Interpretation of Complex Polymer Spectra using KMD Plots

The Kendrick Mass Defect (KMD) plot method is a powerful and convenient tool for assessing information for polymer analysis. This application note will show two examples, a model compound mixture for polyurethane synthesis, where a straightforward interpretation of the observed mass spectra using KMD plots could be performed, and a comparison of different hair care products, where the KMD plots instantly show the differences.

Keywords:
Synthetic polymers;
MALDI-TOF MS;
KMD plot; PolyTools;
Polymerix

Introduction

Introduction to Kendrick Mass Defect (KMD)

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 [1]. 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, and offers valuable insights into hydrocarbon component distribution [2].

KMD Plot in polymer analysis

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, copolymers 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.

Polyurethane synthesis and hair care products

In this application note, we show two examples, a model sample used for polyurethane synthesis (PU) and a selection of hair care products, with straightforward data interpretation by the KMD plots. For an introduction to the KMD features used in PolyTools, please read this application note:

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[1] Anal. Chem., 1963, 35, 13, 2146–2154

[2] Anal. Chem., 73 (2001) 4676-4681

Experimental

Mass spectrometry setup

The autoflex® maX mass spectrometer (Bruker) was used in positive reflector mode for data acquisition of the model sample of the polyurethane synthesis (PU) while the enhanced ultrafleXtreme (Bruker) was used for the hair care products.

Sample preparation

Polymer samples were dissolved in tetrahydrofuran (THF) at a concentration of 10 mg/mL for the PU sample and 20 mg/mL for the hair care products.
A matrix solution of trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyliden] malononitril (DCTB) in THF at a concentration of 20 mg/mL was prepared for the PU sample. 2,4,6-Trihydroxyacetophenone (THAP) as matrix at the same concentration and the same solvent was prepared for the hair care products. For enhanced ionization sodium trifluoroacetate (NaTFA) was prepared in THF at 2 mg/mL as the cationizing agent. The samples were then mixed with the matrix solution and the cationizing agent solution in a typical ratio of 1:20:1 for the PU sample and 10:10:1 for the hair care products. Subsequently, 1 µL of the mixed solution was applied onto the ground steel target plate and allowed to dry.

Data processing and analysis

The acquired mass spectral data were processed by the flexAnalysis software (Bruker) for peak picking and external calibration with the Bruker fleXstandard polymers, followed by data analysis in Polytools 2.0 (Bruker) for KMD plot display and homopolymer assignment. In addition, Polymerix 3.01 (Sierra Analytics) was used for copolymer spectra interpretation.

Results

Polymer mixtures and quality control in Polyurethane synthesis

Today, most of the polymers in our daily life are made from a mixture of different monomers to give them a higher functionality. Polyurethanes (PU) are synthesized from polyols and diisocyanates, but the polyol fraction might contain several monomers and additionally, polyesters might also be present. For quality control purposes it's essential to check incoming goods before the synthesis of the polyurethane is done. Figure 1 shows a spectrum of a polyol fraction used in the polyurethane synthesis. With the extremely high complexity of the spectrum, a manual spectrum interpretation would be very time consuming (see insert for overlapping isotope patterns). Even when PolyTools 2.0 may not be able to identify all series directly, the KMD plot will show the lines of black dots for the unidentified series.

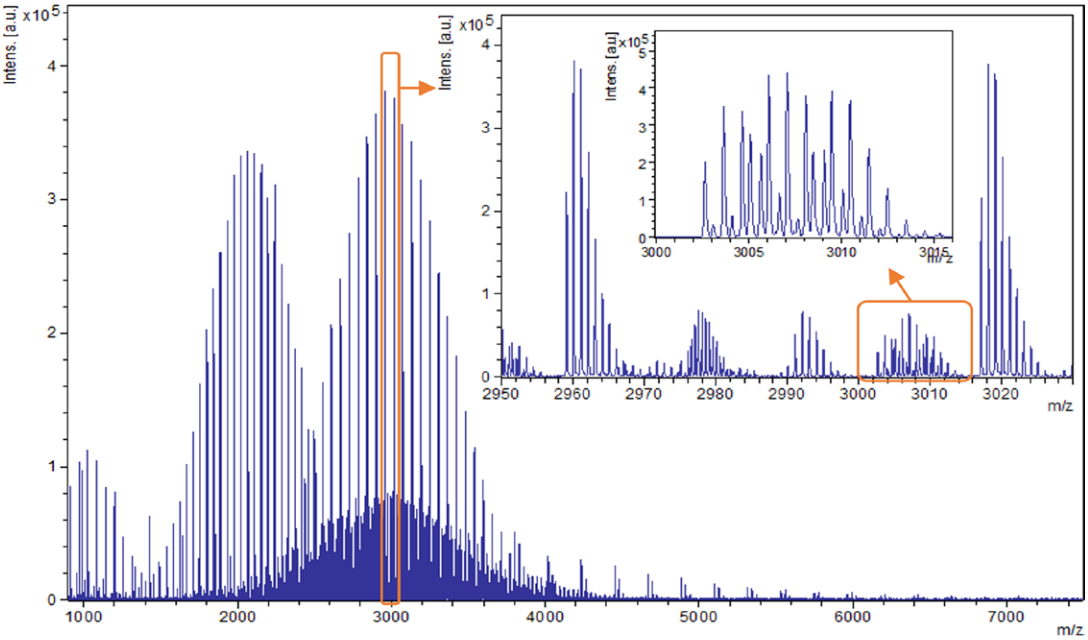


Figure 1. Mass spectrum of a complex mixture of different polymers (polyethers and polyesters, a model sample of a polyol mixture used for polyurethane synthesis).

Visualizing mass spectra with KMD plot in PolyTools

As shown in Figure 2, PolyTools 2.0 enables mass spectrum visualization as a KMD plot for easier interpretation.

As the repeating unit was set to PPG, all polymers containing propylene glycol as monomer show up as horizontal lines, as in the distributions A, E and F. Additionally, the signals in the E- and F-distributions form a grid-like structure in the KMD plot, indicating the presence of copolymers . Even when not all series are identified immediately (black dots), the KMD plot elucidates a negative slope for the series B, C and D indicating a higher presence of oxygen and/or a lower presence of hydrogen in these monomers compared to the selected PPG. The distinctive monomer units are discernible based on the intervals between signals in these series. Based on all this information, the PolyTools result table (Figure 3) is compiled. Component A corresponds to PPG with three different end-groups, B corresponds to PEG with two different end-groups, C corresponds to Poly(Adipic acid-DiEthyleneGlycol) with two different end-groups, and D corresponds to Poly(Phthalic acid-PropyleneGlycol).

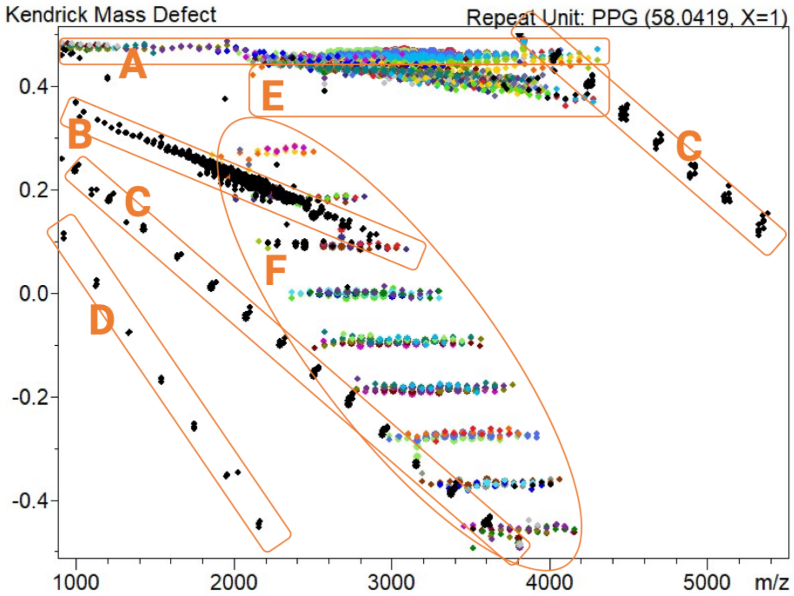
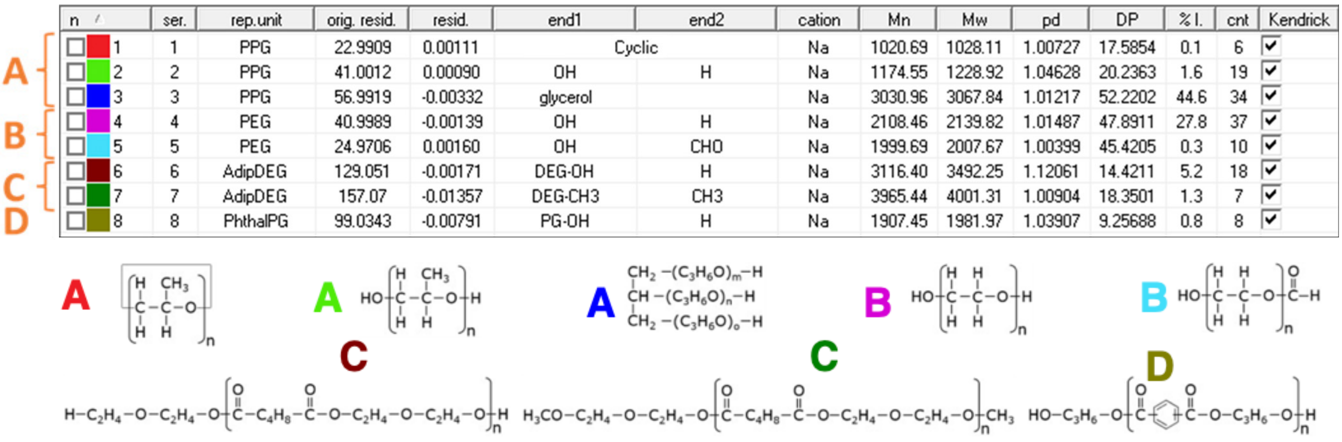


Figure 2. KMD plot of the polyol mixture shown in Figure 1. The mass of the repeat unit was set to 58.0419 Da corresponding to PPG.

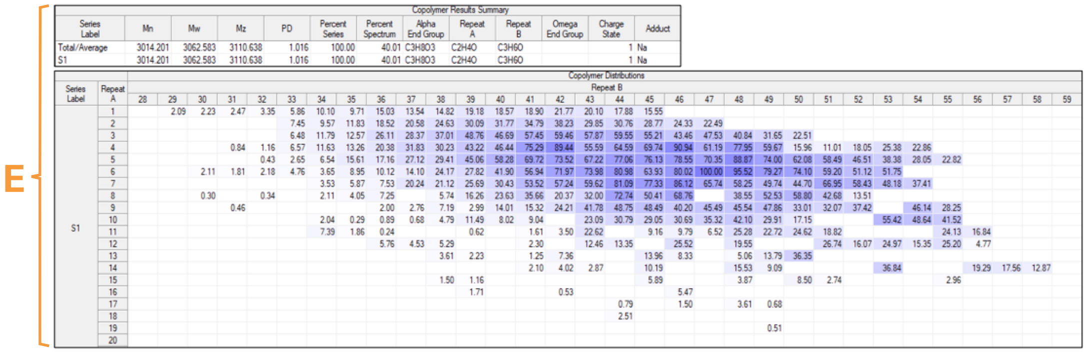


n	ser.	rep.unit	orig. resid.	resid.	end1	end2	cation	Mn	Mw	pd	DP	% I.	cnt	Kendrick
☐ 🟥 1	1	PPG	22.9909	0.00111	Cyclic		Na	1020.69	1028.11	1.00727	17.5854	0.1	6	☑
☐ 🟩 2	2	PPG	41.0012	0.00090	OH	H	Na	1174.55	1228.92	1.04628	20.2363	1.6	19	☑
☐ 🟦 3	3	PPG	56.9919	-0.00332	glycerol		Na	3030.96	3067.84	1.01217	52.2202	44.6	34	☑
☐ 🟪 4	4	PEG	40.9989	-0.00139	OH	H	Na	2108.46	2139.82	1.01487	47.8911	27.8	37	☑
☐ 🟦 5	5	PEG	24.9706	0.00160	OH	CHO	Na	1999.69	2007.67	1.00399	45.4205	0.3	10	☑
☐ 🟥 6	6	AdipDEG	129.051	-0.00171	DEG-OH	H	Na	3116.40	3492.25	1.12061	14.4211	5.2	18	☑
☐ 🟩 7	7	AdipDEG	157.07	-0.01357	DEG-CH3	CH3	Na	3965.44	4001.31	1.00904	18.3501	1.3	7	☑
☐ 🟫 8	8	PhthalPG	99.0343	-0.00791	PG-OH	H	Na	1907.45	1981.97	1.03907	9.25688	0.8	8	☑

Figure 3. End-group assignment of the homopolymer species A-D by Polytools 2.0. The peak list which is extracted from the original data based on *m/z* and KMD values is used. The detailed structures of the polymers A-D are displayed.

Copolymers analysis with KMD plot and Polymerix software

As the distributions E and F in The KMD plot were assigned to copolymers, a further investigation was carried out by the Polymerix software. The result is shown in Figure 4. In both cases the monomer B was defined as propylene glycol displayed on the horizontal axis. In sample E, the second repeating unit was defined as ethylene glycol. In sample F, the second repeating unit was an ester of one propylene glycol with phthalic acid (PGPA). Both copolymers were terminated by glycerol. The most intense signals were found at the masses of glycerol terminated and sodium attached species of EG6PG47 and PGPA7PG28 respectively.



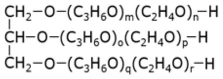
Copolymer Results Summary

Series Label	Mn	Mw	Mz	PD	Percent Series	Percent Spectrum	Alpha End Group	Repeat A	Repeat B	Omega End Group	Charge State	Adduct
Total/Average	3014.201	3062.583	3110.638	1.016	100.00	40.01	C3H8O3	C2H4O	C3H6O		1	Na
S1	3014.201	3062.583	3110.638	1.016	100.00	40.01	C3H8O3	C2H4O	C3H6O		1	Na

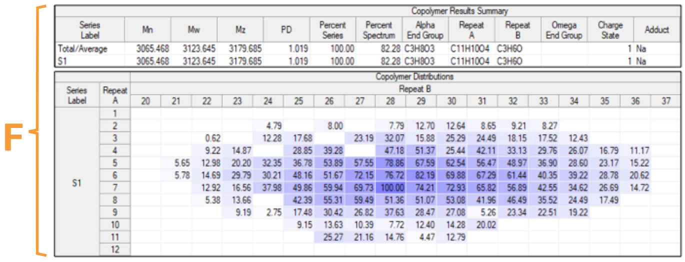
Copolymer Distributions

Repeat B

Series Label	Repeat A	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59
S1	1		2.09	2.23	2.47	3.35	5.86	10.10	9.71	15.03	13.54	14.82	19.18	18.57	18.90	21.77	20.10	17.88	15.55														
	2						7.45	9.57	11.83	18.52	20.58	24.63	30.09	31.77	34.79	38.23	29.85	30.76	28.77	24.33	22.49												
	3						6.48	11.79	12.57	26.11	28.37	37.01	48.76	46.69	57.45	59.46	57.87	59.55	55.21	43.46	47.53	40.84	31.65	22.51									
	4				0.84	1.16	6.57	11.63	13.26	20.38	31.83	30.23	43.22	46.44	75.29	89.44	55.59	64.59	69.74	90.94	61.19	77.95	59.67	15.96	11.01	18.05	25.38	22.86					
	5					0.43	2.65	6.54	15.61	17.16	27.12	29.41	45.06	58.28	69.72	73.52	67.22	77.06	76.13	78.55	70.35	88.87	74.00	62.08	58.49	46.51	38.38	28.05	22.82				
	6			2.11	1.81	2.18	4.76	3.65	8.95	10.12	14.10	24.17	27.82	41.90	56.94	71.97	73.98	80.98	63.93	80.02	100.00	95.52	79.27	74.10	59.20	51.12	51.75						
	7							3.53	5.87	7.53	20.24	21.12	25.69	30.43	53.52	57.24	59.62	81.09	77.33	86.12	65.74	58.25	49.74	44.70	66.95	58.43	48.18	37.41					
	8			0.30		0.34		2.11	4.05	7.25		5.74	16.26	23.63	35.66	20.37	32.00	72.74	50.41	68.76		38.55	52.53	58.80	42.68	13.51							
	9				0.46					2.00	2.76	7.19	2.99	14.01	15.32	24.21	41.78	48.75	48.49	40.20	45.49	45.54	47.86	33.01	32.07	37.42		46.14	28.25				
	10							2.04	0.29	0.89	0.68	4.79	11.49	8.02	9.04		23.09	30.79	29.05	30.69	35.32	42.10	29.91	17.15			55.42	48.64	41.52				
	11							7.39	1.86	0.24			0.62		1.61	3.50	22.62		9.16	9.79	6.52	25.28	22.72	24.62	18.82				24.13	16.84			
	12									5.76	4.53	5.29			2.30		12.46	13.35		25.52		19.55			26.74	16.07	24.97	15.35	25.20	4.77			
	13											3.61	2.23		1.25	7.36			13.96	8.33		5.06	13.79	36.35									
	14														2.10	4.02	2.87		10.19			15.53	9.09				36.84			19.29	17.56	12.87	
	15											1.50	1.16						5.89			3.87		8.50	2.74				2.96				
	16												1.71			0.53				5.47													
	17																	0.79		1.50		3.61	0.68										
	18																	2.51															
	19																						0.51										
	20																																



$$\begin{array}{l} \mathrm{CH_2-O-(C_3H_6O)_m(C_2H_4O)_n-H} \\ | \\ \mathrm{CH-O-(C_3H_6O)_o(C_2H_4O)_p-H} \\ | \\ \mathrm{CH_2-O-(C_3H_6O)_q(C_2H_4O)_r-H} \end{array}$$



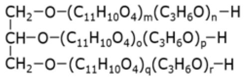
Copolymer Results Summary

Series Label	Mn	Mw	Mz	PD	Percent Series	Percent Spectrum	Alpha End Group	Repeat A	Repeat B	Omega End Group	Charge State	Adduct
Total/Average	3065.468	3123.645	3179.685	1.019	100.00	82.28	C3H8O3	C11H10O4	C3H6O		1	Na
S1	3065.468	3123.645	3179.685	1.019	100.00	82.28	C3H8O3	C11H10O4	C3H6O		1	Na

Copolymer Distributions

Repeat B

Series Label	Repeat A	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
S1	1																		
	2					4.79		8.00		7.79	12.70	12.64	8.65	9.21	8.27				
	3			0.62		12.28	17.68		23.19	32.07	15.88	25.29	24.49	18.15	17.52	12.43			
	4			9.22	14.87		28.85	39.28		47.18	51.37	25.44	42.11	33.13	29.76	26.07	16.79	11.17	
	5		5.65	12.98	20.20	32.35	36.78	53.89	57.55	78.86	67.59	62.54	56.47	48.97	36.90	28.60	23.17	15.22	
	6		5.78	14.69	29.79	30.21	48.16	51.67	72.15	76.72	82.19	69.88	67.29	61.44	40.35	39.22	28.78	20.62	
	7			12.92	16.56	37.98	49.86	59.94	69.73	100.00	74.21	72.93	65.82	56.89	42.55	34.62	26.69	14.72	
	8			5.38	13.66		42.39	55.31	59.49	51.36	51.07	53.08	41.96	46.49	35.52	24.49	17.49		
	9				9.19	2.75	17.48	30.42	26.82	37.63	28.47	27.08	5.26	23.34	22.51	19.22			
	10						9.15	13.63	10.39	7.72	12.40	14.28	20.02						
	11							25.27	21.16	14.76	4.47	12.79							
	12																		



$$\begin{array}{l} \mathrm{CH_2-O-(C_{11}H_{10}O_4)_m(C_3H_6O)_n-H} \\ | \\ \mathrm{CH-O-(C_{11}H_{10}O_4)_o(C_3H_6O)_p-H} \\ | \\ \mathrm{CH_2-O-(C_{11}H_{10}O_4)_q(C_3H_6O)_r-H} \end{array}$$

Figure 4. Polymerix copolymer analysis of the distributions E and F found in the polyol mixture of the polyurethane synthesis. The distribution plots show the relative intensities of the signals for different combinations of the two monomer units and fixed combinations of end groups, i.e. glycerol and the attached sodium ion.

KMD Plot for analyzing hair care product mixtures

Figure 5 showcases another practical application of the KMD plot, particularly beneficial for discerning complex mixtures which are commonly encountered in commercial products such as hair care products. In this case, six hair care products (I-VI) were analyzed. A special focus was set on the presence of siloxanes, i.e. dimethyl siloxane was also selected as the base unit in the KMD plot for the analysis.

Differentiating polymer distributions in hair care products

The hair treatments I-IV contain PDMS, while hair conditioners (V-VI) do not. PEG is very common among all products except VI. The hair treatments I and II are the same brand but different types showing that they are similar with small differences in polymer distribution. The KMD plot aids in identifying the polymer species present in each product, facilitating comparison and differentiation between products, thus demonstrating its relevance in industrial and consumer product analysis.

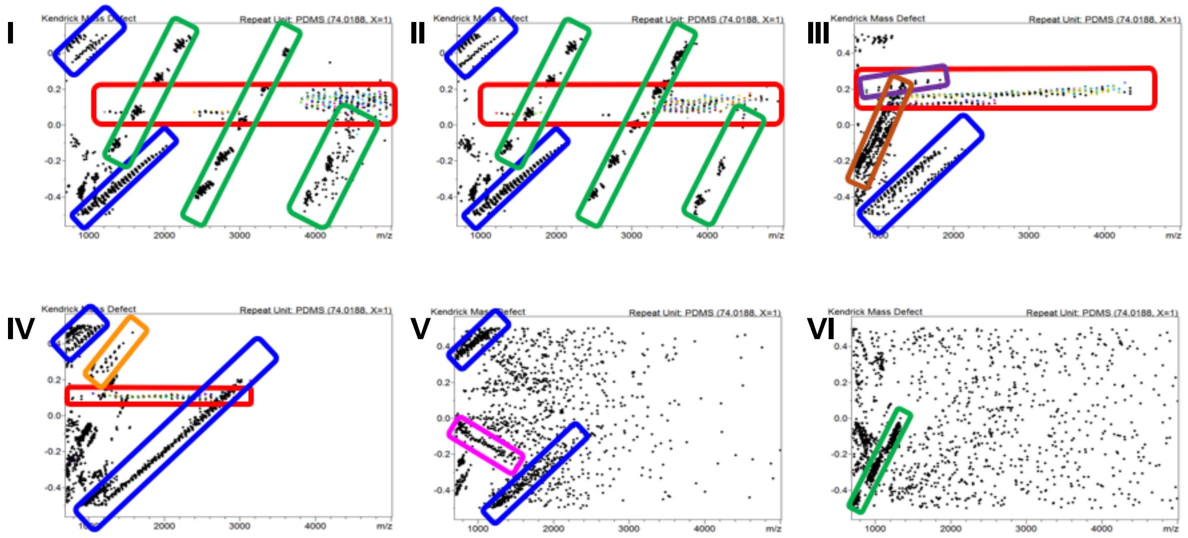


Figure 5. KMD plots of six different hair care products. Polydimethylsiloxane (74 Da / Dimethicone), polyethylene glycol (44 Da / PEG), stearic acid adduct (282 Da / Pentaerythritol polystearate, etc.), polysaccharide (162 Da / hydrogenated starch hydrolysate), probably polypropylene glycol (58 Da / no description in ingredient list), probably polyacrylicacid (72 Da / no description in ingredient list) and probably fatty acid esters (28 Da / no description in ingredient list) could be identified in the samples

Conclusion

KMD plot for quality control

As an example for the quality control of incoming goods, a complete analysis of the ingredients of the polyol fraction used in polyurethane synthesis has been performed. It was shown how the Kendrick Mass Defect plot in PolyTools 2.0 can simplify the interpretation of very complex spectra.

Polymerix software for copolymer species interpretation

Additionally, a detailed interpretation of the copolymer species in the sample was performed using the Polymerix software. As a second example it was shown how the KMD plot can help to distinguish between different samples of the same kind.

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