Recent Developments in:-

GPC/MS

High Temperature ELSD

Analysis of PET

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Overview

Coupling GPC with APCI Mass Spectrometry

- To identify the number of oligomers in a low molecular weight polystyrene sample.
- Accurately identify additives without the need for complete resolution

High Temperature Evaporative Light Scattering Detection (HTELSD)

- Refractive index detection at high temperatures in solvents such as TCB is not without challenges. HT-ELSD has undergone further developments to offer a viable alternative.

Analysing PET in Chloroform

- A novel piece of work showing how the polymer can be dissolved in HFIP and then chromatographed in Chloroform.

GPC/MS

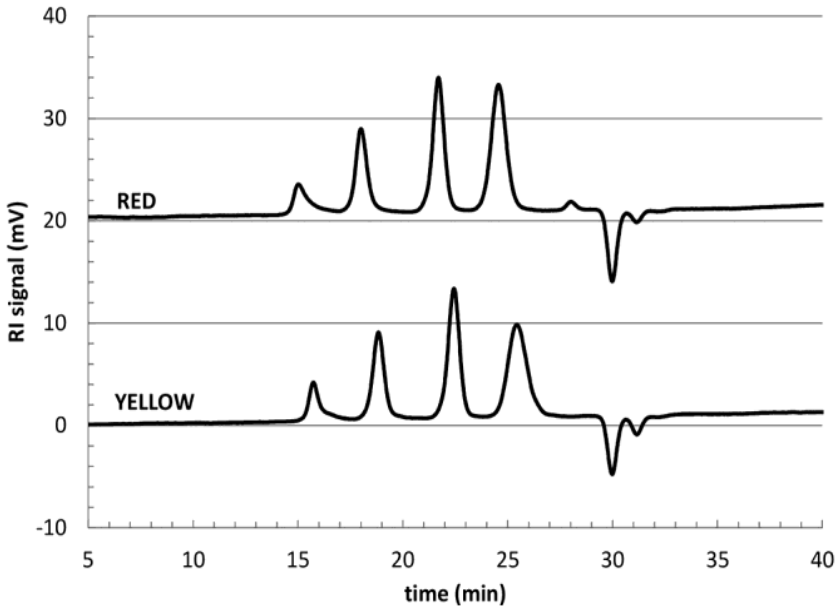
Oligomers & Additives

Introduction – Miniaturization in GPC

- Improved Resolution
- Lower Flow Rates
- Reduced Solvent Consumption

EasiVial (Red) (1.5ml) MW = 6,035,000 / 483,000 / 19,720 / 1,260

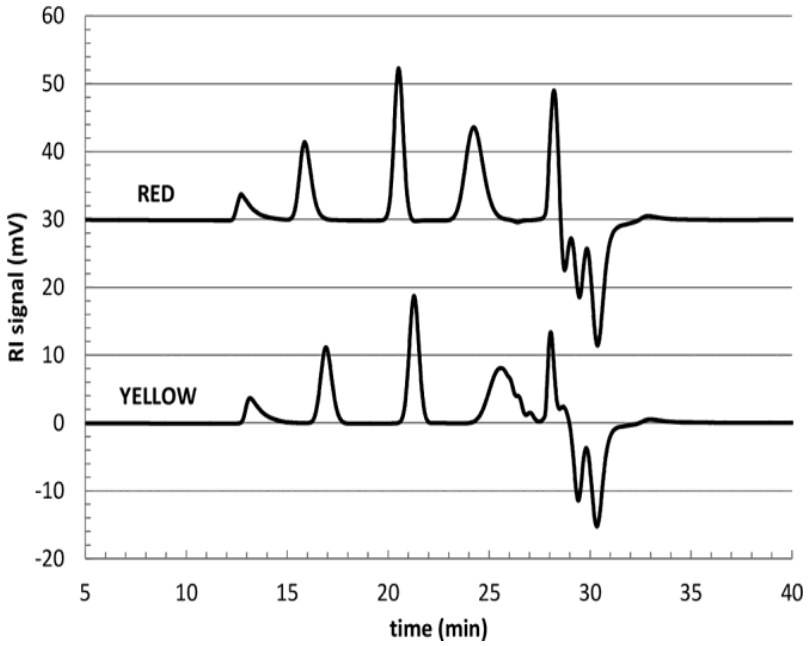
EasiVial (Yellow) (1.5ml) MW = 3,053,000 / 184,900 / 8,450 / 580



3 x 10µmMixed B columns, 300x7.5mm

Conventional RID

THF, flow rate = 1 mL/min

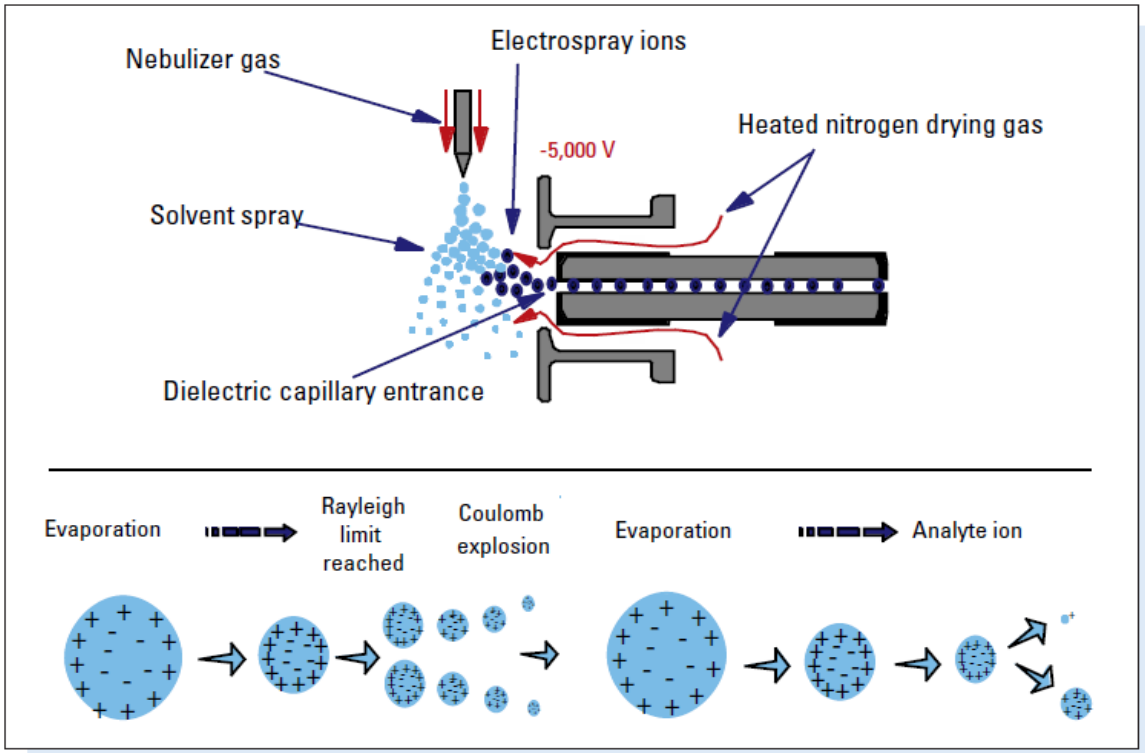


2 x PolyPore columns, 250 x 2.1mm

µRI detector

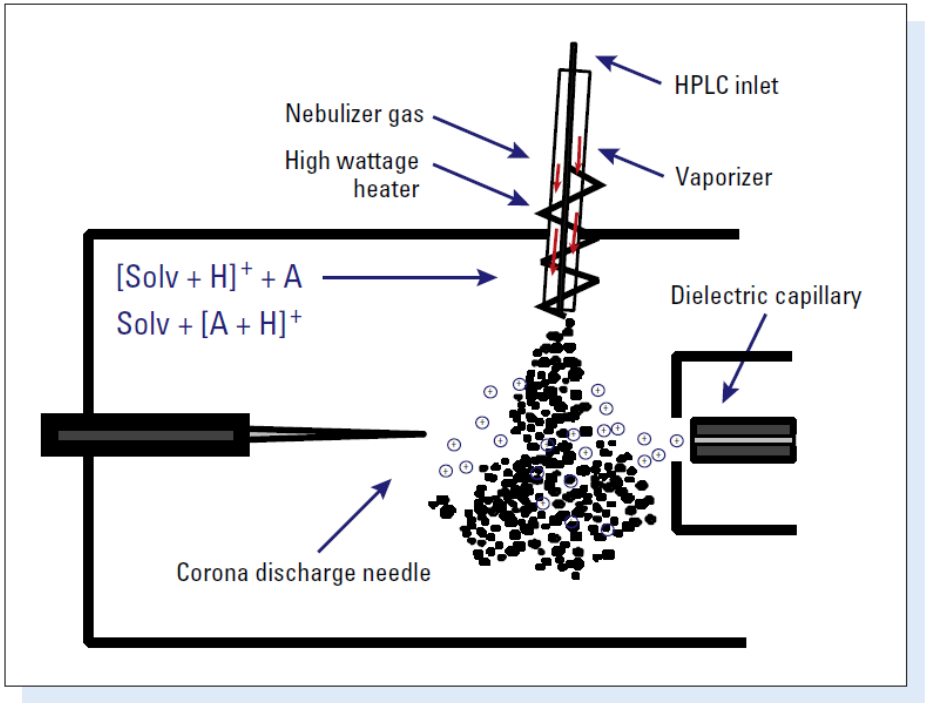
THF, flow rate = 50 µL/min

Atmospheric Pressure Ionization (API-ES)



- The possibility to use a very low solvent flow rate make 2.1mm diameter columns ideal for MS
- The possibility to use volatile solvents and isocratic conditions
- Usually, for GPC the electrospray (ES) process is used, mainly because of the possibility to have multiple ions on the higher molecular weight polymers

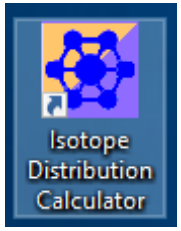
Atmospheric Pressure Chemical Ionization (APCI)



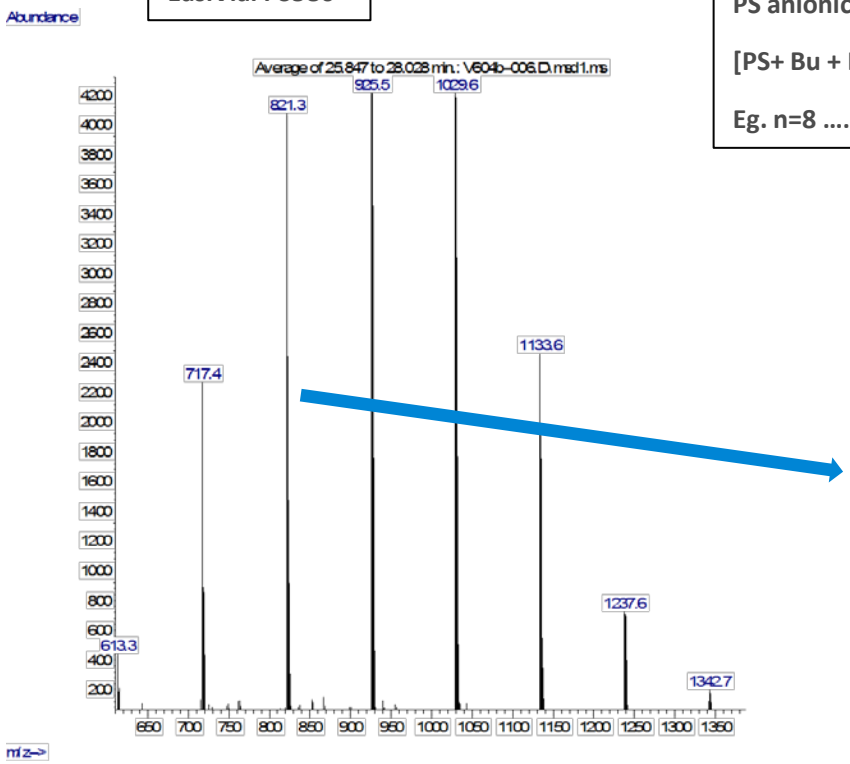
- However the API-ES interface creates multiple ions and complex MS spectra, which can prove difficult to interpret directly without deconvolution.
- APCI produces, under soft ionization conditions, only the molecular ion.
- Although the quadrupole MS with APCI is limited to m < 2000 (because z = 1), this is enough to study the oligomers and the majority of the additives

Theoretical and Measured Distribution of Anionic Polystyrene Oligomers (n=7, C60 H66)

- Chloroform is compatible with both GPC and MS
- Under APCI conditions [M+Cl]- ions are produced (SCAN mode)
- Excellent correlation between theoretical and measured distribution



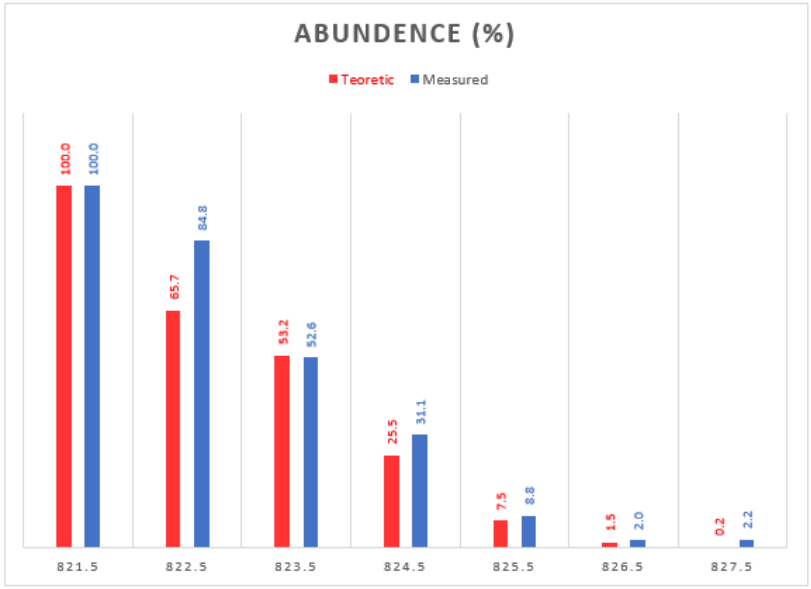
EasiVial PS580



PS anionic; styrene = 104

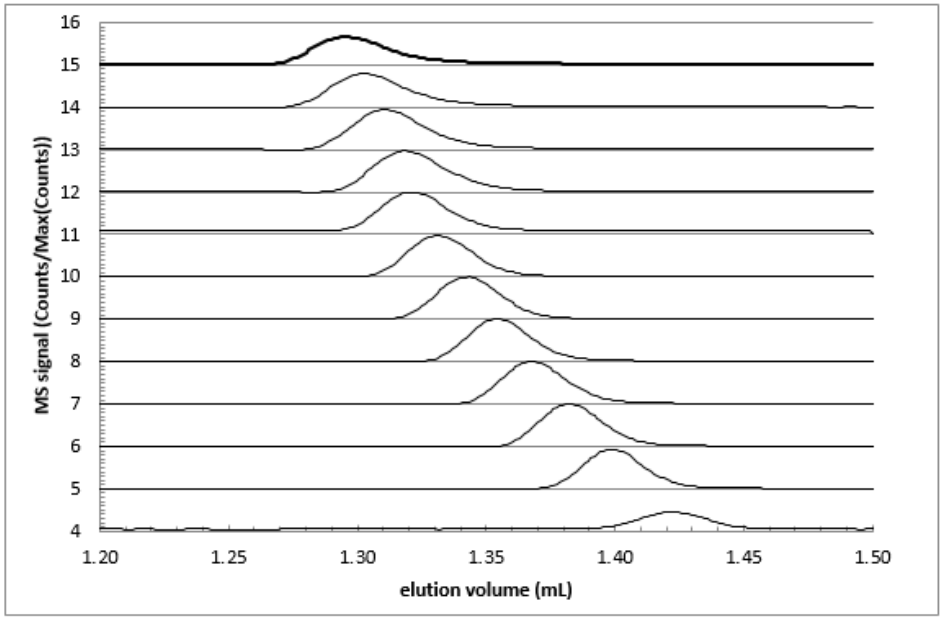
[PS+ Bu + H + Cl] = n*104 + 57 + 1 + 35

Eg. n=8 …… 821



Chromatograms Corresponding to each Oligomer

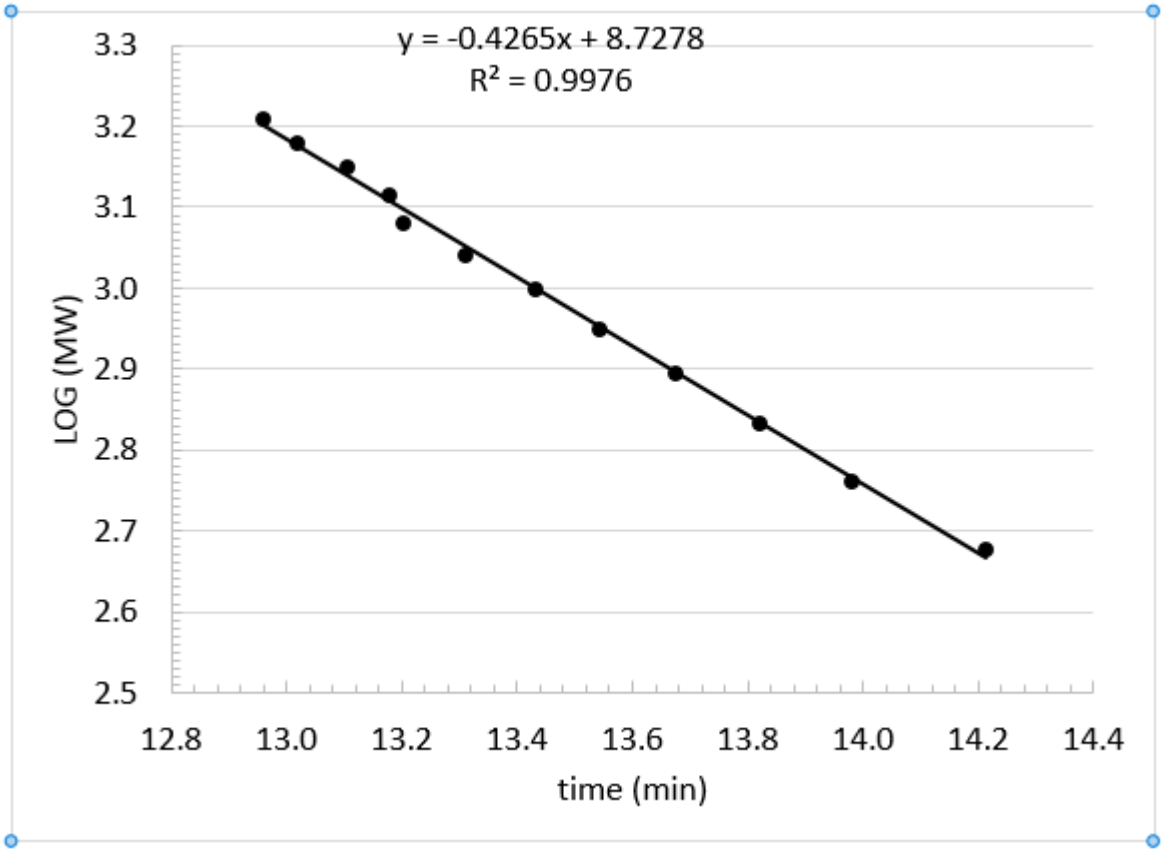
- It is possible to create specific single ion monitoring methods for each targeted molecule in a mixture (SIM Mode)
- Even without a complete separation, GPC-MS can monitor each oligomer
- The method is similar to extracting peaks when using DAD



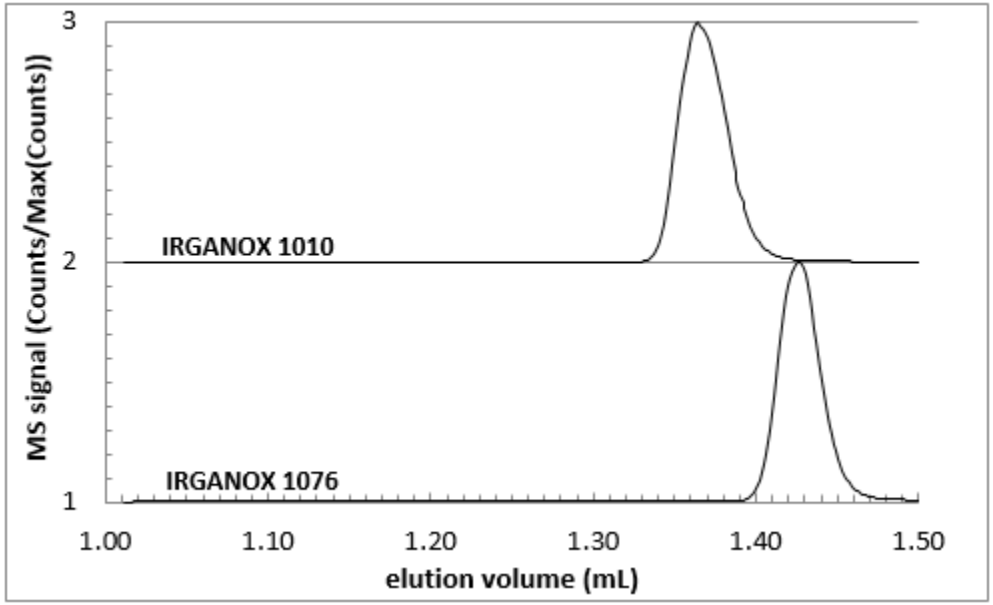
Linear Calibration Curve

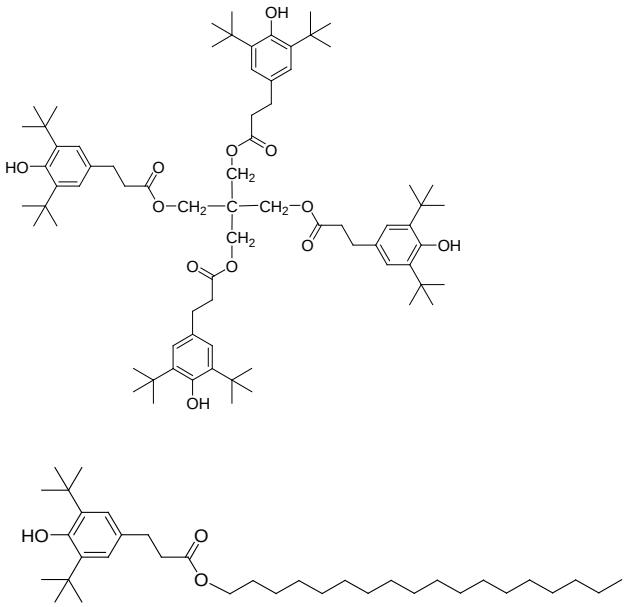
- Each oligomer can be used to create a column calibration
- Separation mechanism is true GPC

Resipore columns 250 x 2.1mm



Identifying and Quantifying Polymer Additives





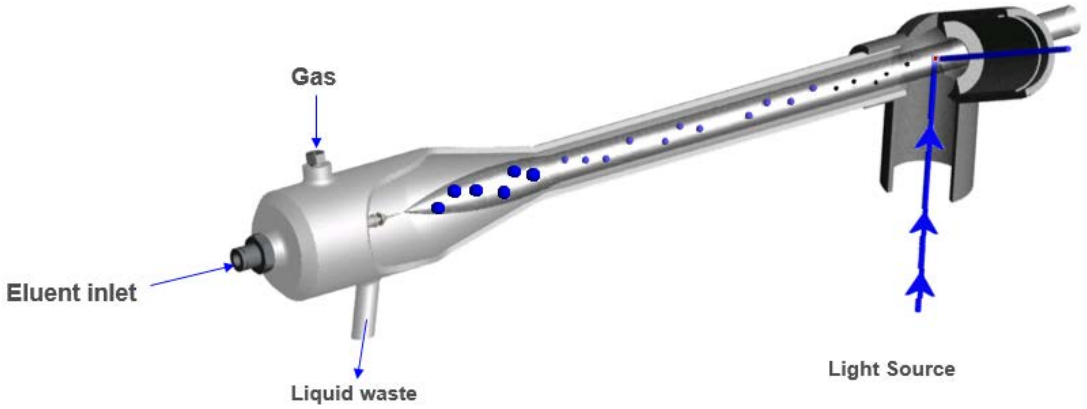
- Even in the case of low resolution separations it is possible to identify and quantify additives

High Temperature ELSD

Polyolefin Characterization

Evaporative Light Scattering (ELSD)

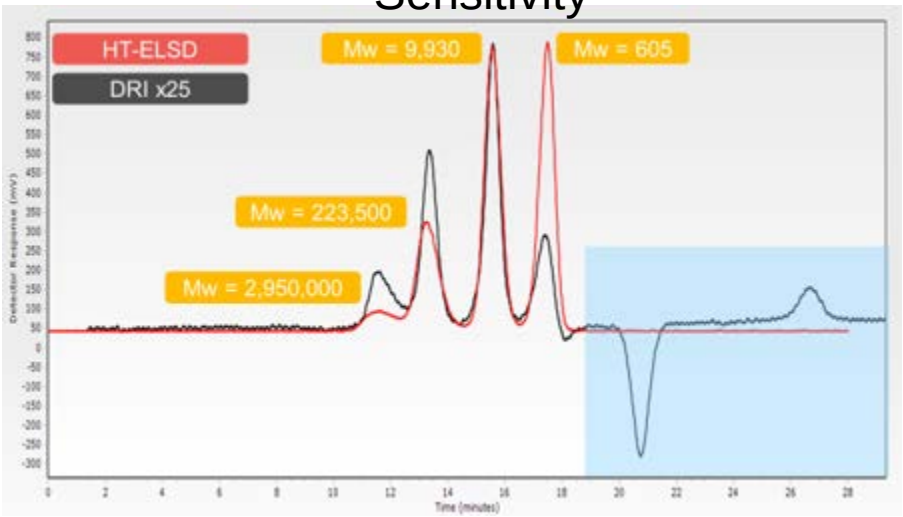
- Nebulisation
  - Liquid flow from the column is nebulised using nitrogen or air to give a plume of fine droplets containing the analyte in solution
- Evaporation
  - The liquid droplets pass into a heated zone where the solvent is removed to leave the dried analyte particles
- Detection
  - The analyte particle is subsequently irradiated with light; and the amount of light scattered by the particle is measured



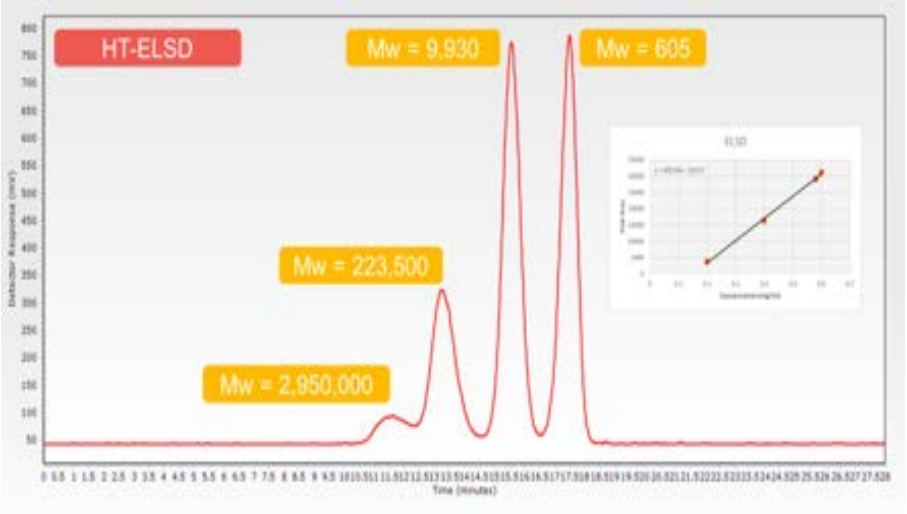
High Temperature Evaporative Light Scattering (HT-ELSD)

- ELSD is independent of any physical or chemical properties of the polymer
- Sensitivity – At least a factor of 10 higher than RID
- Accurately measures the concentration (independent of dn/dc)
- Minimal equilibration time, very stable baselines
- No solvent peaks, positive sample response

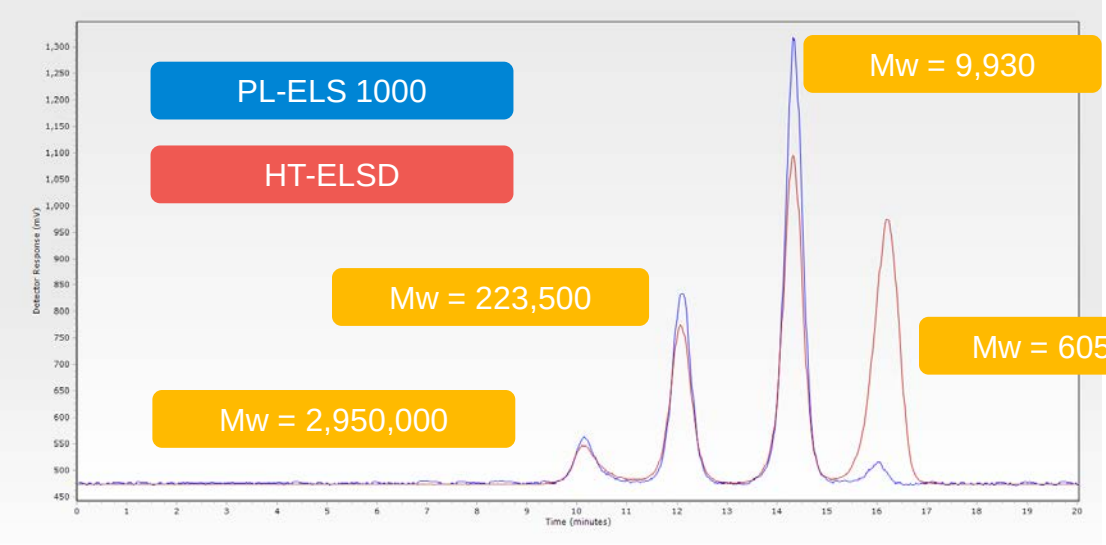
Sensitivity



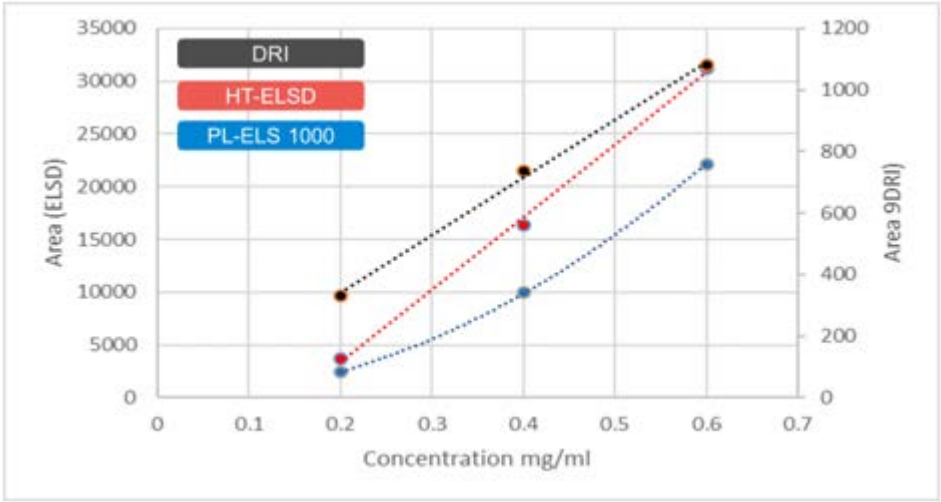
Linearity



How does it compare to its predecessor? (ELS1000)



ELS 1000 data up-scaled by a factor of 10



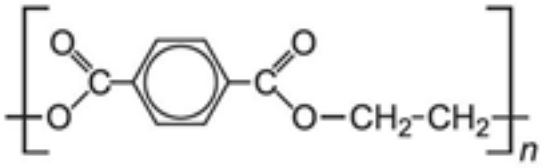
Summary Of HT-ELSD

- Superior sensitivity as compared to a DRI, making it preferable for UHMWPE samples that require very low concentration for dissolution and analysis
- Stable baseline, the removal of solvent peaks, and suitability for high temperature gradient chromatography
- Improved linearity and accuracy in the determination of molecular weights, due to a new nebulizer design, which reduces operating temperatures

Triple Detection

PET Analysis

A novel approach to characterizing PET



Polyesters are used extensively for fibers and packaging – worldwide production of PET is estimated at 40 million tons.

The mechanical and chemical resistance properties of PET make it difficult to dissolve.

GPC Analysis

M-cresol at elevated temperatures to reduce eluent viscosity

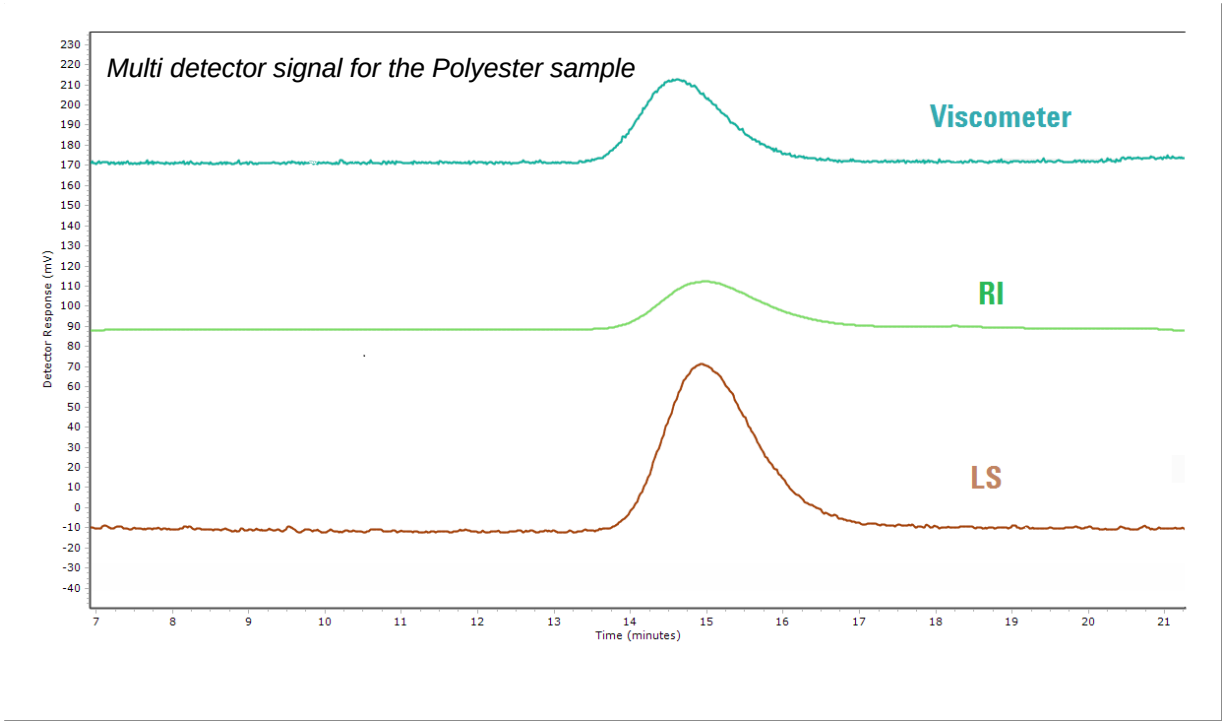
HFIP, lower temperatures, still high viscosity, handle with caution, very expensive

Dissolve the PET in HFIP, Analyze Using Chloroform

In this application we overcome these issues by initially dissolving the polymer in HFIP, but then running the analysis in Chloroform.

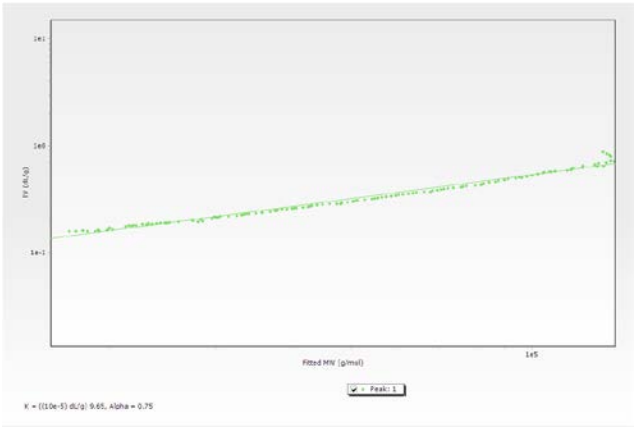
When dissolving a polymer in one solvent, but then analyzing in a different solvent, interaction with the packing material is a potential issue.

600ul of HFIP was added to 43mg of polyester sample in a 10ml flask.
Dissolution time of 3 hours, chloroform then added

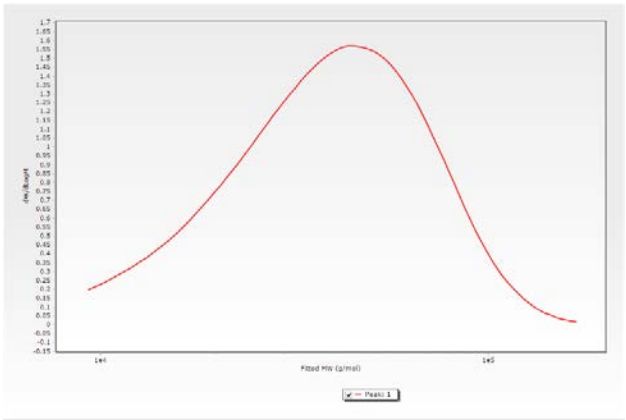


Molecular Weight Using Triple Detection

MH plot for the polyester sample



Molecular weight distribution of the polyester sample



The linear MH plot indicates that there is no change in structure across the molecular weight distribution of the PET. In addition, the slope of 0.75 suggests that the polymer is in a good solvent and has a random coil conformation.
The molecular weight (Mw) calculated by the triple detection analysis for this sample compares very well with the expected value of 45,000
The method of dissolution and analysis of the PET sample by firstly dissolving in HFIP followed by analysis in Chloroform with triple detection produces reliable molecular weight information

	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
PET Sample	43945	33099	44544	57456	70224	55772	1.3

Acknowledgements

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Any Comments

Questions?