

## GPC-Viscosity, GPC-light scattering and Triple Detection Approaches

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*Dr. Jason S. Davies, Smithers Rapra, UK*

In addition to a concentration detector (typically differential refractive index), viscosity (differential pressure) and light scattering detectors are used in combination to provide *true* molecular weight data in circumstances where *equivalent* molecular weight or use of a mathematical correction using a conventional approach would not be acceptable.

The application of these multi-detector approaches may not be appropriate in all circumstances and it is important to note the strengths and weaknesses of each approach.

### Recap of the Conventional Approach

A conventional GPC approach uses the response of a concentration detector, usually differential refractive index (DRI) but may be infrared (IR), ultraviolet (UV), or evaporative light scattering (ELS), to provide *comparative* molecular weight data.

Molecular weight data is obtained via a log molecular weight versus elution volume calibration typically using a series of narrow distribution calibrant polymers of known peak molecular weight (Mp).

The log-linear relationship of the calibration and the fact that this is best defined by a third order relationship means that extrapolation of the calibration at high molecular weight may be questionable. Where possible, chromatography should be kept within the linear range of the fractionation columns selected.

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For GPC systems operating with organic eluents it is typical to use either poly(styrene) or poly(methyl methacrylate) narrow distribution calibrant polymers and therefore the results are expressed as the '*PS*' or '*PMMA*' *equivalent molecular weight*. In some instances it may be practical to apply a mathematical correction to allow for the differences between the sample and calibrant polymer types and expressing the results as for the sample polymer.

A conventional approach is best applied where it is necessary to *compare* the molecular weight distribution of sample polymers of the *same chemical composition and structure (branching)*.

### Combined GPC-Viscosity (Universal Calibration) Approach

The combined GPC-Viscosity approach also makes use of a column calibration however, including the response from a differential pressure (Viscosity) detector and having knowledge of the intrinsic viscosities of the calibrants allows computation of a *Universal Calibration* that is applicable to all polymer types that behave normally in solution. The calibration is therefore not dependent on chemical composition or structure of the polymer. Any extrapolation of the calibration would introduce the same potential errors as the Conventional approach.

It is important to appreciate that in a GPC-Viscosity approach knowledge of the polymer solution concentration is critical in obtaining correct results. Knowledge of the polymer concentration is often not straightforward as most polymers will contain additives or there may be the potential for residual solvents or moisture. Any insoluble polymer (gel) will be removed during solution preparation and would therefore result in a concentration error.

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The best approach to obtaining polymer concentration is by back-calculation from the refractive index (concentration) detector response and knowledge of the differential refractive index increment ( $dn/dc$ ) for the stated polymer / eluent combination. This requires that  $dn/dc$  be accurately known. In practise, this usually means depending on literature values or measuring it on-line for a single sample known (or accepted) to be pure, fully soluble polymer.

The above assumes that the polymer is of a consistent chemical composition (and therefore consistent  $dn/dc$ ) across the whole distribution. This is unlikely to be the case with polymer blends and may not be the case with copolymers.

### **GPC-Light Scattering and Triple Detection GPC**

Classic light scattering experiments to obtain the weight average ( $M_w$ ) molecular weight of polymer involved measurement of the Rayleigh scattered light at a range of angles and concentrations. A 'Zimm' plot was constructed and used to extrapolate to zero concentration and angle in order to calculate  $M_w$ .

Modern on-line light scattering detectors for GPC are based on a laser light source with measurement at specific set angle(s) and simplified calculations and assumptions. Current on-line light scattering detectors used at Smithers Rapra are right-angle light scattering (RALS) systems. The advantage of RALS is that the measurement at right angles gives the best signal to noise response however, large molecules have an angular dependence to scattered light – for large (high molecular weight) polymer it becomes necessary to apply an angular correction based on the response of the viscosity detector.

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The response of the light scattering detector is a function of the polymer concentration and the weight average molecular weight, although the value of  $dn/dc$  also appears as a squared term in the computation. The size of the light scattering response increases dramatically with increase in molecular weight.

Hence for high molecular weight polymer with application of an angular correction, GPC-RALS requires both differential refractive index and viscosity detectors and is best considered as *Triple Detection GPC*.

Polymer solution concentration is a parameter of the same critical importance as for the GPC-Viscosity approach.

It is inevitable that at the high molecular weight end of the distribution there will be a strong light scattering response but minimal differential refractive index (concentration) detector response with the opposite being the case at the low molecular weight end of the distribution. It follows that there are likely to be significant inaccuracies in the computations at the extremes of the distribution and the data handling software will use a degree of extrapolation at these extremes. This issue may be minimal for narrow distribution polymers but likely to be significant for broader distribution materials. As light scattering detectors are insensitive to very low molecular weight polymer GPC-LS and Triple detection GPC approaches are not suitable to these types of study.

For GPC-light scattering or Triple Detection GPC approaches a column calibration is not necessary, instead a detector calibration is performed. A detector constant is set using a calibrant polymer for which molecular weight and concentration is known.

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GPC-Viscosity, GPC-LS and Triple Detection GPC approaches are potentially more complicated in the consideration and management of data handling. Such approaches may not be applicable in all situations. However, they do offer calculation of *true* molecular weight with comparison of  $\log(\text{viscosity})/\log(\text{molecular weight})$  plots and ancillary measurements of branching frequency, radius of gyration etc.