

Statistical Analysis of NIST Interlaboratory Comparison of Polystyrene Molecular Mass Distribution Obtained by MALDI TOF MS

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Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) is becoming a new and important technique in synthetic polymer characterization. Yet much is still unknown about the molecular mass distribution (MMD) which is obtained through the MALDI process. An interlaboratory comparison was conducted by NIST to compile data and learn more about the MMD obtained and the parameters that influence this distribution. Each laboratory was asked to use two different sample preparations, one of which was specified, and to report three repeats for each preparation. This paper describes results from sixteen laboratories analyzing a polystyrene sample of nominal molecular mass 7000 u.

To analyze such a body of data the first consideration is how to reduce the data into estimators, which can then be compared and interpreted. The moments of the MMD were considered. M_n , M_w , & M_z are the traditional moments considered in polymer molecular mass determination [1]. Three other moments were also considered, $M_{1/n}$, $M_{1/w}$, $M_{1/z}$, defined as;

$$M_{1/n} = \frac{\sum N_i}{\sum N_i M_i^{-1}} \quad M_{1/w} = \frac{\sum N_i M_i^{-1}}{\sum N_i M_i^{-2}} \quad M_{1/z} = \frac{\sum N_i M_i^{-2}}{\sum N_i M_i^{-3}}$$

N_i = the number of molecules with a molecular mass of M_i

These moments take into consideration the lower molecular mass end of the distribution. The six moments were then compared using statistical techniques.

These six moments do not represent the entire molecular mass distribution, only the center of the distribution (see figure 1). The tails of the distribution, which are expected to have the greatest variation, will not be well represented in any analysis using these moments.

Another method of reducing the data for analysis is to divide the MMD into a few bins. This method is particularly beneficial to compare the tail regions of the molecular mass distribution. The distribution was separated into eleven equal mass divisions before comparison.

The first step in the data analysis was to identify any outliers. The outliers were identified by examining the distribution of the moments and determining whether any data points fell outside of three standard deviations. The moments of two repeats conducted by one laboratory fell outside of the normal distribution of the moments. These data points were classified as outliers and excluded in further data analysis.

The reduced data, both the moments and the bins, were compared using ANOVA. ANOVA indicates a difference in population means by comparing the variation among the group means with the variation within the groups [2]. Analysis of all of the moments showed the significant parameters to be the laboratory performing the measurement, and the matrix used in sample preparation.

The variation among laboratories was tested for all of the moments and bins by ANOVA. The results indicate that the variation among laboratories is much greater than the variation within laboratories.

When a matrix of all-*trans*-retinoic acid was used in the sample preparation, a M_n of 6614 u and a M_w of 6743 u were obtained. When the polystyrene sample was prepared with a dithranol matrix, a M_n of 6539 u and a M_w of 6689 u were obtained (see figure 2). ANOVA tests were performed on the moments to test variation between matrices. The analysis shows that the variance between the matrices is greater than within the matrices, indicating that the matrix used in the sample preparation has a significant influence on the molecular mass distribution obtained by MALDI.

Also compared was the influence of linear or reflectron modes of the instrument on the molecular mass distribution. When the moments were compared, no difference in variance was

seen between the instrument modes and within the modes. However, the ANOVA of the bin data shows that the linear or reflectron modes affect the tails of the distribution. The null hypothesis, that no difference exists between the linear and the reflectron modes of analysis, is accepted for all of the bins except for those bins representing the tails of the distribution. The data indicate that the reflectron mode is more sensitive to the low mass species, whereas the linear mode is more sensitive to the high mass species.

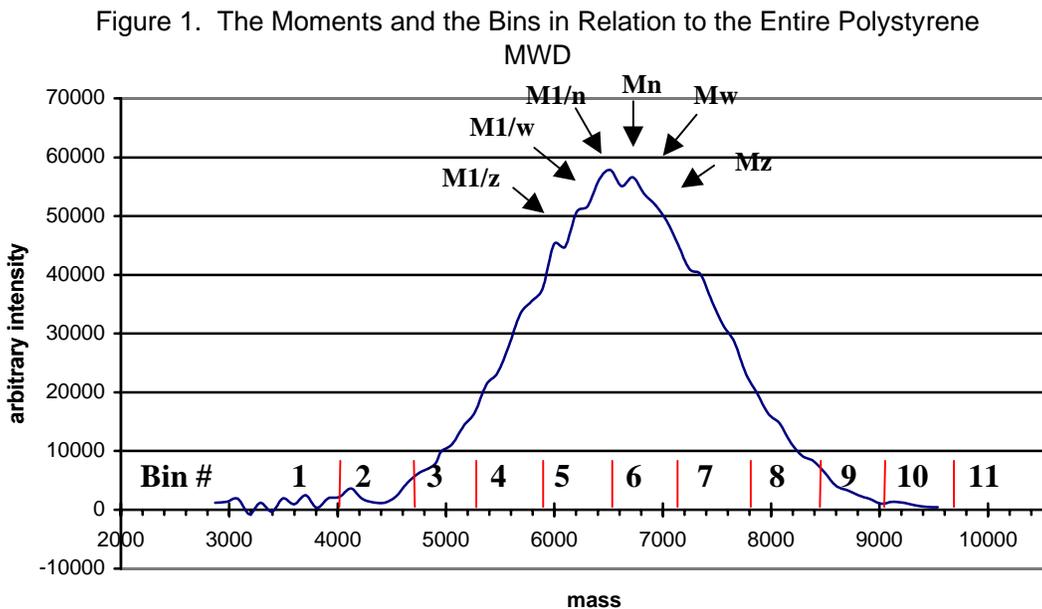
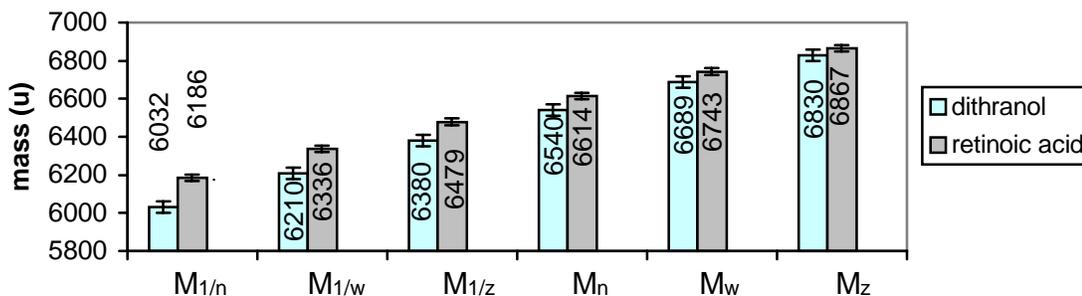


Figure 2. A comparison of the mean moments from two different matrices, retinoic acid and dithranol, used in the sample preparation. The error bars estimate the standard error of the mean.



1. Hiemenz, Paul C., Polymer Chemistry. New York: Marcel Dekker, Inc., 1984 p.36-41.
2. Anderson, T. W., Finn Jeremy D., The New Statistical Analysis of Data. New York; Springer-Verlag, 1996.