



Supercritical Fluid Chromatographic (SFC) Separations of Oligomeric Materials Using Columns Packed with sub 2-um Particles

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Summary



Recently, columns packed with particles of diameters less than 2 μm have become available for use in High Performance Liquid Chromatography (HPLC). These columns have been used with new instrumentation that offers higher pressure capability and reduced extra-column volumes. The combination of the high pressure equipment and sub 2- μm columns has been termed Ultra Performance Liquid Chromatography (UPLC).

With the low viscosity of carbon dioxide used in SFC, the use of elevated flow rates has been possible due to flat van Deemter curves to increase the speed of analysis. The lower viscosity of carbon dioxide mobile phase should also result in lower column pressure drops when used at conventional flow rates. While columns with sub 2- μm particles exhibit high pressure drops in UPLC, the use of these columns in SFC should result in much lower pressure drops across the column, due to the low viscosity of carbon dioxide.

In this study, sub 2- μm particle size columns were evaluated in SFC with conventional instrumentation for separations of oligomeric materials. Lower pressure drops were observed in SFC with these columns than are seen in UPLC. Excellent separations were observed for oligomeric materials such as ethoxylated alkyl phenols, despite higher pressure drops than are normally obtained in conventional SFC. The use of sub 2- μm columns was demonstrated on conventional SFC instrumentation. Significant degradation of column performance due to frictional heating or extra-column system volume was not observed.



Introduction

Some have predicted, based on theoretical treatments, that large column pressure drops could result in efficiency and selectivity losses (1) in SFC. These losses were predicted to be especially severe when working in pressure and temperature regions where the density changes rapidly with pressure. This could have the largest impact on separations of oligomeric materials, where separations are driven by solubility in the mobile phase versus specific column interactions which normally drive separations on packed columns.

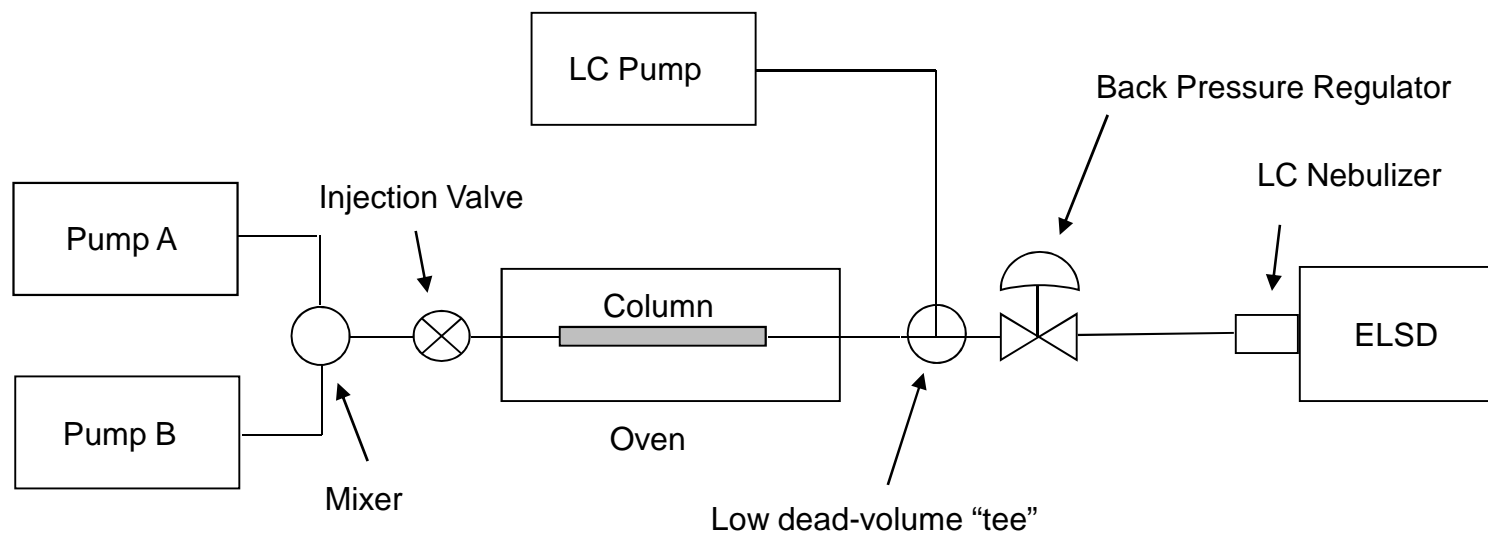
It was the purpose of this study to evaluate sub 2-um columns in SFC for separations of oligomeric materials, where deleterious effects of column pressure drop may be most pronounced. Alkylphenol ethoxylates were chosen for the evaluation since they are commercially available and are detectable with both UV and evaporative light scattering detectors (ELSD). The effect of extra column dead volume associated with ELSD on the separations was also studied.

1. P.A. Peaden and M.L. Lee, *J. Chromatogr.*, **259**, 1 (1983).

Experimental

- SFC Instrument: Jasco PU-2080
- ELSD: Sedex 85, 40°C, 47 psi, Gain 8
- Column: Rx Sil, 10 cm x 4.6 mm i.d., 1.8 μ m
- Mobile phase: Carbon dioxide and methanol
- Mobile phase gradient: 2 to 35% MeOH in CO₂
- Make up fluid: methanol at 0.2 mL/min
- UV Detection: 230 nm
- Temperature: 60°C
- Back pressure: 20 MPa
- Column flow: 1.7 mL/min
- Injection volume: 2 μ L
- Sample prep: 10 mg/mL in methanol

Instrument Configuration Using Liquid Make-up Fluid with ELSD



Observed Column Pressure Drops



Sepax CN, 150 x 2.1 mm, 1.8 μ m, 60°C, B=MeOH, A=CO₂

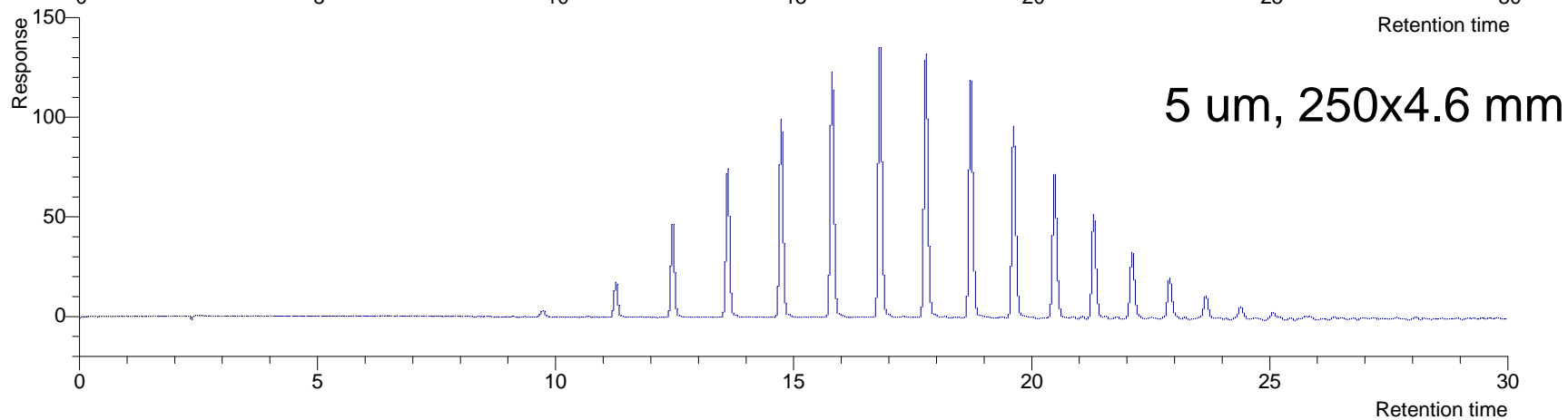
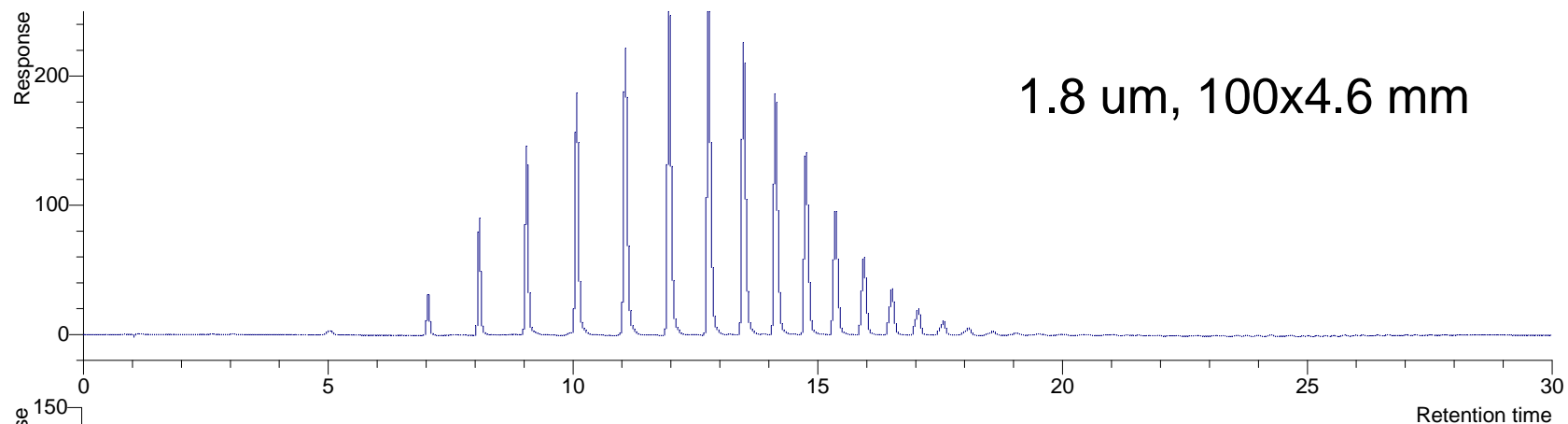
Flow (mL/min)	%B	P2 (MPa)	P1 (MPa)	Δ P (MPa)
1.0	5	22	10	11
1.0	20	26	10	16
1.0	50	40	10	30
0.9	45	37	10	27

RxSil, 100 x 4.6 mm, 1.8 μ m, 60°C, B = MeOH, A = CO₂

Flow (mL/min)	%B	P2 (MPa)	P1 (MPa)	Δ P (MPa)
1.5	2	18.1	15	3
1.5	35	20.3	15	5.3
1.7	35	21.6	15	6.6
1.7	35	26.6	20	6.6
1.7	2	22.9	20	2.9

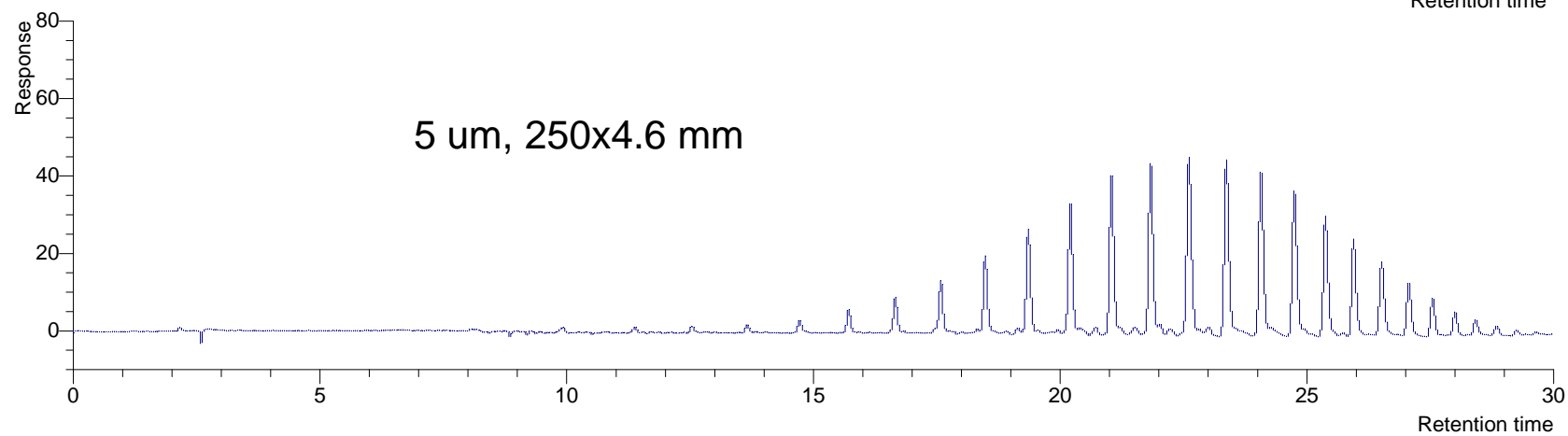
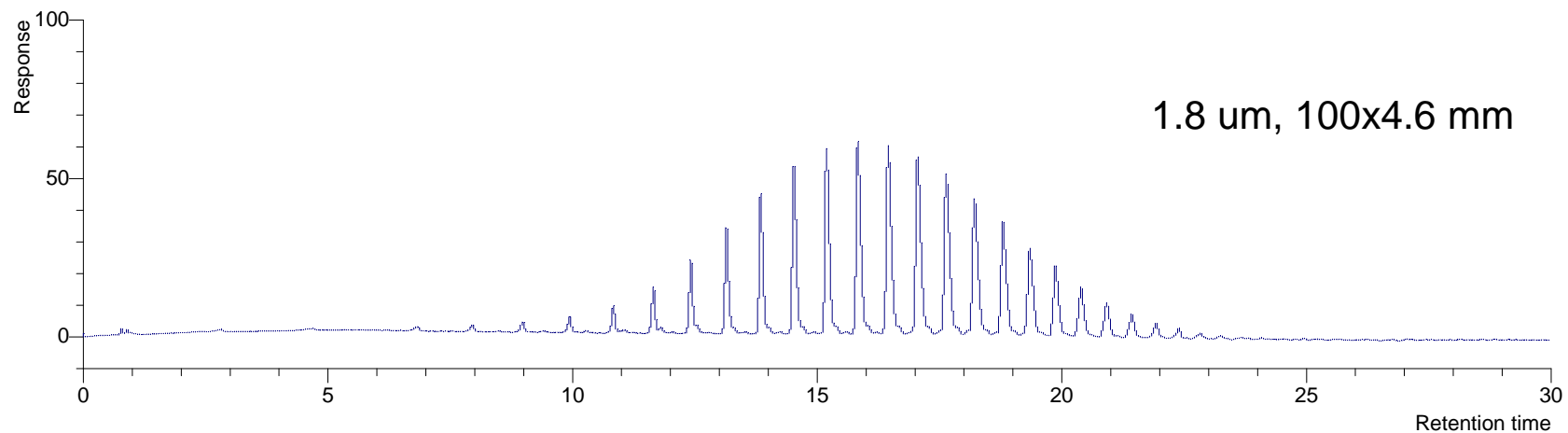


Alkylphenol ethoxylate "X100" by SFC, silica, UV at 230 nm



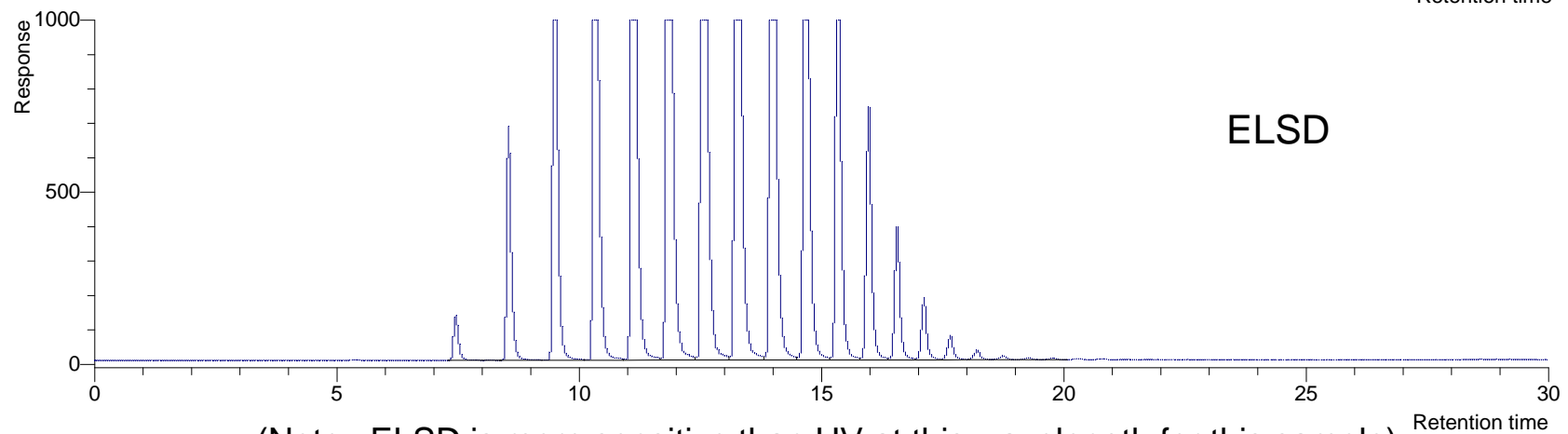
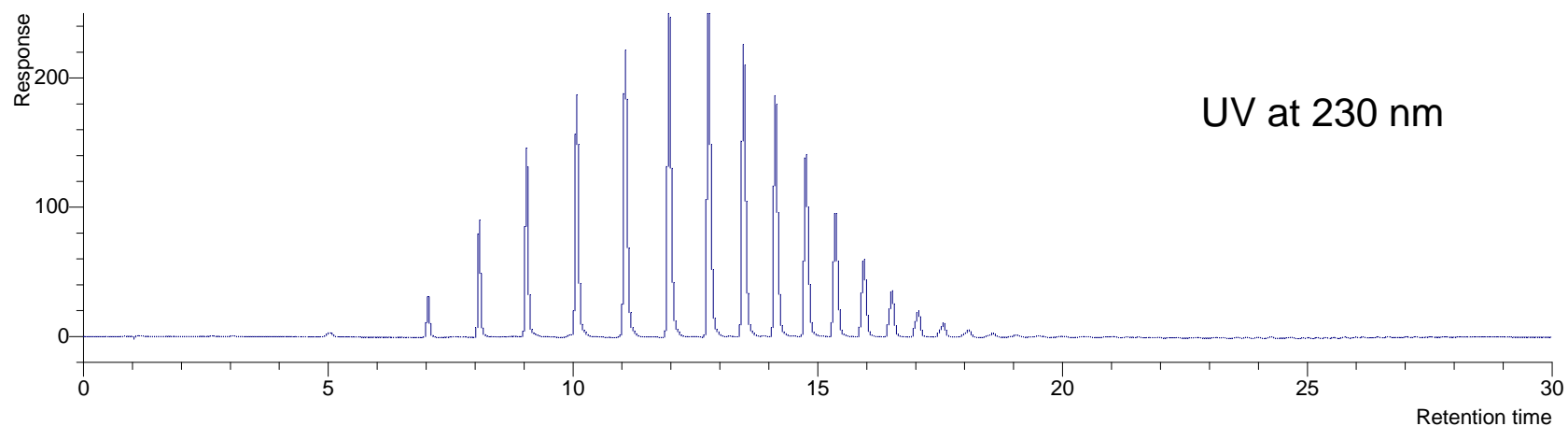


Alkylphenol ethoxylate "X165" by SFC, silica, 230 nm





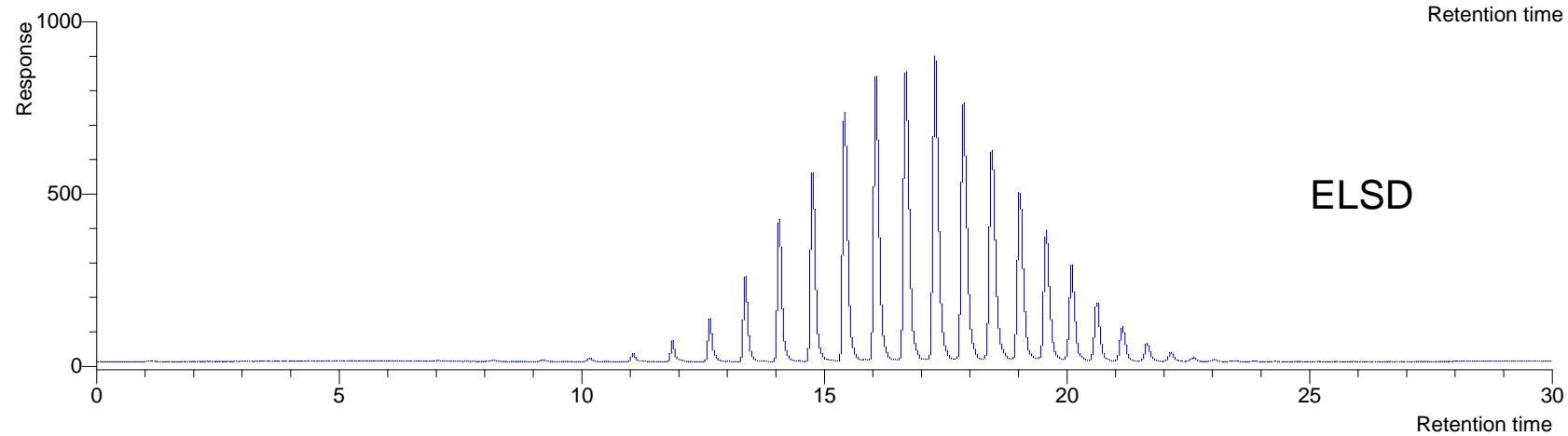
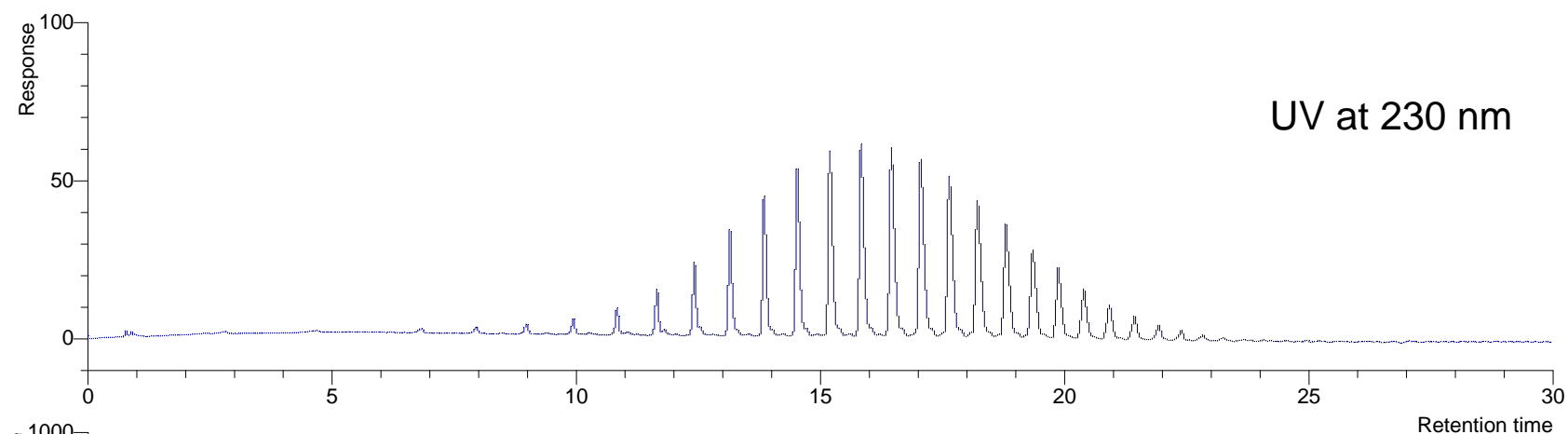
ELSD Detection Using sub 2-um Columns, "X100"



(Note: ELSD is more sensitive than UV at this wavelength for this sample)



ELSD Detection Using sub 2-um Columns, "X165"



Conclusions

- Sub 2-um particle columns can be used in SFC for separations of oligomeric materials
- If efficiency or selectivity losses occur, they are not severe at these conditions
- Significant degradation of column performance due to frictional heating or extra column volume was not observed
- Although some resolution loss due to band broadening was evident when using the ELSD detector, the losses are not significant in most cases
- Frequent column plugging was not observed with the 1.8 um particle columns used in this study
- Rapid, high efficiency separations appear possible with these columns



Advantages of sub 2-um Columns in SFC

- High resolution chromatograms at reduced analysis time appear possible
- Allows reduced mobile phase usage
- Various detectors may be used, including ELSD
- Can be used on conventional SFC instrumentation

Challenges Remaining

- Low extra column dead volumes are desirable
- Higher pressure systems would be advantageous
- Need low dwell volume, effective mobile phase mixing
- Need longer columns
- Need inert columns, efficiently packed
- Need a wider variety of column stationary phases
- Need good column to column reproducibility
- Need column reliability in SFC conditions