize polyetheramines can facilitate workflow in certifying lot-to-lot variation, quality control of raw materials, new product development, and product troubleshooting for both polyetheramine manufacturers and downstream users.

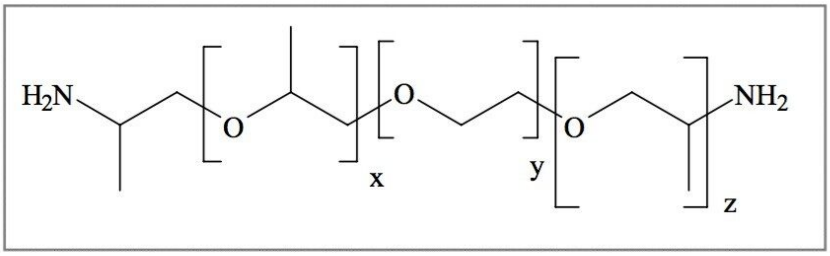


Figure 1. Generic Structure of polyetheramine.

Experimental

UPLC System and Operation Conditions

System:	ACQUITY UPLC with ACQUITY ELSD detector and Waters ZQ 2000
Software:	Empower
Column:	ACQUITY UPLC BEH C_{18} 2.1 x 100 mm
Weak wash:	95:5 Water:CH_3CN (600 µL)
Seal wash:	90:10 Water:CH_3CN (5 min)
Mobile phase A:	0.05% TFA in H_2O
Mobile phase B:	0.05% TFA in CH_3CN

Generic Linear Gradient:	4% B to 50% B in 10 minutes
Flow rate:	0.5 mL/min
Injection:	2 µL
Column temp.:	50 °C

Note: A low dead volume MicroTee was used to split the flow to ELSD (80%) and ZQ (20%).

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

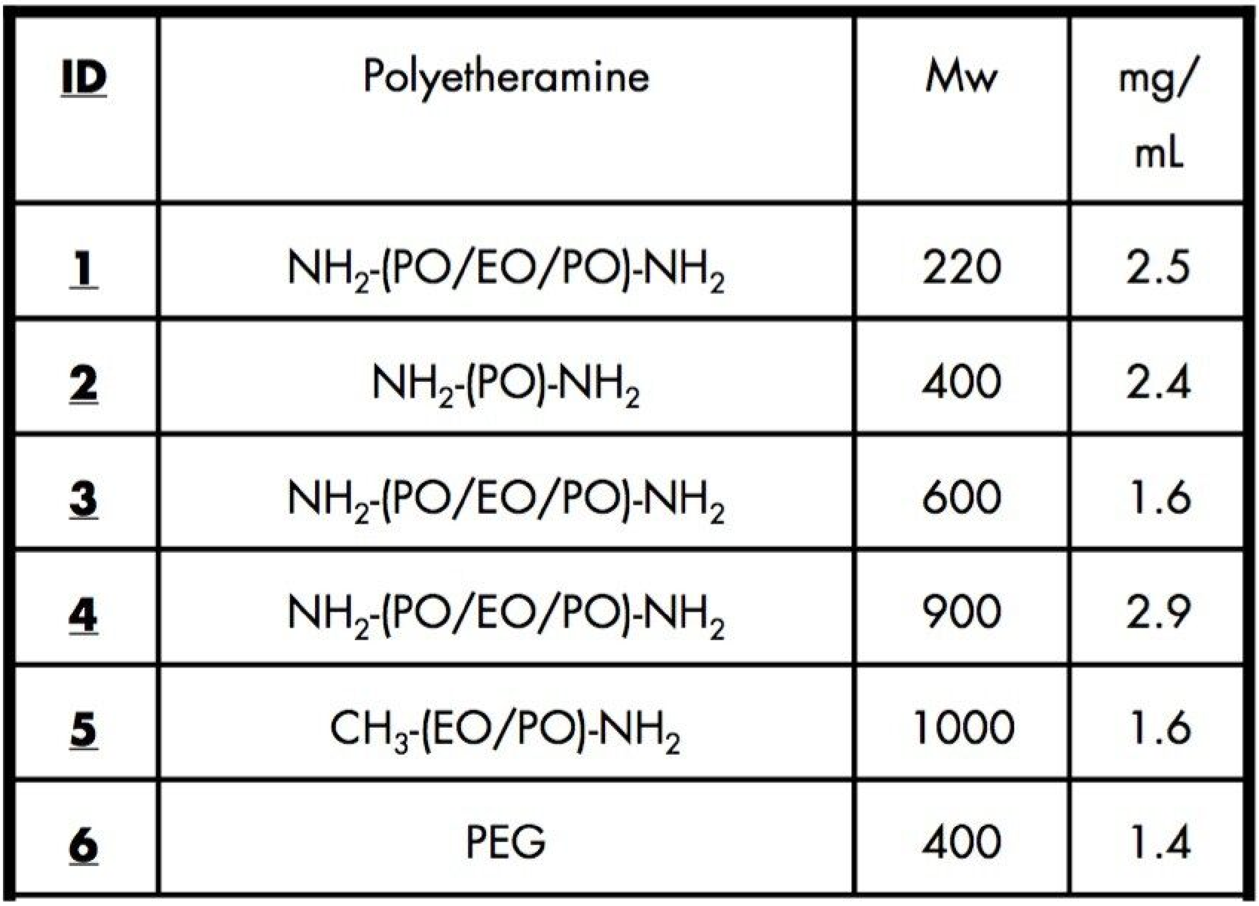
ZQ Parameters

Probe:	ES$^+$
Cone (V):	35
RF Lens (V):	0.5
Source T (°C):	120
Cone Gas (L/Hr):	50

LM Resolution:	15
Ion Energy:	0.3
Scan time:	0.23s
ES capillary (kV):	3.2
Extractor (V):	2
Multiplier:	500
Desolvation T (°C):	400
Desolvation Gas (L/Hr):	750
HM resolution:	15.5
Scan Range:	100 to 1200 Da
Inter-scan delay:	0.1s

Results and Discussion

Table 1 lists the different polymer backbones and average molecular weights of the five commercial polyetheramine samples (1–5) that were analyzed. A polyethylene glycol (PEG) sample was included for comparison.



ID	Polyetheramine	Mw	mg/ mL
1	NH_2-(PO/EO/PO)-NH_2	220	2.5
2	NH_2-(PO)-NH_2	400	2.4
3	NH_2-(PO/EO/PO)-NH_2	600	1.6
4	NH_2-(PO/EO/PO)-NH_2	900	2.9
5	CH_3-(EO/PO)-NH_2	1000	1.6
6	PEG	400	1.4

Table 1. Sample ID and concentration. (All the polymers were dissolved in water. EO is ethylene oxide units. PO is propylene oxide units. PEG is polyethylene glycol. Mw is the reported average molecular weight.)

Figure 2 shows ELSD chromatograms of polyetheramines 1–5 and PEG (6) from applying a ten-minute linear gradient method. Product peaks are well-resolved and symmetric within a ten-minute window, illustrating the benefits of UPLC with BEH column chemistry for the separation of polyetheramines. Under these elution conditions the retentions times of samples 1–6 differ significantly due to dissimilar relative hydrophobicities. Each product has a peak cluster or "finger-print" that can be used for product identification. ELSD chromatograms are useful for QC, troubleshooting, customer support and R&D. In new product development, this approach is also useful in monitoring the progress of chemical reactions based on polyetheramines.

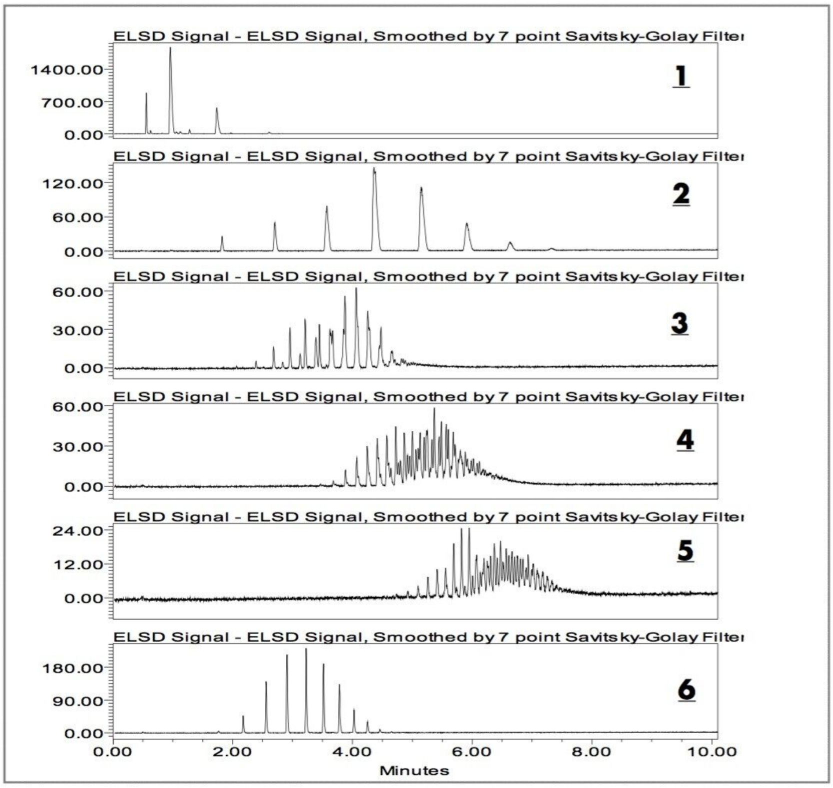


Figure 2. ELSD chromatograms of 1–6 using a linear gradient method (4% to 50% B in ten minutes).

Applying other gradient methods resolves the polymer envelopes even further. The ELSD chromatograms of the higher MW polyetheramines 3 and 5 when applying more shallow gradient methods, are in Figure 3. The polymer envelopes are further resolved relative to Figure 2 and the chromatogram patterns suggest that both 3 and 5 contain multiple series of polymers

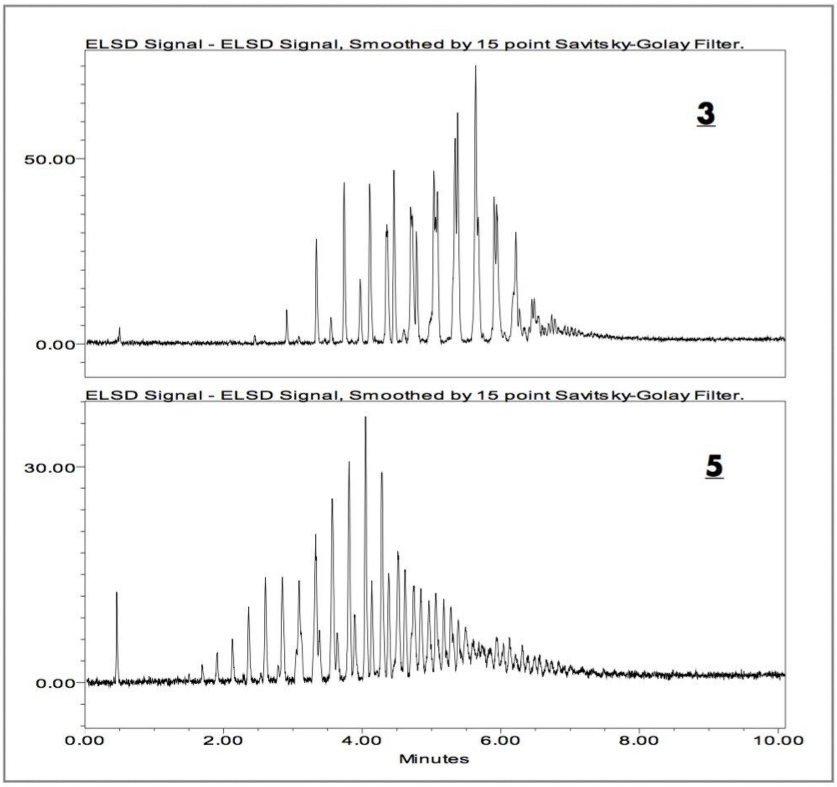


Figure 4 is an overlay of eight replicate injections of ES$^+$ TIC (electrospray positive total ion current) chromatograms. Visual examination shows the overall reproducibility is excellent

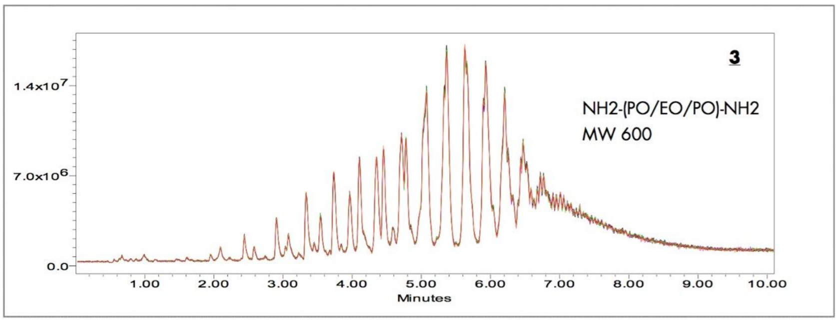


Figure 4. Overlay ES$^+$ TIC chromatograms of eight replicate injections of 3 (4% to 35% B, ten minute linear gradient)

Retention time reproducibility is another indicator of the robustness of UPLC with BEH column chemistry for this class of compounds. The single quad MS detector can provide structural and molecular weight information about these series that the ELSD cannot.

Figure 5 shows the extracted ES positive-ion mass spectra of 3 with peaks at retention times (min): 3.55, 3.74, 3.97, 4.11, 4.35, 4.46, and 4.71. Four series of polymer ions (3-ax, 3-bx, 3-cx, and 3-dx) with 44 Da (ethylene oxide unit) spacing can be recognized. Since 3 is tri-block polyetheramine (PO/EO/PO), the general structures of 3-ax, 3-bx, 3-cx, and 3-dx can be illustrated as follows:

3-ax = $NH_2CH(CH_3)CH_2$-$(OCH_2CH_2)x$-$[OCH_2CH(CH_3)]2NH_2$;
where x = 5, *m/z* = 411; x = 6, *m/z* = 455; x = 7, *m/z* = 499; x = 8, *m/z* = 543

3-bx = $NH_2CH(CH_3)CH_2$-$(OCH_2CH_2)x$-$OCH_2CH(CH_3)NH_2$;
where x = 8, *m/z* = 485; x = 9, *m/z* = 529; x = 10, *m/z* = 573

3-cx = $HOCH_2CH_2$-$(OCH_2CH_2)x$-$OCH_2CH(CH_3)NH_2$;
where x = 7, *m/z* = 428; x = 8, *m/z* = 472; x = 9, *m/z* = 516

3-dx = $HOCH(CH_3)CH_2$-$(OCH_2CH_2)x$-$OCH_2CH(CH_3)NH_2$;
where x = 6, *m/z* = 398; x = 7, *m/z* = 442; x = 8, *m/z* = 486

These results demonstrate the utility of a single quadrupole mass spectrometer5 combined with UPLC for lower MW polyetheramine characterization. For >2000 MW polyetheramines, an ACQUITY UPLC time-of-flight (ToF) MS System can provide characterization information. These experiments were outside the scope of this application note.

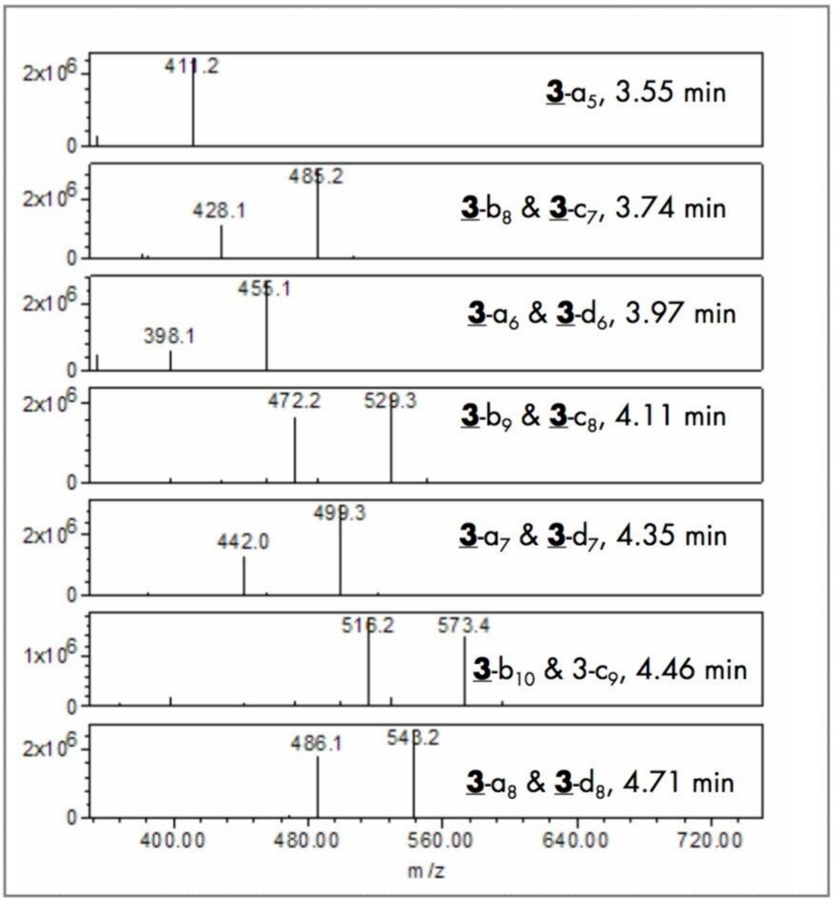


Figure 5. Positive-ion mass spectra of peaks of 3 at retention time (min): 3.55, 3.74, 3.97, 4.11, 4.35, 4.46, and 4.71.

Conclusion

The ACQUITY UPLC System with the ELSD and single quadrupole MS detector provides a tool for the rapid differentiation, identification, and characterization of polyetheramines. This is particularly important as these compounds lack a strong UV response. Reliable, reproducible comparisons of polyetheramines products are easily achieved when running fast gradients with ACQUITY UPLC BEH Column chemistry and a simple mobile phase. Multiple benefits are derived from combining MS and ELS detection with UPLC separation. The retention time of ELSD chromatogram peaks are useful to “finger-print” polymer components; whereas, the extracted mass spectra provide details about molecular weight for chemical structure elucidation. The resolution, separation speed and reproducibility of UPLC can benefit polyetheramine manufacturers and end-users. Applications include batch-to-batch product quality control and troubleshooting as well as monitoring the progress of new reaction products in product development.

References

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