What Is The Mark-Houwink Equation?

For narrow molecular weight fraction linear polymers, log-log plots of the molecular weight dependence on the intrinsic viscosity are linear. The expression describing this empirical relationship is the Mark-Houwink equation shown below, where η is the intrinsic viscosity, M is the molecular weight, and κ & α are solvent-polymer dependent fitting parameters.

$$[\eta] = \kappa M^{\alpha}$$

Extensive tables of κ & α values for various solvent-polymer pairs are readily available, either through reference publications or simple internet searches. Using the above expression, along with known κ & α values, one can estimate the polymer molecular weight from the measured intrinsic viscosity.

An alternate form of the Mark-Houwink equation, suitable for use with dynamic light scattering (DLS) data, is that shown below, where D is the translational diffusion coefficient, M is the molecular weight, and k & a are solvent-particle dependent fitting parameters.

$$D = kM^{-a}$$

Similar to the viscosity form of the Mark-Houwink equation, one can use the above expression to estimate the molecular weight of a particle from the DLS measured diffusion coefficient and known k & a values. As with the viscosity form of the expression, extensive tables of solvent-particle k & a values are available, many of which are listed in the Help file of the DTS software for the Zetasizer Nano system.

It is important to note, that the k & a values used for the diffusion form of the equation differ from the κ & α values used for the viscosity form. For non-interacting particles, the exponents can be shown to be related by $\alpha = 3a - 1$. The "stiffness", α, varies between 0 and 2, for hard spheres and a rigid rods respectively, and typical intrinsic viscosity exponents, a, fall between the limits of 0.33 and 1. The table below gives a model dependent comparison of expected exponent values.

Model	α	a
Hard Spheres	0	0.33
Semi Coils	1	0.66
Rigid Rods	2	1.0

An example of how one might integrate Mark-Houwink parameters into DLS results is given in the following figures and discussion. Traditionally many protein researchers are familiar with chromatography plots wherein signals from the detectors are plotted as a function of elution volume. For columns calibrated with known molecular weight standards, these elution volumes can be converted to molecular weight, allowing the researcher to generate an estimated molecular weight distribution for unknown samples passing through the column. Using known Mark-Houwink parameters, the same type of "molecular weight" distribution can be derived from the intensity particle size distribution measured from a dynamic light scattering experiment.

Figure 1 shows the DLS derived intensity particle size distribution for a hemoglobin sample in phosphate buffered saline. Three particle size families are evident in the intensity distribution – one at 8.5 nm diameter, a second at 121 nm diameter, and a third at around 1630 nm diameter.

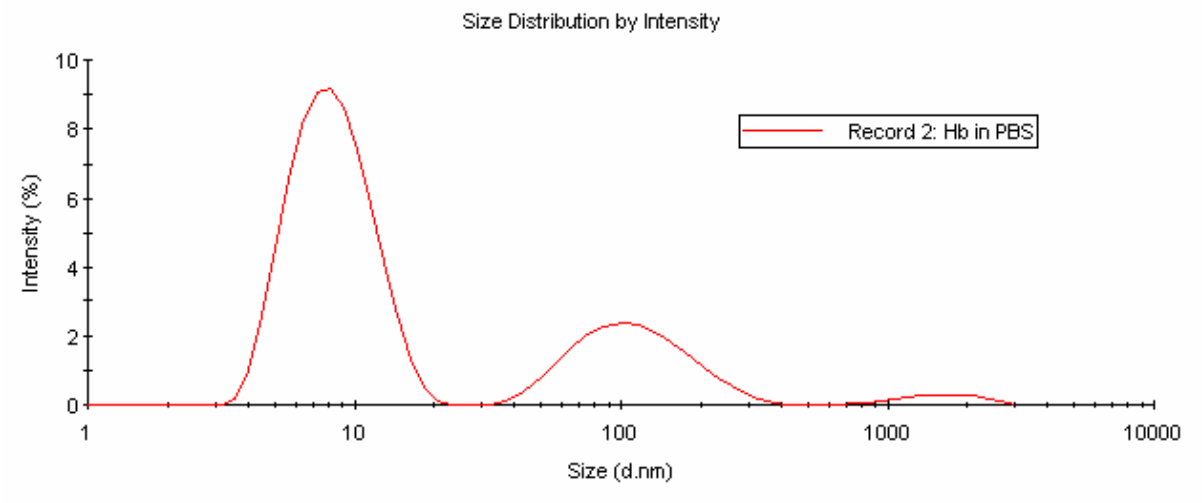

Figure 1: DLS derived intensity particle size distribution for hemoglobin in PBS.

For globular proteins, the empirically determined Mark-Houwink parameters are k ~ 7.67E-05 cm^2/s and a ~ 0.428. For the assumption of globular proteins then, these parameters can be used in the Sample Material properties section of the Zetasizer Nano software to transform the intensity particle size distribution into an estimated molecular weight distribution. To enter the values into the measurement record:

1) Open the Measurement Settings window
2) Select the Sample tab in the Measurement Settings window
3) Click the Define button in the Mark-Houwink Parameters section
4) Enter the k and a values into the text boxes in the MH Parameters window

Note that the Measurement Settings window can be accessed either pre or post measurement. To open the window for pre-measurement entry, use the Measure-Manual option on the Main Tool bar, or use the Configure-Existing SOP option on the Main Tool bar to add the parameters to an existing SOP. To open the window for post-measurement entry, use the Edit-Edit Result option on the Main Tool bar.

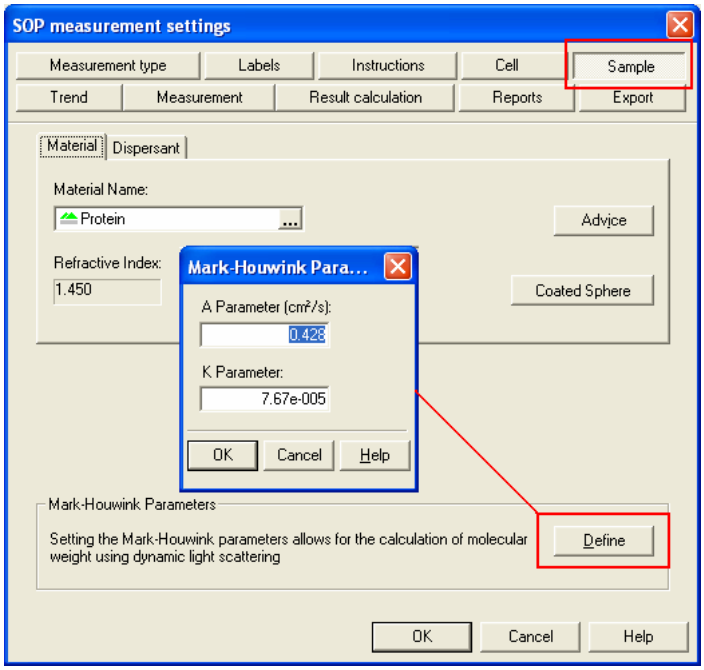

Figure 2: Zetasizer Nano software screen shots detailing the entry of Mark-Houwink k & a parameters for use in generating estimated molecular weight distributions. Note that the units given in the software are currently mislabeled, in that a should have no units and k should have units of cm^2/s.

To transform the measured intensity particle size distribution into an estimated molecular weight distribution, select one of the "size distribution" reports from within the Zetasizer Nano software, and then right click the figure to open the Size Graph Properties window. As seen in Figure 3, the drop down list box within the Display section includes a Weight/Intensity option. Selection of this option will transform the intensity distribution into an estimated molecular weight distribution.

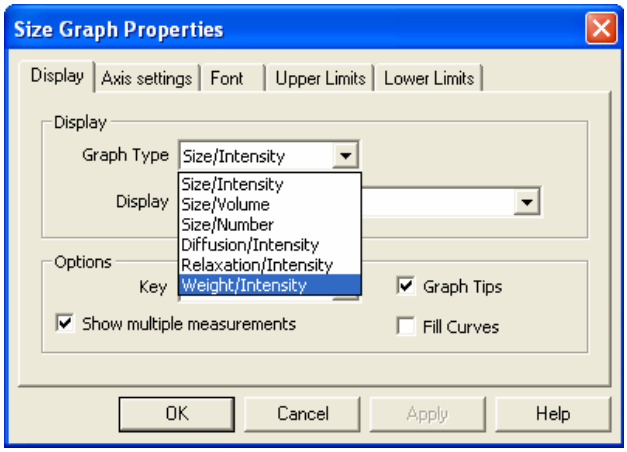

Figure 3: Size Graph Properties window from the Zetasizer Nano software, accessed by right clicking any report figure.

The figure below shows the estimated molecular weight distribution derived from the intensity particle size distribution measured for Hb in phosphate buffered saline, shown earlier in Figure 1. As seen by comparison of Figures 1 & 4, the distributions are identical, with the exception that the X axis for the Mark-Houwink distribution has been transformed into estimated molecular weight, using the k and a parameters for globular proteins.

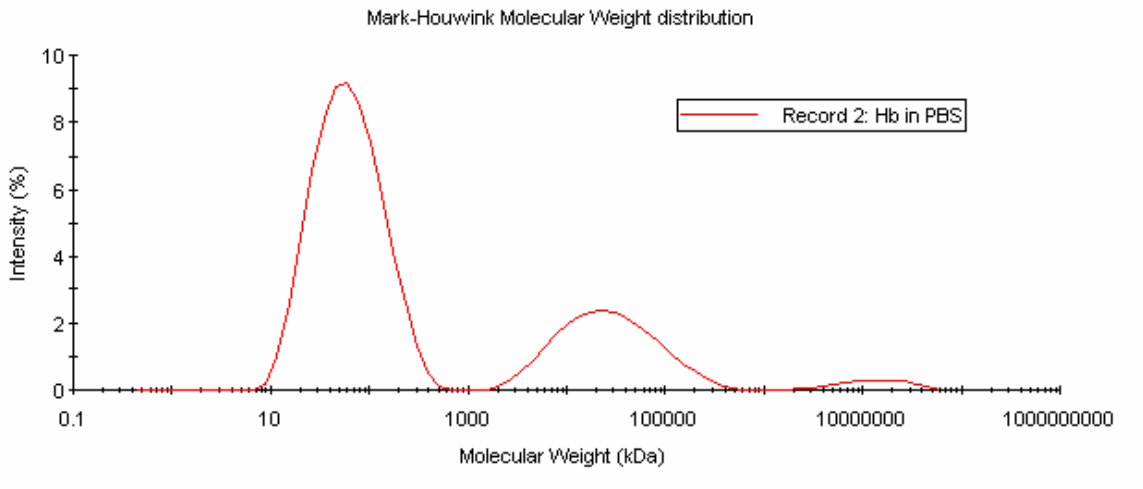

Figure 4: Estimated molecular weight distribution, transformed from the measured intensity size distribution using the Mark-Houwink equation.

A note of caution that should be remembered regarding DLS derived molecular weight distributions is that the MW distribution is only an estimate, and is based upon a number of limiting assumptions, include the assumptions that the aggregates are globular and that there is NO error (or inherent polydispersity) in the intensity distribution. If the protein is not globular the MW could easily be off by a factor – although the order of magnitude should still be correct.

Malvern Instruments Ltd

Enigma Business Park • Grovewood Road • Malvern • Worcestershire • UK • WR14 1XZ
Tel: +44 (0)1684 892456 • Fax: +44 (0)1684 892789

Malvern Instruments Worldwide

Sales and service centers in over 50 countries for details visit www.malvern.com/contact