



# Kendrick Mass Defect Plots for the Easy Visualization of Information in Polymer Spectra

The Kendrick Mass Defect (KMD) plot method is a powerful and convenient tool for assessing information for polymer analysis. This application note is an introduction to the theory of KMD and its application in polymer analysis. KMD plots are useful in polymer research, as they provide a clear and intuitive way to analyze samples and uncover valuable insights about their composition and structure.

## Introduction

The concept of KM and KMD (Kendrick Mass Defect) was originally introduced by Edward Kendrick in the 1960s as a method for analyzing mass spectral data<sup>1</sup>. Since then, the KMD plot, derived from these principles, has found widespread utility across various scientific disciplines, including petrochemical analysis, environmental chemistry, and lipid characterization, offering valuable insights into hydrocarbon component distribution<sup>2</sup>.

Traditionally utilized in these fields, the KMD plot has emerged as a powerful tool in polymer analysis, facilitated by advancements in mass spectrometry techniques. In polymer spectra, typically signals from different degrees of polymerization are observed. These pose challenges for interpretation, particularly in complex samples containing multiple polymer species, such as blends or those with diverse end groups.

The benefit of the KMD plot lies in its ability to simplify the interpretation of complex polymer

spectra. By plotting polymer signals on a two-dimensional plane based on their KMD values, a clear linear trend emerges with the addition of repeat units, facilitating easier interpretation even for mixed samples. This unique feature makes the KMD plot invaluable for unraveling the composition and structure of intricate polymer mixtures.

In this application note, we delve into the visualization of the KMD plot and showcase its practical applications through illustrative examples, demonstrating its use on homopolymers, polymer blends and copolymers

### Keywords:

Synthetic polymer, MALDI-TOF MS, KMD plot, PolyTools

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## Experimental Procedure

The autoflex maX mass spectrometer was utilized in positive reflector mode for data acquisition. Polymer mixture samples were dissolved in tetrahydrofuran (THF) at a concentration of 10 mg/mL. A matrix solution containing *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) in THF at a concentration of 20 mg/mL, along with sodium trifluoroacetate (NaTFA) in THF at 2 mg/mL as the cationizing agent was prepared. The samples were then mixed with the matrix solution and the cationizing agent solution in a typical ratio of 1:20:1. Subsequently, 1  $\mu$ L of the mixed solution was applied onto the ground steel target plate and allowed to dry.

The acquired mass spectral data were processed using flexAnalysis software for peak picking, followed by data analysis in Polytools 2.0 (Bruker) for KMD plot display and homopolymer assignment.

## Theory of KMD Plot

The **Kendrick Mass (KM)** is a normalized mass value obtained by dividing the nominal mass of an ion by a defined base unit mass. It is calculated using the following equation:

$$KM(R) = m/z \times \frac{\text{round}(R)}{R}$$

Where:

- $m/z$  is the exact mass observed in the spectrum.
- $R$  is the exact mass of the fundamental repeat unit within the sample, such as the mass of the  $C_2H_4O$  unit (44.026215 Da) in polyethylene glycol.
- $\text{Round}(R)$  is the rounded mass of the repeat unit  $R$  (such as 44 Da in polyethylene glycol).
- $KM(R)$  is the Kendrick mass based on repeat unit  $R$ .

The **Kendrick Mass Defect (KMD)** is a normalized mass defect value obtained by subtracting the nearest integer Kendrick mass from the Kendrick mass of an ion. It is calculated using the following equation:

$$KMD = KM - \text{round}(KM)$$

Where " $\text{round}(KM)$ " represents the nearest integer Kendrick mass to  $KM$ .

The KMD represents the fractional deviation of the Kendrick mass from the nearest integer Kendrick mass. It provides a unique signature for compounds within a sample, facilitating the identification of structural features, such as polymer end groups or repeating units, based on their KMD values.

The KMD plot is a two-dimensional plot where the x-axis represents the mass of ions  $m/z$  and the y-axis represents the KMD values of ions. The bubble diameter represents the signal intensity. In the KMD plot, ions with similar structural features or repeating units align along a chain line with a slope depending to the selected base unit mass.

The KMD plot allows a visual representation of the distribution of compounds within a sample for the identification of homologous series, polymer end groups, and other structural motifs. It simplifies the interpretation of complex mass spectra and aids in the elucidation of sample composition and structure.

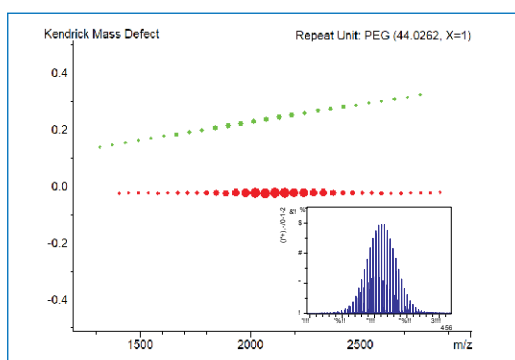
KMD values can range from -0.5 to + 0.5 by definition. However, series of the same monomer with just minor variations of the end groups (like a  $CH_2$  unit) cover only a small part of this range. Therefore, the resolution-enhanced KMD (reKMD) plot was developed<sup>3</sup> as:

$$KM(R,X) = m/z \times \frac{\text{round}(R/X)}{R/X}$$

By changing the divisor  $X$  between values from *round* ( $2/3R$ ) to *round* ( $2R$ ), the resolution of the KMD plot can be adjusted to expand the Y-axis gaps between peak series that are packed in a small range (e.g., -0.03 to 0.15 in Figure 2A) to the actual full Y-axis (theoretically -0.5 to +0.5 at maximum, as shown in Figure 2B). Despite expanding the available range of the Y-axis, the mass error within each peak series is maintained, so the relative mass error against the gaps between each peak series becomes smaller.

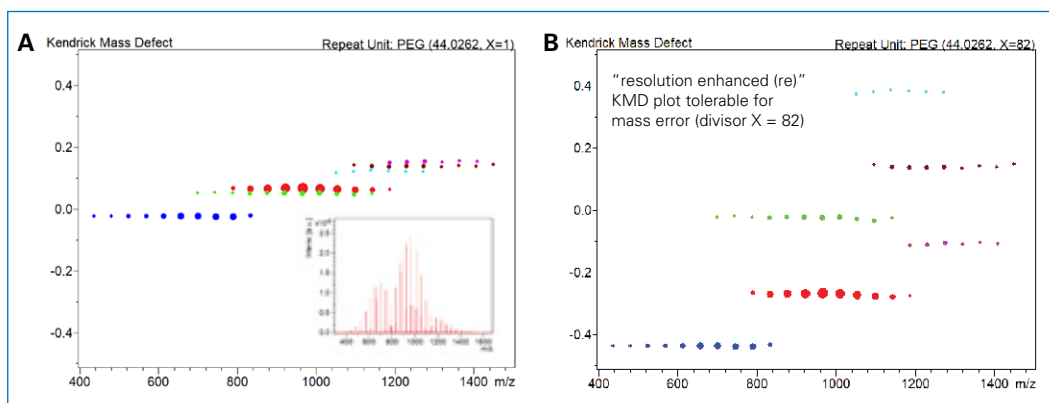
## Results

In Figure 1, a basic illustration for polymer mixtures of standard polyethylene glycol (PEG) and polypropylene glycol (PPG) is presented to introduce the visual appearance of the Kendrick Mass Defect (KMD) plot. The inset of the figure is the original spectrum which was acquired and transformed into the KMD plot. It consists of two polymer distributions which overlap and complicate the spectrum. In the KMD plot, two distinct lines are observed: one horizontal and one diagonal. Given that the Kendrick mass unit is set to 44.0262 as the repeat unit of PEG, the red horizontal chain line is attributed to PEG, while the diagonal green line represents a polymer species distinct from PEG. By examining the signal interval within the green diagonal line, the polymer type can be determined as PPG (58 Da). This is also confirmed by the positive slope of the green PPG series, showing the higher relative hydrogen content of this monomer.



**Figure 1**  
Typical aspects of mass spectra and corresponding KMD plots of a mixture of different polymers.

In Figure 2A, an example of a mixture containing PEG standards with varied end group structures is presented. All lines depicted are horizontal, indicative of PEG species. The presence of six parallel lines signifies a mixture of six different end group combinations, further demonstrating the versatility of the KMD plot in analyzing complex polymer compositions. As seen in Figure 2B, the reKMD plot largely improves the visualization of the various chain lines.

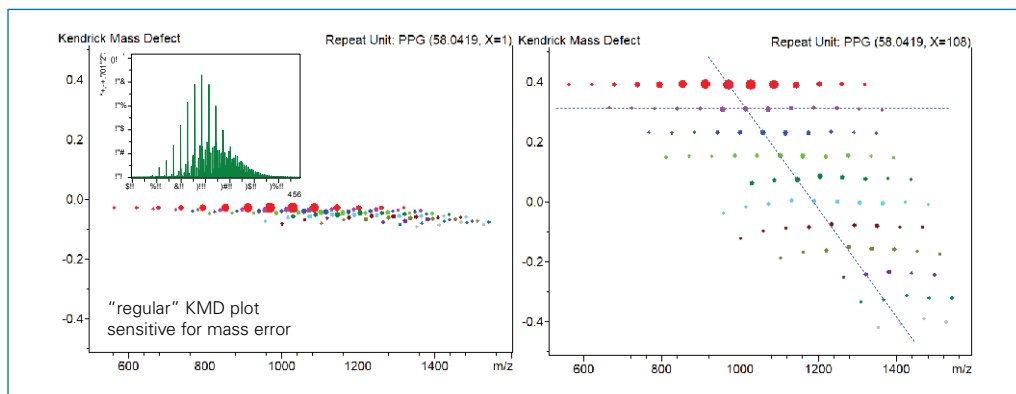


**Figure 2**  
Typical aspects of mass spectra and corresponding KMD plots of a mixture of different end groups. (A) regular KMD plot, (B) resolution-enhanced KMD plot which increases the resolution of the display and generates an improved distinction of the various end groups.

Figure 3 shows the interpretation of a copolymer sample which features a standard composition of PEG and PPG. The distinct KMD plot pattern exhibits the different copolymer species. Again, the regular KMD plot is compared with a reKMD plot to show the improved separation of the different series. For the calculation of the KMD plot, PG (propylenglycol) was selected as the repeat unit. Thus, horizontal lines show PPG distributions which each contain a constant number of PEG units. Here, horizontal lines and diagonal lines coalesce, forming a diagonal grid pattern. This pattern reveals the inclusion of copolymer species within the sample, showcasing the ability of the KMD plot to differentiate between copolymers and homopolymer blends.

**Figure 3**

Typical KMD plots for copolymers, like poly(ethylene glycol)-block-poly(propylene glycol). Left: regular KMD, right: reKMD with an enhanced resolution and differentiation of the various series. The grid pattern points to the presence of constant PEG units within the PPG series.



## Conclusion

Polymer mass spectra typically contain numerous signals representing different degrees of polymerization, resulting in complex spectra even for standard samples. Moreover, polymer samples often comprise mixtures of various monomer units or end group structures, further complicating the spectra. By utilizing the Kendrick Mass Defect (KMD) plot or its resolution-enhanced version, signals align into straight lines on a two-dimensional plane. This alignment enables intuitive recognition of polymer series, providing insights into the types of monomer units present and the number of polymer series in the sample. Additionally, this approach facilitates the distinction between polymer blends and copolymers.

## References

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