

Use of High Speed/High Resolution Size Based Chromatographic Separation of Surfactants and Oligomeric Materials with Single Quadrupole Mass Spectrometry Detection

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INTRODUCTION

Recent developments in polymerization processes have utilized a wide array of strategies. The development has evolved from simple polymer chains to complex polymers capable of performing multiple functions within a single molecular chain. As these new materials evolve their control and understanding has come under intense scrutiny utilizing a wide range of analytical technology ranging from chromatographic separation to advanced mass spectrometry.

Addressing the challenges of material characterization has often been focused on hyphenated detection techniques coupled with separation. This approach utilizes a concentration detector such as a refractive index (RI) detector as well as a viscosity detector and a multi angle light scattering detector and more recently the use of Mass Spectrometry (MS) detectors.

With the introduction of high speed-high resolution size based separation techniques, a novel approach to the design of the separation equipment including the separation column as well as the entire flow path are used to yield a high speed / resolution separation maintained from injection to detection with traditional detector options such as RI and UV detection. However, the use of this high speed high resolution separation technique has seen limited pairing with MS detection due to the need to control material ionization and solvent matrix effects.

In this study the expansion of the APC approach to the size based separation is presented. A single system control platform is evaluated to pair the chromatographic system to the MS detector system allowing for a high throughput/ high resolution evaluation of size based separation of polymeric material while allowing for controlled MS ionization without interfering with the chromatographic separation.¹

METHODS

The test conditions are based on using a high speed, high resolution ACQUITY APC SEC system¹ coupled to a Waters SQD Detector 2 single quadrupole mass spectrometer. The two detectors are managed by using a post column split flow at a fixed 1:1 ratio, (see figure 1). Samples evaluated are PEG and Tergitol surfactants dissolved in the chromatographic system mobile phase.

SEC Conditions

- Eluent (PEG): 20/80 Methanol/Water 0.05% Formic
- Eluent (Tergitol): 95/5 Methanol/Water
- Columns 2 Waters 4.6X150 mm BEH SEC 125 Å

Mass Detector Conditions

Ionization mode: ESI+ or APCI+

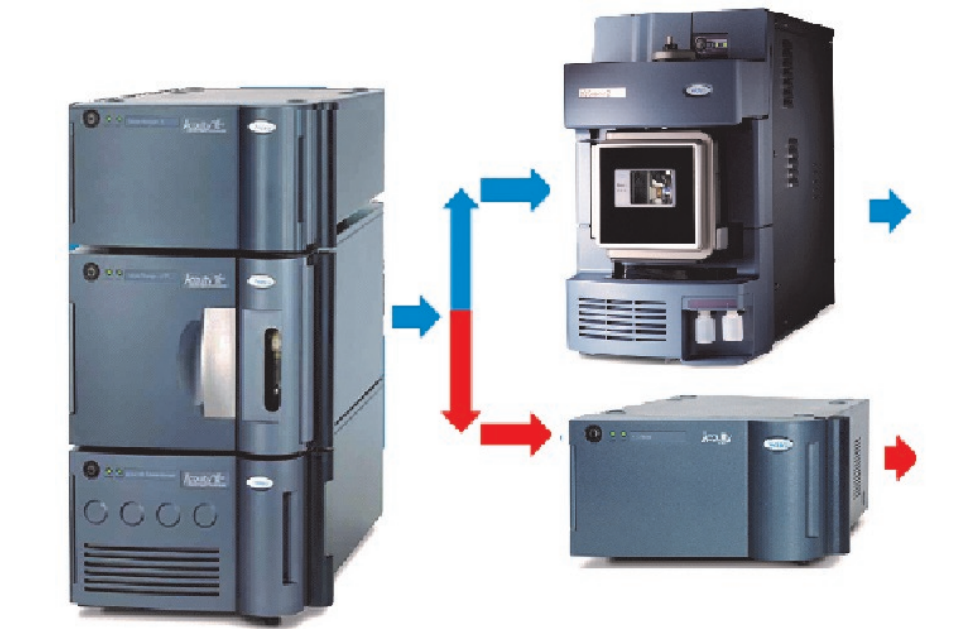


Figure 1. Waters ACQUITY Core 1 APC system with post column split flow to ACQUITY RID and SQD 2 Mass Spectrometer

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RESULTS

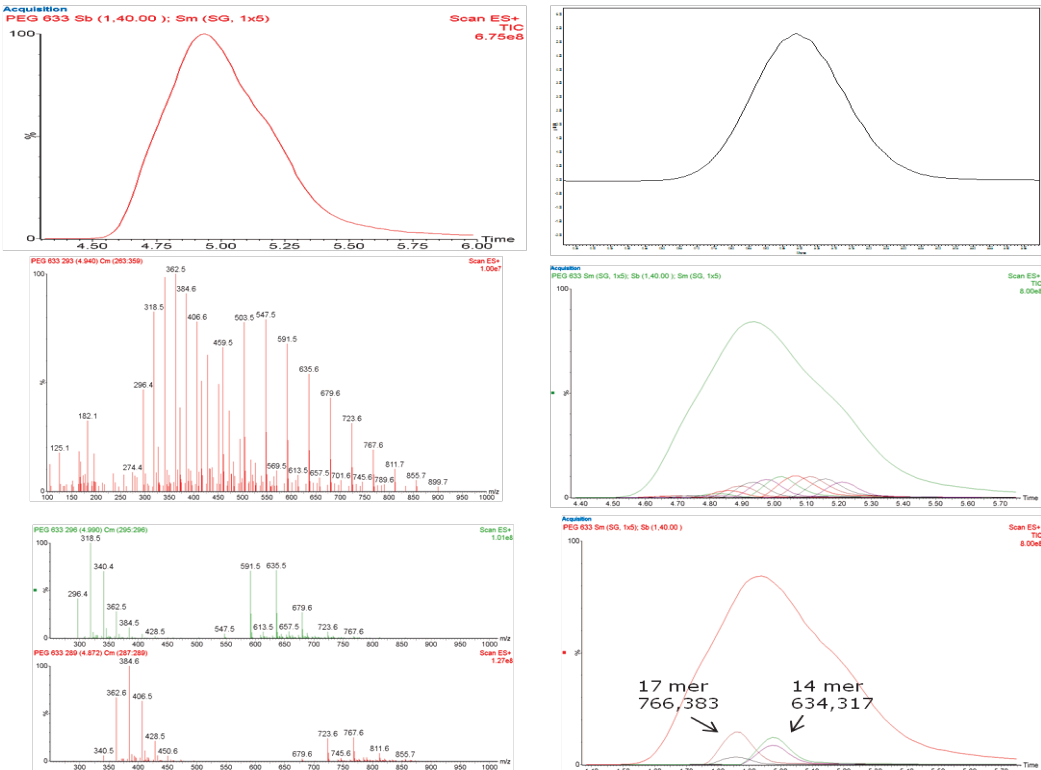


Figure 2. The top left image shows the Total Ion Chromatograph (TIC) using ESI conditions of a '633' Da PEG standard and the top right the corresponding RI signal from the same injection. The mid left spectra is the ESI collected across the entire size distribution showing the mass of each molecule separated by 44 Da (each EO unit or mer) as well as a second lower mass series separated by 22 due to the mass of each mer divided by the double charge (M/z). The mid right chromatogram shows the TIC for the sample and the Extracted Ion Chromatogram (XIC) for the different chains lengths present in the 'narrow standard'. The bottom left spectral set shows the spectra of two chromatographic (size) slices showing the impact of the charge 1 and charge 2 state of the sample. The bottom right overlaid chromatogram set shows the distribution of the sample and that of the 17 and 14 mer chain length. The overlapping peaks are due to the 2 charge states of the molecule.

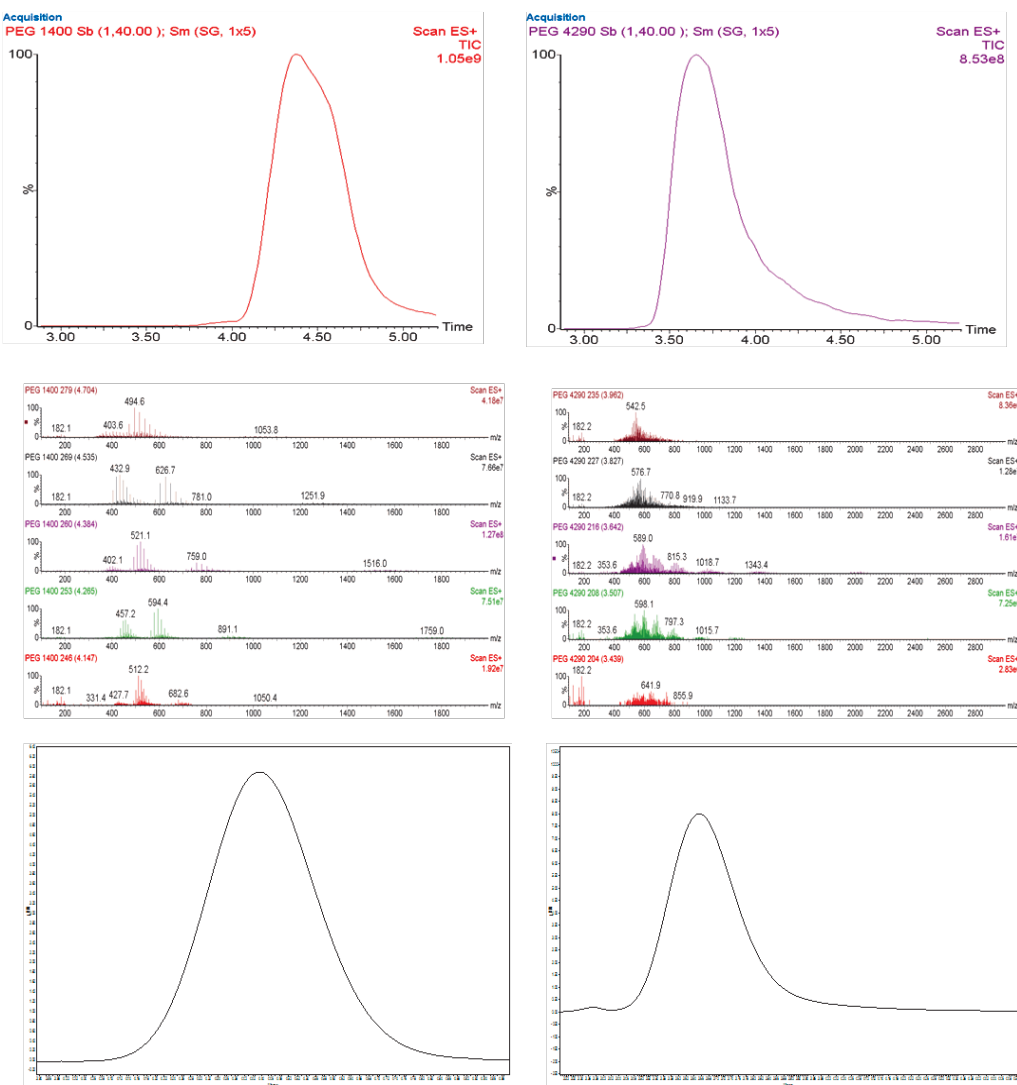


Figure 3. Top left image is the total ion chromatograms (TIC) using ESI conditions of a '1400' Da PEG standard, the mid left is the individual mass spectra as a function of retention time (size) showing +1, +2, +3 and +4 with increasing charging with chain length and the bottom left is the corresponding RI chromatographic trace for the polymer sample. Top right image is the total ion chromatograms (TIC) using ESI conditions of a '4000' Da PEG standard, the mid right is the individual mass spectra as a function of retention time (size) showing +2, +3, +4, +5, +6 and +7 with increasing charging with chain length (note, +7 dominating) and the bottom right is the corresponding RI chromatographic trace for the polymer sample.

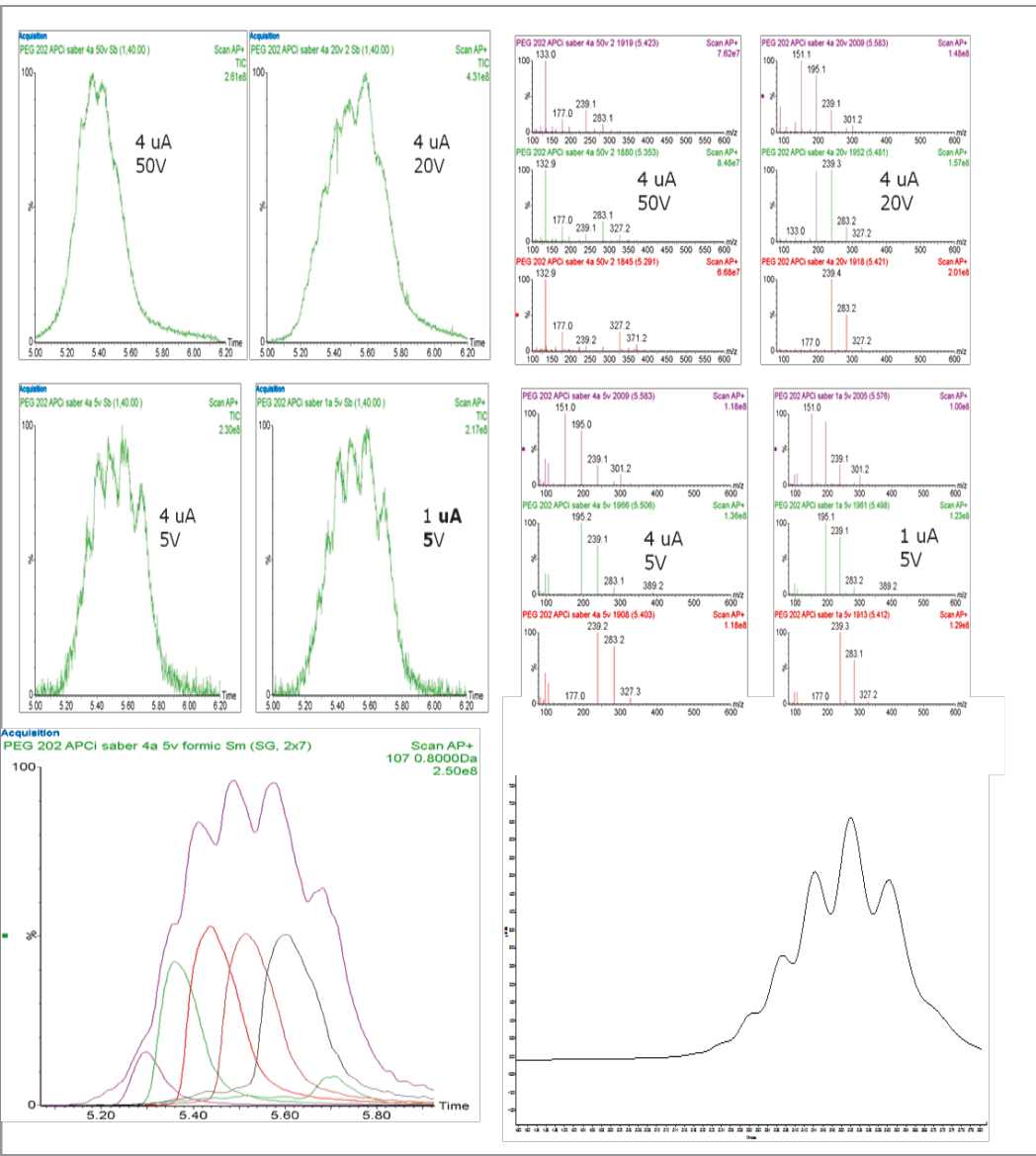


Figure 4. Top left set of images are the TIC of PEG '202' standard collected using Atmospheric Chemical Ionization (APCI) with varied corona current and cone voltage settings. Top right are spectra collected from each ionization condition extracted at the elution time corresponding to the signal maxima. Bottom left image is the overlay of the smoothed TIC data of the PEG standard and the XIC spectra of the individual components in the mixture using the optimized cone voltage (5V) and corona current (4uA) settings. The bottom right image is the corresponding RI chromatographic trace for the polymer sample.

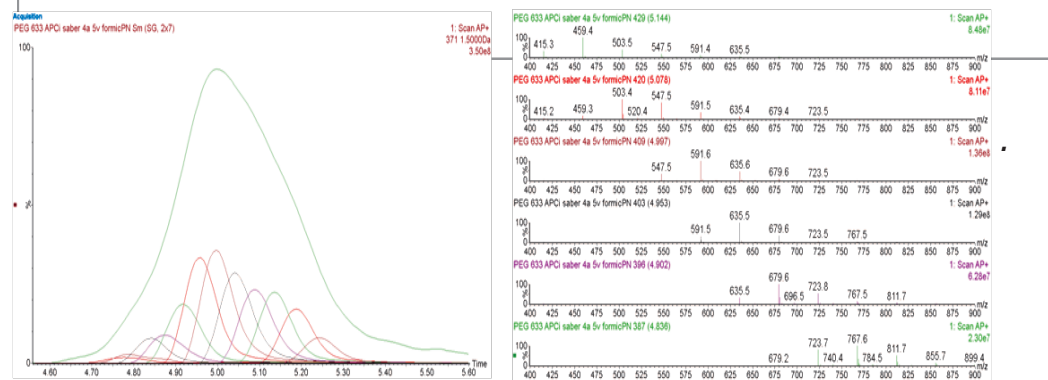


Figure 5. Left image TIC and XIC of '633' PEG using APCI. Right is the mass spectra of the components of PEG 633.

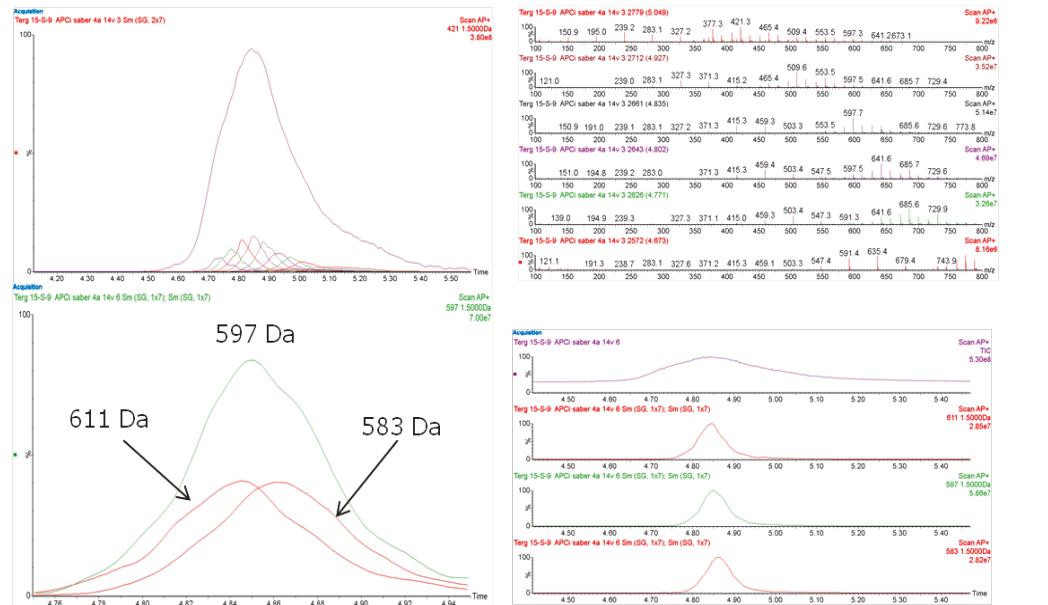


Figure 6. Top left image TIC and XIC of Tergitol⁴ ($\text{CH}_3(\text{CH}_2)_{14}(\text{C}_2\text{H}_4\text{O})_5\text{H}$) using APCI. Top right are spectra collected from each ionization condition extracted at the elution time corresponding to the signal maxima. Bottom left are the XIC of fixed EO content and varied CH₂ length. Bottom right XIC relative to the full sample distribution

CONCLUSION

- Using a single quadrupole shows a potential for coupling MS to APC for rapid polymer analysis and MS optimization.
- Use of ESI yields rich data sets for interrogation but caution must be taken when evaluating the data due to charging effects with increasing chain length with increasing charge dominating the signal.
- Use of APCI allows for simplifying the mass spectral signal allowing for a simplified sample evaluation.