COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY WITH UHP SEC IN THE SECOND DIMENSION FOR SEPARATION OF INDUSTRIAL POLYMERS

Elena Uliyanchenko, 27 Sept. 2016
OUTLINE

• Introduction to SABIC
• The need for multidimensional LC for polymers
• HPLC×SEC advantages and limitations
• UHPSEC in the second dimension: advantages and limitations
• Conclusions
SABIC IN NUMBERS

1976 – SABIC founded

2015 (Forbes):
3rd largest global diversified chemical company
116th biggest public company in the world

91 B$ total assets
50 B$ annual revenue

40,000 employees
50 countries

65 world-class plants worldwide
5 key geographies with innovation hubs
150 new products each year
10,640 global patents

Pictures © SABIC
SABIC’S STRATEGIC BUSINESS UNITS

CHEMICALS
- Olefins and gases
- Oxygenates
- Aromatics and chlor-alkali
- Glycols,…

POLYMERS
- Polyolefins (PE, PP)
- Polycarbonate (PC)
- Polyvinyl chloride (PVC)
- Polystyrene (PS), …

METALS
- Long steel
- Flat steel

AGRI-NUTRIENTS
- Urea
- Ammonia
- Phosphates

SPECIALTIES
- Polyphenylene ether
- Polyether imide
- PC copolymers
- Specialty film and sheet

Analytical Technology Supports all Business Units
OUR GLOBAL TECHNOLOGY AND INNOVATION CENTRES

GLOBAL CHROMATOGRAPHY TEAM WITH > 40 MEMBERS WORLDWIDE
POLYMER CHARACTERIZATION AT SABIC

- Optimization of production process
- Development of materials with new properties
- Improvement of material performance
- Understanding of degradation mechanism
- Detailed structural information
CHARACTERIZATION OF POLYMER MOLECULAR DISTRIBUTIONS

- **Molar-mass distribution**
  - Size-exclusion chromatography (SEC)
  - Hydrodynamic chromatography (HDC)

- **Chemical-composition distribution**
  - Gradient-polymer elution chromatography (GPEC)

- **Distribution of functionality**
  - Liquid chromatography at critical conditions (LCCC)

- **Molecular architecture**
  - Size-exclusion chromatography (SEC) with multiple detectors

- **Etc.**
ONE-DIMENSIONAL ANALYSIS OF PC/PC-COPOLYMER BLEND

Size-exclusion separation

Gradient liquid chromatography separation

ONLY INFORMATION ON AVERAGE MW OF THE BLEND CAN BE OBTAINED BY SEC
ONLY SEPARATION OF COMPONENTS BUT NO MW INFORMATION CAN BE OBTAINED BY GPEC
IUPAC:

**Two-dimensional chromatography** - A procedure in which parts or all of the separated sample components are subjected to additional separation steps. This can be done e.g. by conducting a particular fraction eluting from the column into another column (system) having different separation characteristics.

IUPAC Recommendations, *PAC* 65 (1993) 819
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IUPAC Recommendations, PAC 65 (1993) 819
TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY - ADVANTAGES

- Higher separation capacity (two-dimensional space)
- Visual representation of 2D sample distribution
- Great amount of information in a single analysis
- Information on mutual dependence of two distributions (for polymers)

SINGLE-DIMENSIONAL SEPARATIONS ARE NOT ABLE TO REVEAL DIFFERENCES
COMPREHENSIVE ON-LINE 2D LC

Position 1

Advantages:
• Does not require intensive manual work
• Relatively fast (within few hours)
• Automated data processing possible
• All information in a single analysis (less prone to experimental errors)

Disadvantages:
• Experimental conditions in both dimensions need to be adjusted
• Limited sample amount can be injected

Position 2
2D LC APPLICATION TO STUDY MATERIAL DEGRADATION*

*Data from Stephan Moyses (SABIC SLK, currently STC-H), ISPAC 2012 presentation
LIMITATIONS OF CONVENTIONAL 2D LC

Analysis speed
Fast SEC in 2D: 2-3 min
Loop size: <200 µL
Flow rate in 1D: <100 µL/min
Analysis time: 3-4 hrs
Polymer peak width: >10 min
Good resolution of ca 5 fractions per peak

Resolution
Fast SEC in 2D: 2-3 min
Loop size: >200 µL
Flow rate in 1D: >100 µL/min
Analysis time: 1-2 hrs
Polymer peak width < 10 min
Low resolution of < 5 fractions per peak

Solvent consumption
Fast SEC in 2D at 5 mL/min
Ca. 1 L of (organic) solvent per analysis!
### ULTRA-HIGH PRESSURE LC IN THE SECOND DIMENSION

<table>
<thead>
<tr>
<th>Fast SEC</th>
<th>APC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>3 - 10 μm</td>
</tr>
<tr>
<td>Column dimensions</td>
<td>20x50 mm</td>
</tr>
<tr>
<td>Max. pressure for the column</td>
<td>15 MPa</td>
</tr>
<tr>
<td>Extra-column variance</td>
<td>≥ 40 μL²</td>
</tr>
<tr>
<td>Column chemistry</td>
<td>Polymer based</td>
</tr>
<tr>
<td>System flexibility</td>
<td>Limited</td>
</tr>
</tbody>
</table>

\[ H = A d_p + \frac{B D_m}{u} + C \frac{d_p^2 u}{D_m} \]

- Ethylene bridges
- Divinylbenzene
- Styrene

System flexibility: Limited | High
QUESTIONS/CONCERNS

• Are the molecular weights provided by SEC and APC comparable?
• Does switching of solvents influence separation repeatability in APC?
• Do we have higher polymer degradation in APC vs SEC?
• Does APC provide better trade-off between resolution and analysis time in 2D LC in practice?
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### ARE THE MOLECULAR WEIGHT IN SEC AND APC COMPARABLE?

<table>
<thead>
<tr>
<th>Polymer type</th>
<th>SEC (12 min)</th>
<th>APC (6 min)</th>
<th>Fast APC (1 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn (Da)</td>
<td>Mw (Da)</td>
<td>PD</td>
</tr>
<tr>
<td>PC</td>
<td>14885</td>
<td>34138</td>
<td>2.29</td>
</tr>
<tr>
<td>PEI</td>
<td>19277</td>
<td>44892</td>
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<tr>
<td>PPE</td>
<td>22204</td>
<td>55680</td>
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<tr>
<td>PBT</td>
<td>38177</td>
<td>113660</td>
<td>2.98</td>
</tr>
</tbody>
</table>

- The Mw and Mn data measured by SEC and APC are statistically different
- APC provided stable response (RSD for Mw < 1%)
- The data comparison was found to be suitable for 2D LC experiments
• Are the molecular weights provided by SEC and APC comparable?

• **Does switching of solvents influence separation repeatability in APC?**

• Do we have higher polymer degradation in APC vs SEC?

• Does APC provide better trade-off between resolution and analysis time in 2D LC in practice?
APC SYSTEM AND COLUMNS ROBUSTNESS

Polycarbonate samples regularly injected after measuring other polymers at different column temperatures and with different solvents.

**Solvents previously run**
- THF
- DCM
- CHCl$_3$ + DBA
- CHCl$_3$ + HFIP
- 100% HFIP
- CHCl$_3$ + HFIP, DCM
- CHCl$_3$ + HFIP + TFA
- CHCl$_3$ + DBA + butanol
- CHCl$_3$ + HFIP + FA
- CHCl$_3$ + DBA
- CHCl$_3$ + HFIP + butanol

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RSD ~5%
QUESTIONS/CONCERNS

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POLYMER DEGRADATION

Study of PS degradation in UPLC

- Polymers were injected on UPLC column at different flow rates, collected and re-injected
- No significant degradation of PS with Mw up to ca 3 MDa at common conditions
- The onset of degradation was only slightly lower that reported for SEC

NO DEGRADATION IS EXPECTED FOR MOST POLYMERS UP TO 2 MDa (AVAILABLE SEPARATION RANGE OF APC)

QUESTIONS/CONCERNS

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• Does switching of solvents influence separation repeatability in APC?

• Do we have higher polymer degradation in APC vs SEC?

• **Does APC provide better trade-off between resolution and analysis time in 2D LC in practice?**
APC VS FAST SEC COLUMNS – PS STANDARDS

**Fast SEC**
- Column: 20 x 50 mm, SDV Linear M, 5 µm
- Flow rate 5 mL/min, $t_0 = 2.7$ min

**APC**
- Columns: APC XT 125 + APC XT 450, 4.6 x 75 mm, 2.7 µm
- Flow rate 2 ml/min, $t_0 = 1.25$ min

### Peak Resolution

<table>
<thead>
<tr>
<th></th>
<th>Red Std</th>
<th>Mw, kDa</th>
<th>R</th>
<th>Yellow Std</th>
<th>Mw, kDa</th>
<th>R</th>
<th>Green Std</th>
<th>Mw, kDa</th>
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<tbody>
<tr>
<td>Red Std</td>
<td>990</td>
<td>1.24</td>
<td></td>
<td>126</td>
<td>1.20</td>
<td></td>
<td>19.5</td>
<td>1.18</td>
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<tr>
<td></td>
<td>126</td>
<td>1.20</td>
<td></td>
<td>74.8</td>
<td>1.34</td>
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<td>1.26</td>
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<tr>
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<tr>
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<td>2.93</td>
<td>1.32</td>
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<th>R</th>
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<th>Mw, kDa</th>
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<tbody>
<tr>
<td>Red Std</td>
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<td>2.51</td>
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</tr>
</tbody>
</table>

- $R > 1.5$
- $R > 2.5$
CHROMATOGRAPHIC RESOLUTION IN SEC

\[ R = \frac{\ln\left(\frac{M_2}{M_1}\right)}{2D_2(\sigma_1 + \sigma_2)} \approx \frac{\Delta \ln M}{4\sigma D_2} \]

- \( M_1 \) and \( M_2 \) – polymer molar masses
- \( \sigma \) – peak standard deviation
- \( D_2 \) – slope of the calibration curve

CALIBRATION CURVES FOR FAST SEC AND APC

Fast SEC column – mixed bed linear M: MW range 100-1000000
APC – combination of two single pore-size columns of 125 Å and 450 Å, MW range: 1000 - 400000

SELECTIVITY (D) IS ONLY SLIGHTLY BETTER FOR APC COLUMN
PEAK STANDARD DEVIATION IN SEC

\[ \sigma^2_{observed} = \sigma^2_{PDI} + \sigma^2_{chrom} + \sigma^2_{extra-column} \]

Band-broadening due to polymer Mw distribution: desired contribution

Band-broadening on the chromatographic column

Band-broadening in the extra-column system volume

Depends on selectivity

Depends on the stationary phase, mobile phase, analyte

Depends on the instrument
H VS U CURVE FOR TOLUENE

\[ H_{\text{observed}} = H_{\text{chrom}} + H_{\text{extra-column}} \]

EXTRA-COLUMN CONTRIBUTION IS THE SAME AS THE SAME SYSTEM USED
APC CAN OFFER UP TO 50% IMPROVEMENT IN PLATE HEIGHT AT MUCH FASTER ANALYSIS TIMES
# Plate Numbers for Toluene

## Fast SEC

<table>
<thead>
<tr>
<th>Flow rates, mL/min</th>
<th>N (5 cm column)</th>
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<tr>
<td>0.5</td>
<td>362</td>
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<tr>
<td>1</td>
<td>565</td>
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<tr>
<td>2</td>
<td>775</td>
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<td>908</td>
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<tr>
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<td>5.5</td>
<td>940</td>
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<td>6</td>
<td>989</td>
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</table>

## APC

<table>
<thead>
<tr>
<th>Flow rates, mL/min</th>
<th>N (15 cm column)</th>
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</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2828</td>
</tr>
<tr>
<td>0.4</td>
<td>4134</td>
</tr>
<tr>
<td>0.6</td>
<td>4906</td>
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<td>0.8</td>
<td>5342</td>
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<tr>
<td>1.4</td>
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<td>1.6</td>
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<tr>
<td>1.8</td>
<td>4809</td>
</tr>
<tr>
<td>2</td>
<td>4818</td>
</tr>
</tbody>
</table>
CALCULATED $h$ vs. $v$ CURVES FOR SEC

Is the polymer behavior comparable to toluene?

\[ \lambda = \frac{R_{\text{polymer}}}{R_{\text{pore}}} \]

The slope of $h$ vs. $v$ curves depends on the analyte / pore size ratio $\lambda$. The chromatographic band broadening has maximum at $\lambda \approx 0.8$. The pore size of the two columns in different!
DEPENDENCE OF H VS U CURVE ON THE MOLECULAR WEIGHT

Depending on the Mw fast SEC or APC show better performance

Note: APC has somewhat better selectivity and therefore higher PDI contribution
REAL CONDITIONS IN D2 – HIGH INJECTION VOLUME

For PSS column extra-column contribution in total peak widths is small and does not significantly affect plate number.

For APC column extra-column contribution in total peak widths is large.

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For APC column extra-column contribution in total peak widths is large.
SUB-CONCLUSIONS

• APC can offer a better trade-off between resolution and analysis time
• The benefits of APC over fast SEC decrease with increasing injection volume in D2 and change with polymer molecular weight
• APC is especially advantageous for high-resolution 2D LC separations
HPLC×APC IN PRACTICE – HIGH-RESOLUTION SEPARATION OF SAN POLYMER

HPLC×SEC

2.5 min slices

6 fractions across 1st-dimension peak

HPLC×APC

1 min slices

14 fractions across 1st-dimension peak

*HPLC×SEC chromatogram courtesy Stephan Moyses (SABIC SLK, currently STC-H)
HPLC×APC IN PRACTICE – ANALYSIS OF PC COPOLYMER BLEND

PC homopolymer

1OH

2OH

copolymer oligomers

Fully end-capped

PC copolymer

PC-OLIGOMERS ARE WELL-RESOLVED
HPLC×APC AND HPLC×SEC IN PRACTICE – ANALYSIS OF PC COPOLYMER BLEND

HPLC×APC

PC homopolymer

PC copolymer

oligomers

HPLC×SEC

30 min

PC homopolymer

PC copolymer

1.5 hrs
CONCLUSIONS

Fast SEC

Advantages:

• Legacy stationary phase, minimal differences in Mw expected compared to “normal” SEC
• Available in broad pore size range
• Less sensitive to high injection volumes in D2

Disadvantages:

• High solvent consumption
• Short columns – low plate number
• Difficult to exchange solvent
• Lower sensitivity due to high dilution

APC

Advantages:

• Fast separations (e.g. down to 1 min)
• Low solvent consumption
• Higher sensitivity due to lower dilution
• Flexible: solvent can be easily replaced

Disadvantages:

• Mw data can differ from legacy SEC methods
• Limited pore sizes available, no linear columns
• Sensitive to high injection volumes in D2
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• WATERS and PSS

Thank you all!
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