What can we do for you?

Focus areas: By technique

Separations

- Chromatography (LC)
- Field Flow Fractionation (FFF)
- CRYSTAF, TREF, CEF

Spectroscopy

- Infrared
- Raman
- NMR

Thermal

- DSC
- TGA
- Pyrolysis GC-MS

Imaging

- Infrared-microscopy
- Raman-microscopy
- Polarized light microscopy
- Electron Microscopy

THE POWER OF LIQUID CHROMATOGRAPHY

Photo: Fraunhofer

Fraunhofer

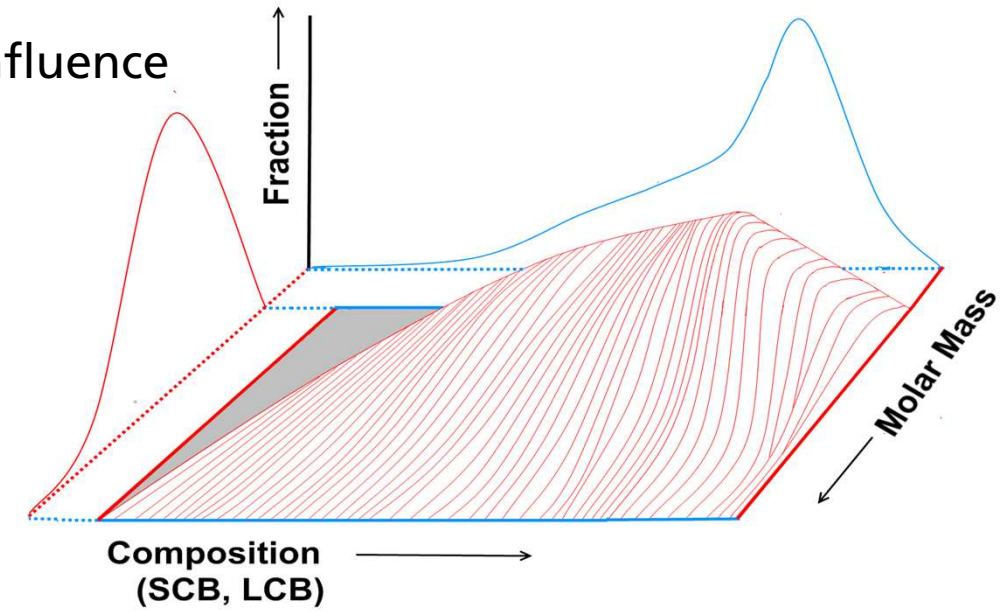
Challenges in polymer analysis

Multivariate molecular distribution

- Polymers show distributions in various molecular metrics e.g.: molar mass, architecture, end-capping
- Complex molecular properties influence macroscopic behavior

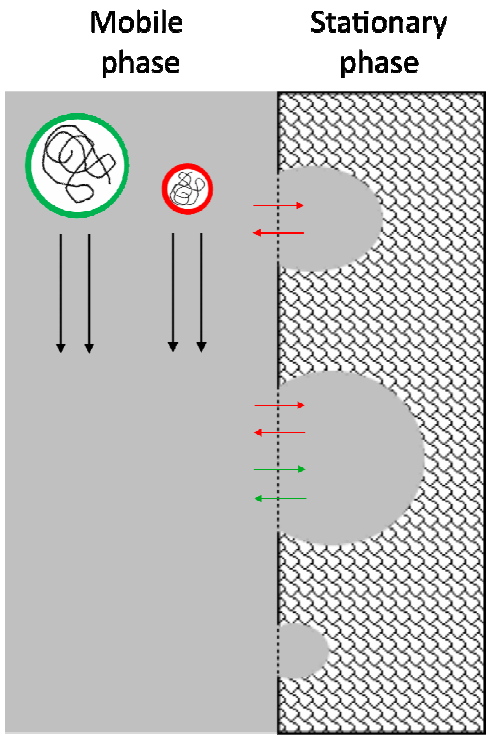
➔ Polymer represent highly complex materials

➔ No characterization techniques that allow a simultaneous and comprehensive analysis of all molecular metrics



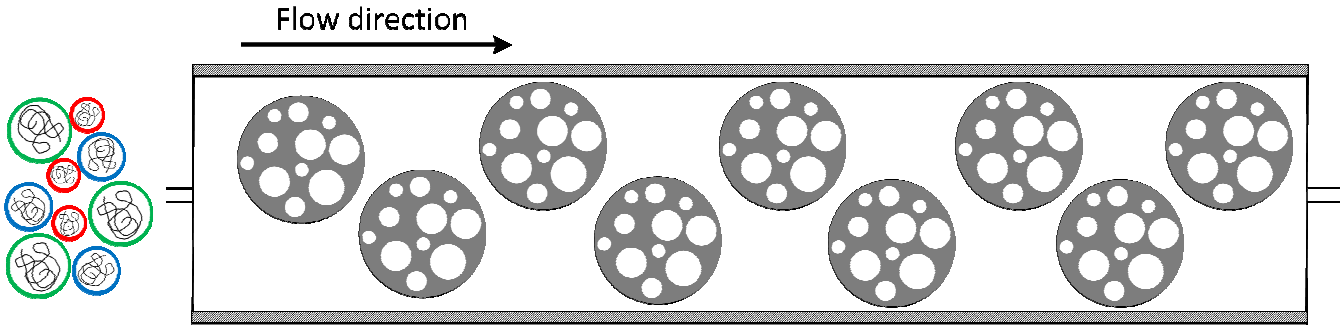
Size-exclusion chromatography

Basic separation principle



- Size-exclusion effect: macromolecules permeate in pores of the stationary phase
- Larger molecules are partially excluded from pores
- ➔ Inverse sieve effect based on entropic processes

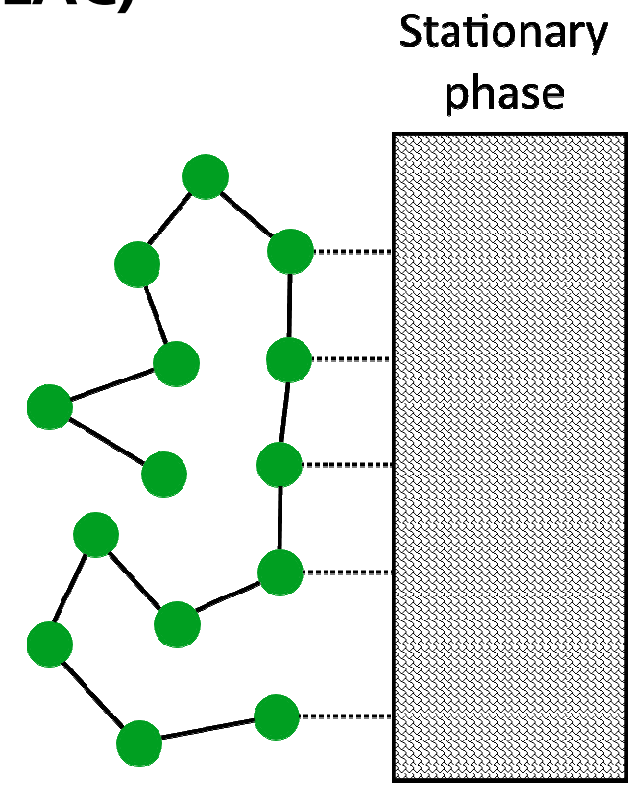
➡ molar masses↑ → elution volume↓

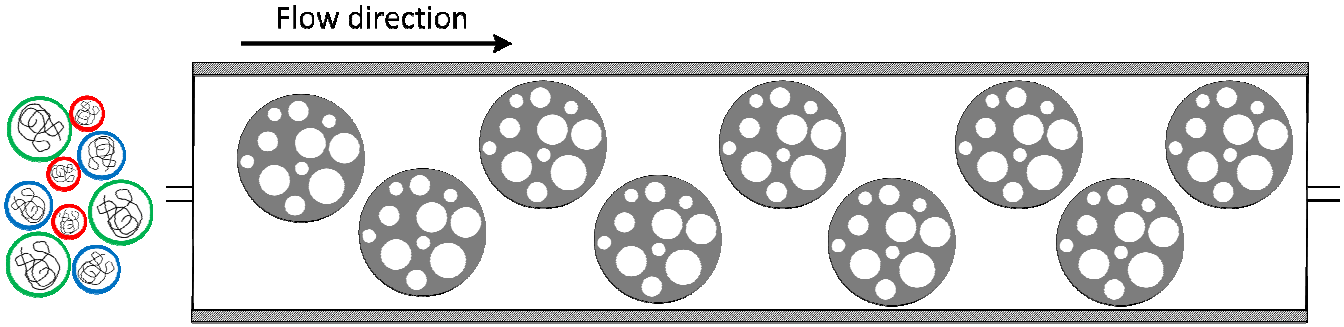


Liquid adsorption chromatography (LAC)

Basic separation principle

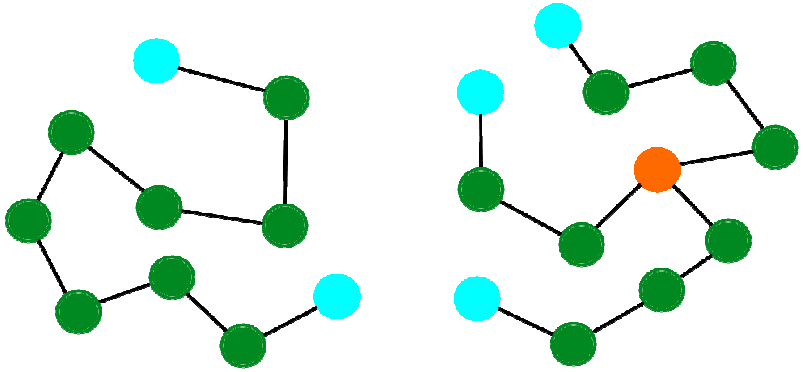
- Each repeating unit can interact with column
- molar masses↑ → elution volume↑
- Separation according to molar mass and chemical composition



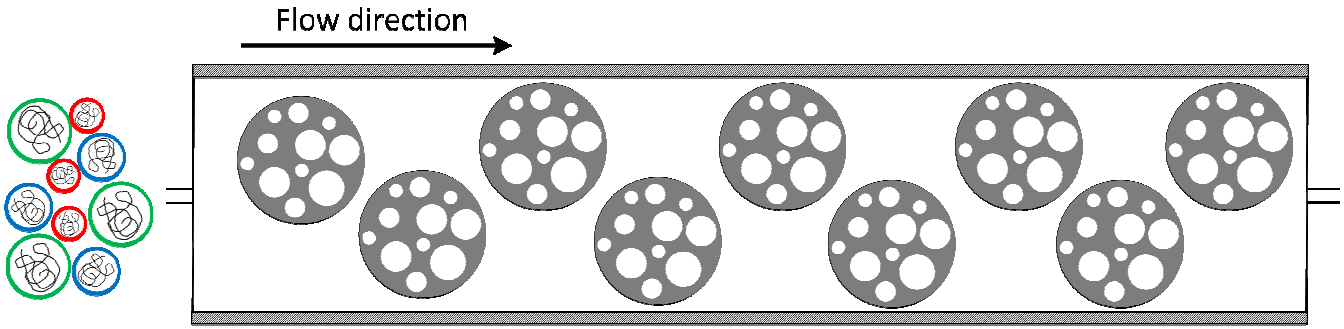


Liquid chromatography under critical conditions

Basic separation principle

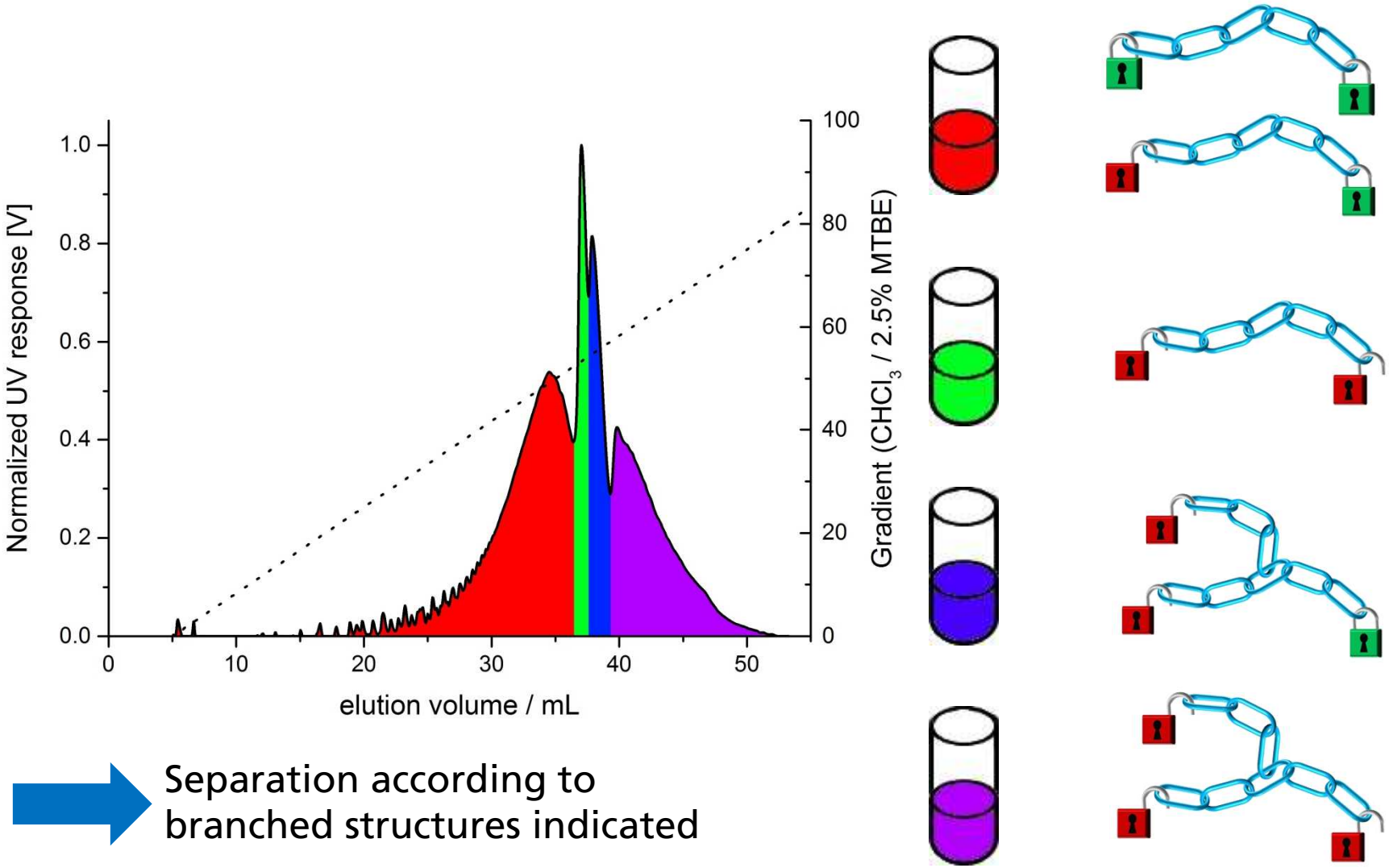


- Size-exclusion effects and interactions are balanced out
- Polymer backbone becomes “invisible”
- Separation according to end-groups or branching units is possible
- Separation is possible according to branching based on end-group moiety or branching units of the polymer



Solvent gradient at near-critical conditions (SG-NCC)

Fractionation



Separation according to branched structures indicated

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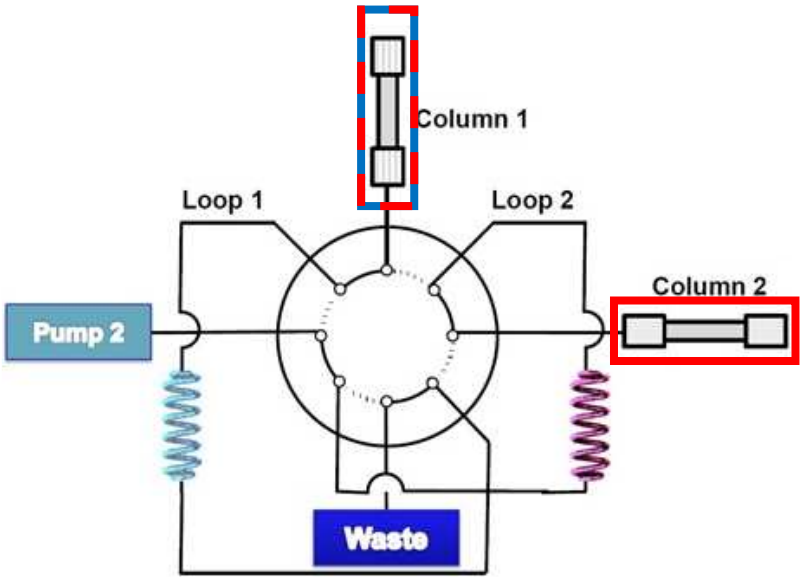
Two-dimensional liquid chromatography (2D-LC)

- 1D: Solvent gradient at near-critical conditions (SG-NCC)
- 2D: Size-exclusion chromatography (SEC)
- Improvement in separation: **chemical structure** and **molar mass**

➔ Comprehensive analysis of branched structures



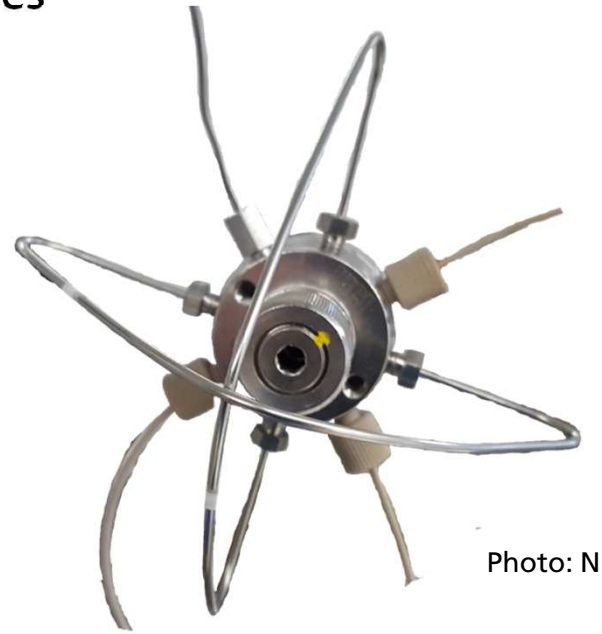
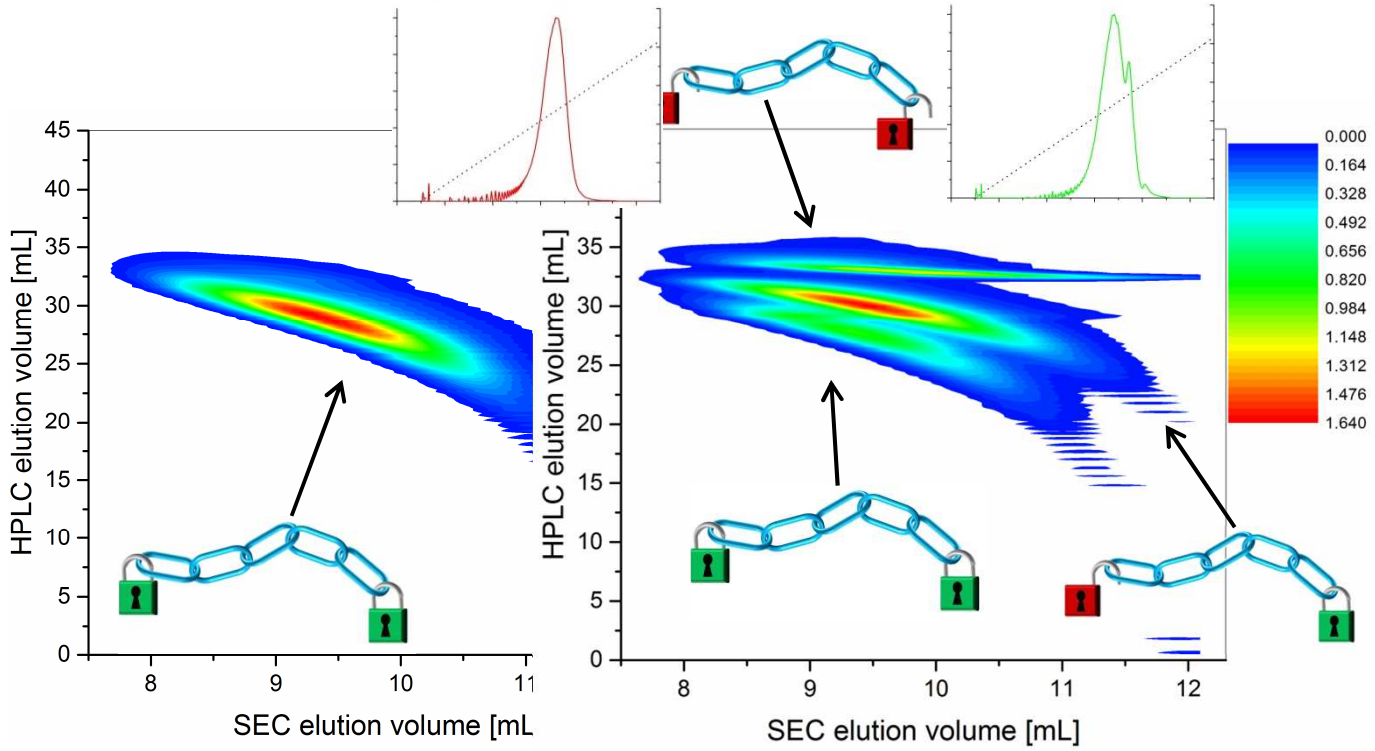


Photo: N. Apel

Two-dimensional liquid chromatography (2D-LC)

End-capped + **linear** **Un**-capped + **linear**



Complete separation according to end-groups

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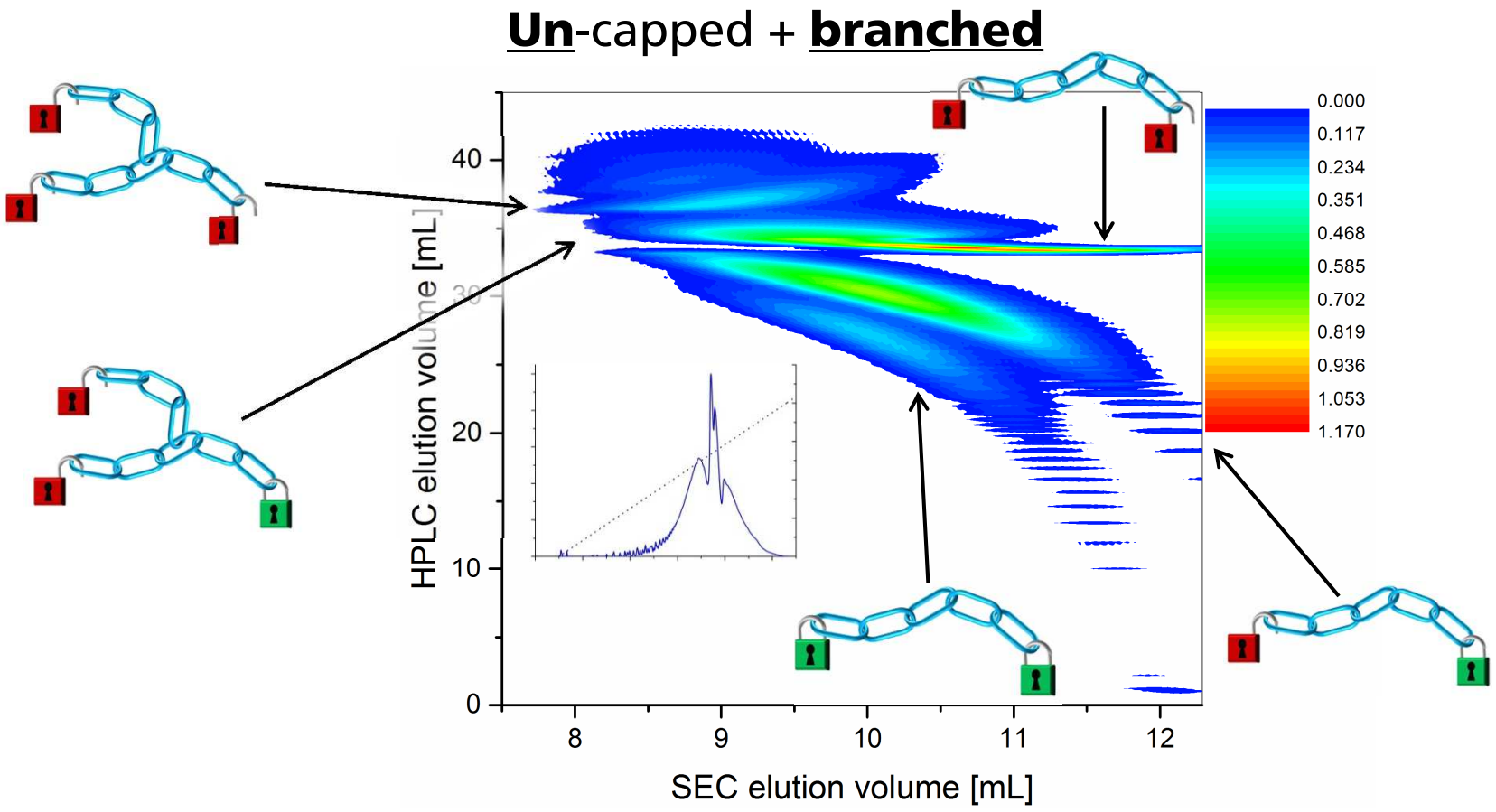
Two-dimensional liquid chromatography (2D-LC)



Separation according to branched structures

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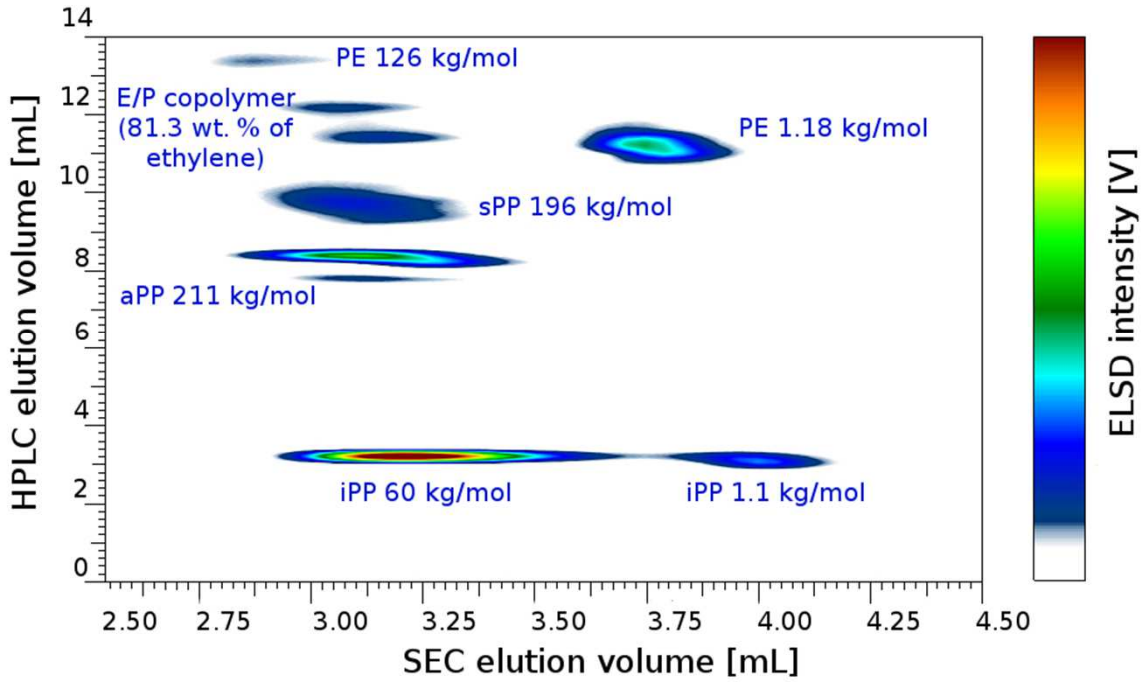
HT 2D-LC of polyolefins



HPLC: Hypercarb™, 1-decanol → TCB, 0.1 mL/min, 140 °C

SEC: PL Rapide™ H, TCB, 2.5 mL/min, 160 °C

A. Ginzburg, T. Macko, V. Dolle, R. Brüll, *J. Chromatog. A* **2010**, 1217, 6867

A. Ginzburg, T. Macko, V. Dolle, R. Brüll, *Eur. Polym. J.*, **2011**, 47, 319

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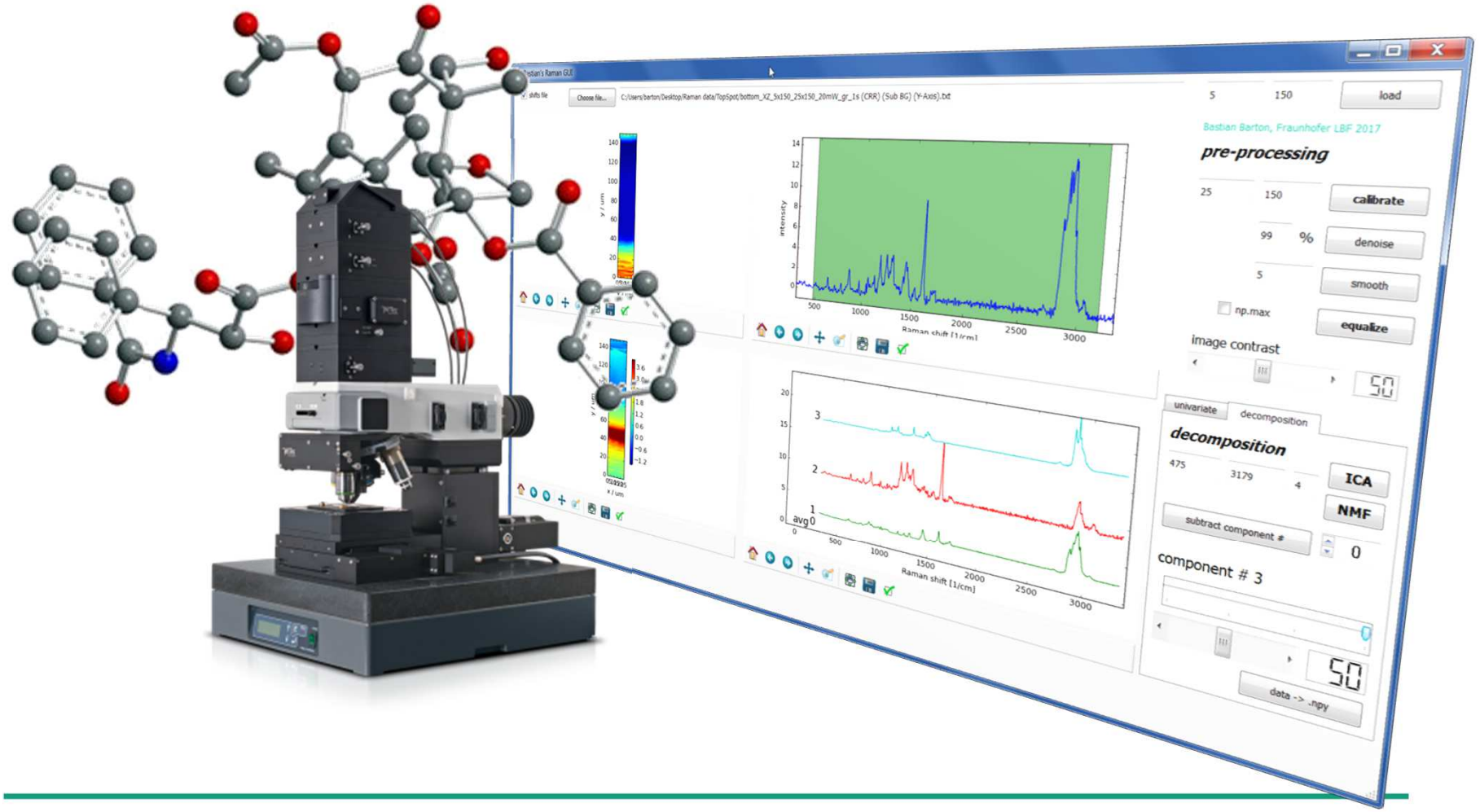
What liquid chromatography can do for you:

- TD-SEC: Monitoring of branching along the molar mass distribution
- SG-NCC: Separation according to end-capping level and branching
- 2D-LC: Individually separated linear and branched end-group species
- 2D-LC with TD-SEC: Detailed determination on branching parameters for individual branched species

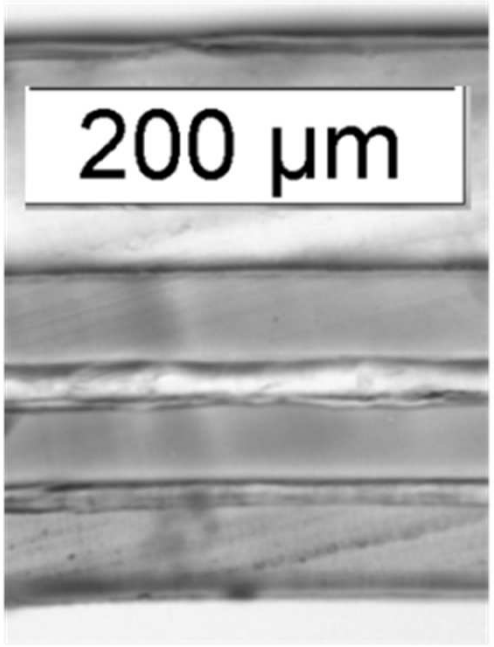
HIGH RESOLUTION CHEMICAL MICROSCOPY OF INDUSTRIAL POLYMERS



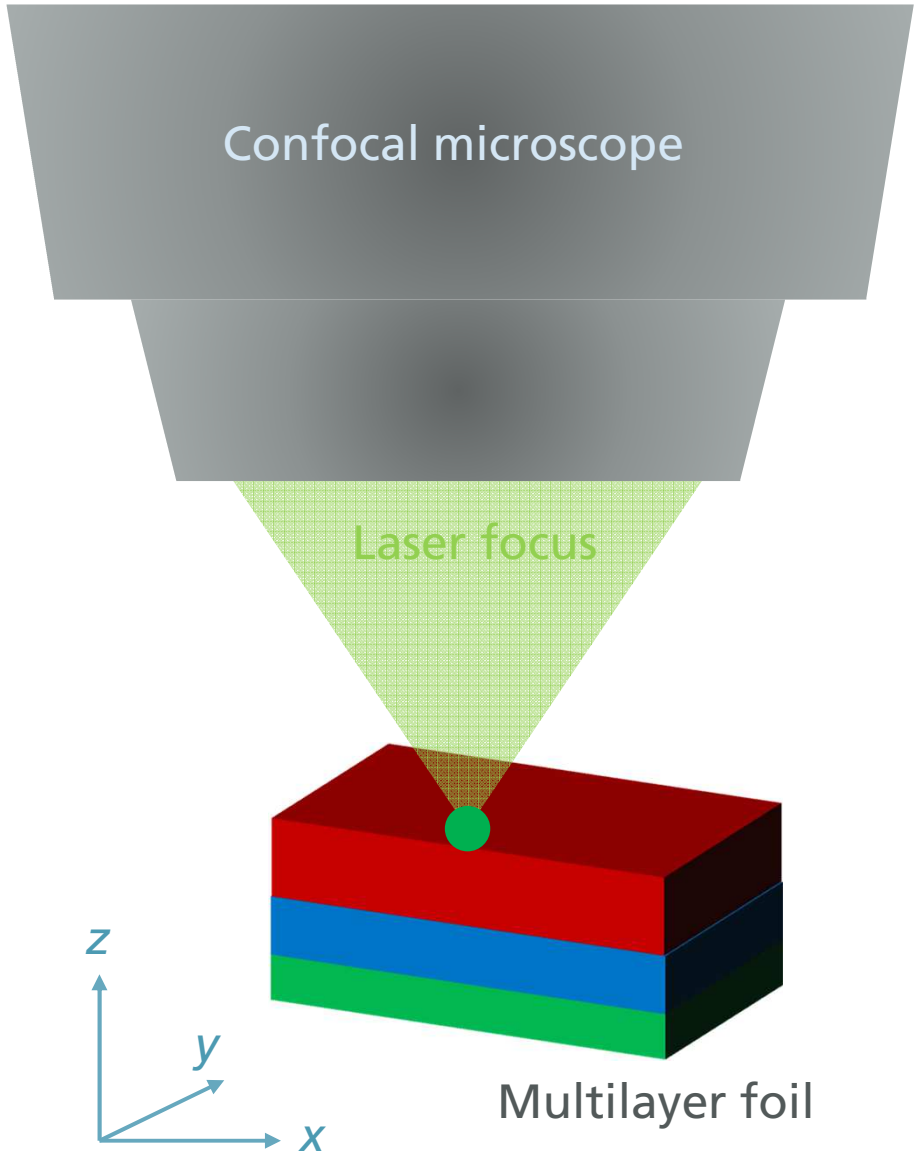
Analyzing multilayer foils by confocal Raman microscopy

- Resolution < 1 µm in *xyz*
- Layers are identified by their polymer chemistry
- Layer thickness, thickness variations, distortions, intermixing,… can be mapped
- Adhesives can be identified and their distribution mapped
- No need for microtome sectioning

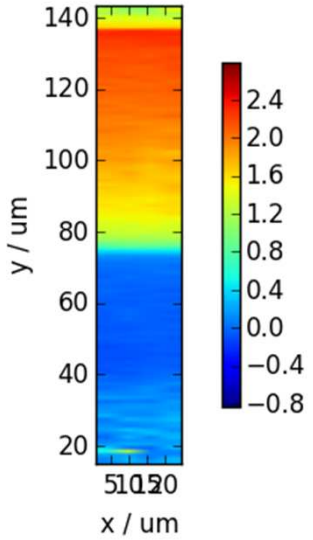
  → no mechanical artifacts
- Even the morphology of individual layers can be mapped, e.g. semi-crystalline areas



Light microscopy of microtome cross-section



Raman XZ image



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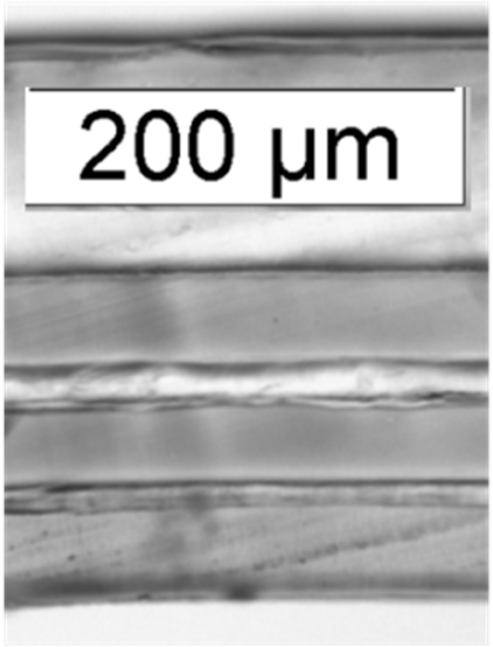
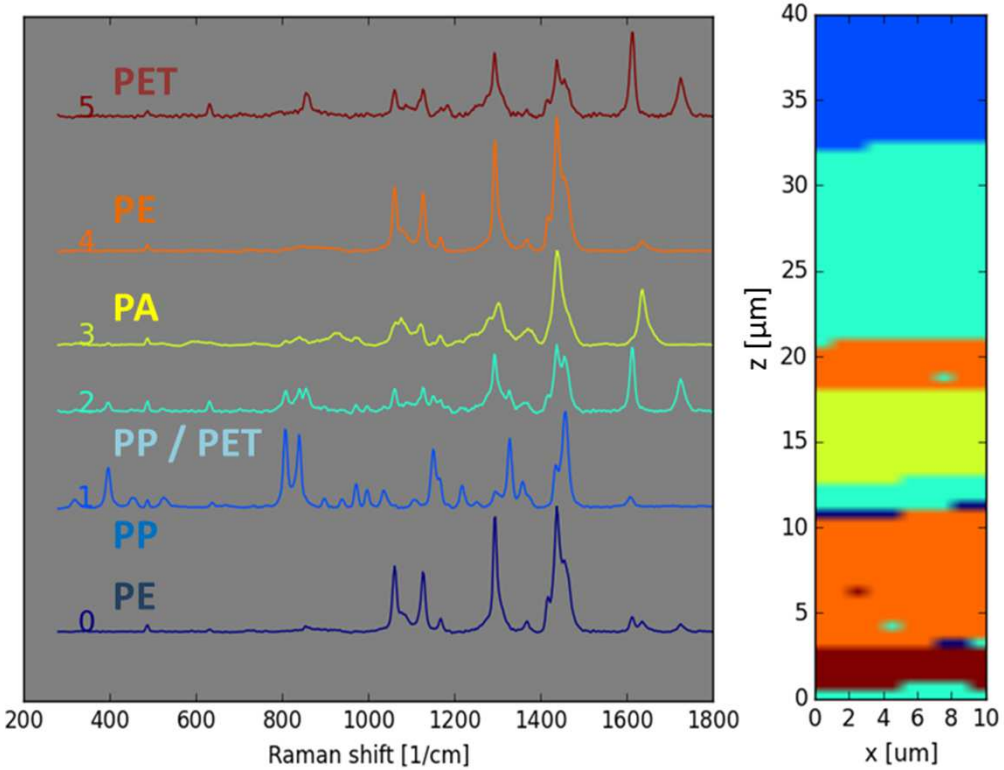
Chemical imaging XZ imaging

of a complex (7-layer) multilayer packaging foil



Light microscopy of microtome cross-section



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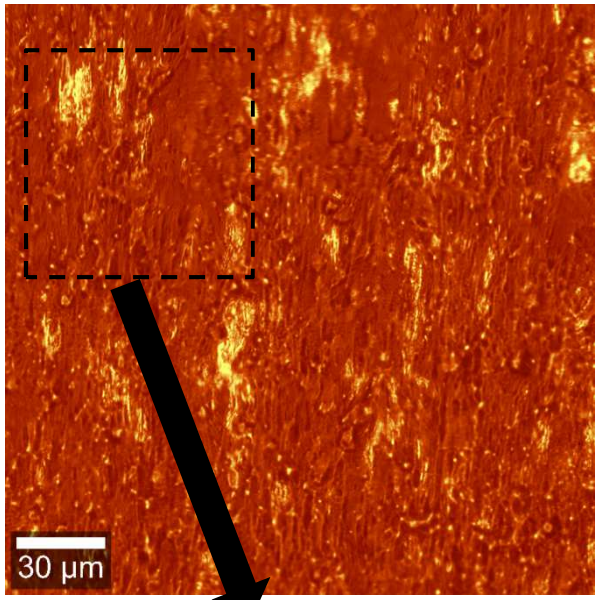
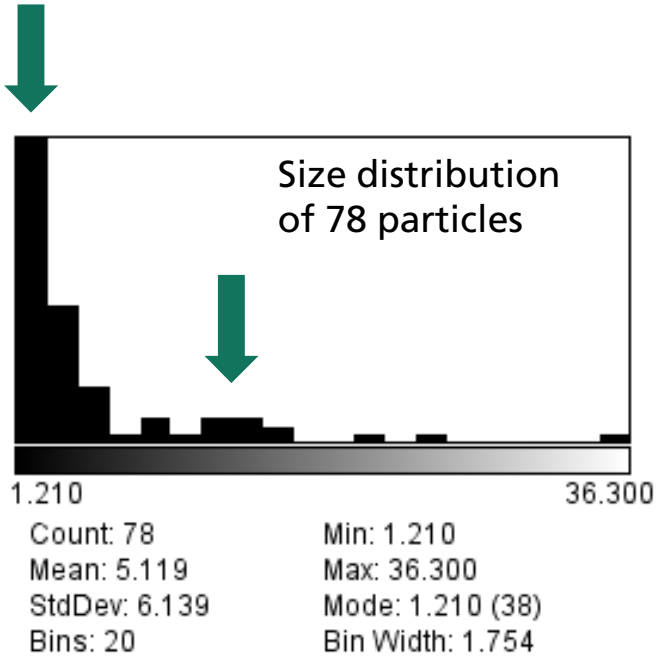
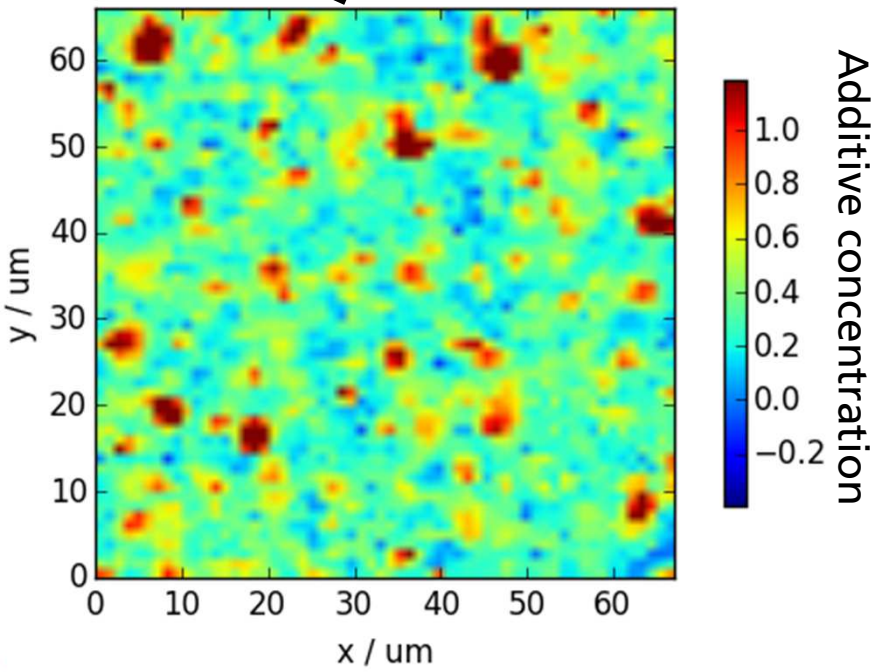
High resolution imaging of additive distribution within POM

- Approx. 270.000 particles per mm^3
- Most particles have diameter < 1 µm
- Some have diameters ~ 5 µm







Fraunhofer

‘ANALYTICS OF STABILIZERS‘ - INNOVATIVE APPROACHES FOR THE LIQUID CHROMATOGRPAHY ANALYSIS OF ADDITIVES IN POLYMERS

Forschungsnetzwerk Mittelstand

Industrielle Gemeinschaftsforschung

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Additive Analysis

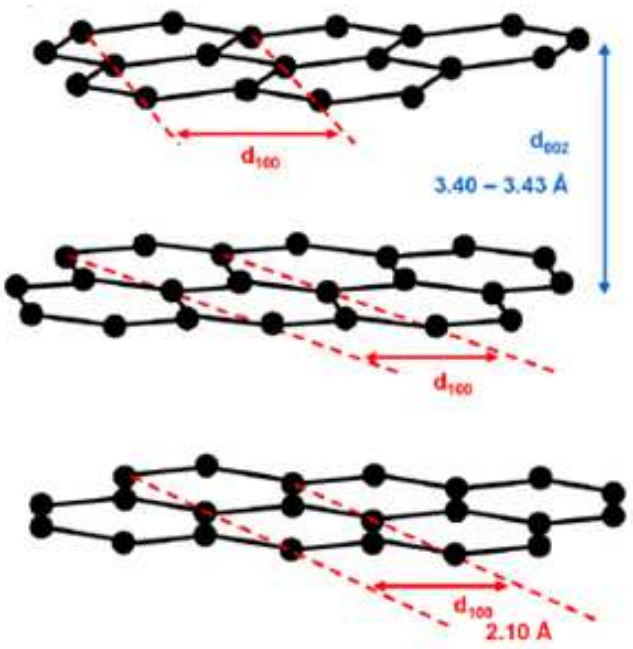
‘Generation of an analytical method for the qualitative and quantitative characterization of modern stabilizers and their degradation products in thermoplastic materials‘

- Benefits of this method:

  - Separation of additives with high molecular weigths and polymers

  - Precise quantification

  - Analysis of a variety of stabilizers in an one-shot approach



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Objective

I. Separation of polyolefins (PE, PP) and additives (antioxidants, UV absorbers, HALS) using solid phase extraction (SPE)

II. Qualitative and quantitative characterization of additives and their degradation products – separation of additives and their degradation products using HPLC

State of the art

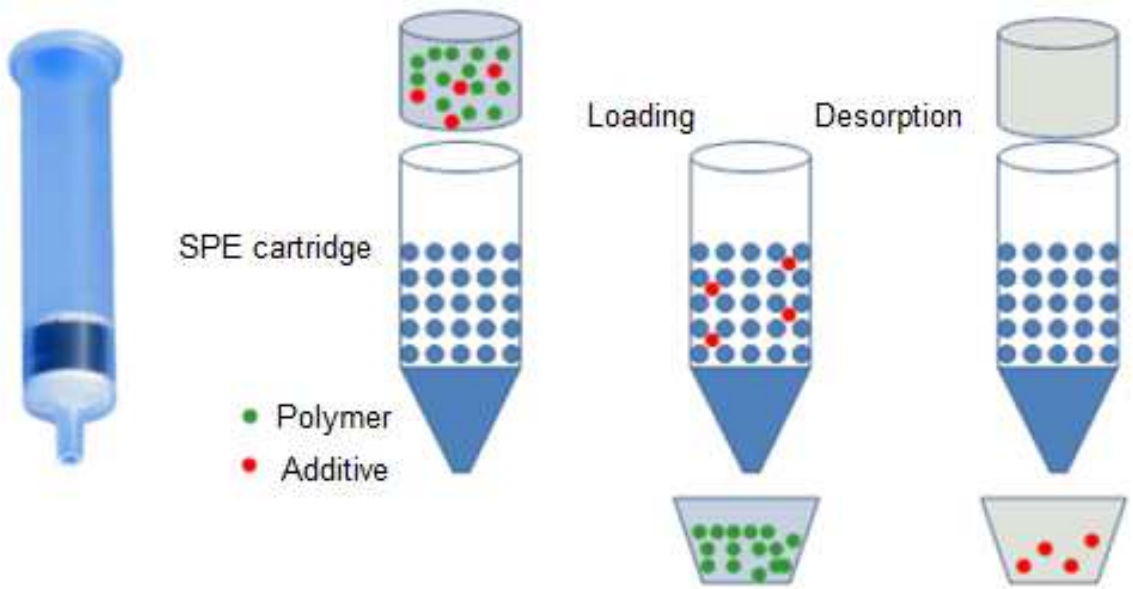
- OIT measurements

- IR spectropsopy
- Precipitation of the polymer in solution

- Soxhlet extraction (partly improved extraction, duration of extraction from 6 to 48 h)
- Supercritical Fluid Extraction (SFE)

Realization

- Method: Solid Phase Extraction, SPE



- Separation and analysis of the polymer and additive fractions are performed with the same material as for the HPLC and SPE

Realization

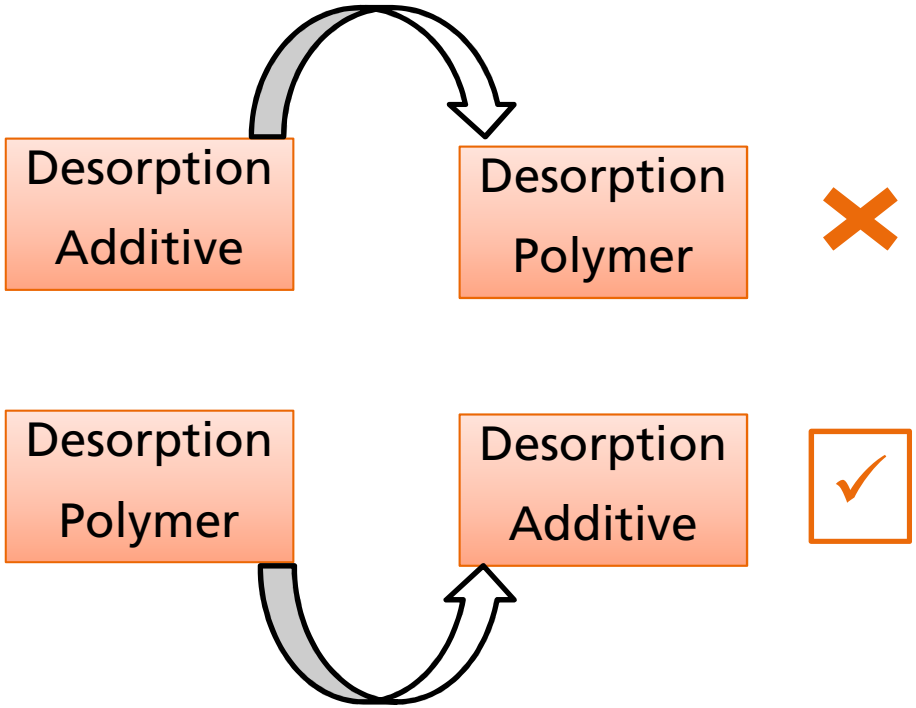
- Oxygen sensitivity of polymer additives

- Approach:
  - Flooding the system with nitrogen or argon
  - Controlling the reproducibility and the extent of the error

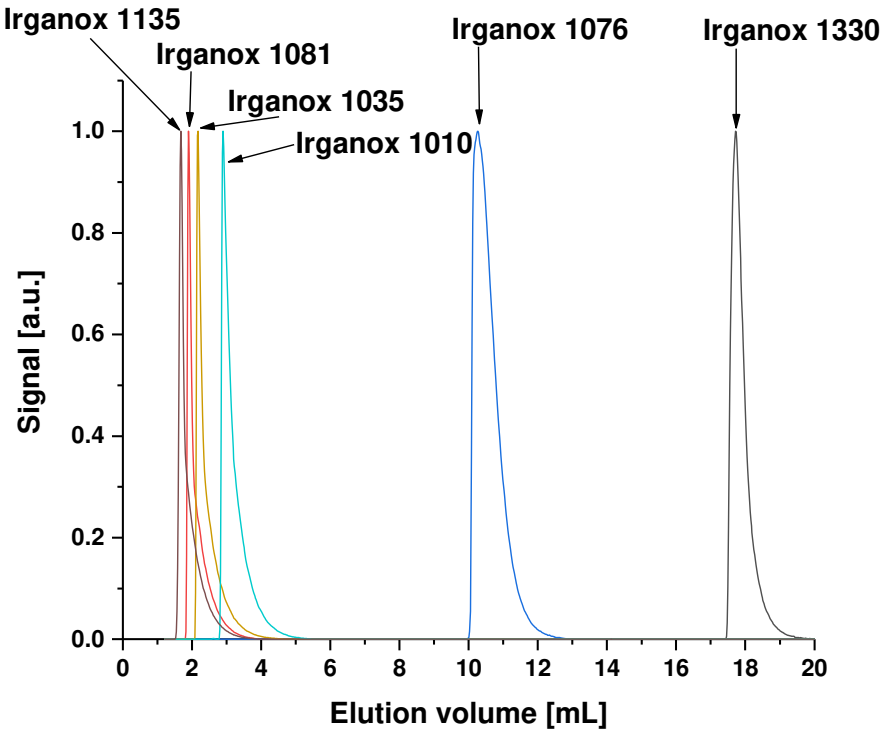
- Verification of the received results with a well-known method (e.g. Soxhlet extraction)

Limitation of the method

- Limitation by solubilitiy
- Limitation by adsorption



Separation of antioxidants



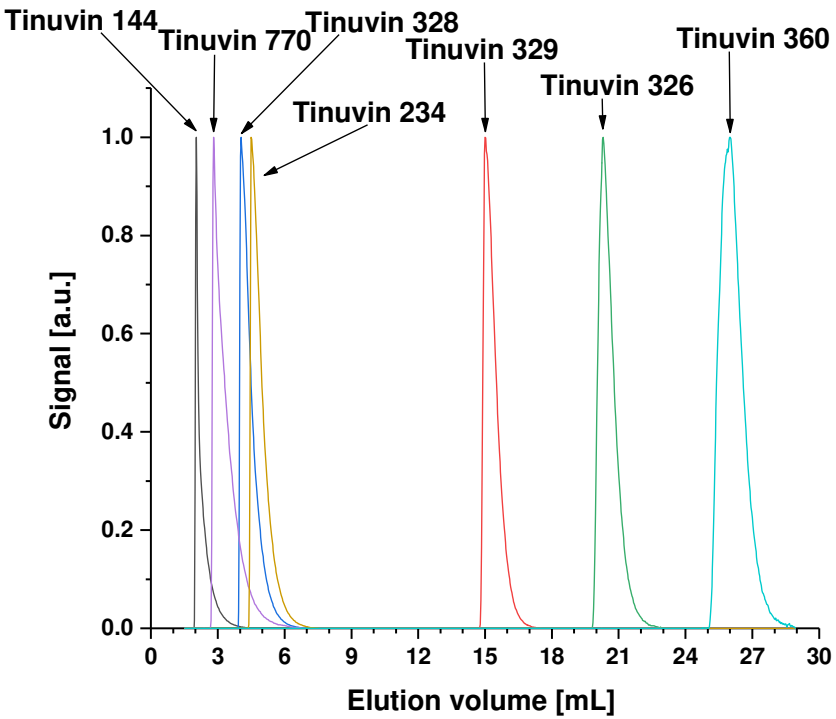
I. 0 min: 100% MTBE, 0 % $CHCl_3$

II. 5 min: 100% MTBE, 0 % $CHCl_3$

III. 15 min: 0% MTBE, 100 % $CHCl_3$

IV. 30 min: 0% MTBE, 100 % $CHCl_3$

Separation of UV absorbers



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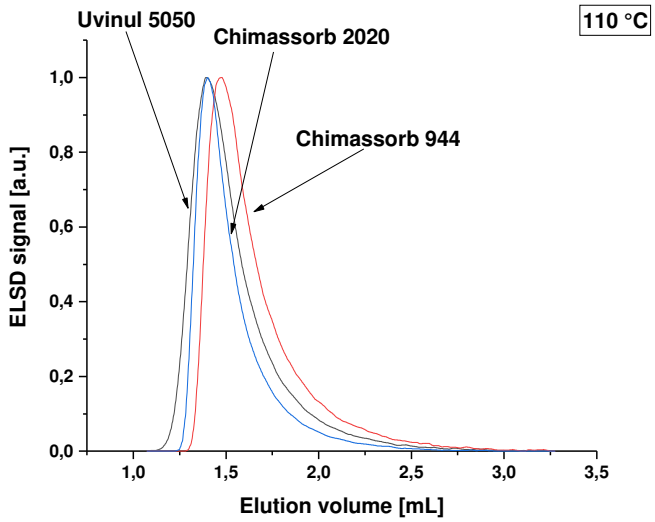
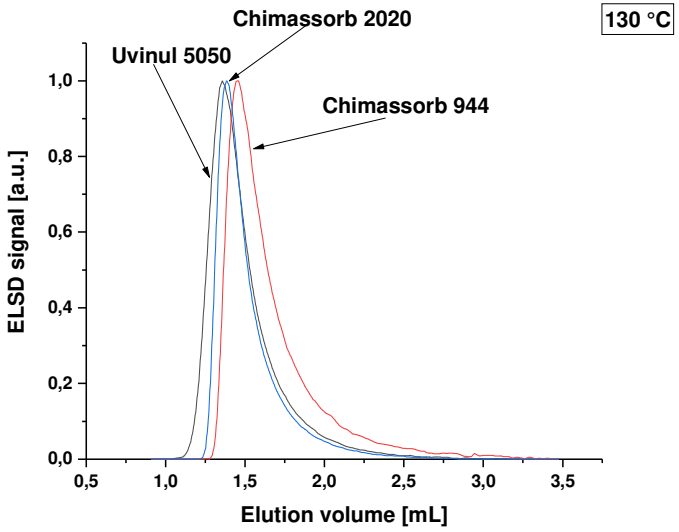
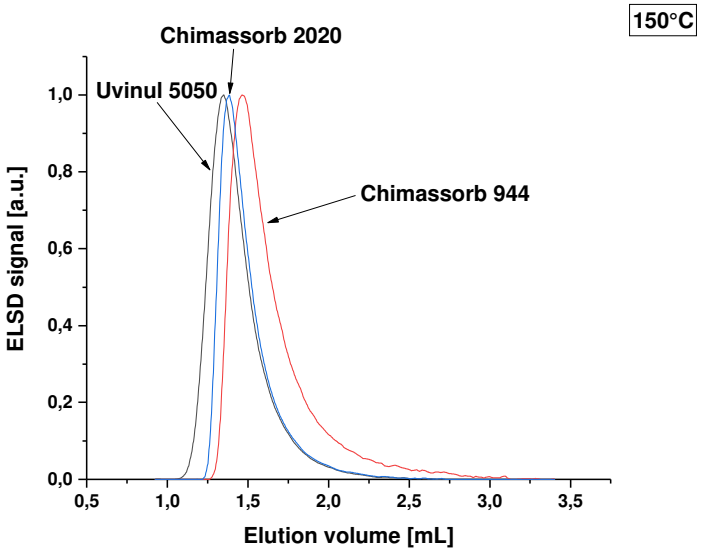
Desorption of oligomeric HA(L)S with mesitylene







- Adsorbent: Toluene
- Desorbent: Mesitylene
- Xylene is a desorbent, but first at 150 °C

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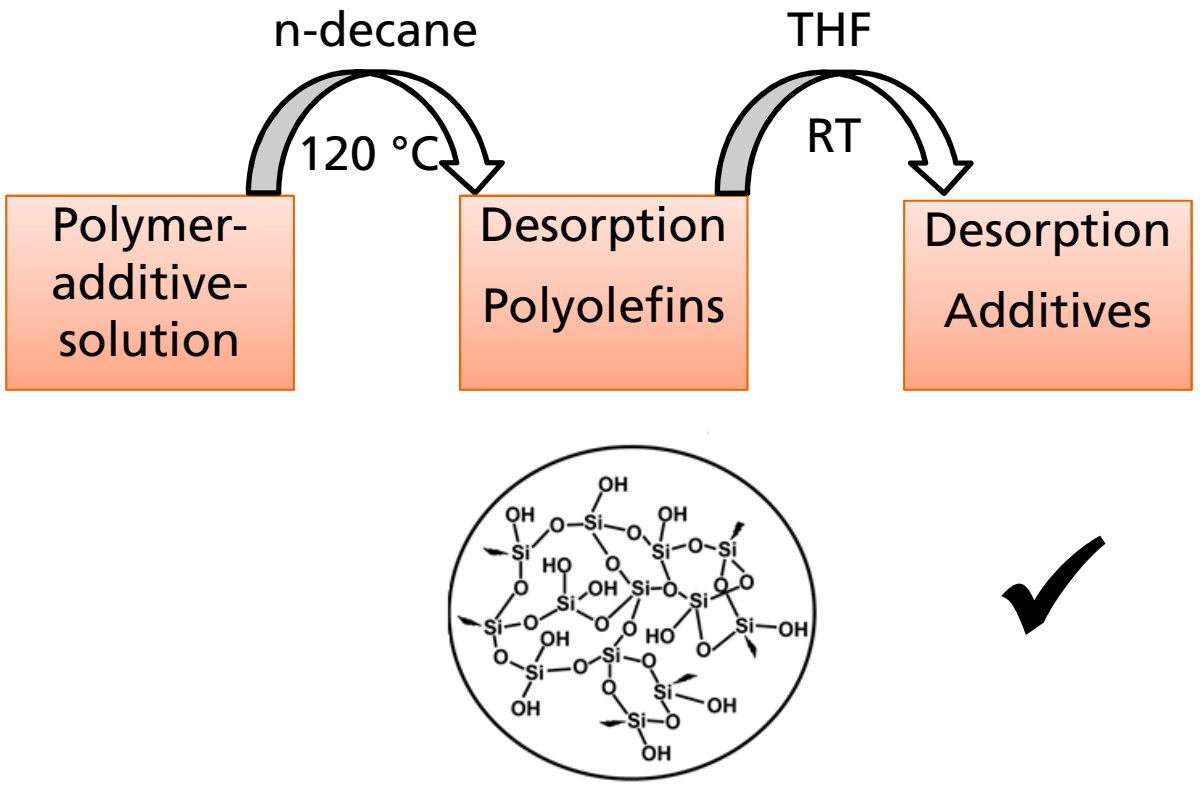
Separation of polyolefins and additives using silica as stationary phase



- Result: Separation of polyolefins and additives with silica is possible

Outlook

- Construction of an HT-SPE apparatus
- Separation of polymers and HA(L)S additives
- Quantitative characterization of polymer additives by HPLC