



**Figure 3:** Representative mass spectra of the oligomers in PEG\_480 (A)  $m/z=571.5$  and (B)  $m/z=615.5$ .

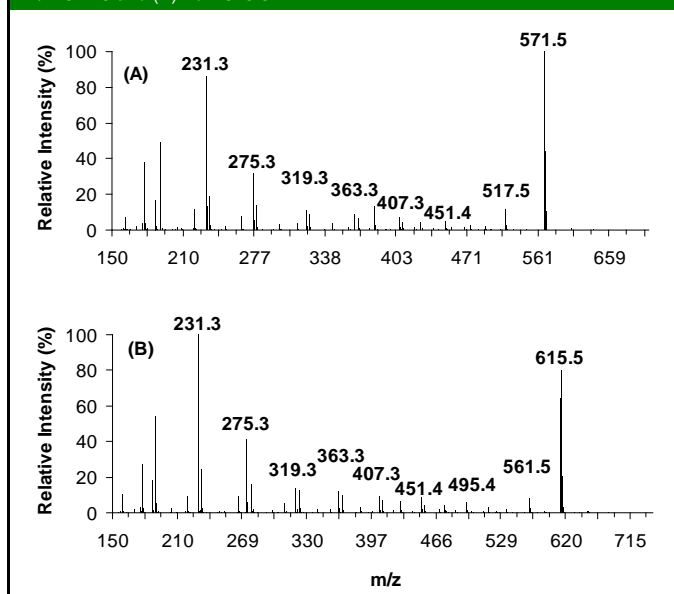


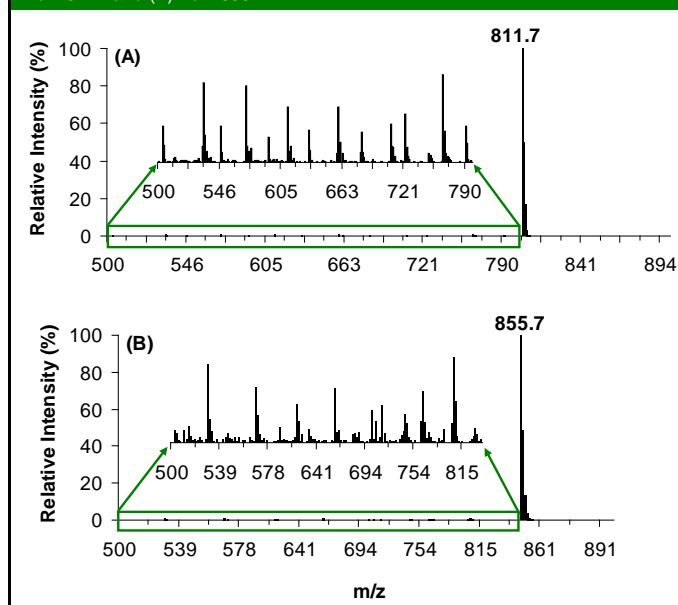
Figure 4 shows the mass spectra of the two most abundant oligomers in PEG\_1000, with retention times of 18.3 and 19.2 min, respectively. Contrary to the case of PEG\_480, the most abundant oligomer in PEG\_1000 has a molecular mass of 811.7 Da, lower than the expected molecular mass of 1000 Da. Instrument settings, such as cone voltage, can easily alter the relative intensity of oligomer peaks; hence, the overall nominal mass distribution of the oligomers. Extreme caution must be exercised in molecular weight determinations for polymers/oligomers using a single quadrupole mass spectrometer. It is also noted that the in-source fragmentation for PEG\_1000 is much weaker than that in PEG\_480. Since fragmentation of protonated poly(ethylene oxides) is a charge-induced and/or charge-remote process; likely, the energy is more easily dissipated along a longer backbone before causing a cleavage for a PEG with higher molecular weight.

Commercial Tween 80<sup>®</sup> formulation consists of not only the ethoxylated oligomers with a different fatty acid side chain, but also the oligomers of the ethoxylated sugars and poly(ethylene glycol) (PEG) oligomers [4]. This complexity is shown in Figure 5. There are at least three identifiable series of oligomers, as indicated by the circle, star and triangle symbols. Based on the  $m/z$ , all three series can be assigned to the poly(ethylene glycols) and isosorbide polyethoxylates [4]. Unfortunately, under the current gradient condition, the main component of Tween 80<sup>®</sup>, polysorbate monooleate, was not observed.

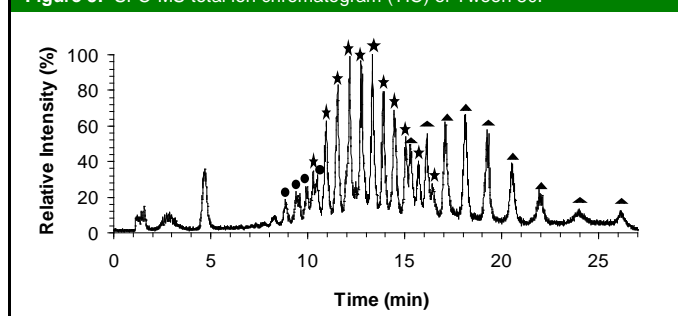
## Conclusions

In this application note, the high resolving power of SFC and the wealth of structural information attainable by MS were demonstrated by the analyses of two straight-chain PEG oligomers and Tween 80<sup>®</sup> using a simple modifier gradient and APCI ion source. Under APCI conditions, in-source fragmentations of the protonated oligomers were observed; from which, end-group information can be easily deduced. However, the nominal mass distributions in both cases deviated from the expected ones. Due to the complexity of Tween 80<sup>®</sup>, only the poly(ethylene glycols) and isosorbide polyethoxylates in the formulation were observed.

**Figure 4:** Representative mass spectra of the oligomers in PEG\_1000 (A)  $m/z=811.7$  and (B)  $m/z=855.7$ .



**Figure 5:** SFC-MS total ion chromatogram (TIC) of Tween 80.



## References

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