



## GPC/SEC Troubleshooting

# Unexpected peak shapes – different shapes than others

*Daniela Held, PSS GmbH, Mainz, Germany*

**Q: I have measured calibration standards to create a calibration curve and they look different from the manufacturer's peaks. What is wrong?**

### *Comment:*

GPC/SEC is used to measure the molar mass distribution (MMD). If the GPC/SEC analysis is done properly, the MMDs obtained in different laboratories should be identical within the expected measurement uncertainty of the method.

However, the first (visual) information obtained in GPC/SEC, the elugram or chromatogram, can not be easily compared between different laboratories. The signals in the elugram depend on a sample related part (PDI, molar mass) and on system parameters (mainly number and type of columns, tubing length, system dead volume). So different peak widths, sometimes even shapes, or different elution volumes are common.

**A:** In contrast to HPLC, broad sample peaks in GPC/SEC are quite common. GPC/SEC is used to separate and characterize the different sized chains (different molar masses) within a macromolecule. In the low molar mass region, it is possible to use GPC/SEC column combinations that can separate oligomers into single peaks. For higher molar masses (approx. above 1000 Da) it is not possible to see single peaks; a broad peak including a variety of chains appears.

Without additional information (e.g., the calibration curve) it is not possible to deduce from the width of an elugram peak the molar mass distribution. A peak can look broad,

because of good resolution, without having automatically a broad molar mass distribution. In contrast, if the resolution is poor or the columns are not optimized for this molar mass range, a narrow looking peak can have a broad molar mass distribution.

However, if a calibration curve is measured it is possible to get the MMD with the polydispersity index (PDI) and the molar mass averages and to see if the resolution is good. A good resolution always requires a flat/shallow slope of the calibration curve.

If the slope of the calibration curve is steep, the resolution will not be good. Therefore, it is always worth

Figure 1

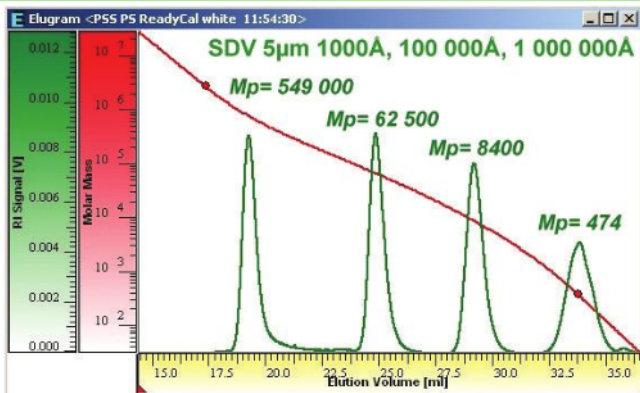


Figure 1: Four different polystyrene molar mass standards on a column bank for medium molar masses (100 to 3 000 000 Da). Red dots in the calibration curve show highest and lowest molar mass used to create the calibration curve.

Figure 2

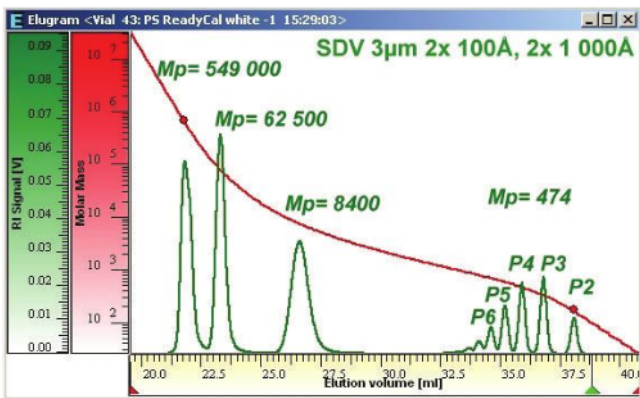


Figure 2: The same polystyrene molar mass standards on a column bank for oligomers and low molar masses (100 to 60 000 Da).

visually inspecting the calibration curve and to also overlay it with the sample elugram. This will show if all sample parts elute in the calibrated region and if the chosen column combination shows a flat slope and therefore provides good resolution.

Figures 1 and 2 show both elugrams of a mixture of 4 different polystyrene molar mass standards. Figure 1 shows the peaks on a column combination optimized for separations in the molar mass range 100 to 3 000 000 Da.

For Figure 2, a column combination with highest resolution in the oligomeric region is used (optimum molar mass: 100 to 60 000 Da). Here the oligomeric polystyrene is nicely separated into the single chains with the indicated degree of polymerization. However, this is because of the high resolution in the low molar mass region. This was not possible on the other column combination in Figure 1. Here only a broad peak appears, as this column combination is optimized to also separate higher molar masses and the resolution is less.

However, if the calibration is done correctly the obtained molar mass averages and the PDI should be the same, although the molar mass distribution has much less information.

## Tip: Increasing the resolution

1. Use column banks or column combinations to increase the resolution over a wide molar mass range.

2. Addition of an analytical GPC/SEC column of the same porosity (dimensions, and particle size) increases the resolution by a factor of approximately 1.4 meaning that the slope of the calibration curve will be flatter.

Daniela Held studied chemistry at the University of Mainz. Her PhD work was on the characterization of star-branched polymers using GPC/SEC and hyphenated techniques. She joined PSS in 2000 and is responsible for customer training and support.