CASE STUDY

Polyethylene Molecular Weight Determination using Standardized GPC and Light Scattering

OBJECTIVE

The purpose of this work was to compare the molecular weight values generated using standardized GPC and Tetradetection GPC with Light Scattering.

ANALYTICAL STRATEGY

A NIST 1475a polyethylene certified reference material and a low density polyethylene were tested using standardized GPC versus polystyrene standards and using Tetradetection GPC with light scattering to compare the utility of the two methods.

CONCLUSIONS

Both methods were able to distinguish differences in the molecular weight distributions for two polyethylene samples and to estimate the magnitude of those differences. The absolute values determined by the two methods were found to differ. The weight average molecular weight determined for the NIST reference sample was in line with expectations when determined by Light Scattering (53,070 vs 52,481). In contrast, the value determined by standardized GPC was nearly a factor of two larger (108,637). This is a result of the difference in hydrodynamic volume for polystyrene and polyethylene.

These results emphasize the importance of selecting the appropriate method for the intended purpose. GPC-H is a comparative method which should be used to assess differences between samples such as in routine lot QC. GPC-HT is an absolute method providing high accuracy for determination of absolute molecular weights and for examination of polymer architecture (branching).

Read the following report to see the full analysis.

MATERIAL SOLUTIONS. UNCOMPROMISING INTEGRITY.
4 Mill St, Bellingham, MA. 02019 USA
Tel: +1 (508) 966-1301 Fax: +1 (508) 966-4063
JORDI

Final Report

Company Name
Client Name

Date:

Released by:
Dr. Mark Jordi
President
Jordi Labs LLC

Report Number: JXXXXX

Company Name Confidential

Date

Client Name
Company Name

P: xxx-xxx-xxx
E: xxxxx@xxxx.com

Dear Client,

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

1. NIST 1475a Polyethylene Certified Reference Material
2. Low Density Polyethylene

The following tests were performed:

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

Summary of Results

The purpose of this work was to determine the absolute and standardized molecular weight of two polyethylene samples. **Table I** shows the molecular weight values as determined by GPC-H. **Table II** shows the molecular weight values as determined by GPC-HT.

The values for the weight average molecular weight were found to differ by nearly a factor of two for the two methods. This is a result of the difference in the hydrodynamic volume for polystyrene and polyethylene and the effects of polymer branching. ***This result emphasizes the need to use the appropriate methodology for the intended purpose.*** GPC-H is a comparative tool which should be used to assess differences between samples. GPC-HT is an absolute method providing high accuracy for determination of absolute molecular weights.

Individual Test Results

A summary of the individual test results is provided below. All accompanying data, including spectra.

<u>GPC-HT</u> – Analysis by GPC requires that a suitable solvent be found to dissolve the samples. Samples were dissolved in 1,2,4-trichlorobenzene (TCB) with 0.5 mg/mL 2,6-di-*tert*-butyl-4-methylphenol (BHT). **Tables I & II** show the resulting molecular weight values as determined by GPC-H and GPC-HT respectively.

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, Mz 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, the intrinsic viscosity (IV) and the radius of hydration (Rh). Intrinsic viscosity is the inverse molecular density and can be used as an indication of the extent of polymer branching and shape. Rh 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:

$[IV] = K \times M^a$

Where [IV] is the intrinsic viscosity, K and "a" 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 + a*Log [M]

This equation is linear and has the form:
Y = m*X+b

Where m is the slope and b is the intercept. The Mark Houwink relationship therefore has a slope of "a" and an intercept of Log K. The slope can be 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.

System Calibration:

Polystyrene standards with molecular weights of 8,910,000, 4,410,000, 1,040,000, 454,000, 184,000, 130,000, 17,600, 9,730, 3,250, 474 were analyzed to prepare the calibration curve for GPC-H. The resulting calibration plot is included in the data section of this report. A polystyrene standard with a weight average molecular weight of 99,420 was used for system calibration for GPC-HT. **Table III** shows the results for the standard analyzed for system calibration in GPC-HT.

Results:

Table I shows the calculated molecular weight for a NIST 1475a reference material and a low density polyethylene as determined by standardized GPC ***versus polystyrene standards***. **Table II** shows the calculated molecular weights as determined by light scattering (GPC-HT). The method of known dn/dc was applied for GPC-HT analysis. ***As is expected,*** the values by standardized GPC were found to overestimate the weight average molecular weight of the sample by nearly a factor of two. This is a result of the difference in the hydrodynamic volume for polystyrene and polyethylene. Differences in branching characteristics for the two polyethylenes and the linear polystyrene standard also affect the results of GPC-H.

Values as determined by GPC-HT were found to show good agreement with the known values as reported by NIST. ***This result emphasizes the importance of utilizing the appropriate method for the intended purpose.*** GPC-H is appropriate when a comparison of the molecular weight of two samples is desired relative to an external standard. GPC-H is capable of ***demonstrating differences*** in the two polyethylene samples and provides an indication of the magnitude of those differences. It is appropriate for routine QC and can be used to measure changes in lot to lot consistency. GPC-HT is the preferred method when an accurate absolute value is desired or when changes in molecular architecture (branching) may affect the results. **Figure I** compares the molecular weight distributions for the two samples by GPC-H and **Figure 2** shows the same plot as measured by GPC-HT. Both plots show the difference between the samples but the absolute values differ.

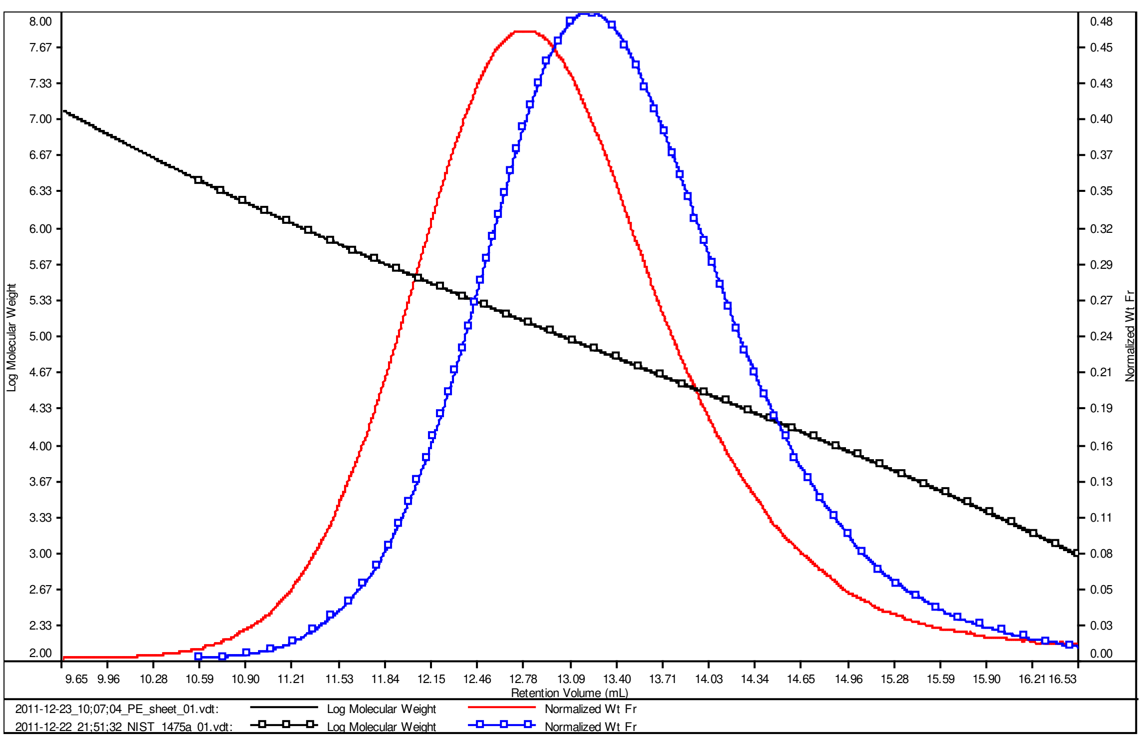


Figure 1: Molecular weight distribution plot by GPC-H for NIST 1475a (blue) and Low Density Polyethyelene (red).

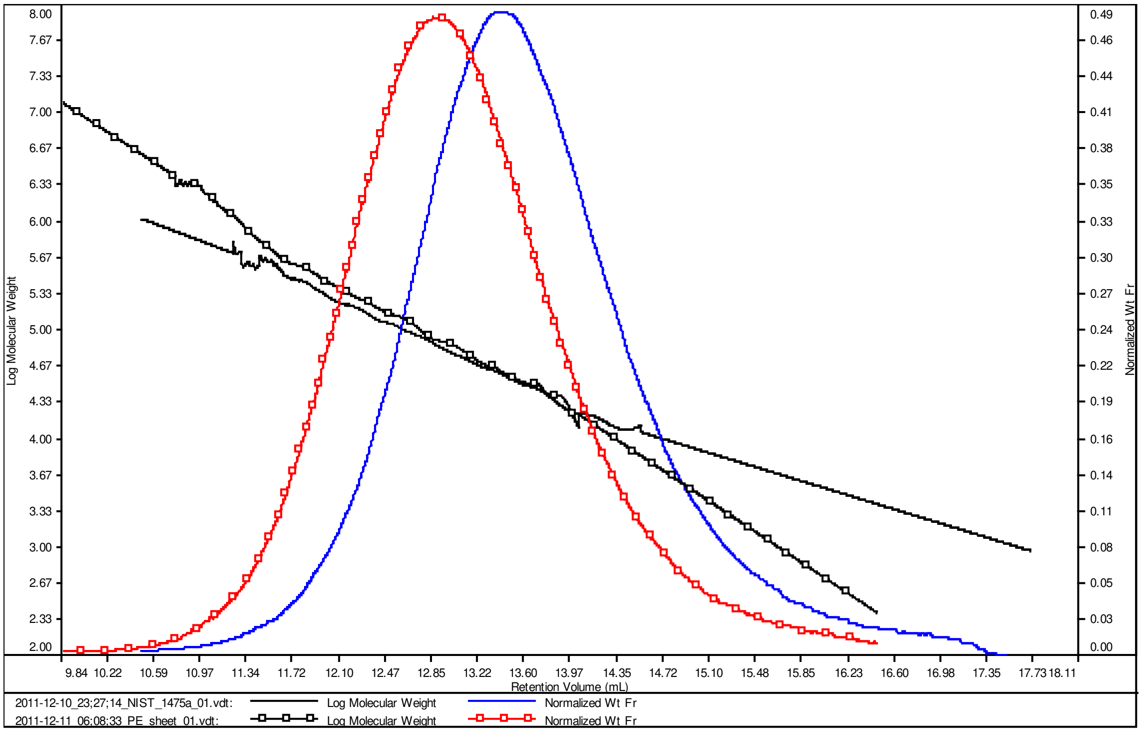


Figure 2: Molecular weight distribution plot by GPC-HT for NIST 1475a (blue) and Low Density Polyethyelene (red).

Table I. Analysis of Samples by GPC-H

NIST 1475a Linear Polyethylene Analysis
(Mn = 18,310 Mw = 53,070 Mz = 138,000)

Sample	Mn	Mw	Mz	Mw/Mn
2011-12-22_21;51;32_NIST_1475a_01.vdt	25,538	108,196	304,223	4.237
2011-12-22_22;58;23_NIST_1475a_02.vdt	23,600	109,078	304,348	4.622

Low Density Polyethylene Analysis

Sample	Mn	Mw	Mz	Mw/Mn
2011-12-23_10;07;04_PE_sheet_01.vdt	39,254	200,175	718,915	5.099
2011-12-23_11;13;57_PE_sheet_02.vdt	39,015	202,133	689,982	5.181

Table II. Analysis of Samples by GPC-HT

NIST 1475a Linear Polyethylene Analysis
(Mn = 18,310 Mw = 53,070 Mz = 138,000)

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
2011-12-10_23;27;14_NIST_1475a_01.vdt	18,545	51,472	138,140	2.776	0.7696	7.79
2011-12-11_01;40;58_NIST_1475a_03.vdt	18,409	53,489	139,683	2.906	0.7472	7.81

ID	dn/dc	Conc
NIST	0.1040	1.7966
NIST	0.1040	1.8511

Low Density Polyethylene Analysis

Sample	Mn	Mw	Mz	Mw/Mn	IV	Rh
2011-12-11_06;08;33_PE_sheet_01.vdt	15,851	140,356	879,057	8.854	1.1232	11.81
2011-12-11_07;15;25_PE_sheet_02.vdt	15,221	143,843	879,398	9.450	1.1320	12.00

ID	dn/dc	Conc
PE sheet	0.1040	2.0150
PE sheet	0.1040	2.0150

Table III. Standard for GPC-HT Calibration

Run 1 Standard Analysis (GPC-T)
(PS 99,420)

Sample	Mn	Mw	Mz	Mw/Mn
2011-12-11_22;51;40_PS99K_99420Da_01.vdt	98,776	101,848	111,489	1.031

ID	dn/dc	Conc
PS99K_99420Da	0.0520	2.5920

Analysis Conditions

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	Trichlorobenzene (TCB)/0.5 mg/mL BHT
FLOW RATE	1.0 mL/min
INJECTION VOLUME	200 μL
COLUMN TEMPERATURE	150°C
CONCENTRATION	~2.5 mg/mL
COLUMN	2 x Varian PLGel Mixed-B LS 30cm x 7.5mm
RUN TIME	60 Minutes
INTEGRATION METHOD	Known dn/dc

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,

Mark Jordi

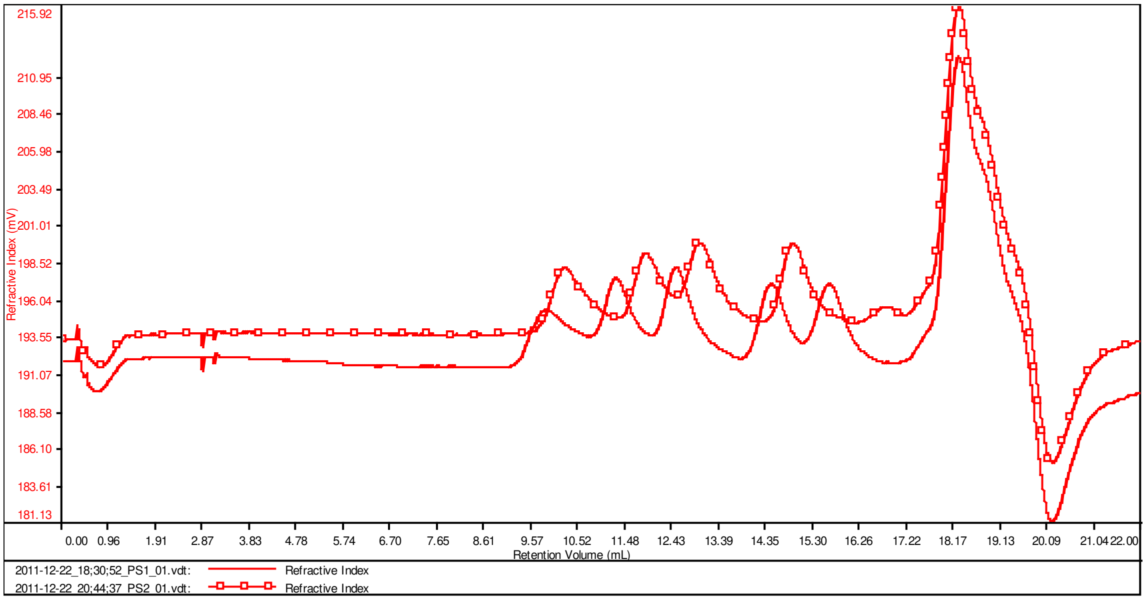
Mark Jordi, Ph. D.
President
Jordi Labs LLC

Appendix

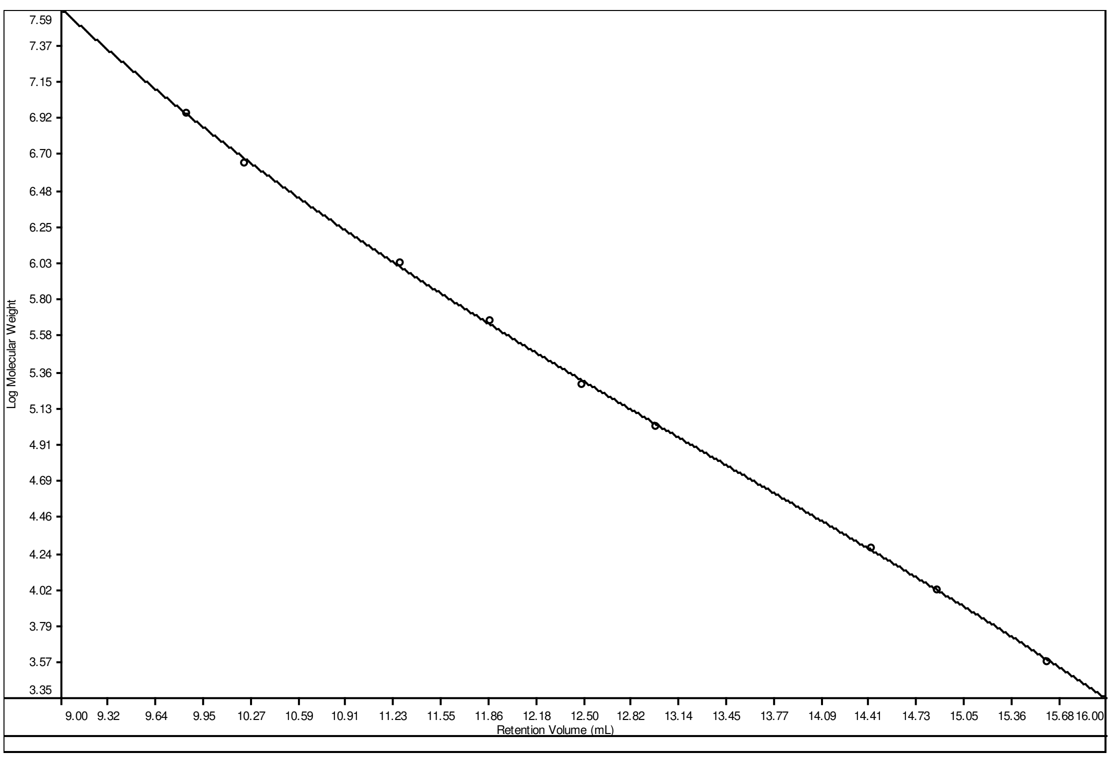
Table of Contents

GPC-H

System Calibration using PS 8,910,000, 4,410,000, 1,040,000, 454,000, 184,000, 130,000, 17,600, 9,730, 3,250, 474



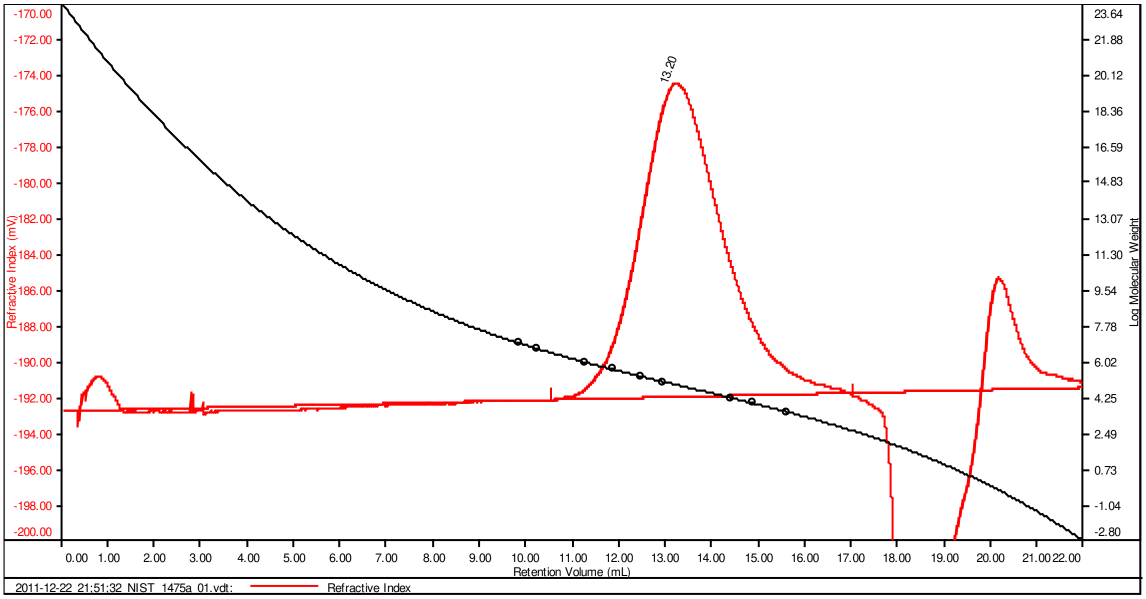
PS Standards: RI Overlay Chromatogram



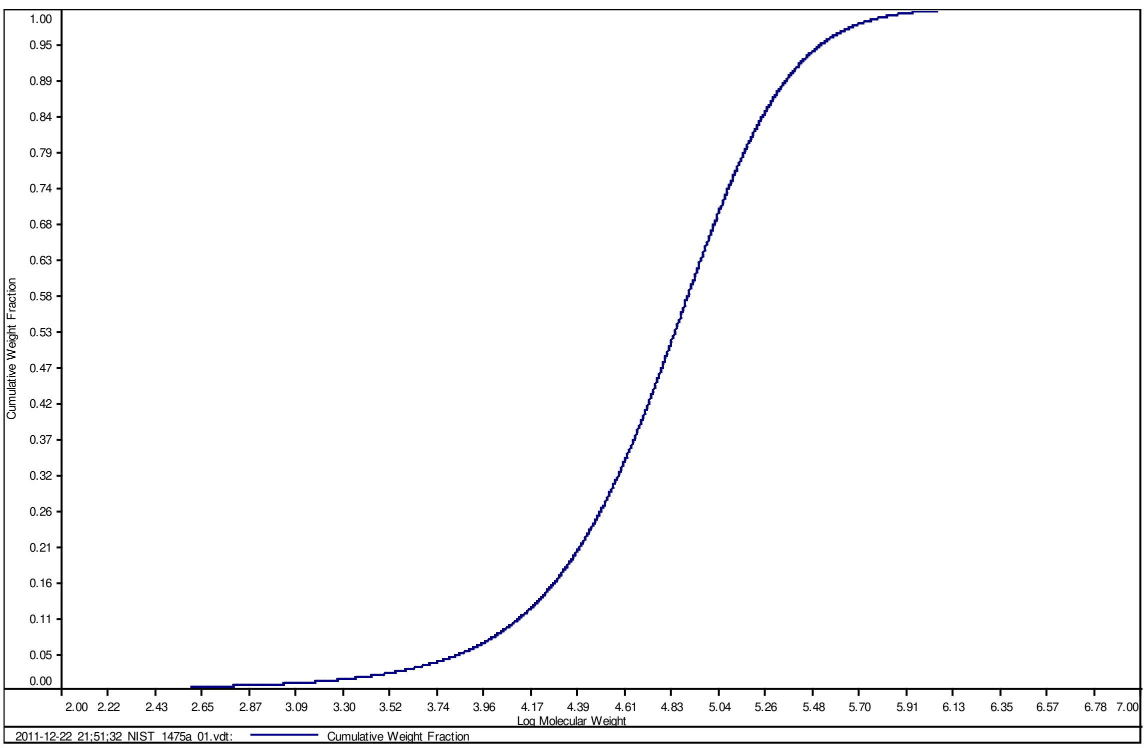
PS Standard Calibration

GPC-H

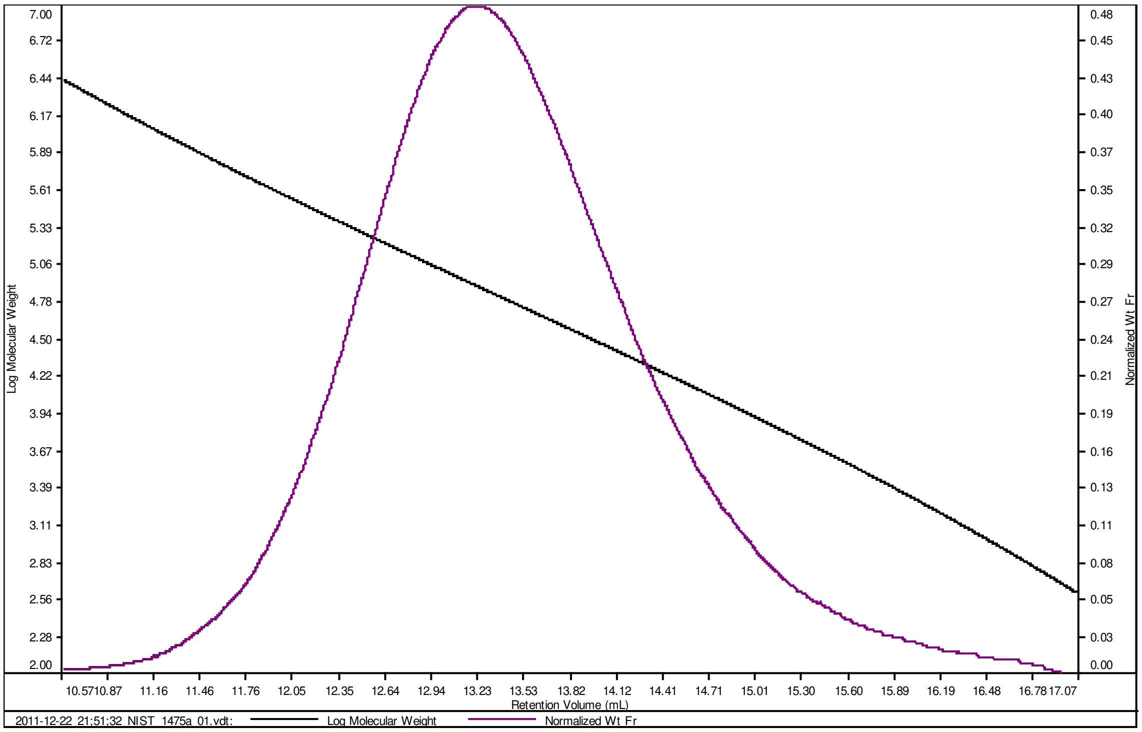
NIST 1475a Linear Polyethylene



NIST 1475a Linear Polyethylene: RI Chromatogram



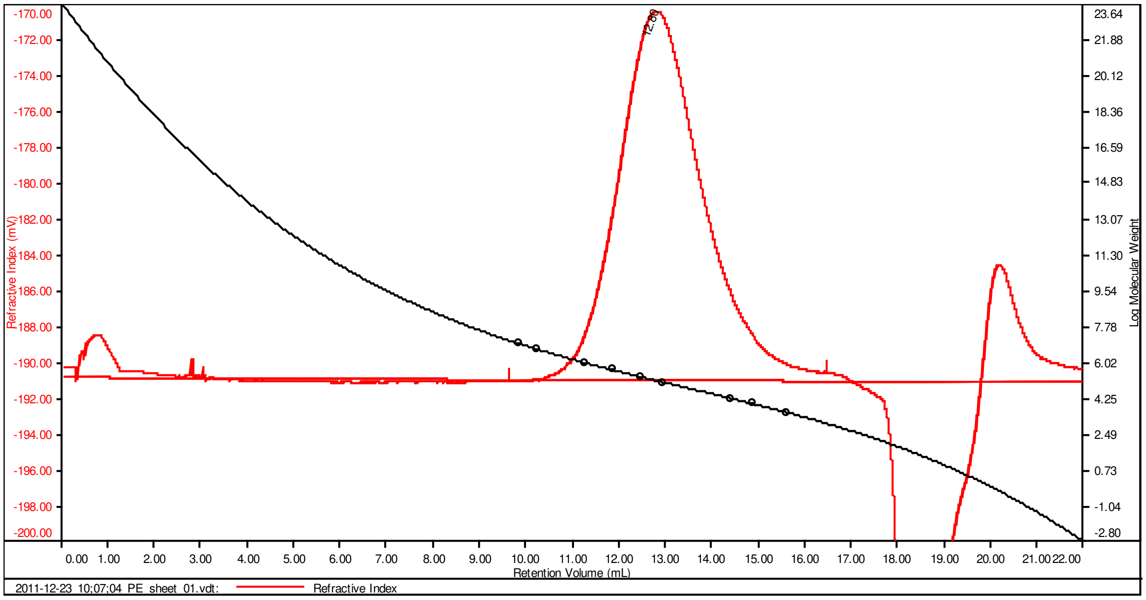
NIST 1475a Linear Polyethylene: Cumulative Weight Fraction Curve



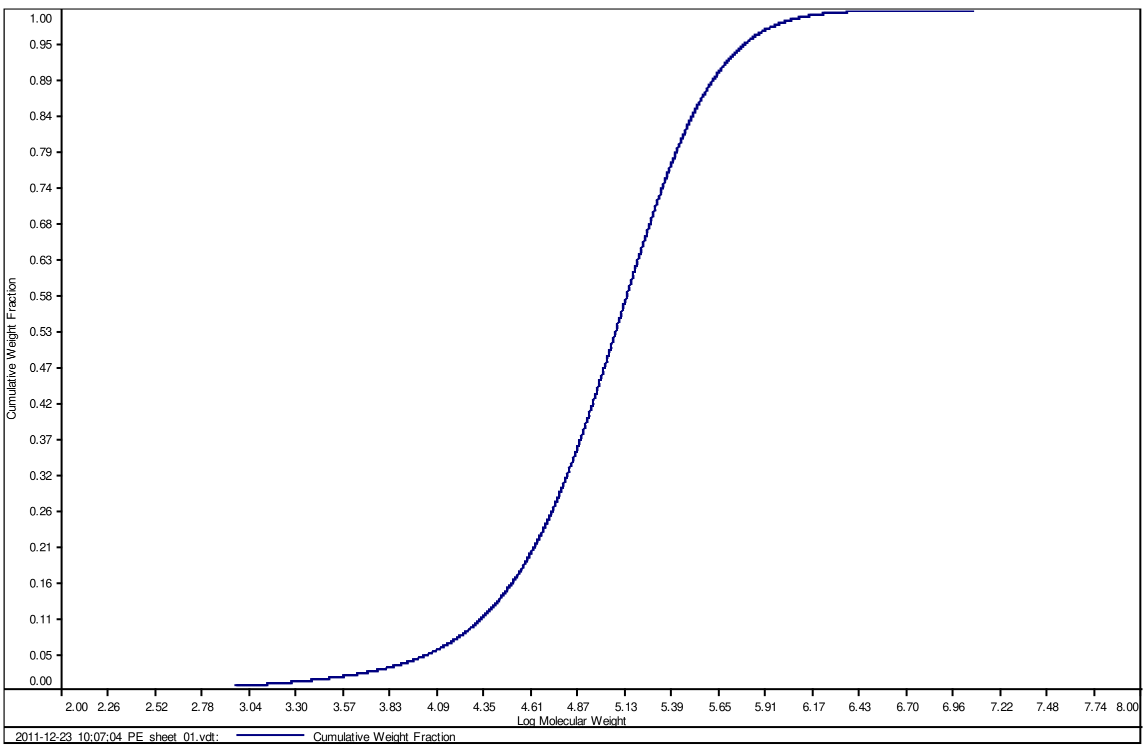
NIST 1475a Linear Polyethylene: MW Distribution Curve

GPC-H

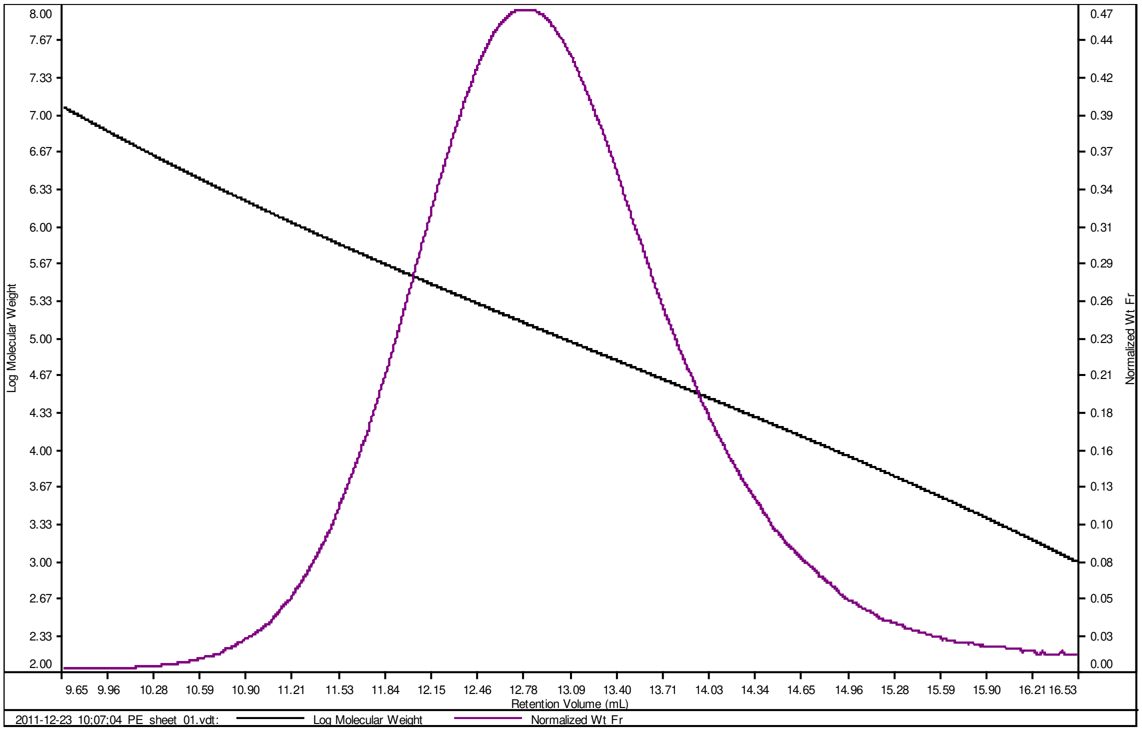
Low Density Polyethylene



Low Density Polyethylene: RI Chromatogram



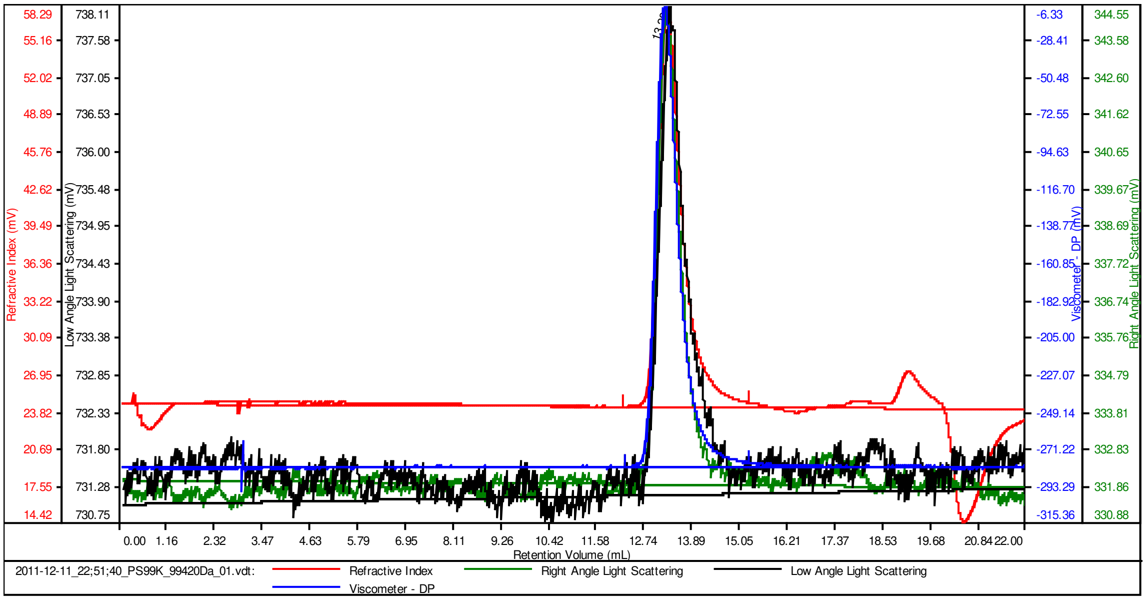
Low Density Polyethylene: Cumulative Weight Fraction Curve



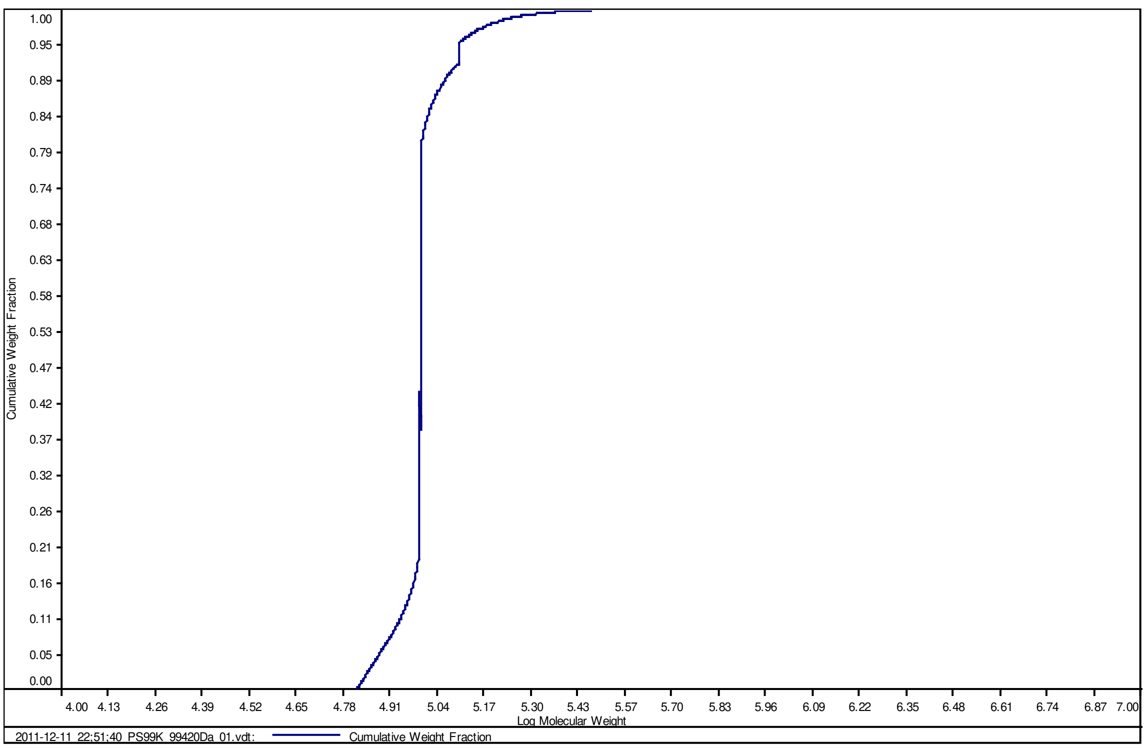
Low Density Polyethylene: MW Distribution Curve

GPC-HT

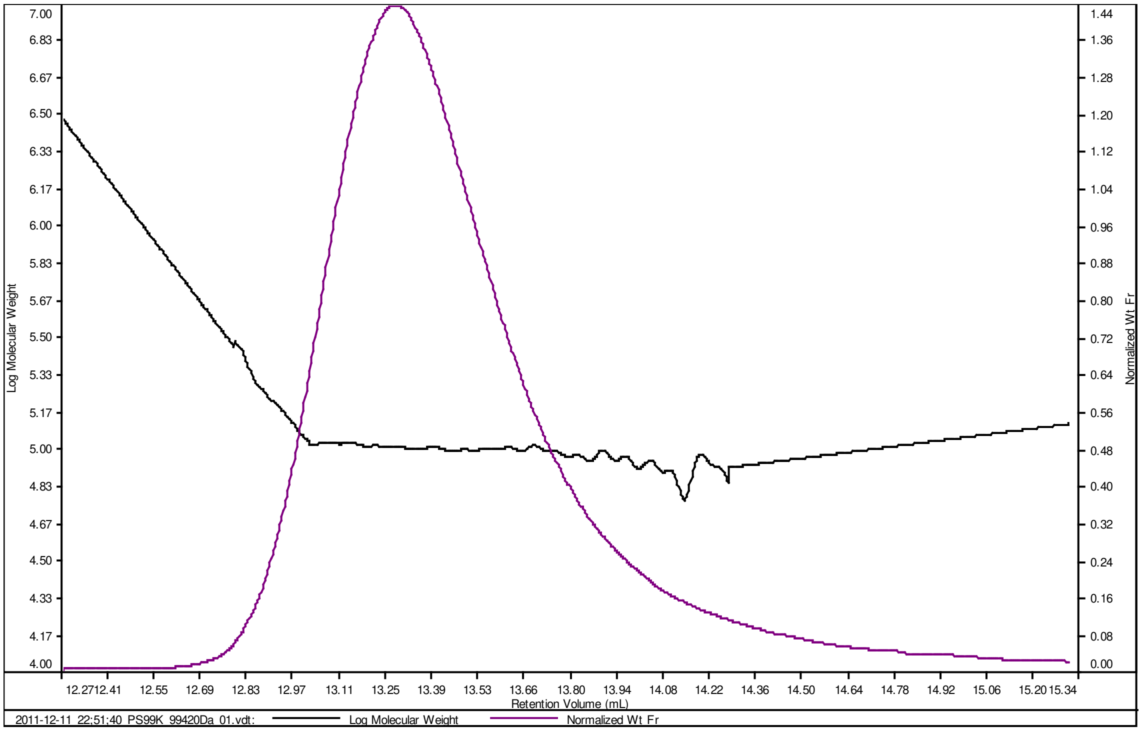
System Calibration using PS 99,420 (PS99K)



PS 99K: RI, RALS, LALS DP Overlay Chromatogram



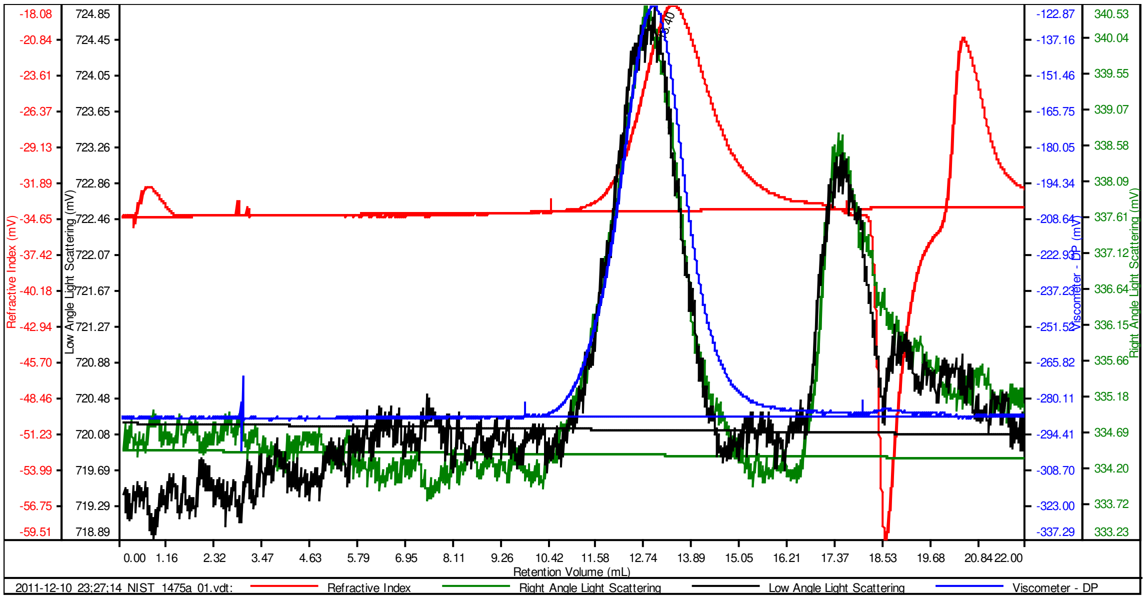
PS99K: Cumulative Weight Fraction Curve



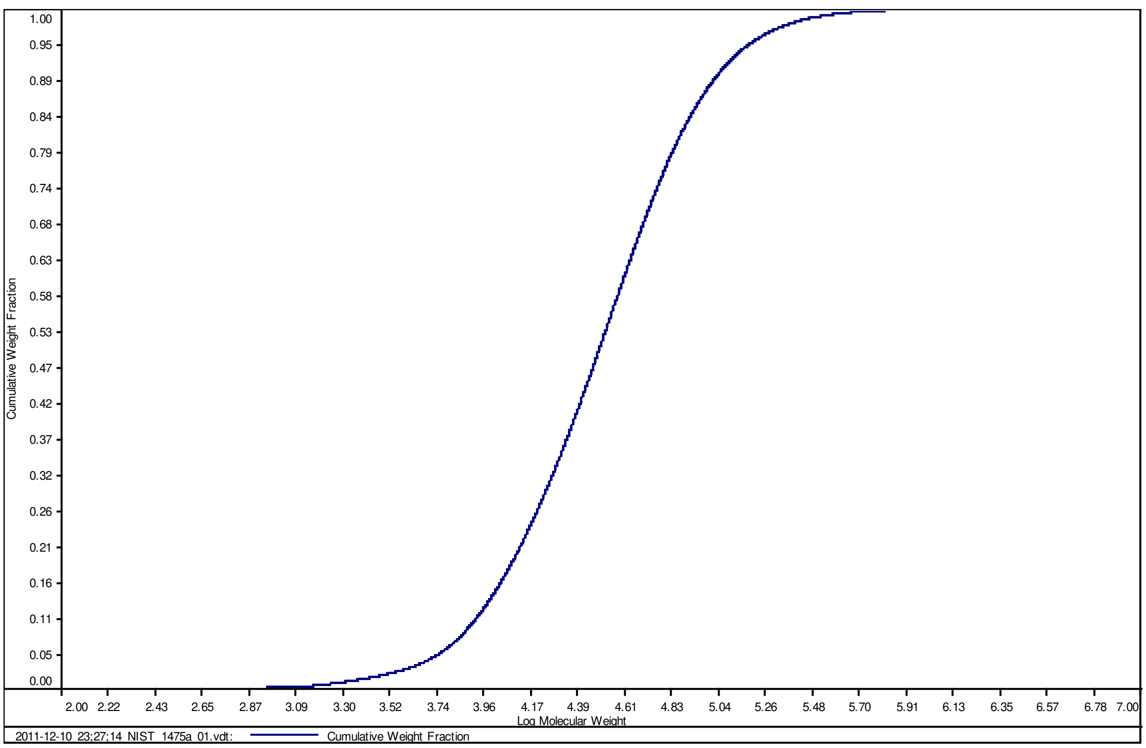
PS99K: MW Distribution Curve

GPC-HT

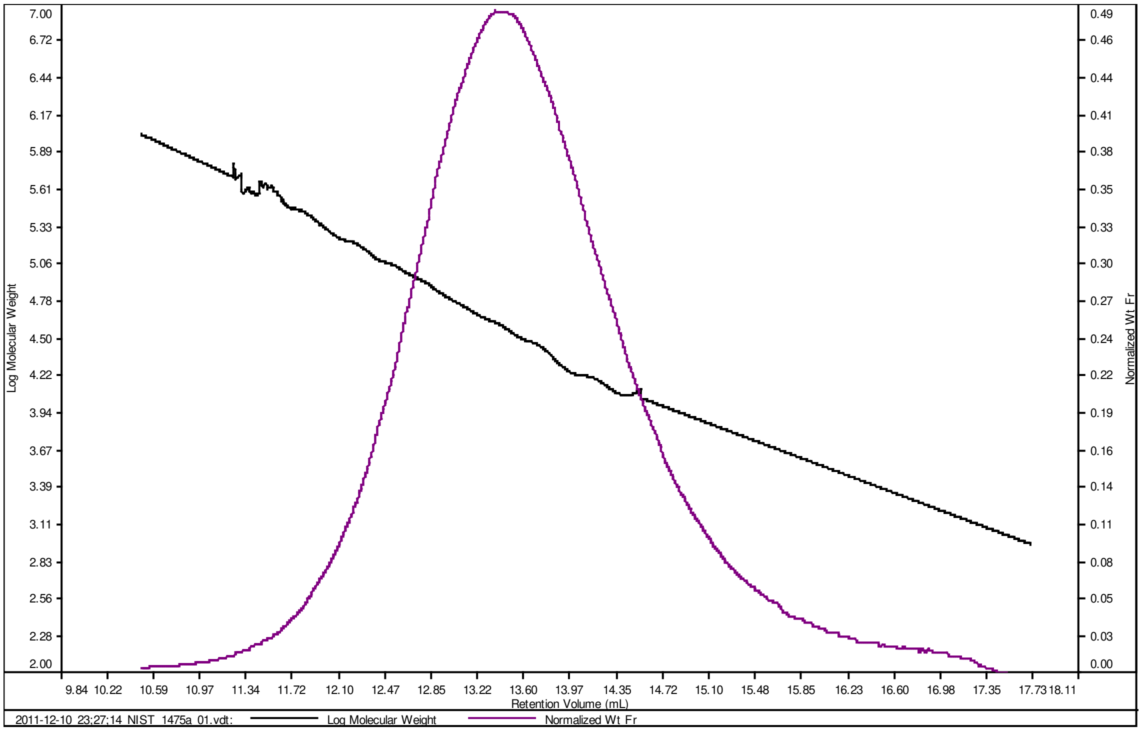
NIST 1475a Linear Polyethylene



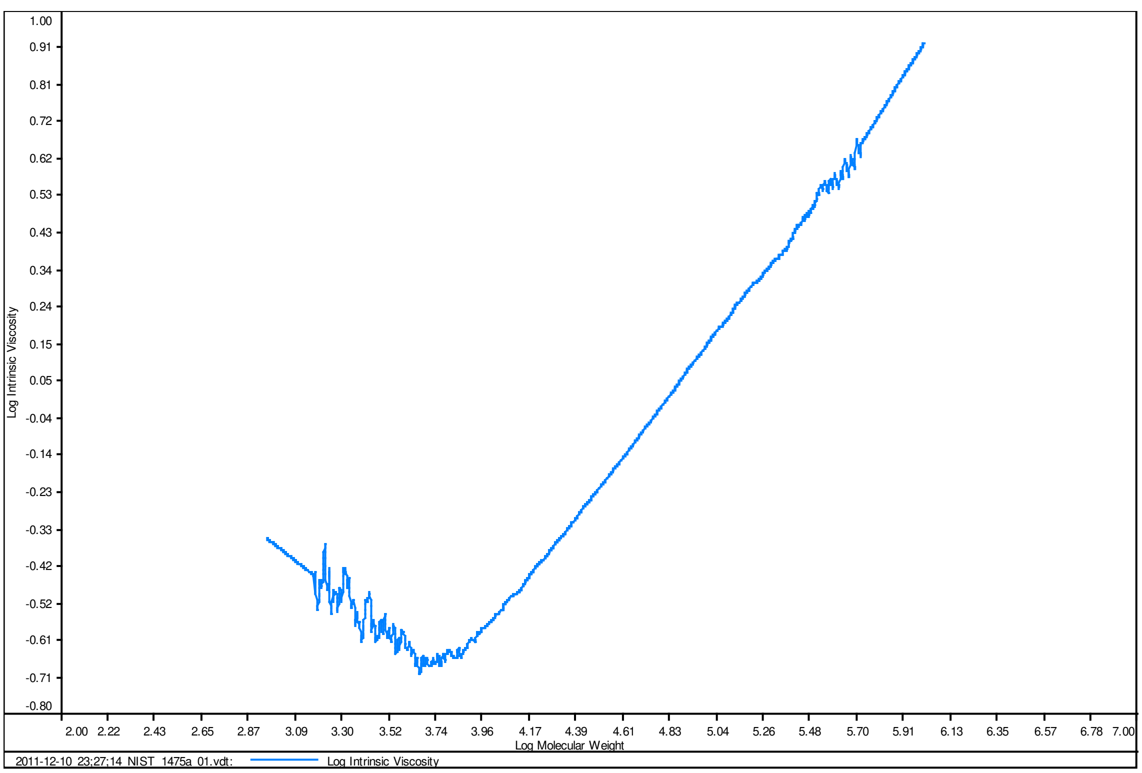
NIST 1475a Linear Polyethylene: RI, RALS, LALS DP Overlay Chromatogram



NIST 1475a Linear Polyethylene: Cumulative Weight Fraction Curve



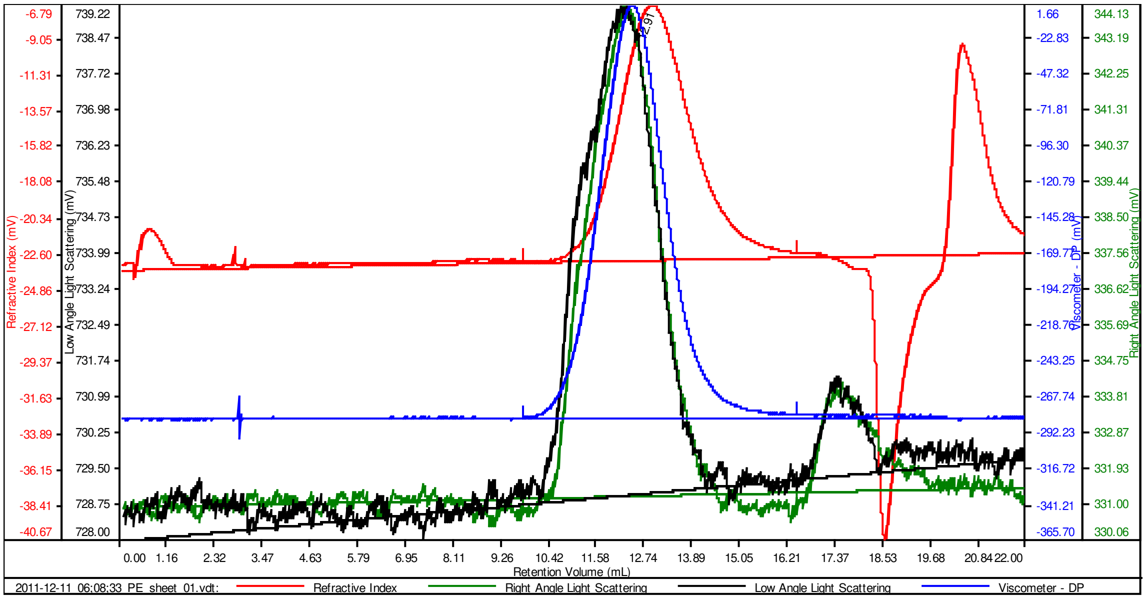
NIST 1475a Linear Polyethylene: MW Distribution Curve



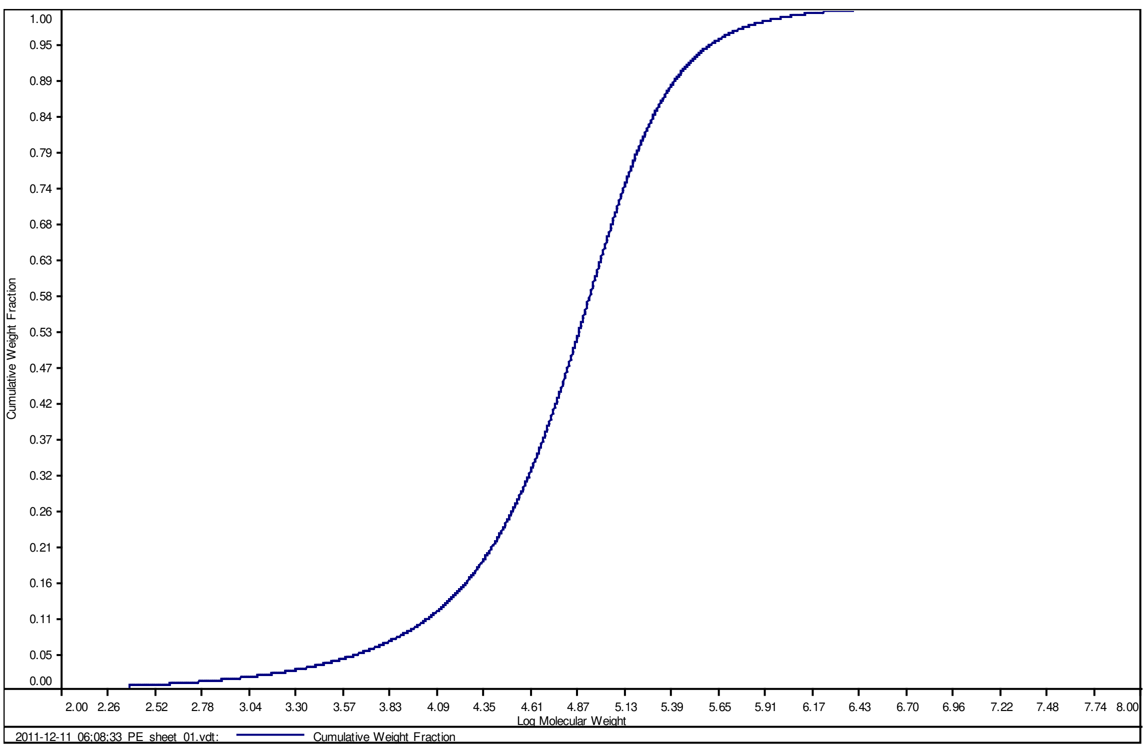
NIST 1475a Linear Polyethylene: Mark Houwink Plot

GPC-HT

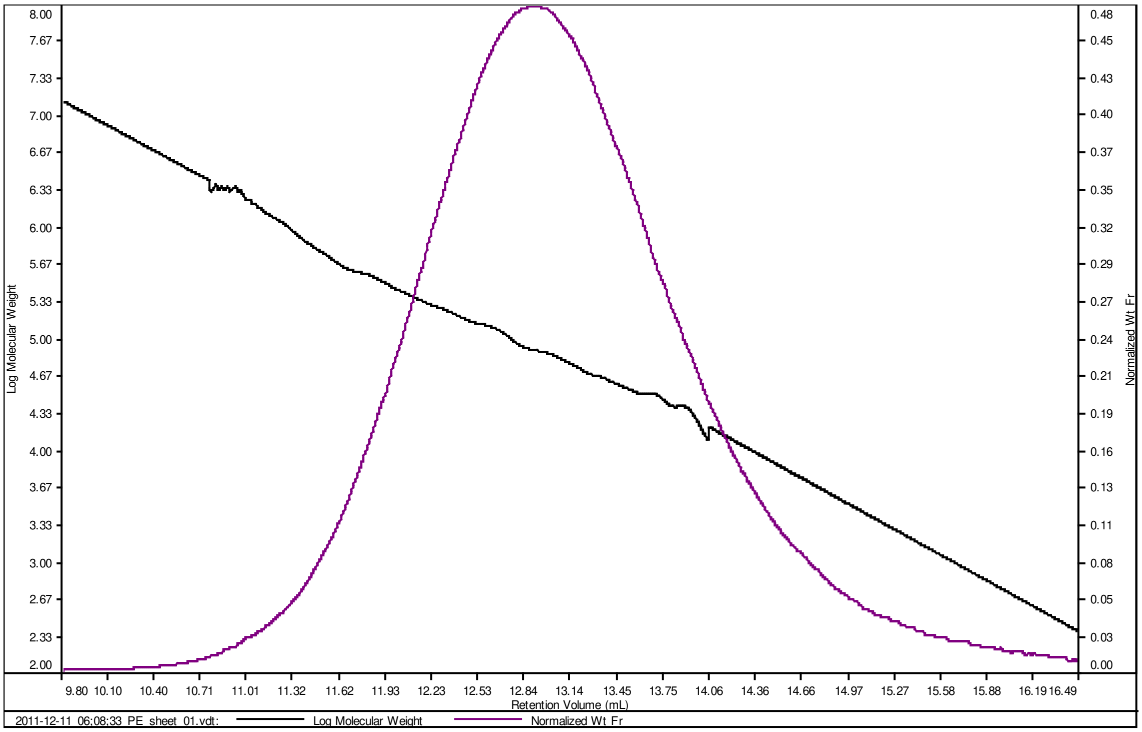
Low Density Polyethylene



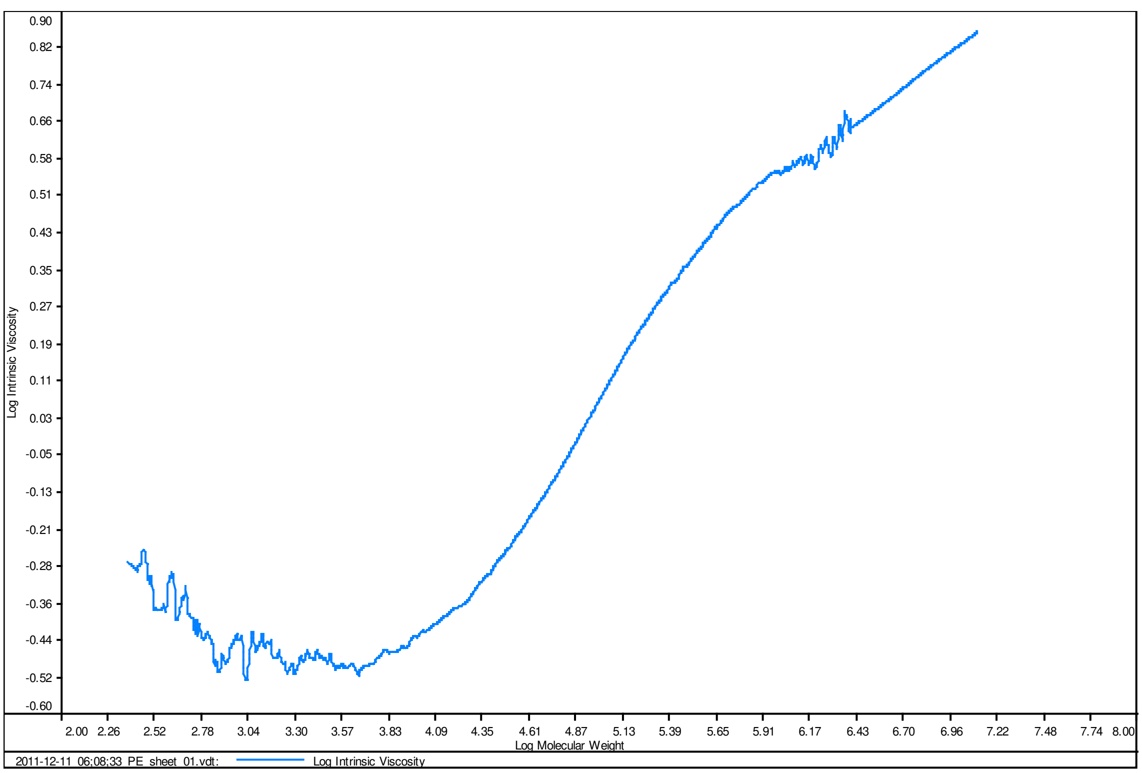
Low Density Polyethylene: RI, RALS, LALS DP Overlay Chromatogram



Low Density Polyethylene: Cumulative Weight Fraction Curve



Low Density Polyethylene: MW Distribution Curve



Low Density Polyethylene: Mark Houwink Plot