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Dr. John Scheirs

Released by:

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President

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February 8, 2016

Dr. John Scheirs
ExcelPlas
31 Louden Road
Dalby, Queensland 4405
Australia

E: John@excelplas.com

Dear John,

Please find enclosed the test results for your samples described as:

1. IPLEX
2. CCC #5607/5
3. HCC 276/18

The following tests were performed:

1. High Temperature Gel Permeation Chromotagraphy (GPC-H)
2. High Temperature Tetradetection Gel Permeation Chromatography (GPC-HT)

Objective

The goal of this analysis was to determine the relative molecular weight distribution and modality of the HDPE samples.

Summary of Results

Three samples were subjected to GPC-H and GPC-HT analysis. The results for GPC-H and GPC-HT are summarized in **Table 1** and **Table 3**, respectively. **Table 4** includes the Mark Houwink data. It is expected that the GPC-HT results are a more accurate reflection of the true sample molecular weight than the GPC-H results, because the polystyrene calibrant is structurally different from the sample polyethylene being characterized. This has a significant effect on the calculated molecular weight averages.

In addition, based on the Mark Houwink plots of the three samples, a downward curvature of the plot at high molecular weight indicated that the samples are branched polymers (long chain branching). The branch frequency in the samples was calculated using a NIST linear standard and are shown in **Table 4**. Samples IPLEX, CCC #5607/5 and HCC 276/18 showed branching frequencies per 1000 carbons of 4.8, 1.5 and 3.7 respectively.

Individual Test Results

A summary of the individual test results is provided below. All accompanying data, including spectra, has been included in the data section of this report.

GPC

GPC Background: A polymer is a large molecule which is formed using a repeating subunit. A polymeric sample does not have a single molecular weight but rather a range of values and thus an average value is used to indicate its molecular weight.

Three different molecular weight averages are commonly used to provide information about polymers. These are the number average molecular weight (Mn), the weight average molecular weight (Mw), and the Z average molecular weight (Mz).

Mn provides information about the lowest molecular weight portion of the sample. Mw is the average closest to the center of the peak and Mz represents the highest molecular weight portion of the sample. The different molecular weight averages can each be related to specific polymer properties such as material toughness, tensile strength, and total elongation.

By comparing the different averages, it is possible to define a fourth parameter called the polydispersity index (PDI). This parameter gives an indication of how broad a range of molecular weights are in the sample.

Enclosed are refractive index chromatograms for each sample, as well as their cumulative weight fraction curves, molecular weight distribution curves and summary reports. A second summary report for each sample is included to show the reproducibility of the data. A calibration curve and chromatographic overlay of the standards are included. Also, please find an overlay of the sample with standards.

Results: Analysis by GPC requires that a suitable solvent be found to dissolve the sample. The sample was found to dissolve in Trichlorobenzene (TCB). Enclosed is a refractive index chromatogram for the sample, as well as its cumulative weight fraction curve, and molecular weight distribution curve. A calibration curve and chromatographic overlay of the standards are included. The average molecular weights are summarized in **Table 1**.

Table 1.
Average Molecular Weight
Relative to polystyrene standards

NIST Polyethylene 1484a
(Mw= 119,600 Da)

Sample	Mn	Mw	Mz	Mw/Mn
2016-01-29_19;30;12_PE_linear_NISt_std_1484a_01.vdt	281,229	329,170	385,848	1.170
2016-01-29_20;33;45_PE_linear_NISt_std_1484a_02.vdt	272,778	331,956	398,649	1.217

NIST Polyethylene 1475a
(Mw= 53,070 Da)

Sample	Mn	Mw	Mz	Mw/Mn
2016-01-29_21;37;19_PE_linear_NIST_std_1475a__01.vdt	42,325	157,845	503,338	3.729
2016-01-29_22;40;53_PE_linear_NIST_std_1475a__02.vdt	42,082	157,887	498,944	3.752

IPLEX

Sample	Mn	Mw	Mz	Mw/Mn
2016-01-30_07;09;36_IPLEX_01.vdt	18,202	401,051	1.603 e 6	22.033
2016-01-30_08;13;09_IPLEX_02.vdt	18,729	388,312	1.613 e 6	20.732

CCC #5607/5

Sample	Mn	Mw	Mz	Mw/Mn
2016-01-30_09;16;45_CCC#5607_5_01.vdt	19,894	508,972	2.478 e 6	25.583
2016-01-30_10;20;21_CCC#5607_5_02.vdt	19,118	496,870	2.413 e 6	25.989

HCC 276/18

Sample	Mn	Mw	Mz	Mw/Mn
2016-01-30_11;23;55_HCC_276_18_01.vdt	15,378	464,439	2.326 e 6	30.200
2016-01-30_12;27;31_HCC_276_18_02.vdt	15,397	453,539	2.318 e 6	29.455

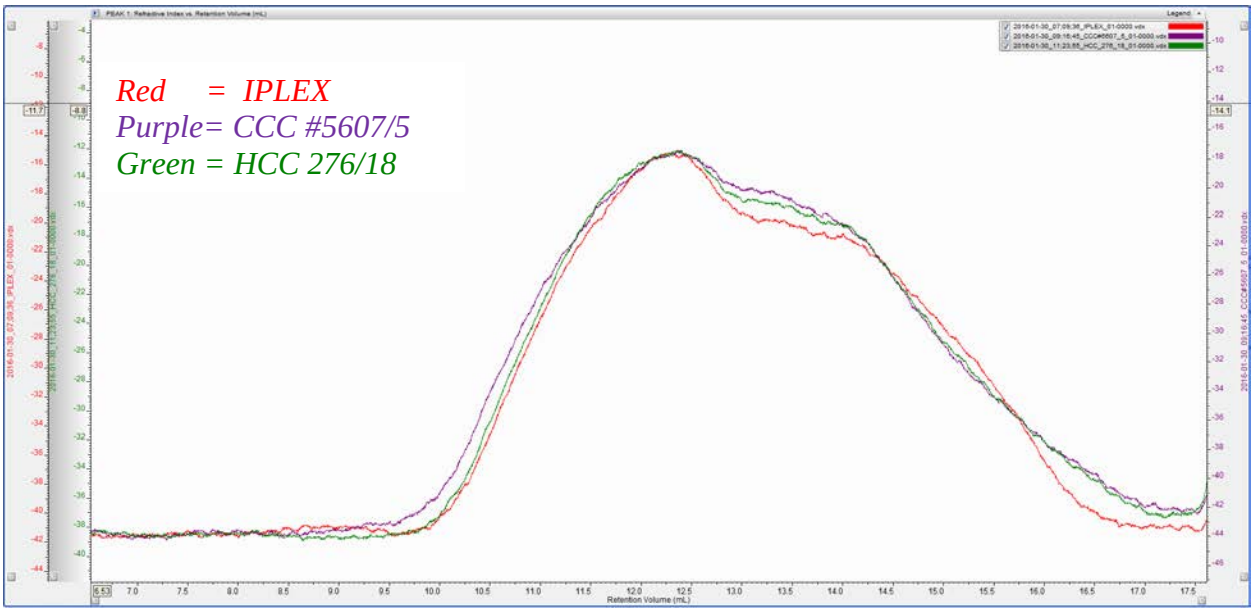


Figure 1. Normalized overlay of refractive index (RI) chromatograms of the samples.

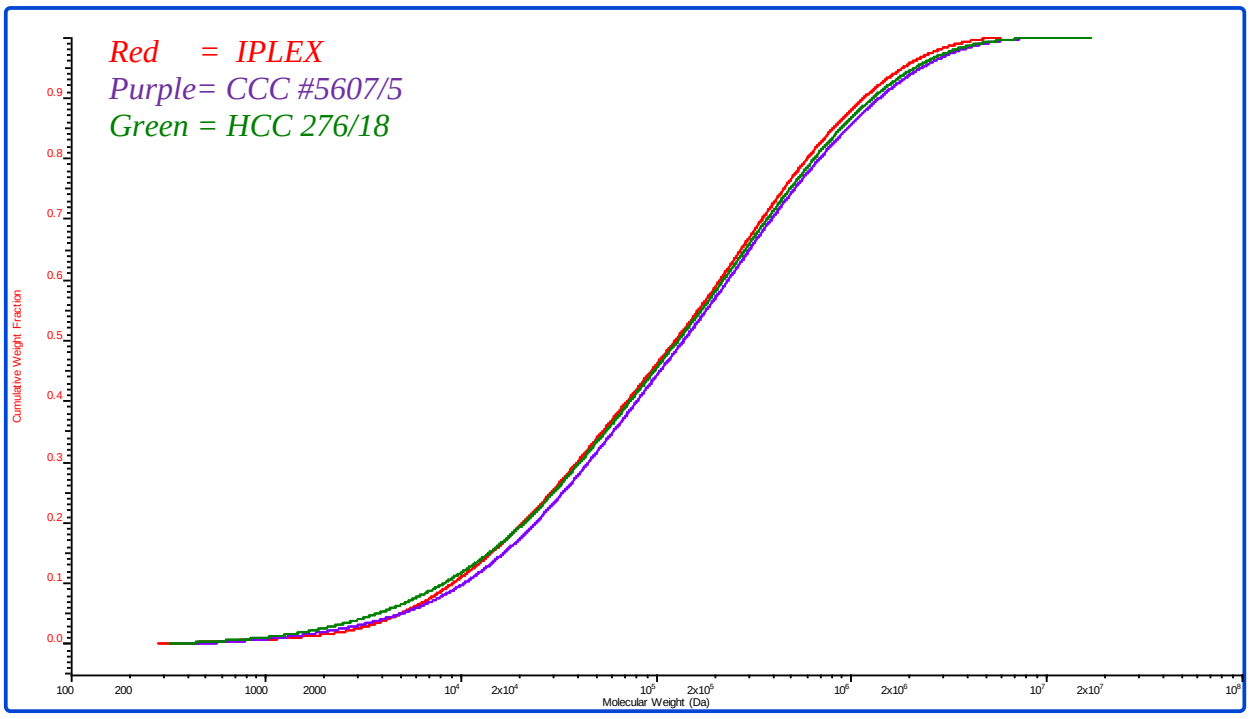


Figure 2. Overlay of cumulative weight fraction curves for the samples.

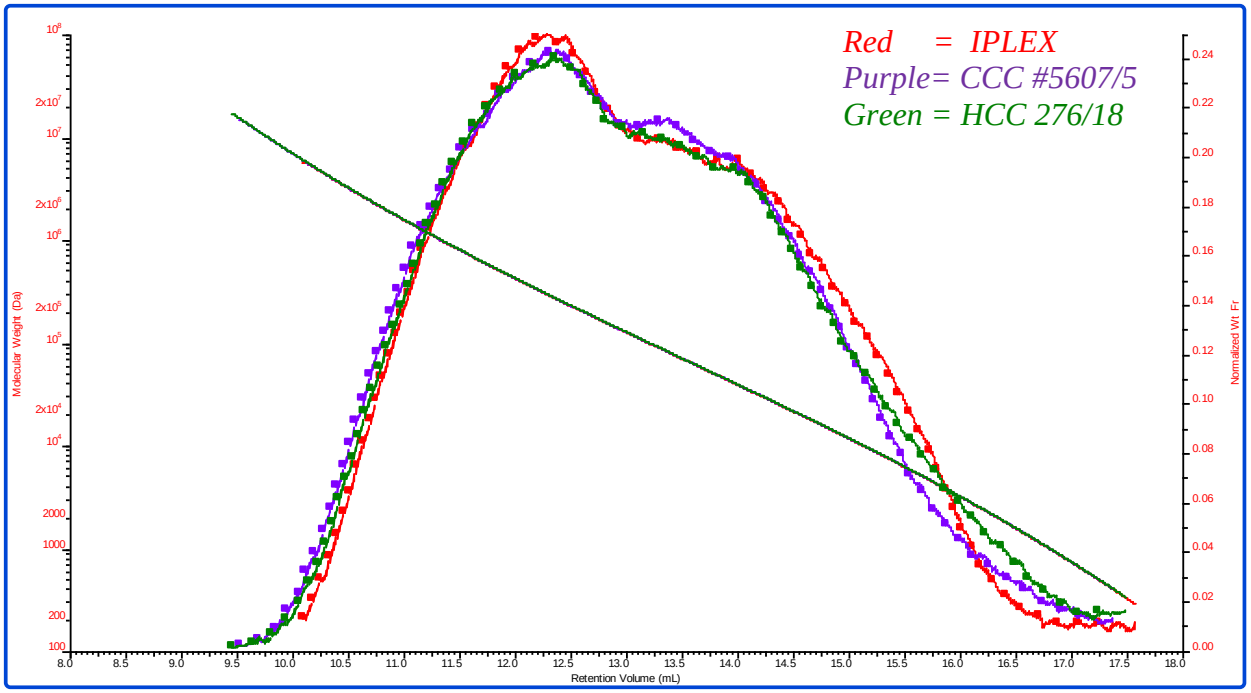


Figure 3. Overlay of molecular weight distribution curves for the samples.

GPC-T

Background

A polymer is a large molecule which is formed using a repeating subunit. A polymeric sample does not have a single molecular weight but rather a range of values and thus an average value is used to indicate its molecular weight.

Three different molecular weight averages are commonly used to provide information about polymers. These are the number average molecular weight (M_n), the weight average molecular weight (M_w), and the Z average molecular weight (M_z). M_n provides information about the lowest molecular weight portion of the sample. M_w is the average closest to the center of the peak and M_z represents the highest molecular weight portion of the sample. The different molecular weight averages have been related to specific polymer properties. As an example, the highest molecular weight portion of the sample is typically related to material toughness.

By comparing the different averages, it is possible to define a fourth parameter called the polydispersity index (PDI). This parameter gives an indication of how broad a range of molecular weights are in the sample.

Two other parameters were calculated during this analysis. They are the intrinsic viscosity (IV) and the radius of hydration (R_h). Intrinsic viscosity is the inverse molecular density and can be used as an indication of the extent of polymer branching and shape. R_h is a measure of the size of the polymer molecule.

Mark–Houwink Equation

The Mark Houwink equation describes the dependence of the *intrinsic viscosity* of a polymer on its relative molecular mass (molecular weight) and has the form:

$[IV] = K \times M^{\alpha}$

Where [IV] is the intrinsic viscosity, K and α are constants, the values of which depend on the nature of the polymer and solvent as well as on temperature and M is the molecular mass.

Taking the Log of this equation results in:

Log [IV]= Log K + α*Log [M]

This equation is linear and has the form:

Y = mX+b

Where m is the slope and b is the intercept. The Mark Houwink relationship therefore has a slope of α and an intercept of Log K. The slope is an important indicator of how the molecule behaves in solution. A solid sphere will have a Mark Houwink slope of zero, a rigid rod has a slope of two and a random coil should have a slope of 0.7. Thus, the slope is a function of molecular shape.

Results

Table 2 shows the results of the system suitability standards. One narrow standard (PS 105,453 Da) was used to calibrate the instrument. A broad standard (PS 234,425 Da) was used as a reference standard to verify system performance.

Table 3 shows the results for the samples. **Figures 1 – 6** show overlays of the Refractive Index (RI), Right Angle Light Scattering (RALS), Viscometer (DP), Molecular Weight Distribution and Mark Houwink curves.

Table 4 includes the Mark Houwink data.

Table 2. Standards

Calibration Standard (GPC-T)
(PS 104,966 Da)

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh (nm)
2016-01-29_16;19;30_PS_105k_CAL_STD_01.vdt	102,332	104,584	107,606	1.022	0.3319	8.17

ID	dn/dc (mL/g)	Conc (mg/mL)
PS 105k CAL STD	0.0520	2.5270

Reference Standard (GPC-T)
(PS 244,483 Da)

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh (nm)
2016-01-29_17;23;04_PS_broad__01.vdt	124,085	239,744	500,718	1.932	0.5704	12.22
2016-01-29_18;26;36_PS_broad_01.vdt	120,073	236,289	476,353	1.968	0.5614	12.08

ID	dn/dc (mL/g)	Conc (mg/mL)
PS broad	0.0520	4.7836
PS broad	0.0520	4.8784

Table 3. Analysis of Samples

NIST Polyethylene 1484a
(Mw= 119,600 Da)

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh(w) (nm)
2016-01-29_19;30;12_PE_linear_NISt_std_1484a_01.vdt	103,722	119,658	209,505	1.154	1.7483	14.61
2016-01-29_20;33;45_PE_linear_NISt_std_1484a_02.vdt	101,815	115,719	217,494	1.137	1.8342	14.71

ID	dn/dc (mL/g)	Conc (mg/mL)
PE linear NISt std 1484a	0.1040	0.4200
PE linear NISt std 1484a	0.1040	0.4069

NIST Polyethylene 1475a
(Mw= 53,070 Da)

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh(w) (nm)
2016-01-29_21;37;19_PE_linear_NIST_std_1475a__01.vdt	23,389	51,197	184,439	2.189	0.8747	8.14
2016-01-29_22;40;53_PE_linear_NIST_std_1475a__02.vdt	23,062	50,899	187,004	2.207	0.8912	8.19

ID	dn/dc (mL/g)	Conc (mg/mL)
PE linear NIST std 1475a	0.1040	0.7918
PE linear NIST std 1475a	0.1040	0.7837

IPLEX

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh(w) (nm)
2016-01-30_07;09;36_IPLEX_01.vdt	28,191	259,213	1.348 e 6	9.195	1.6198	14.97
2016-01-30_08;13;09_IPLEX_02.vdt	28,529	247,322	1.393 e 6	8.669	1.5590	14.54

ID	dn/dc (mL/g)	Conc (mg/mL)
IPLEX	0.1040	1.4280
IPLEX	0.1040	1.4954

CCC #5607/5

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh(w) (nm)
2016-01-30_09;16;45_CCC#5607_5_01.vdt	23,071	176,282	583,768	7.641	1.8046	14.35
2016-01-30_10;20;21_CCC#5607_5_02.vdt	23,283	172,045	586,939	7.389	1.7568	14.05

ID	dn/dc (mL/g)	Conc (mg/mL)
CCC#5607_5	0.1040	1.4053
CCC#5607_5	0.1040	1.4395

HCC 276/18

Sample	Mn (Da)	Mw (Da)	Mz (Da)	Mw/Mn	IV (dL/g)	Rh (nm)
2016-01-30_11;23;55_HCC_276_18_01.vdt	20,831	186,723	725,837	8.964	1.6364	13.91
2016-01-30_12;27;31_HCC_276_18_02.vdt	21,515	187,158	748,085	8.699	1.5854	13.67

ID	dn/dc (mL/g)	Conc (mg/mL)
HCC 276_18	0.1040	1.4769
HCC 276_18	0.1040	1.4949

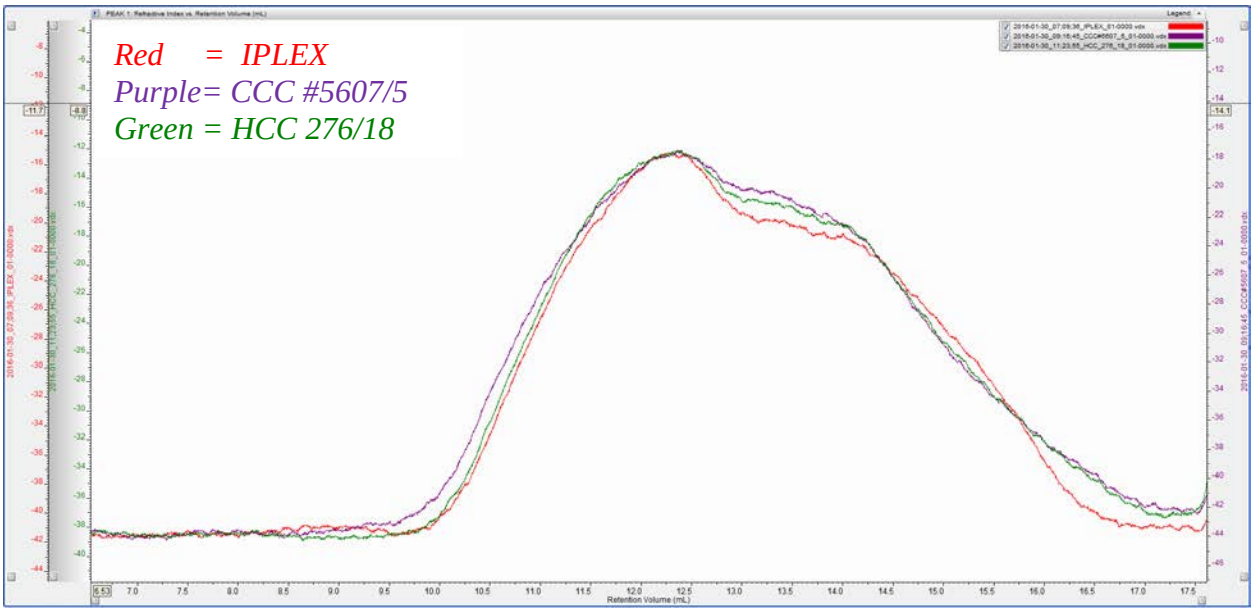


Figure 4. Overlay of normalized refractive index (RI) sample chromatograms.

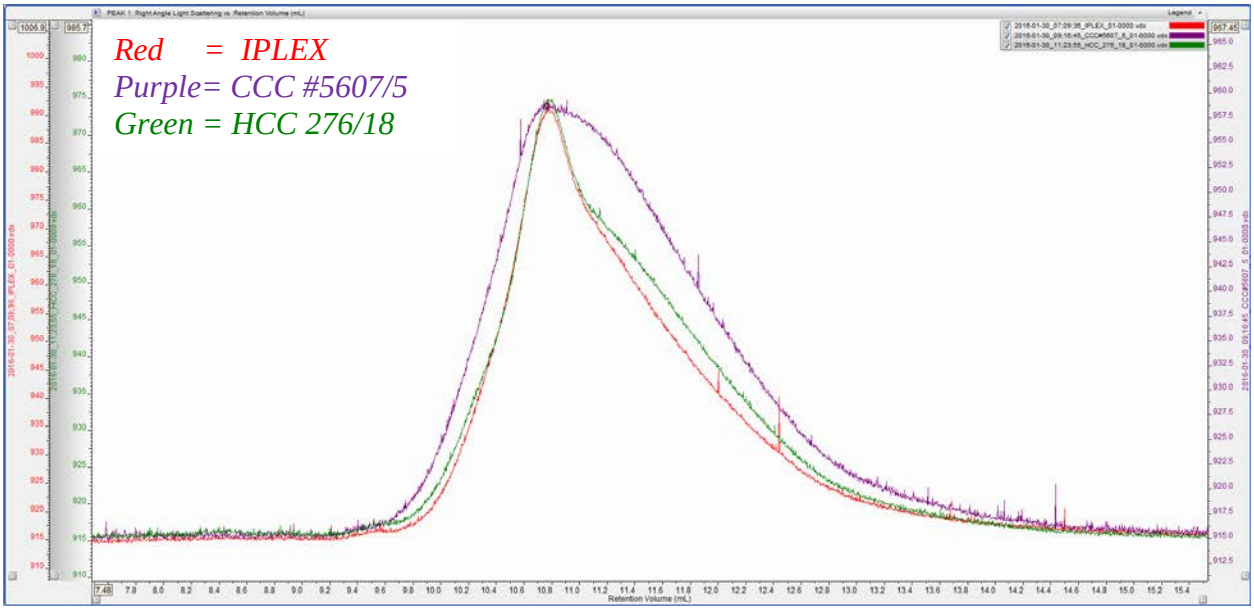


Figure 5. Overlay of normalized right angle light scattering (RALS) sample chromatograms.

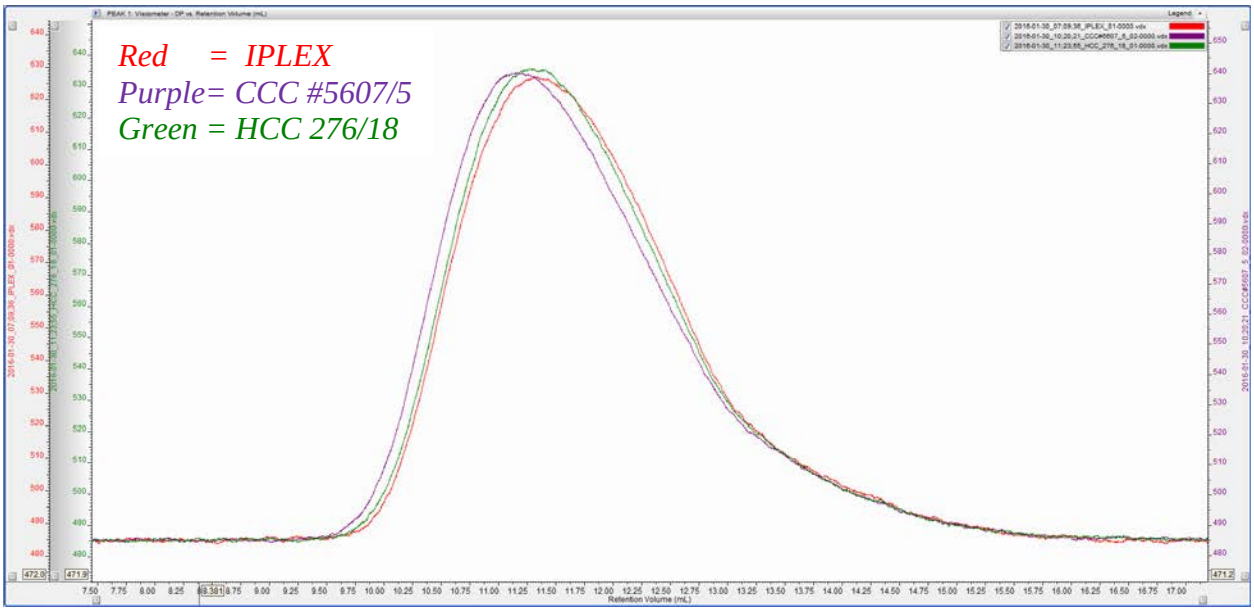


Figure 6. Overlay of normalized Viscometer (DP) sample chromatograms.

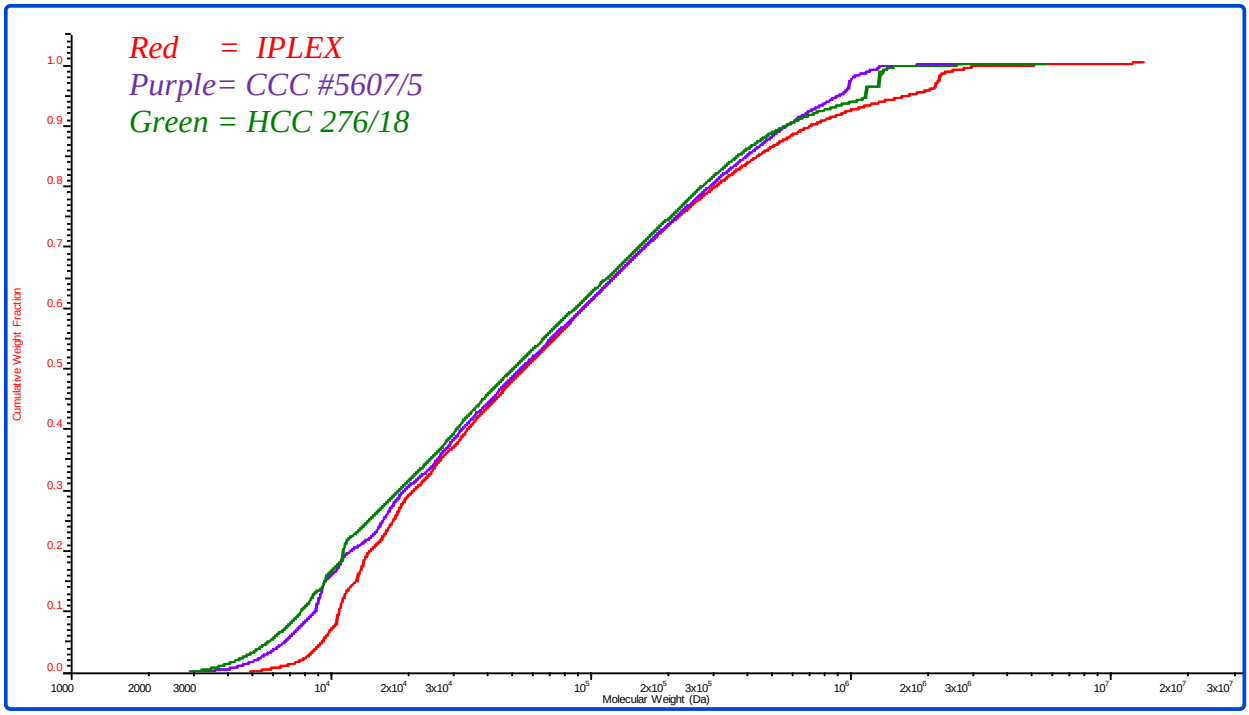


Figure 7. Overlay of cumulative weight fraction curves for all samples.

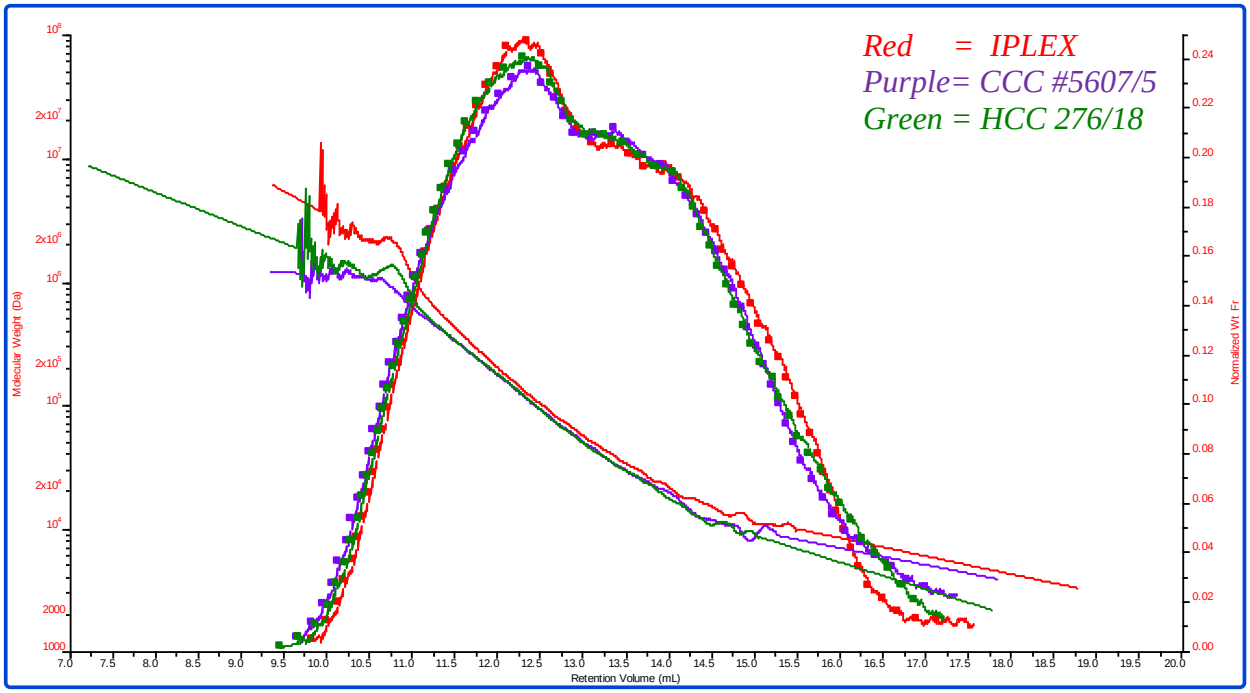


Figure 8. Overlay of weight fraction and log molecular weight curves for all samples.

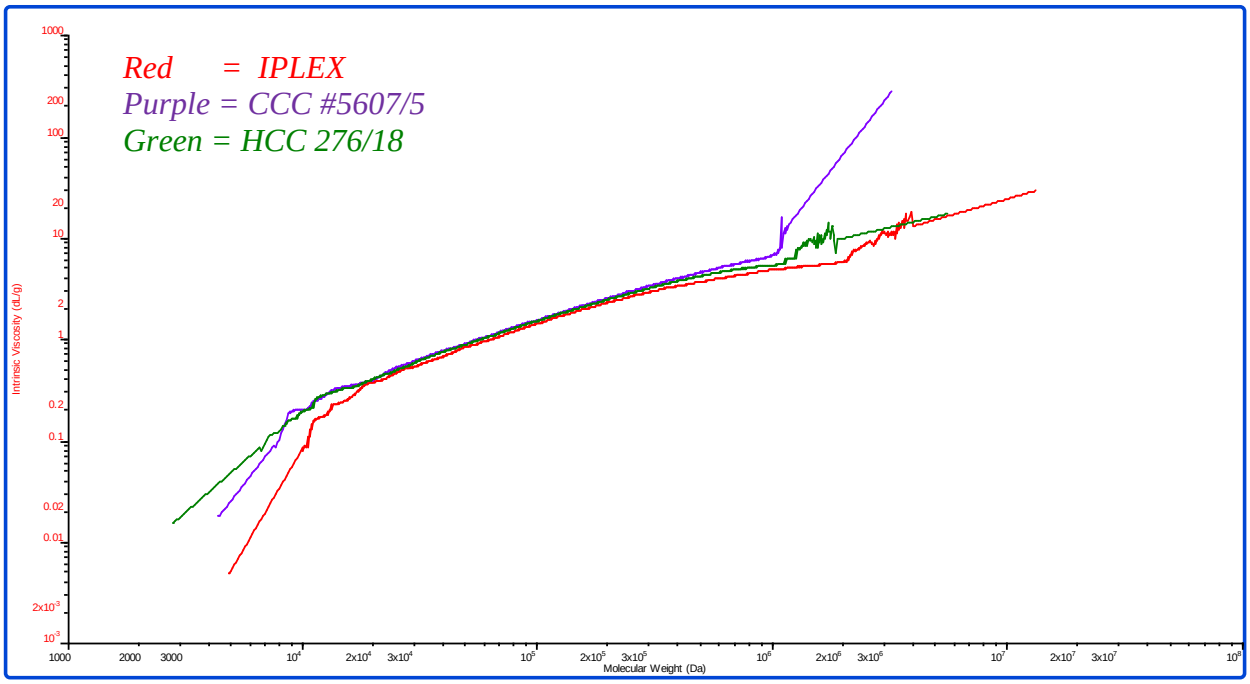


Figure 9. Overlay of Mark Houwink plots for all samples.

Table 4. Mark Houwink Data							
Sample	**Inj**	**α**	**avg. α**	**logK**	**avg. logK**	**Branches***	**Avg. Branches**
NIST 1484a Polyethylene standard	1	0.593	0.639	-2.749	-2.971	0.656	0.359
	2	0.685		-3.193		0.061	
NIST 1475a Polyethylene standard	1	0.734	0.730	-3.462	-3.440	0.320	0.218
	2	0.726		-3.417		0.116	
IPLEX	1	0.681	0.649	-3.498	-3.330	5.624	4.791
	2	0.617		-3.161		3.958	
CCC #5607/5	1	0.719	0.727	-3.426	-3.469	1.435	1.449
	2	0.735		-3.511		1.462	
HCC 276/18	1	0.705	0.720	-3.381	-3.466	2.507	3.699
	2	0.735		-3.550		4.891	

*-branches per 1000 carbons

†-Branches are calculated based on the NIST 1475a Mark Houwink constant α and logK values

Analysis Conditions

GPC-H

The samples were dissolved in Trichlorobenzene (TCB) to a concentration of ~2.5 mg/ml with 1.0 mg/ml antioxidant added. The samples were placed on a 150°C stir plate for 75 minutes for dissolution prior to analysis. The samples were then filtered using a high temperature filtration unit, and stored at 120° C.

The system was run at a flow rate of 1.0 ml/min on 3x Jordi 13µm Resolve Mixed Bed columns, 300 x 7.5 mm (ID). The column temperature was maintained at 160°C. Injection size was 200µL of the sample solution. Polystyrene standards with a concentration of 0.5 mg/ml were used (Molecular weight as follows: 3090K, 990.5K, 508K, 215K, 74.8K, 29.15K, 10.11K, 4.43K, 1.37K & 580) with injection size of 200 µL. The samples were monitored using a Viscotek 350A HT-GPC instrument. Data acquisition and handling was made with VISCOTEK OMNISEC software.

GPC-HT

Samples were monitored using a HT-GPC Module 350A detector array by VISCOTEK. Data acquisition and handling were made with VISCOTEK software.

Data were obtained under the following conditions:

Solvent:	1,2,4-Trichlorobenzene (TCB) with 500 ppm butylhydroxy toluene (BHT)
Flow Rate:	1.0 mL/min
Injection Volume:	200 uL
Column Temperature:	160°C
Concentration:	~2.5 mg/mL
Column:	3 x Jordi 13µm Resolve Mixed Bed columns, 30cm x 7.5mm each
Run Time:	50 Minutes
Integration Method:	Known dn/dc (.104 for PE)
Dissolution Conditions:	75 minutes at 150 °C, stored at 120 °C

Closing Comments

Jordi Labs' reports are issued solely for the use of the clients to whom they are addressed. No quotations from reports or use of the Jordi name is permitted except as authorized in writing. The liability of Jordi Labs with respect to the services rendered shall be limited to the amount of consideration paid for such services and do not include any consequential damages.

Jordi Labs specializes in polymer testing and has 30 years experience doing complete polymer deformulations. We are one of the few labs in the country specialized in this type of testing. We will work closely with you to help explain your test results and solve your problem. We appreciate your business and are looking forward to speaking with you concerning these results.

Sincerely,

Longxi Xiao

Longxi (Jesse) Xiao, Ph. D.
Senior Chemist
Jordi Labs LLC

Mark Jordi

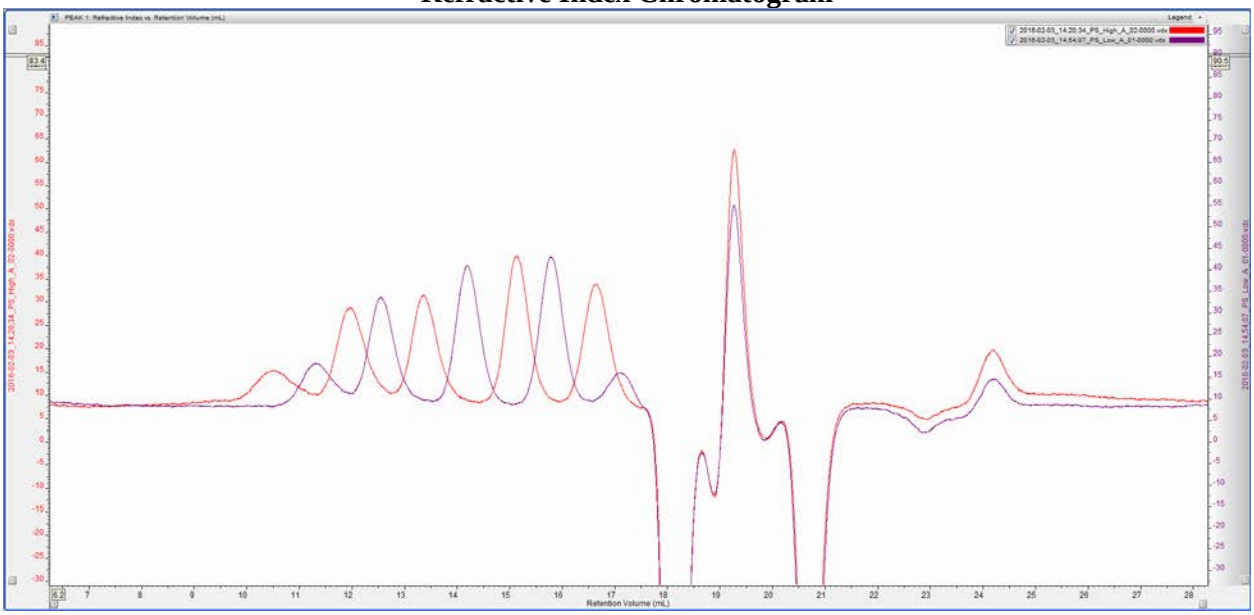
Mark Jordi, Ph. D.
President
Jordi Labs LLC

Appendix

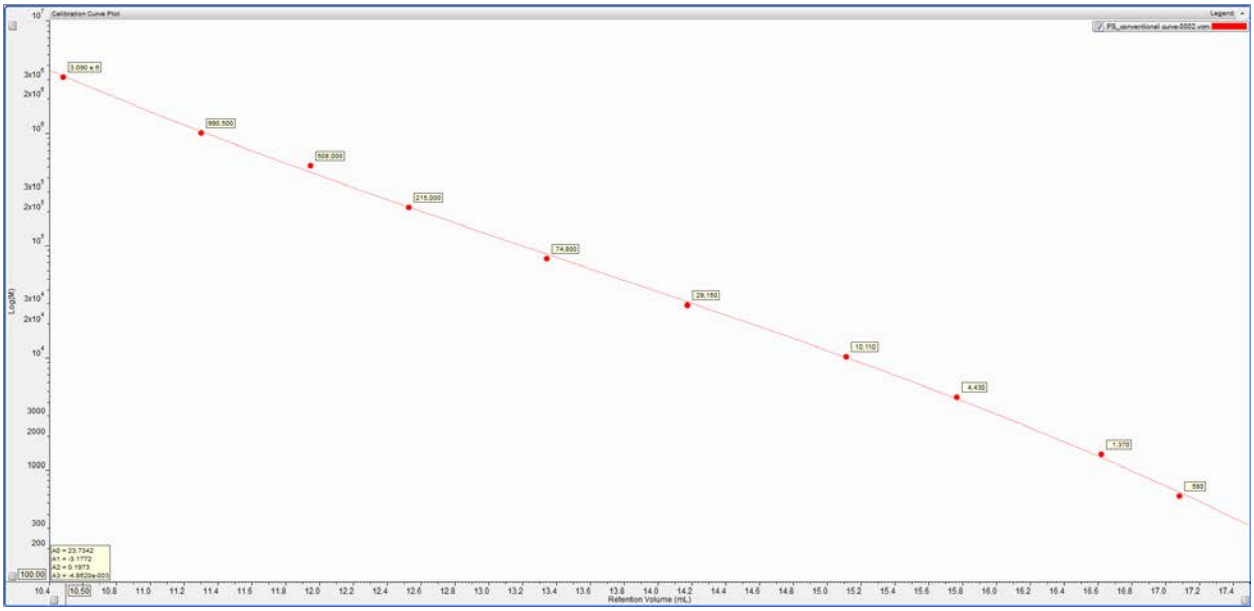
- Pages 16 – 19 GPC Data
- Pages 20 – 38 GPC – T Data

GPC-H Data

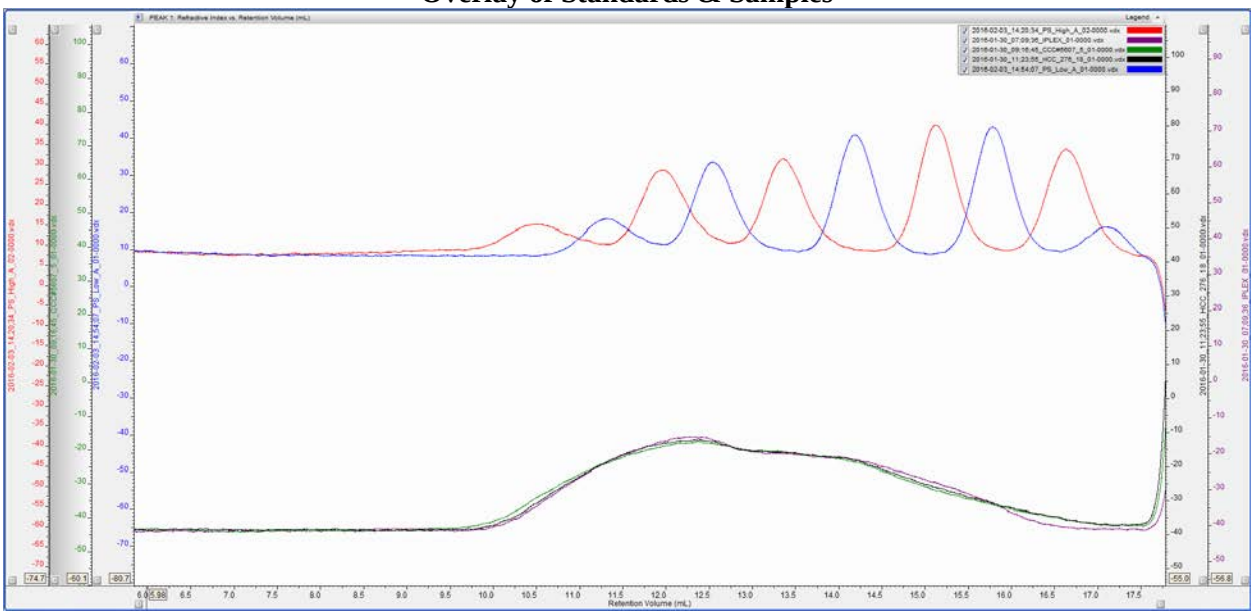
Normalized Overlay of PMMA Standards
Refractive Index Chromatogram



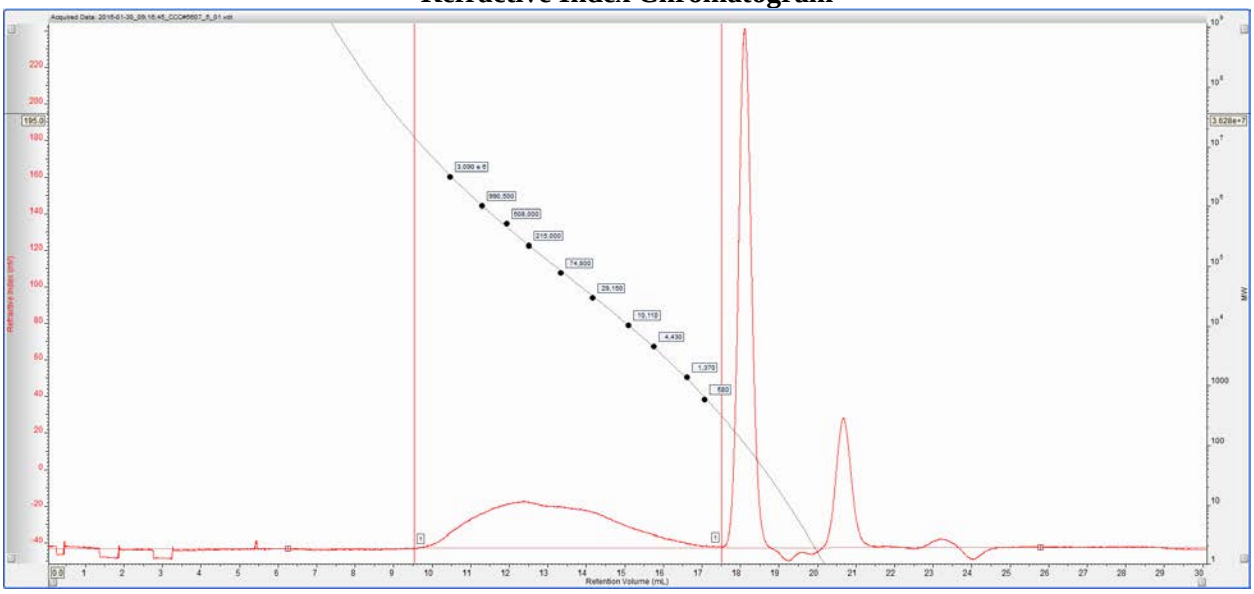
Calibration Curve



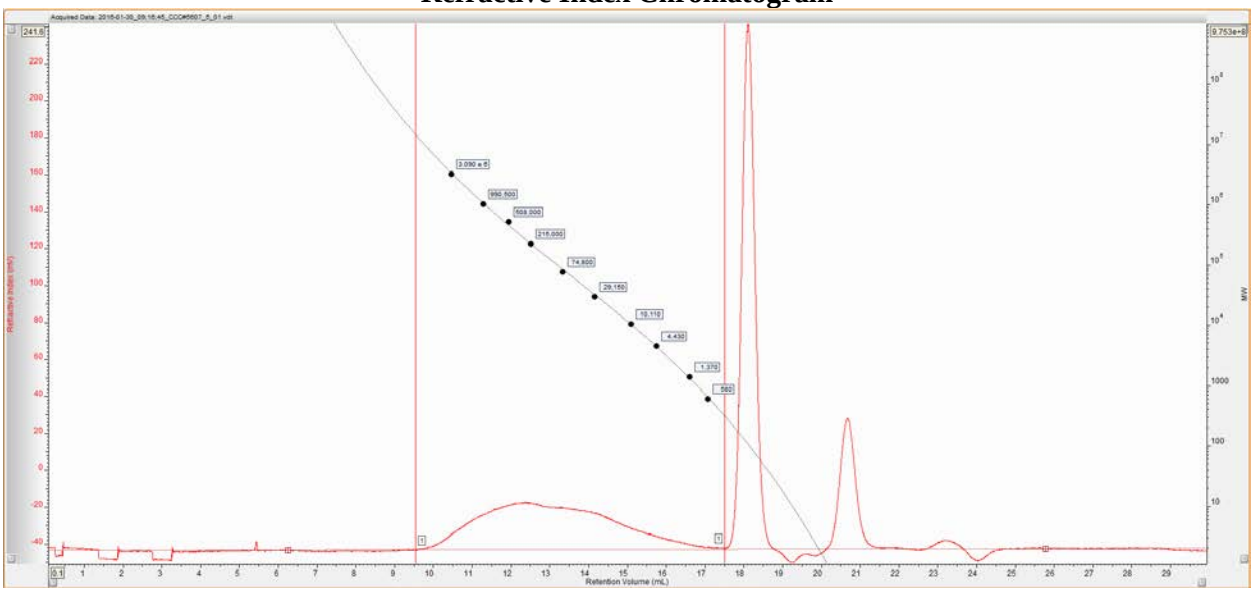
Overlay of Standards & Samples



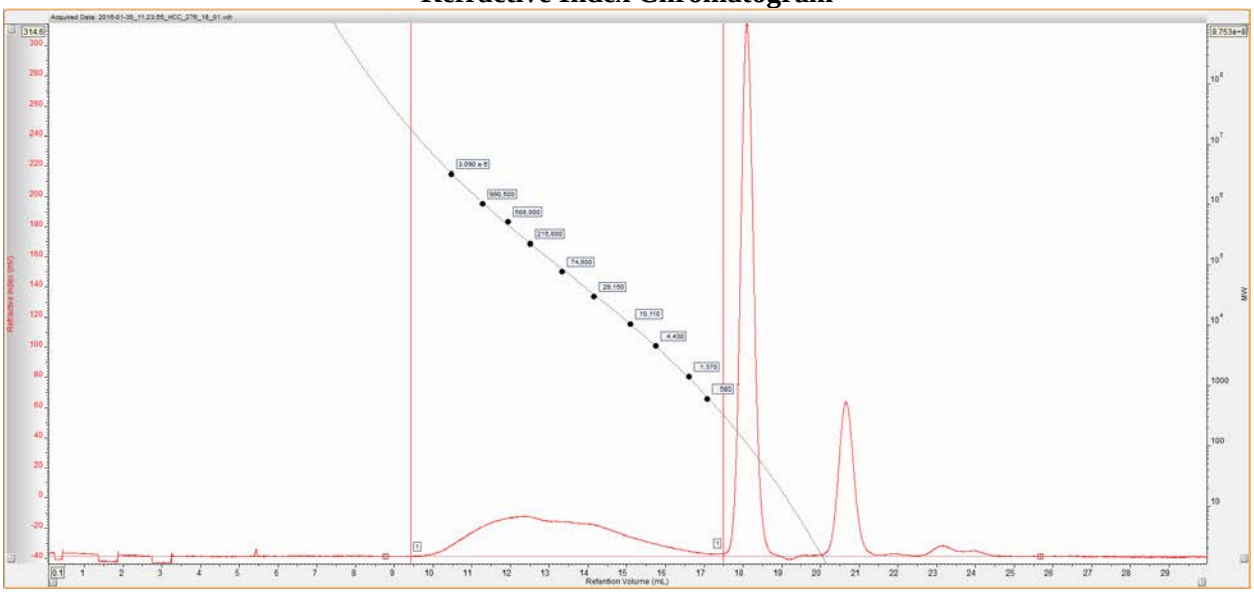
Sample IPLEX
Refractive Index Chromatogram



Sample CCC #5607/5
Refractive Index Chromatogram

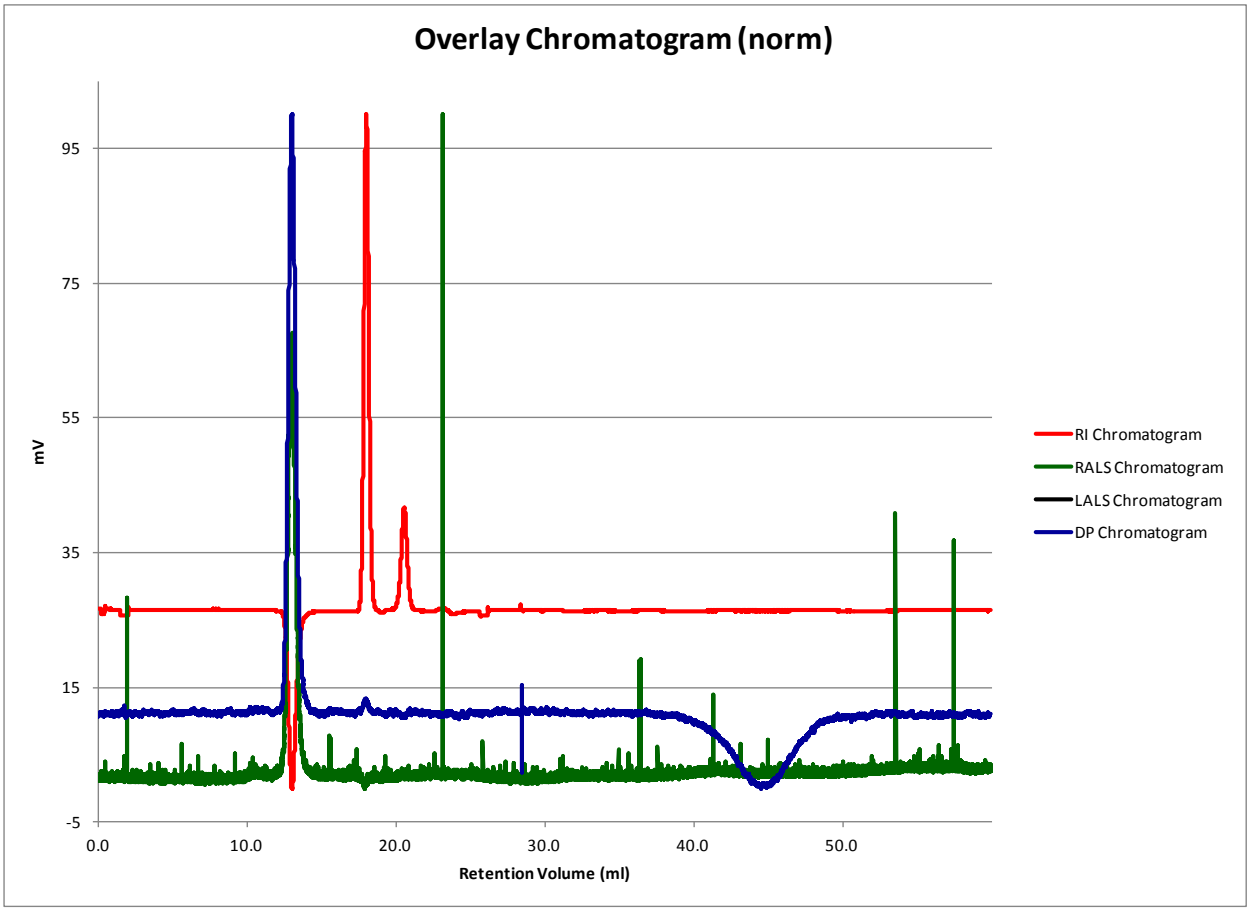


Sample HCC 276/18
Refractive Index Chromatogram



GPC-HT Data

2016-01-29_16;19;30_PS_105k_CAL_STD_01



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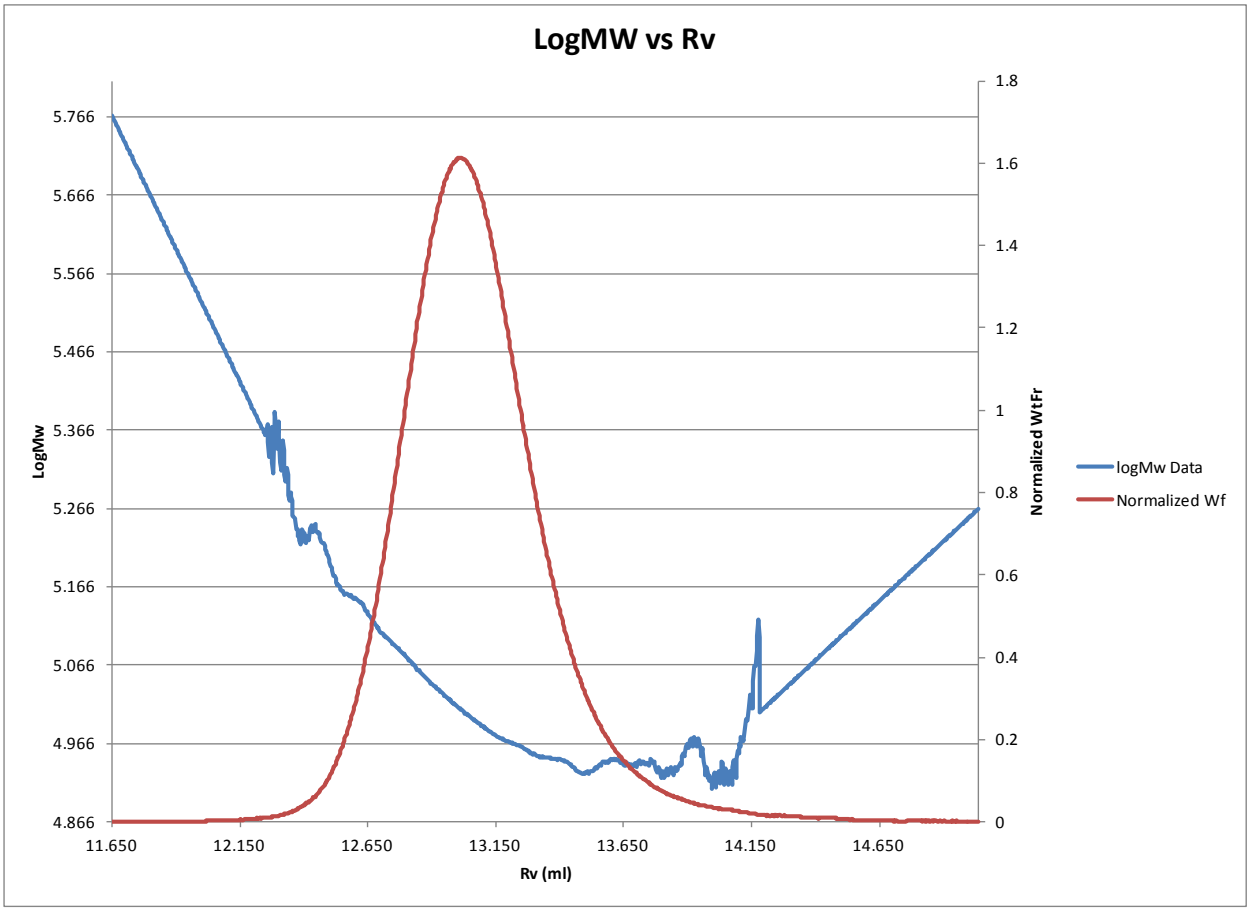

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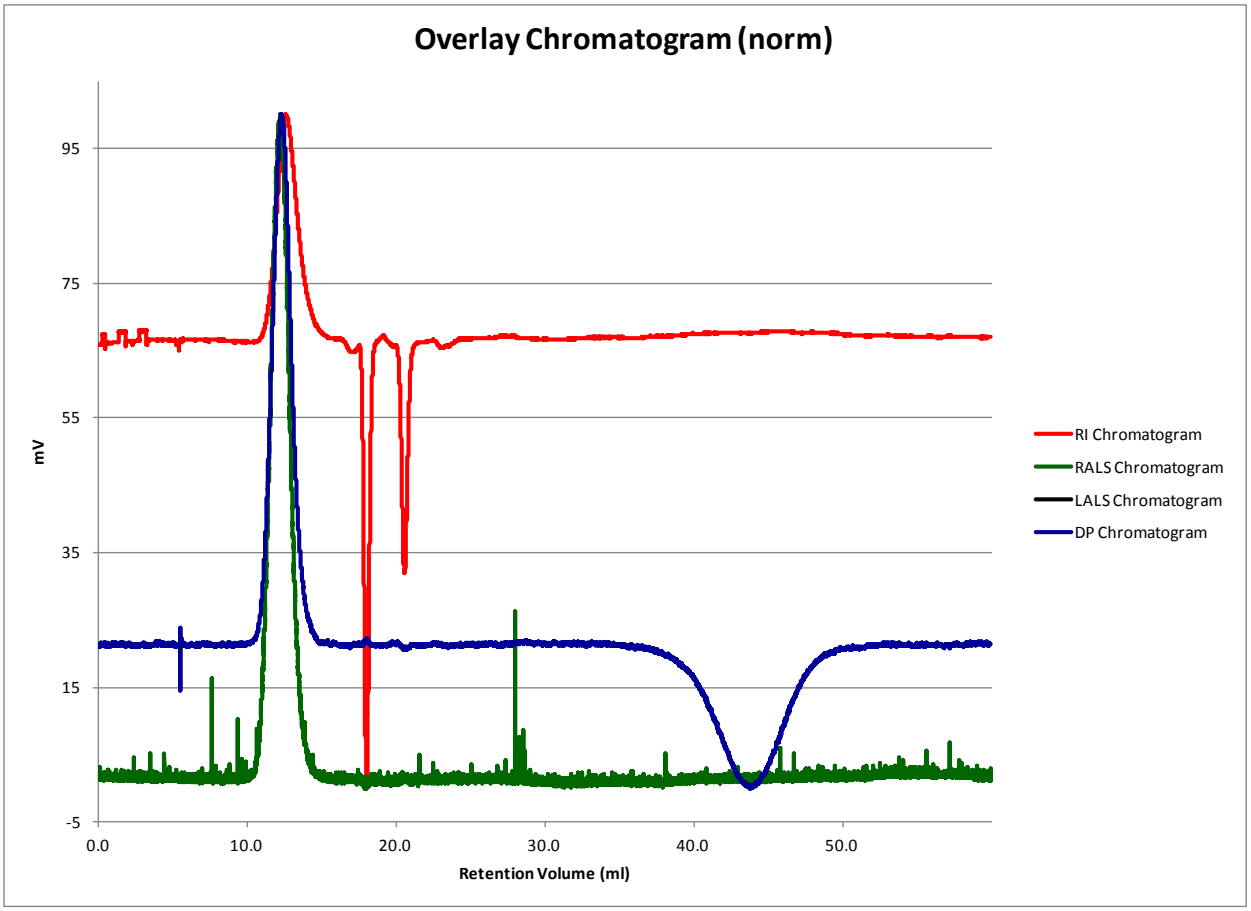

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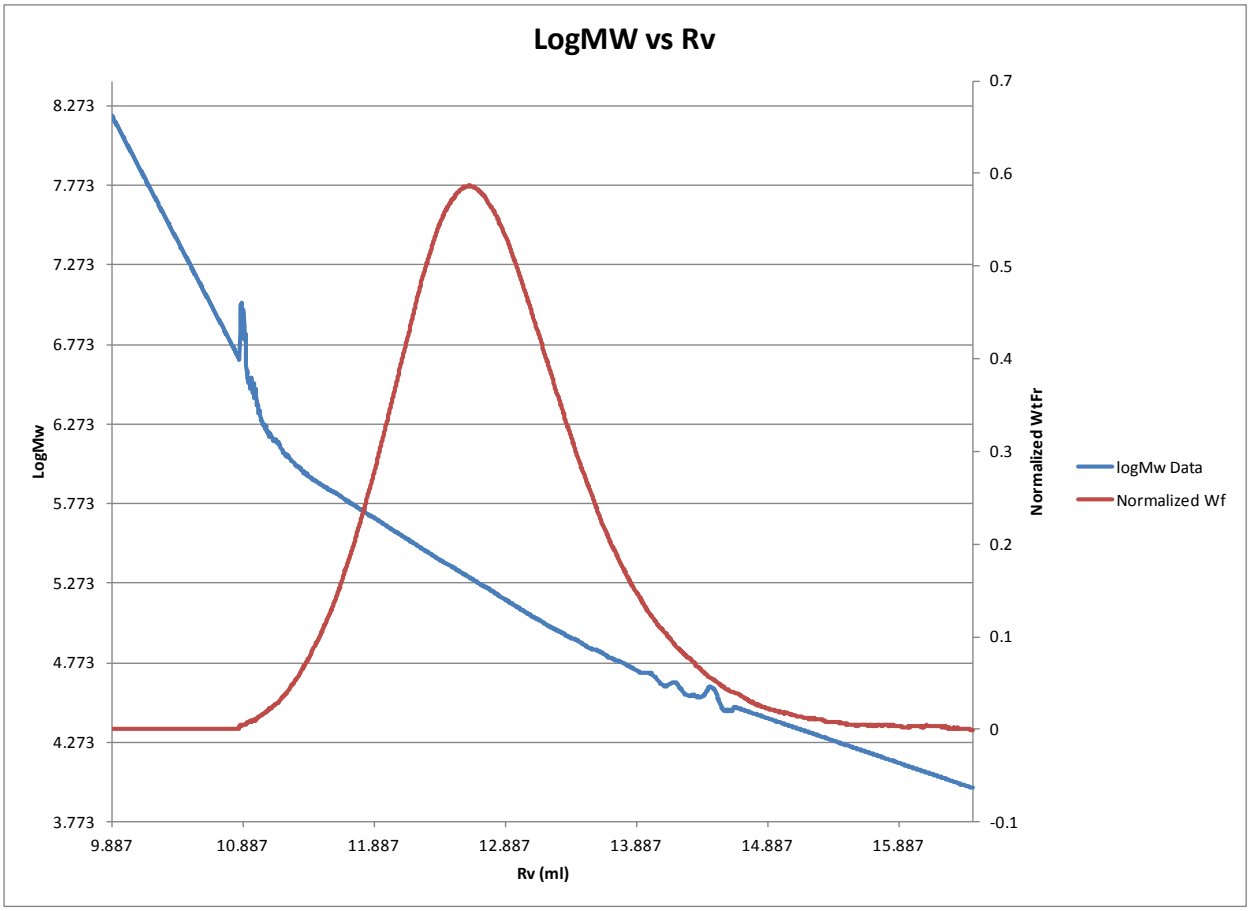

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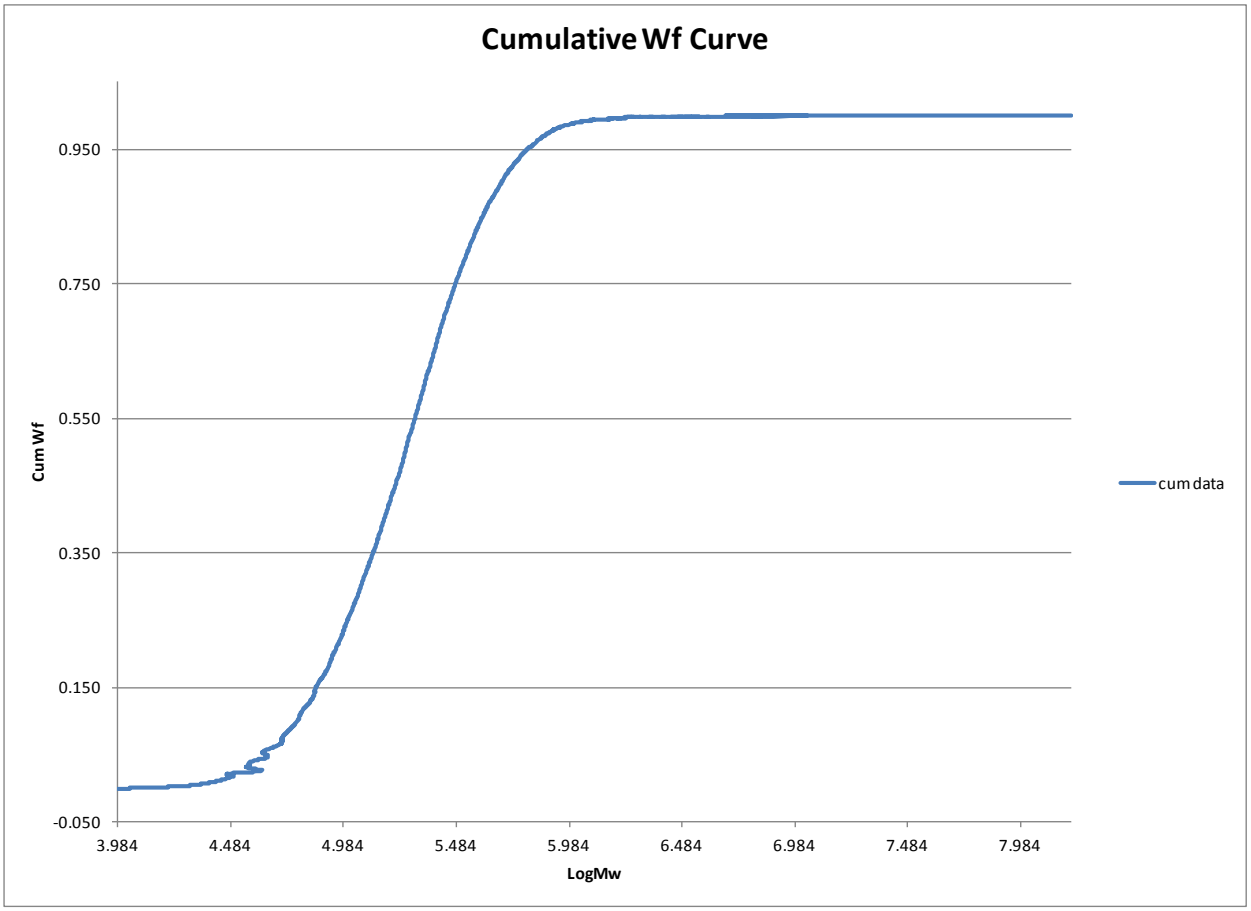

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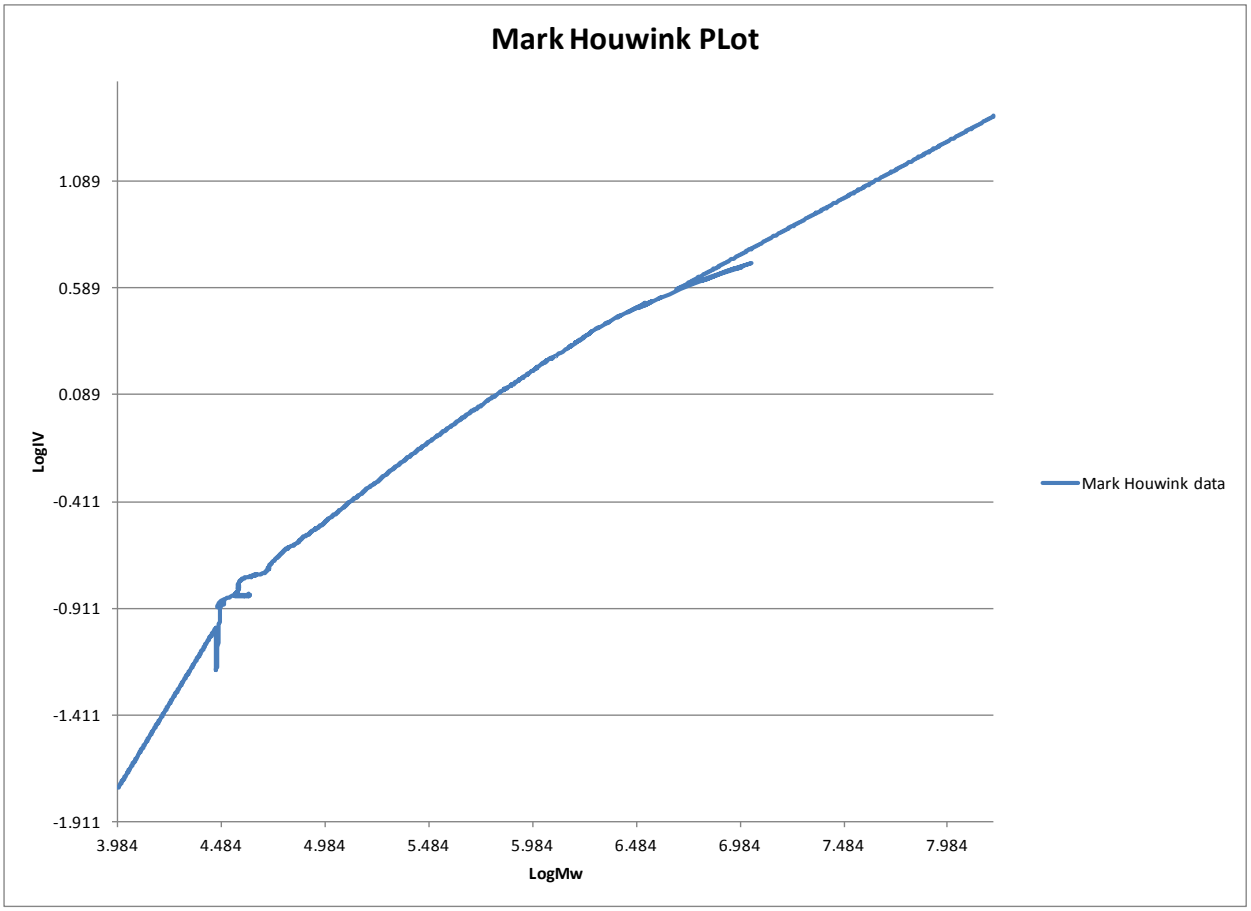
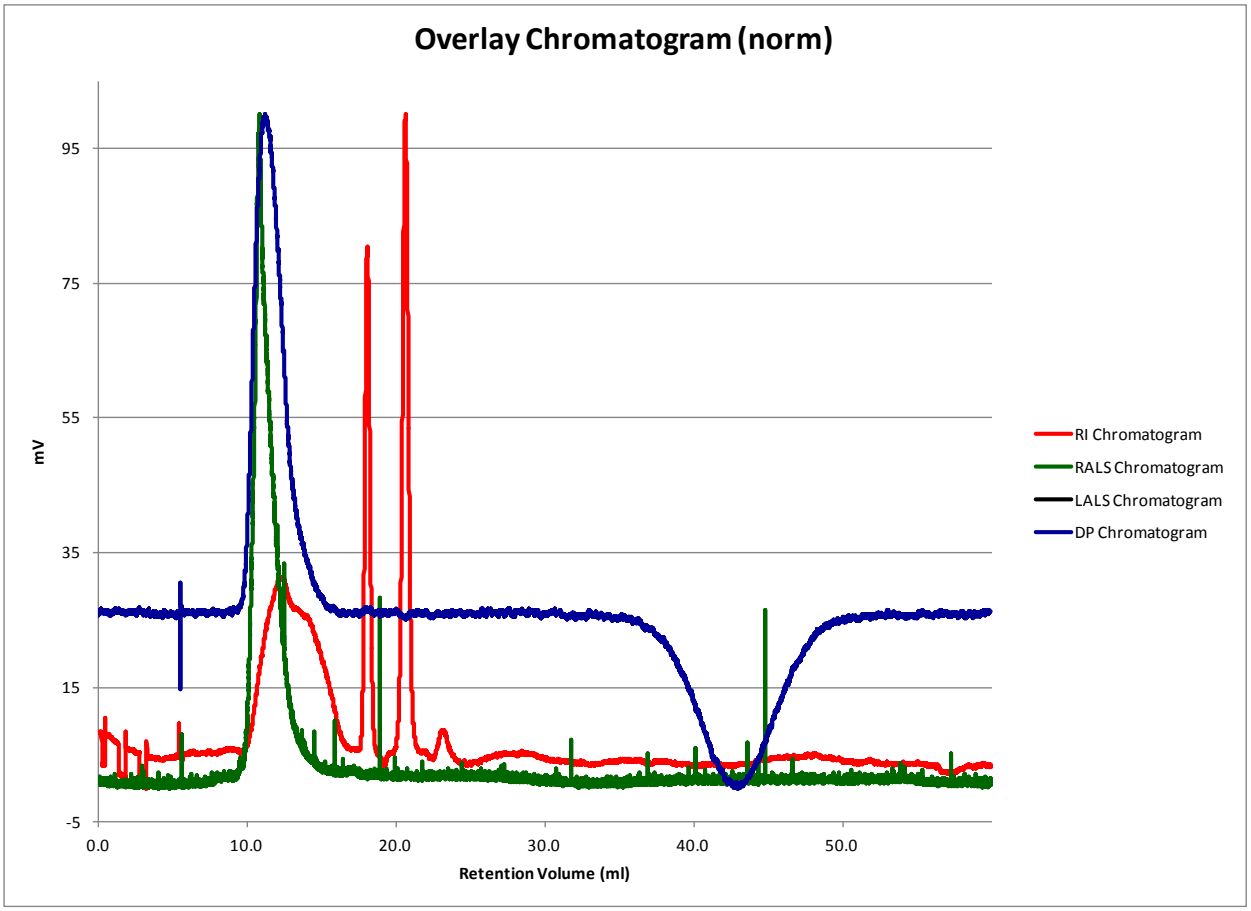


2016-01-30_07;09;36_IPLEX_01



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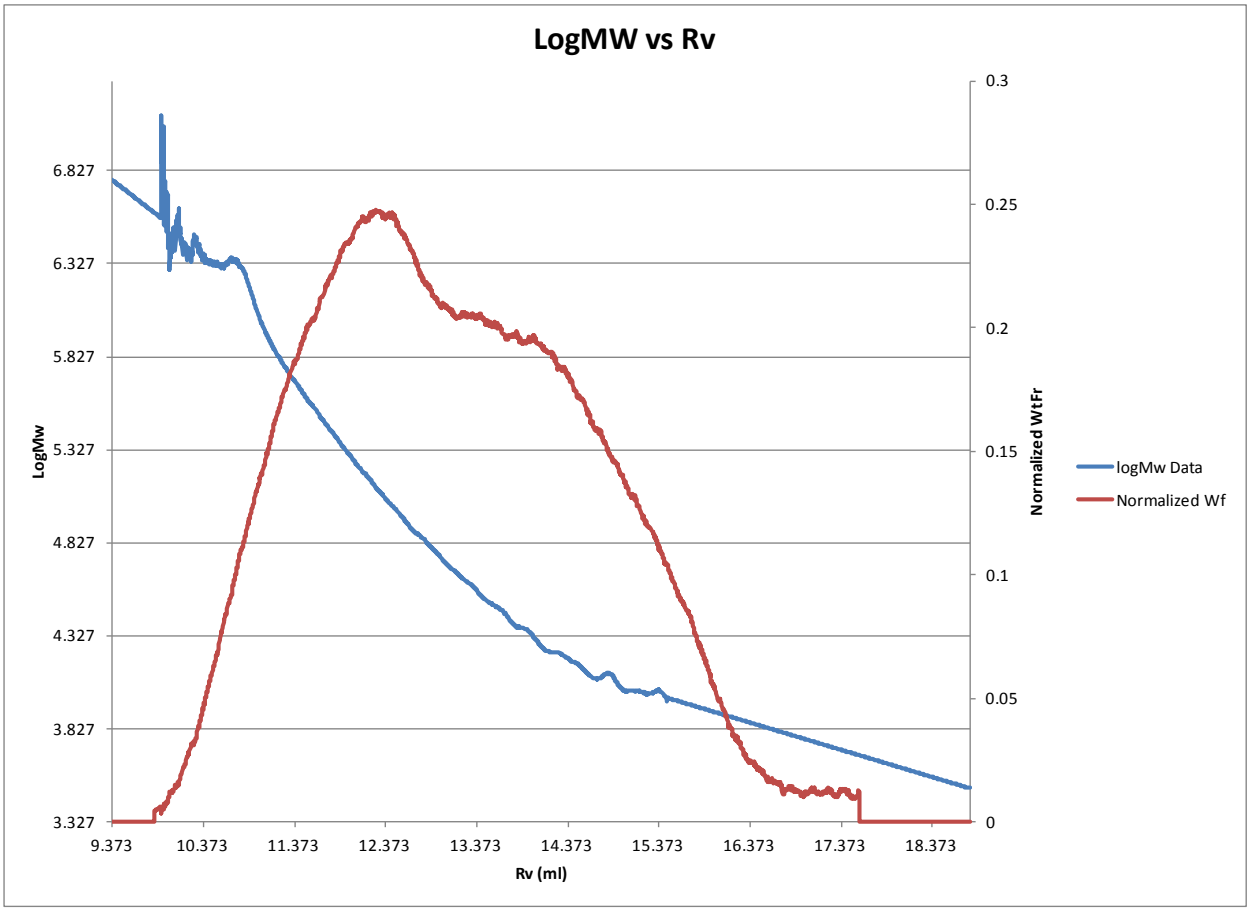

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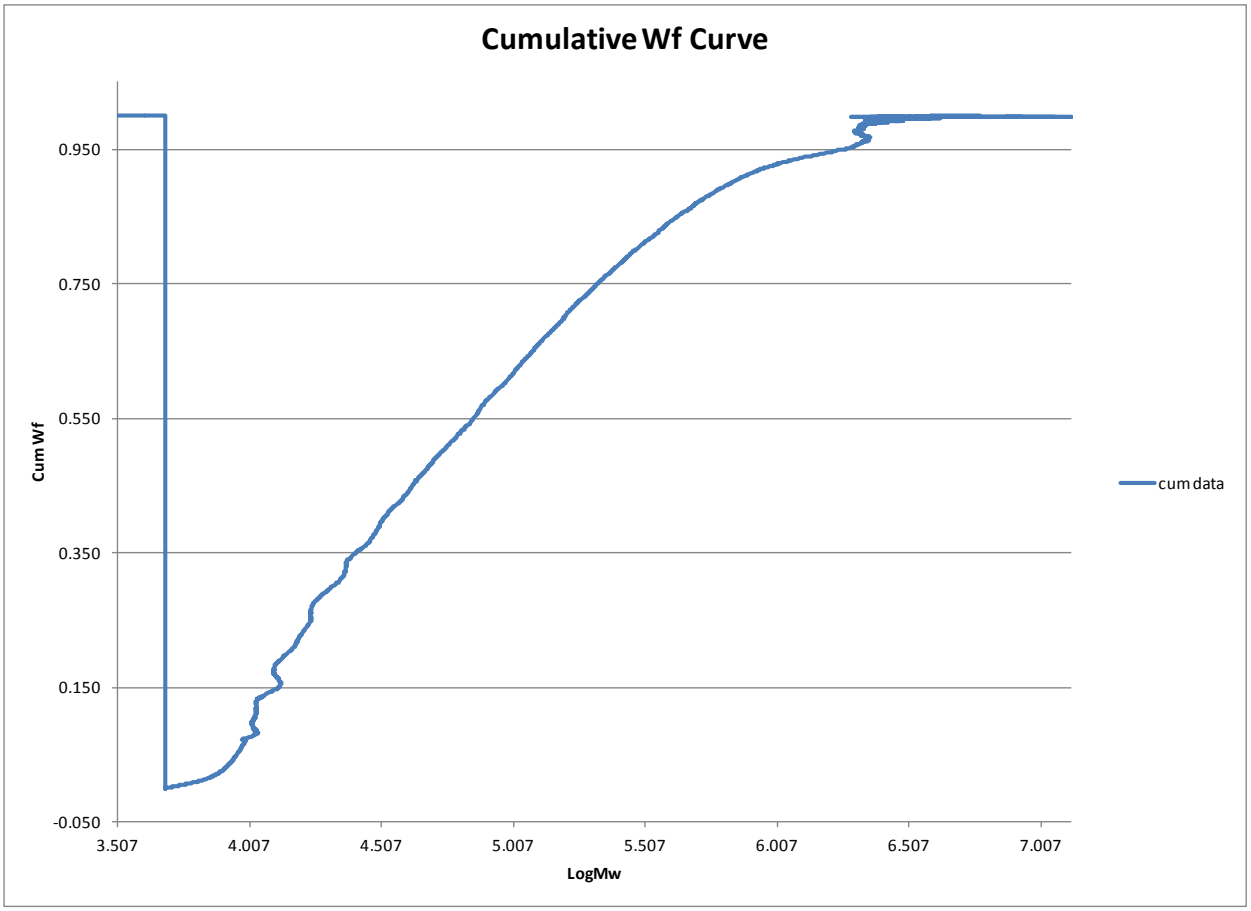

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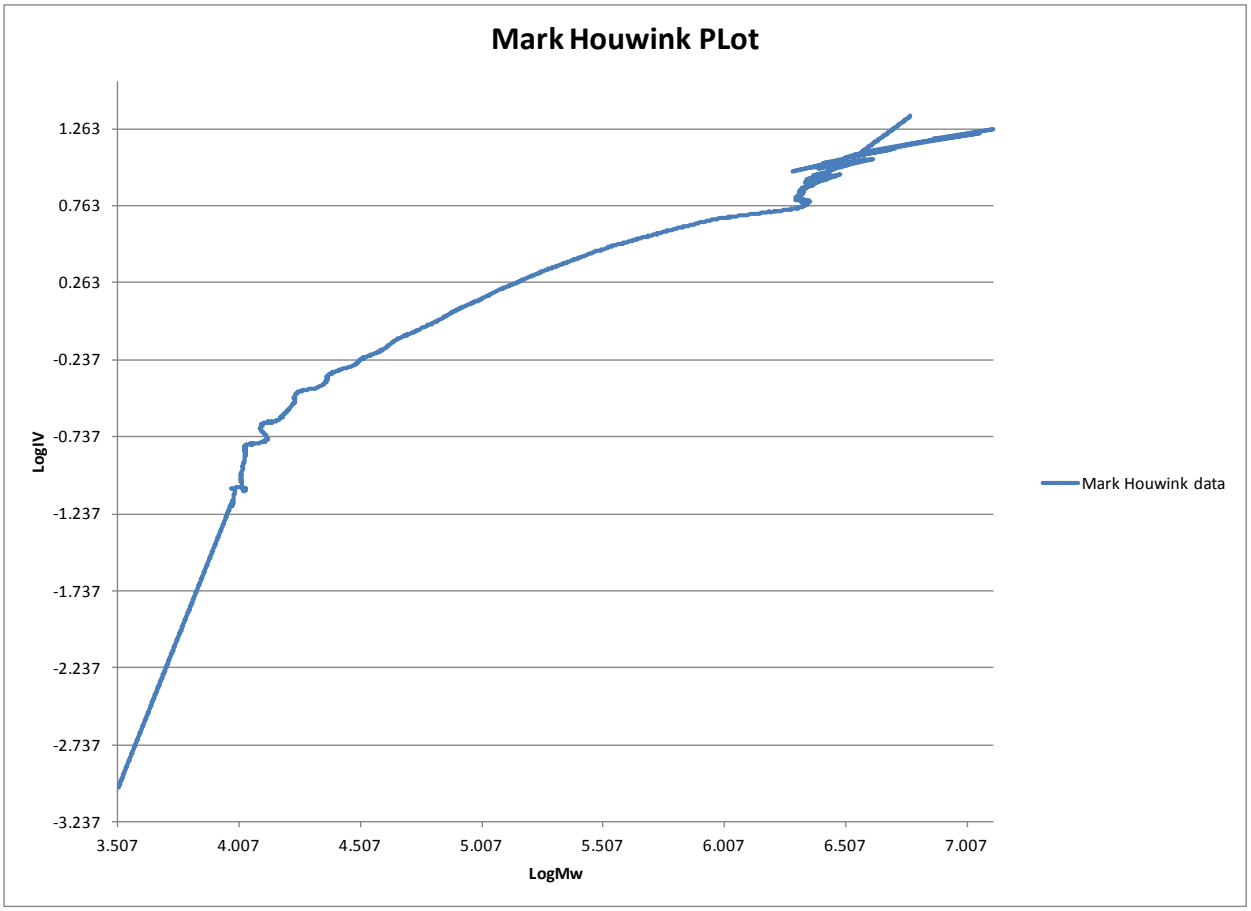

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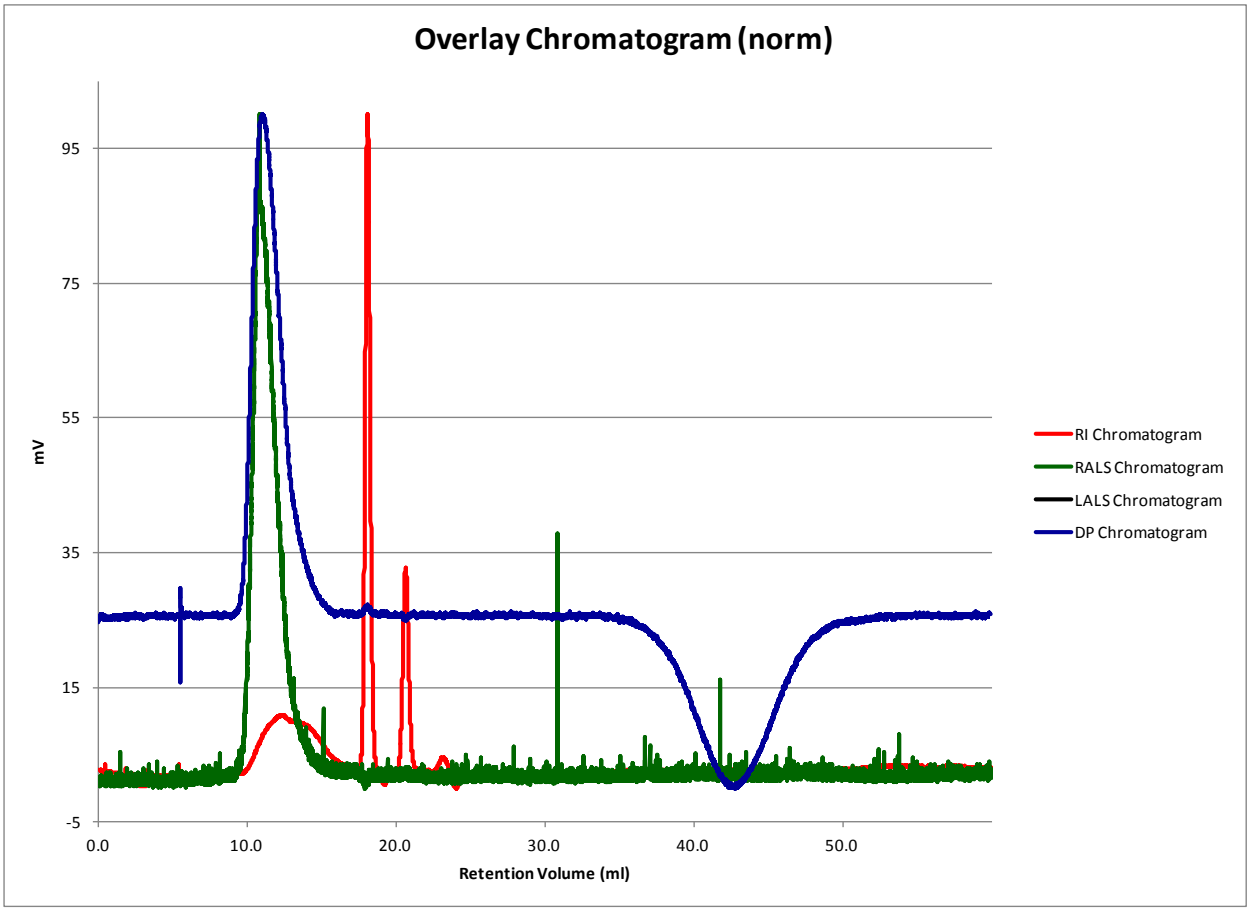

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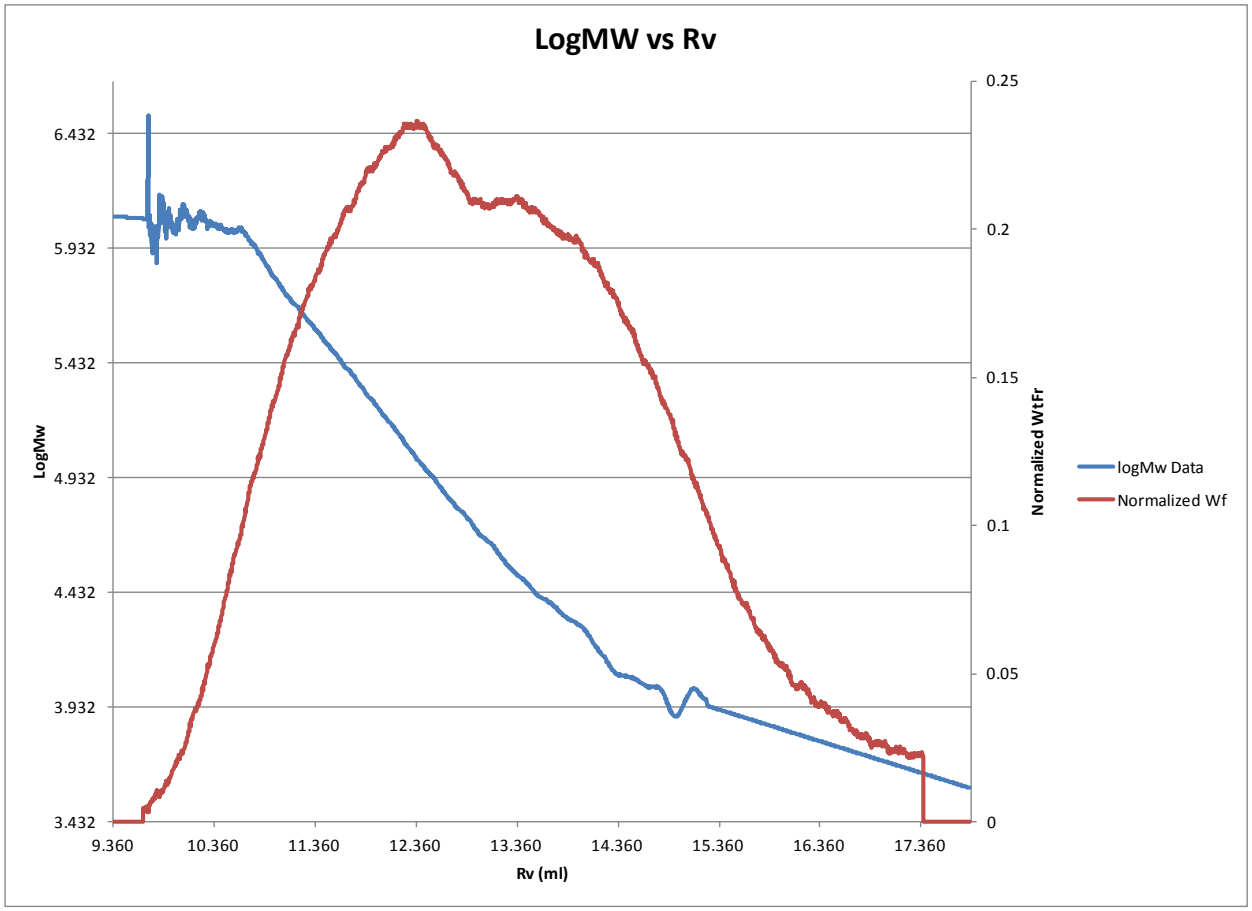

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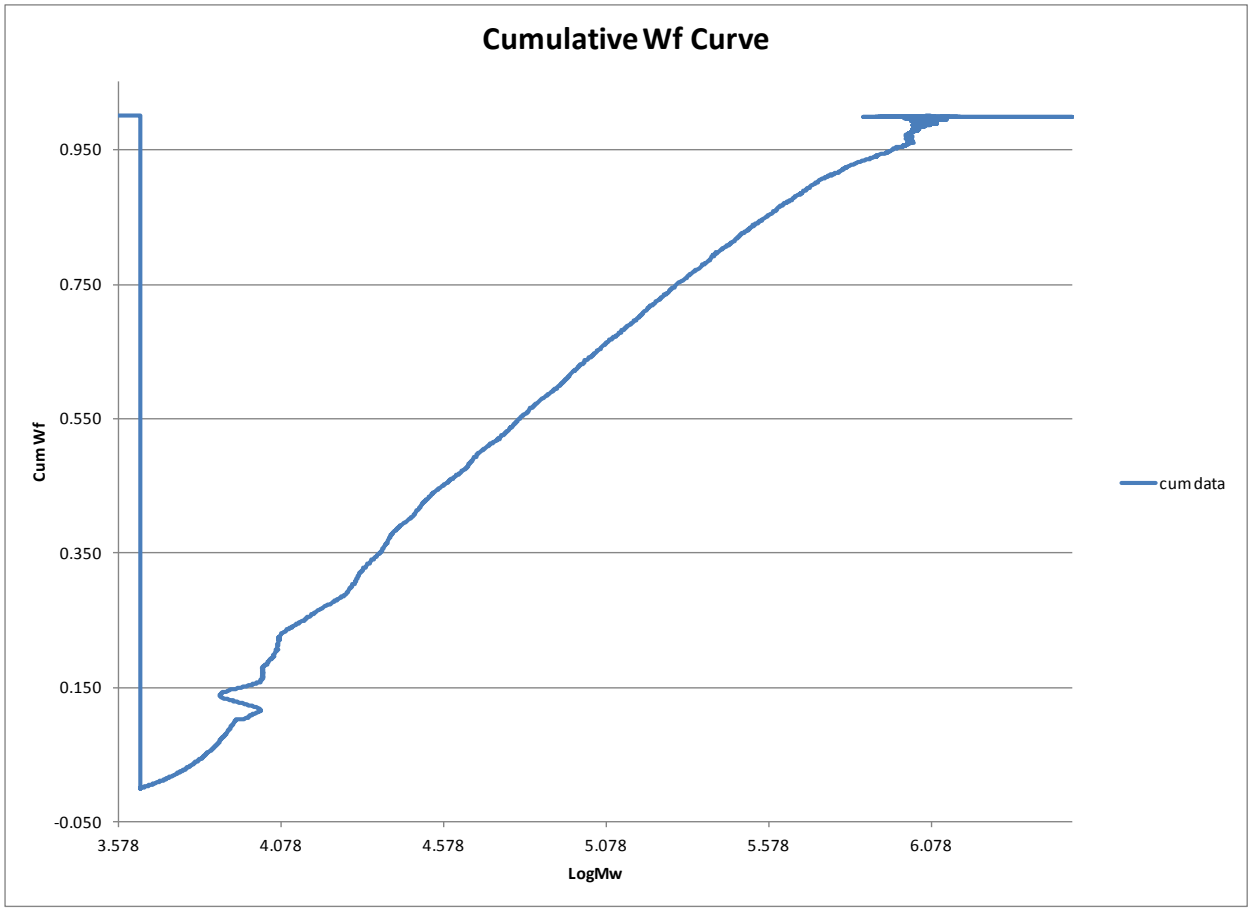

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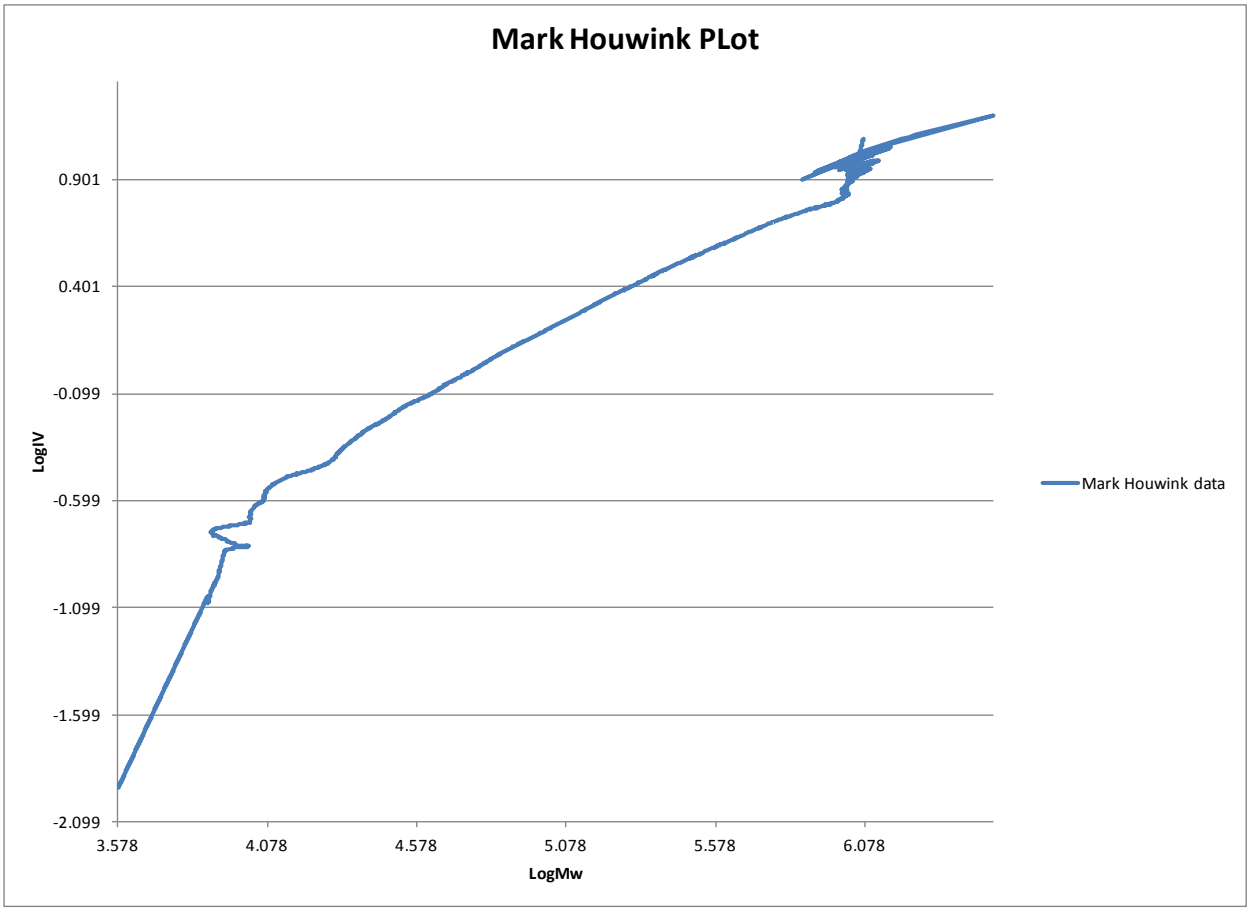

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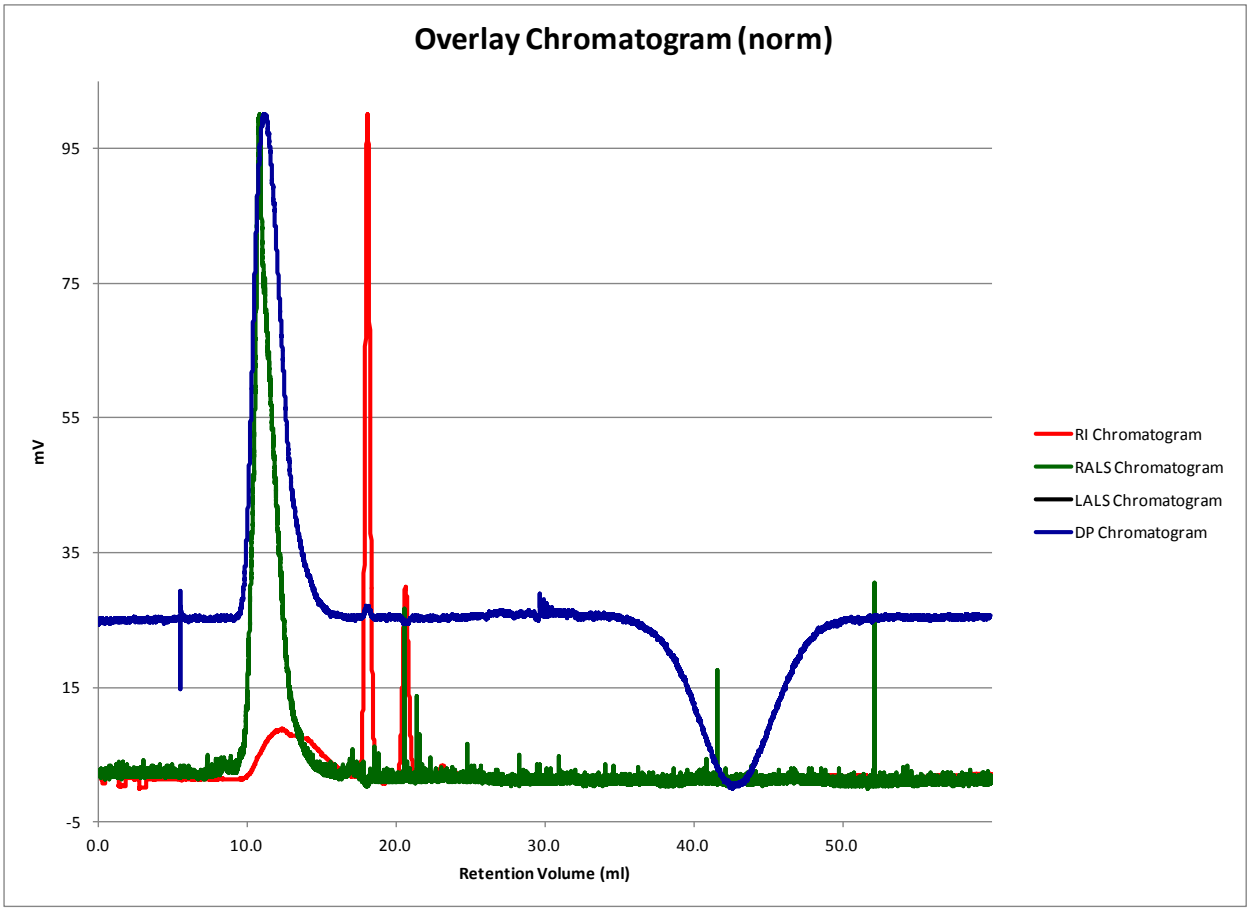

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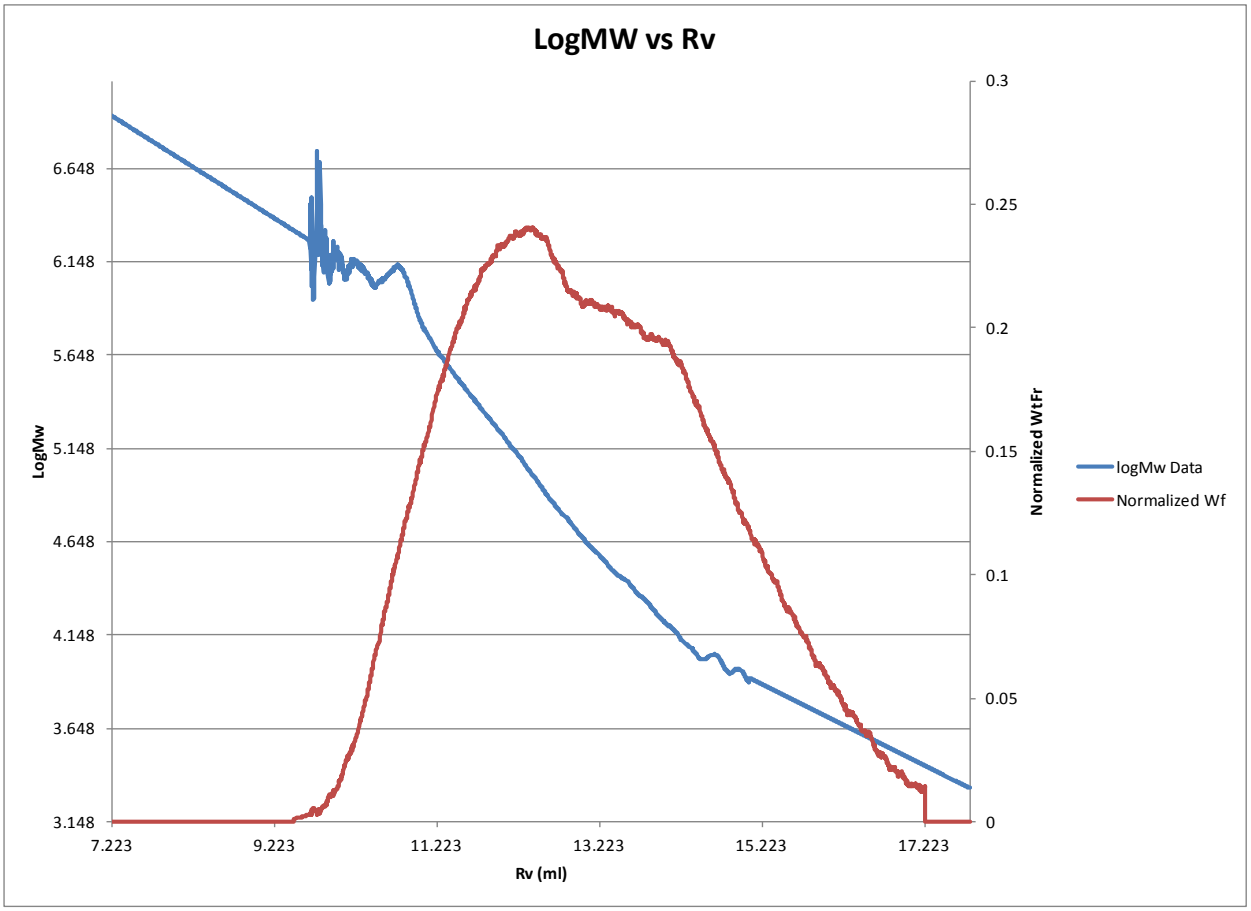

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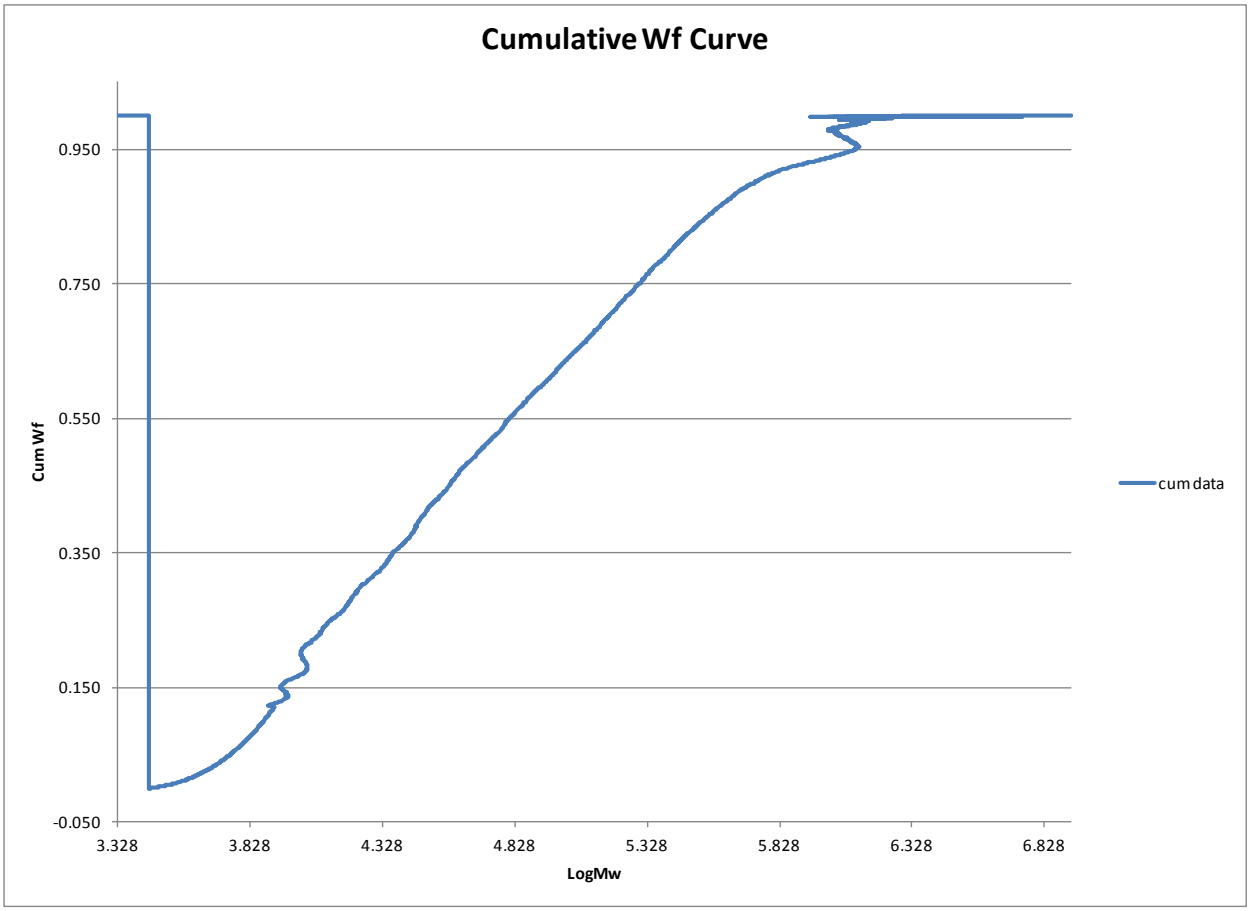

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