WYATT TECHNOLOGY

APPLICATION NOTE

AN1307: SEC-MALS analysis of cellulose/DMAC molecular weight distributions

Introduction

Cellulose, a biopolymer of great importance to the fiber and paper industries, is difficult to characterize because of its high molar mass. Its intractable nature means it cannot be dissolved in conventional solvents without chemical modification. With tedious effort, it can be modified so that it can be dissolved in an easy-to-use solvent like THF, but when the cellulose is so-modified it is degraded and the analysis does not represent the source material.

Unmodified cellulose can be dissolved in dimethyl acetamide (DMAC) with LiCl added. The problem remains, how to characterize it without reference to column calibration standards that typically do not have the same conformation as cellulose and therefore do not provide accurate calibration curves. Absolute characterization is performed by combining multi-angle light scattering with size exclusion chromatography (SEC-MALS) to determine molar mass, independently of elution standards.

Materials and Methods

Separations were performed on a set of SDV-GPC columns in DMAC / LiCl. The separation columns were followed by the HPLC's UV detector, a Wyatt DAWN® MALS detector and a Wyatt Optilab® differential refractive index (dRI) detector.

Data collection and analysis were performed in the ASTRA® software using empirically-determined differential refractive index increments (*dn/dc*). Polymer molar mass *M* was calculated at each elution volume using signals from the two detectors.

The differential refractive index, used both to calculate concentration with a dRI detector and to analyze light scattering, depends on the solvent as well as the analyte. It may be determined experimentally by injecting a series of known concentrations into the Optilab and fitting the dRI/concentration dependence to a linear regression (performed by ASTRA). Accurate concentrations are often obtained by dry weight and subsequent dissolution in the SEC mobile phase.

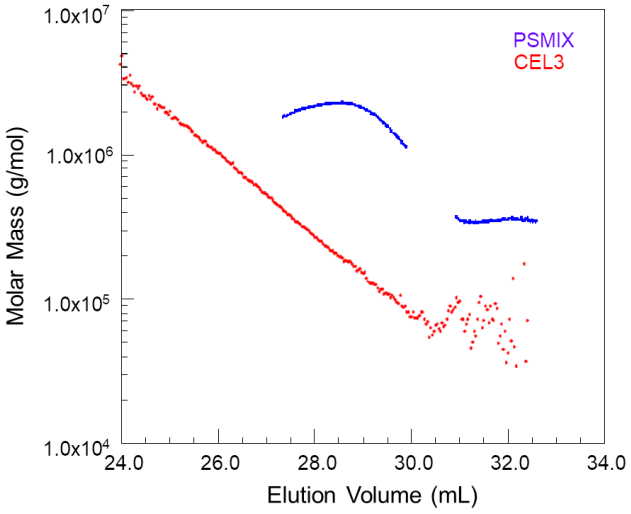


Figure 1. Two narrow polystyrene standards and a cellulose. Note that at the same elution volume, the "standard" gives a molar mass 10 times larger than the cellulose value.

Results and Discussion

Molar masses determined by MALS in Figure 1 follow the usual logarithmic variation with elution volume, indicating excellent chromatography. For the sake of comparison, a run of two mixed polystyrene standards is overlaid in a plot of molar mass versus elution volume.

As can be clearly seen, a calibration based on polystyrene standards would overestimate the molar mass by more than a factor of five. This discrepancy is usually a result of branching, typical for cellulose in the MW range of 10^5 – 10^6 and above.

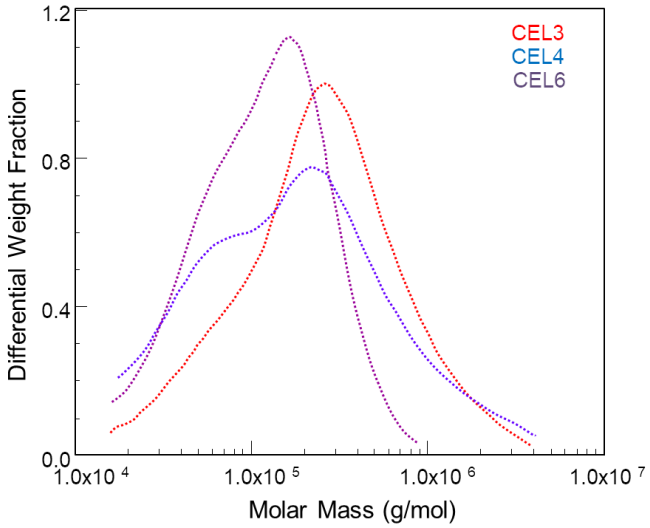


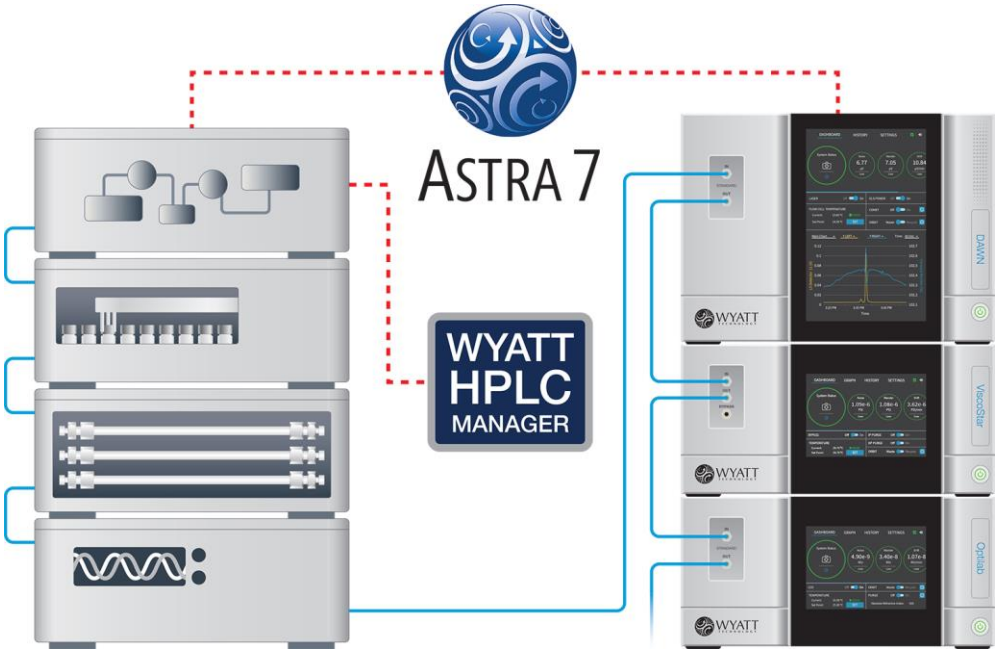
Figure 2. ASTRA's Differential Weight Distribution plot shows how different extraction processes create large variations in cellulose molar mass distributions

Branching can be further explored through conformation plots (log-log plots of rms radius R_g or hydrodynamic radius R_h vs. molar mass) or Mark-Houwink Sakurada plots (log-log plots of intrinsic viscosity $[\eta]$ vs. molar mass).

The technical process of extracting the cellulose from the wood pulp can have a profound effect on the molar mass distributions. Figure 2 shows the differences in molar mass distributions arising from different extraction processes. In addition, moments of the distribution may be calculated readily and tabulated with ASTRA's EASI Table. With the ability to rapidly reveal and quantify those differences, DAWN/Optilab instrument sets for SEC-MALS have become important tools in optimizing the production processes for cellulose.

Conclusions

The SEC-MALS results prove that the lengthy process of solubilizing the cellulose has been mastered, enabling the manufacturer to optimize the cellulose extraction process.



WYATT TECHNOLOGY