

TEMPERATURE GRADIENT INTERACTION CHROMATOGRAPHY: PRINCIPLE AND APPLICATIONS

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ABSTRACT

Overcoming the limitations of the conventional Size Exclusion Chromatography (SEC) separation based on size exclusion principle, Temperature Gradient Interaction Chromatography (TGIC) has been applied to synthetic polymers and pushed the precision of molecular characterization of polymers onto a new dimension. TGIC exploits the thermodynamic interactions of polymer molecules with the stationary phase of chromatographic columns, in which the column temperature is controlled during the elution. TGIC exhibits much higher resolution than SEC in the separation according to the molar mass and it allows many useful detectors for polymer characterization to be utilized, which is impossible in the solvent gradient elution.

TGIC have been applied to resolve a number of long-standing problems in polymer characterization such as 1) rigorous determination of molar mass distribution of the anionic- polymerized polymers, 2) effective separation/characterization of polymer mixtures including a purification of block copolymers from their homo-polymer precursors, 3) separation according to chain architectures demonstrating clearly that the branched polymers or ring polymers prepared by the current state-of-art synthesis/purification process are still contaminated by a large amount of byproducts enough to influence their rheological property significantly, 4) characterization/fractionation of individual blocks of block copolymers demonstrating that so-called “monodisperse” block copolymer prepared by anionic polymerization has a block length distribution large enough (more than 10%) to exhibit various morphology from lamellar, HPL, gyroid, to cylinder, 5) separation according to stereoregularity, 6) separation according to functionality or end-groups.

MULTI-DIMENSIONAL CHROMATOGRAPHY OF MACROMOLECULES GOING MAINSTREAM?

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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.

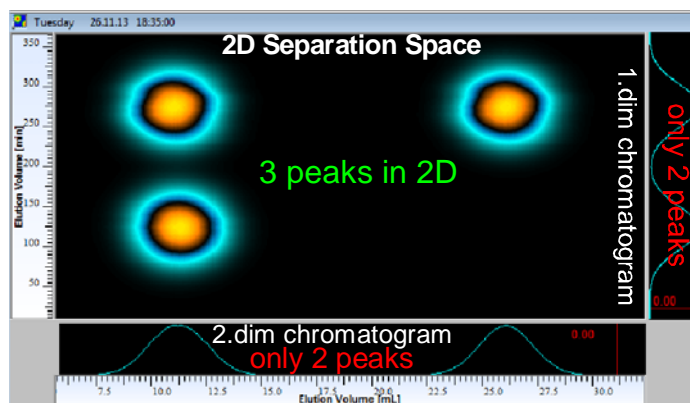
Multi-dimensional chromatography has been adopted in many laboratories to characterize complex macromolecular structures, elucidate synthetic routes to maximize yield and optimize structural features [2]. In contrast to conventional chromatographic techniques which rely on a single separation process, 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:

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CHARACTERIZATION OF LIGNIN BY MULTI-DETECTOR GPC

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ABSTRACT

Lignin is a complex polymer found in vascular plants binding the cells and cellulose fibre in wood. It is the second most abundant natural polymer formed of aromatic alcohols known as monolignols.

With a plethora of actual and potential applications, from bio-fuel to asphalt antioxidant, understanding the distribution of molecular weight, molecular structure and viscosity of this natural polymer is critical to the understanding of the materials performance and end-product properties.

Gel-permeation chromatography (GPC) is the most widely used tool for the measurement of molecular weight and molecular weight distribution of natural and synthetic polymers. Historically, the elution volume of an unknown sample was compared with that of known standards to estimate molecular weight and distribution. However, this so-called 'conventional calibration' is limited by the structural differences between standards and samples, meaning that the measured molecular weight is only a relative value if the standards and samples are different polymers. This is particularly true for lignin due to its unusual molecular structure in solution.

Static light scattering (SLS) detectors measure the intensity of light scattered by the sample as it elutes from the chromatographic column. Since the intensity of the scattered light is proportional to the samples molecular weight and concentration, they allow the direct measurement of the sample molecular weight independent of its elution volume. A viscosity detector can be used to measure the intrinsic viscosity which can be combined with the molecular weight data to calculate hydrodynamic radius. These data allow detailed structural information of a polymer to be generated in a single GPC measurement which can be compared with other samples by the use of Mark-Houwink plots.

A major challenge that needs to be overcome while working with lignin is that it often fluoresces in solution. Light scattering data can then be distorted due to the interference originating from the fluorescent molecules adding to the amount of light scattered during the measurement.

In this paper, we analyzed a set of lignin samples, using several techniques, highlighting these difficulties and illustrating how reliable information can be obtained by careful choice of experimental conditions and methods.

CHEMICALLY SENSITIVE SEC DETECTION BASED ON ONLINE COUPLED FTIR SPECTROSCOPY

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ABSTRACT

Polymers have three important molecular characteristics, which influence their material properties: the molecular weight distribution (MWD), the chemical composition and the topology. The MWD is usually determined using size exclusion chromatography (SEC). Information on chemical composition and topology is normally gained separately using spectroscopic methods, because the SEC detectors commonly in use, such as refractive index detectors, light scattering or viscometers, do not provide any information about the chemistry or topology. Especially when analyzing modern, complex materials like copolymers, blends or unknown samples, the correlated measurement of size and chemical properties is of special interest, not only to better understand the influence of molecular properties on material characteristics, but also for industrial quality control, material design and product development.

Coupling spectroscopy with SEC seems a promising approach to gain this correlated information. An inherent problem to this pairing is the low concentration necessary for SEC, which normally results in high solvent signals. Several approaches, mostly with highly complex or expensive equipment have been reported in literature and reviewed in [1].

Fourier transform infrared spectroscopy (FTIR) is universally applicable to all polymers and is comparably cheap. Here we present an online coupled method consisting of an optimized, highly sensitive FTIR spectrometer and a SEC with specialized flow cells. The method is based on a newly developed mathematical solvent suppression routine.[2] The FTIR spectrometer here works as a chemically sensitive SEC detector that can identify and quantify different analytes and is also able to measure samples that other detectors fail to measure, such as, for example, isorefractive samples.

The general setup, the newly constructed flow cells, the mathematical solvent suppression, the influence of column dimensions as well as several application examples will be presented.

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