MULTI-DIMENSIONAL CHROMATOGRAPHY OF MACROMOLECULES GOING MAINSTREAM?

Peter Kilz*, Wolfgang Radke

PSS Polymer Standards Service, POB 3368, 55023 Mainz Germany, info@pss-polymer.com

ABSTRACT

Modern synthetic and bio-based macromolecules contain multiple chemical and structural features to meet their application requirements. While GPC/SEC is the standard technique for macromolecular characterization, it cannot reveal (in general) the complex nature of current products like copolymers, branched and/or functionalized polymers [1]. Product quality and the efficiency of polymerization processes require the determination of by-products which can be difficult to evaluate by conventional techniques if the main product and the by-product are structurally similar or are present only at trace levels.

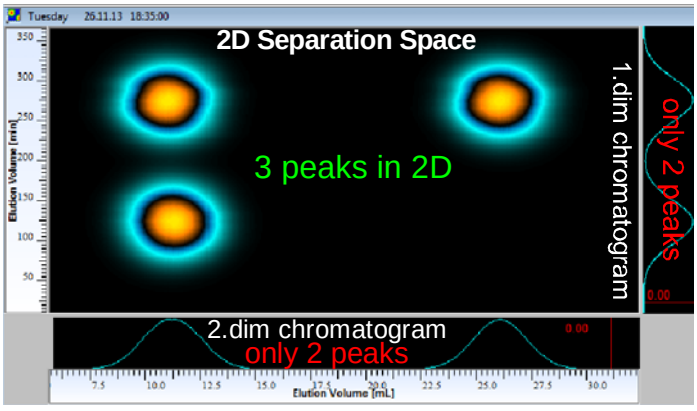
Multi-dimensional chromatography has been adopted in many laboratories to characterized complex macromolecular structures, elucidate synthetic routes to maximize yield and optimize structural features [2]. In contrast to conventional chromatographic techniques which rely on a single separation process, multi-dimensional methodologies apply different separation principles to cover a wider separation space [3, 4].

This presentation will focus on the use of two-dimensional separations and on what can be revealed and understood by applying more sophisticated chromatographic techniques in research and quality control laboratories. Recent advances in instrument and software development make the experimental setup and result generation more user-friendly and allow more laboratories to implement modern chromatographic characterization methods.

Two-dimensional experiments can be used to study:

- binary property distribution without bias, e.g. in block and graft copolymers
- variation in product formulations
- comprehensive out-of-spec tests
- nature and amount of by-products, aggregates, etc
- investigation of chain defects on molecular level
- chemical heterogeneity
- homopolymer contamination in copolymers
- functionalization efficiency
- branch points in star and comb polymers

The adjacent figure shows an example of the superior resolution of a sample which contains 3 compounds which cannot be separated into more than two peaks either in GPC/SEC nor in HPLC. However, two-dimensional chromatography clearly reveals and identifies all 3 components. The application of appropriate detection or calibration allows to determine the molar mass distribution and chemical composition distribution and their numerical averages for each species separately.



References:

[1] Held, D., Kilz, P.; "GPC/SEC as a Key Tool for Assessment of Polymer Quality and Determination of Macromolecular Properties", in: W. R. Reed, A. M. Alb (eds.), Monitoring Polymerization Reactions: From Fundamentals to Applications, Chapter 9, Wiley, New York, 2014

[2] Kilz, P., Radke, W.; Application of two-dimensional chromatography to the characterization of macromolecules and biomacromolecules, Analytical and Bioanalytical Chemistry, **407**, 193 (2015)

[3] Kilz, P., Pasch, H.; Coupled LC Techniques in Molecular Characterization in: Encyclopedia of Analytical Chemistry (R.A.Meyers, ed.), Vol 9, pp 7495-7543, Wiley, Chichester 2000

[4] Kilz, P.; Enhanced Characterization and Comprehensive Analysis by Two-Dimensional Chromatography, in HPLC Made to Measure; S. Kromidas (Ed.), Wiley, Weinheim 2006