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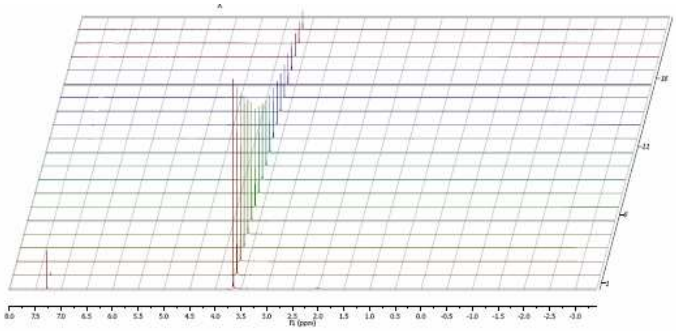
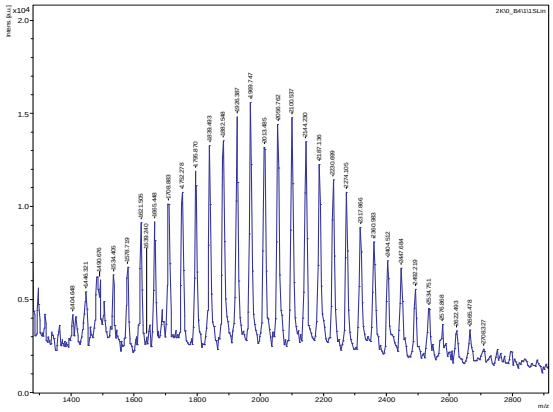
Determination of Polymer Molecular Weight Distributions: DOSY, MALDI, GPC

Poly(ethylene glycol)

PEG





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University Honors Program Research Project

APPROVAL PAGE

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Full title of project as it should appear in Graduation Program and transcript:

"Determination of Polymer Molecular Weight Distributions: DOSY, MALDI, GPC"

Abstract:

This report describes the background theory, procedures, and results of research about polymer molecular weight distributions. The project involved investigating six samples of poly(ethylene glycol), or PEG. The samples had molecular weights of 1,000 Da, 2,000 Da, 5,000 Da, 10,000 Da, and 20,000 Da. The samples were analyzed by diffusion (DOSY) and relaxation (T1, T2) measurements using nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy measurements using matrix-assisted laser desorption ionization (MALDI), and gel permeation chromatography (GPC). This report addresses the concept of molecular weight in polymers from the perspective of the molecular weight distribution and polydispersity. This report also discusses the theory and procedure of each of the methods used along with the results and conclusions of the investigation. This report concludes by presenting information about possible future actions and other techniques that are available to study the molecular weight of polymers.

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Abstract

This technical report describes the background theory, procedures, and results of research about polymer molecular weight distributions. The project involved investigating six samples of poly(ethylene glycol), or PEG. The samples had molecular weights of 1,000 Da, 2,000 Da, 5,000 Da, 10,000 Da, and 20,000 Da. The samples were analyzed by diffusion (DOSY) and relaxation (T1, T2) measurements using nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy measurements using matrix-assisted laser desorption ionization (MALDI), and gel permeation chromatography (GPC). This report addresses the concept of molecular weight in polymers from the perspective of the molecular weight distribution and polydispersity. This report also discusses the theory and procedure of each of the methods used along with the results and conclusions of the investigation. This report concludes by presenting information about possible future actions and other techniques that are available to study the molecular weight of polymers. This document includes twenty-two figures, two tables, and a collection of obtained spectra for each sample. This report will be submitted for the EH 301-03 technical writing course, the Honors Program senior thesis, and the Department of Chemistry senior research project.

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Introduction: Polymers and Molecular Weight Distributions

Terminology within the field of polymer chemistry tends to be somewhat circular. For example, *Contemporary Polymer Chemistry* defines a monomer as "any substance that can be converted into a polymer" (Allcock and others 2003, p 3). Polymers, on the other hand, tend to be defined as high molecular weight substances composed of repeating monomeric subunits and are named by the monomer(s) used (Lide 2006; Scholz 2009).

Given the circular and uninformative description above, a specific example will better serve the purpose of defining monomers and polymers. To do this I will use poly(ethylene glycol), the polymer I investigated for this project, as a case in point. Poly(ethylene glycol) is more commonly called PEG for brevity, and I will use the acronym throughout the rest of this document. Figure 1 at the right shows the structures of ethylene glycol (Figure 1a) and PEG (Figure 1c). In Figure 1c, the lowercase *n* outside the right bracket is used to depict repetition of the monomeric subunit. Ethylene oxide (Figure 1b) is a more common monomer that can be polymerized to form PEG. Consequently, PEG is sometimes called poly(ethylene oxide) or PEO. The names PEG and PEO are used interchangeably, but generally PEG is used for lower molecular weight samples and PEO for higher molecular weight samples (Scholz 2009).

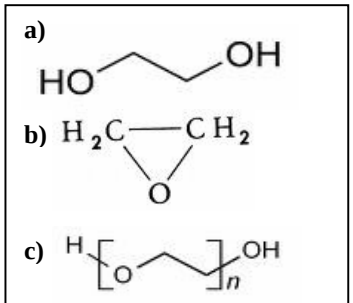

Figure 1: Monomers of PEG
a) ethylene glycol (monomer)
b) ethylene oxide (monomer)
c) PEG (polymer)

Source: Google Images

Polymer Criteria

Polymers are more effectively defined by their observed general properties. In 1920, Hermann Staudinger demonstrated the existence of polymers using four tests to compare low molecular weight and high molecular weight compounds. First, he showed that small molecules dissolve in water whereas polymers swell before dissolving. Then, he showed that the viscosity (resistance of flow) of a one percent solution is low for small molecules but high for polymers. Next, he showed that polymers do not undergo dialysis through a semi-permeable membrane whereas small molecules do. Last, and most importantly, he showed that small molecules have a unique particle size whereas polymers do not (Scholz 2009). The results of his tests are summarized below.

Staudinger's Criteria for a Polymer (Scholz 2009)

Criterion	Small Molecule	Polymer
Swelling	No	Yes
Viscosity of a 1% Solution	Low	High
Possibility of Dialysis	Yes	No
Unique Particle Size	Yes	No

Using Staudinger's criteria, a polymer may, therefore, be defined as a high molecular weight substance which is composed of repeating monomeric subunits, swells in water before dissolving, produces highly viscous solutions, does not undergo dialysis, and does not have a unique particle size. These criteria are still the most commonly used factors in identifying an unknown sample as a polymer or not (Scholz 2009).

Average Molecular Weight

As mentioned above, polymers, unlike small molecules, do not have a single, specific molecular weight (Allcock and others 2003). For example, ethylene oxide has a molecular weight of 44.05 daltons (a unit of molecular weight typically used by polymer chemists). On the other hand, I analyzed six samples of PEG with molecular weights of 1,000 Da, 2,000 Da, 5,000 Da, 10,000 Da, 20,000 Da, and 30,000 Da. However, these numbers are also misleading in that they suggest that sample one had a molecular weight of exactly 1000 Da. This is not the case. Polymer samples have a "distribution of different molecular weights in the same sample of material…it is necessary to speak of average molecular weights rather than a single defining value" (Allcock and others 2003, p 11). Therefore, sample one contained molecules with a variety of molecular weights and the average of all those molecular weights was 1000 Da. Figure 2a shows the mass spectrum of a small molecule (the peak at 135 is the discrete molecular weight while the other peaks correspond to fragments of the whole molecule), and Figure 2b shows the molecular weight distribution of a polymer (chain length is directly proportional to molecular weight).

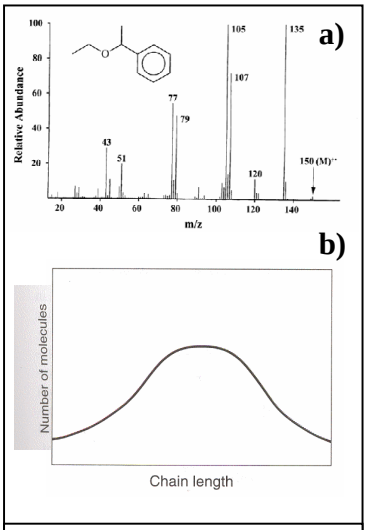

Figure 2: Molecular Weight
a) Mass spectrum of a small molecule (discrete value) Source: Vogler 2009
b) Molecular weight distribution of a polymer Source: Allcock and others 2003, p 11

The molecular weight of a polymer is influenced primarily by two factors: the weight of the individual subunits and the number of subunits present in the polymer. For this project, I only investigated PEG so the individual subunits were always ethylene oxide. From the previous, ethylene oxide always has a molecular weight of 44.05 Da. Therefore, in this experiment, the only factor affecting the molecular weight distribution of my samples was the number of repeated ethylene oxide subunits. The number of repeated subunits in a polymer directly correlates to the chain length: the greater the number of subunits, the longer the chain (Allcock and others 2003).

Effect of Synthesis Method on Molecular Weights

The length of the chain is influenced by the method of polymerization. There are three phases of every polymer synthesis: initiation, propagation, and termination. Initiation prepares a monomer to react with another monomer and thereby begin the

polymerization. Propagation refers to adding subsequent monomers to the end (usually) of the chain. Termination produces the final product, which is not reactive (Allcock and others 2003, p 59).

The efficiency of propagation and the ease of termination are the major factors which affect the length of the polymer chain. For example, a polymerization which propagates slowly but terminates easily is likely to produce low molecular weight polymers. A reaction that is difficult to terminate, on the other hand, will typically generate high molecular weight polymers. The distribution of molecular weights results from the interplay of these two processes. More specifically, the distribution relies on the relation of propagation and termination in the particular polymerization method used and how easily the synthesis may be controlled (Allcock and others 2003).

In a very simplified example, suppose two monomers are initiated at the same time in one solution. The first reacts with seven subsequent monomers and then terminates, and the second reacts with nine subsequent monomers before terminating. As a result, the second has a higher molecular weight and a longer chain than the first. However, these two chains are in the same sample so the average chain length is eight monomers. Consequently, the description of polymer molecular weights is a matter of probability and statistics.

Polydispersity and Molecular Weight Distributions

The two major points regarding polymer molecular weights are that polymers have a distribution of molecular weights and that the referenced molecular weight of a polymer is an average value. The number average (M_N) and the weight average (M_W) are two slightly different descriptive values that are commonly used to describe the molecular weight distributions. A third, less common value is the z-average molecular weight (M_Z) (Scholz 2009). A fourth parameter, the M_P is the molecular weight corresponding to the highest point of the distribution (Weimer 2010). The formulas for computing the M_N, M_W, and M_Z values are given below and Figure 3, at the right, relates these parameters to a generic molecular weight distribution.

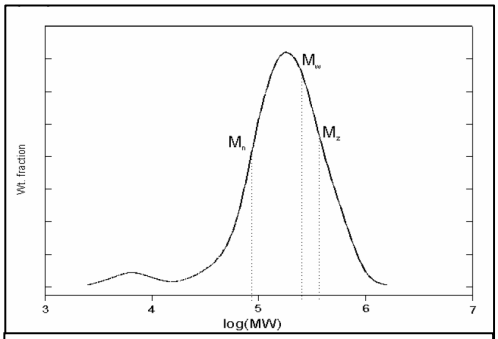

Figure 3: Generic Distribution with Parameters

Source: Scholz 2009

- Number average MW ($\bar{M}_n$). $\frac{\Sigma(M_i N_i)}{\Sigma(N_i)}$
- Weight average MW ($\bar{M}_w$). $\frac{\Sigma(M_i^2 N_i)}{\Sigma(M_i N_i)}$
- Z average MW ($\bar{M}_z$). $\frac{\Sigma(M_i^3 N_i)}{\Sigma(M_i^2 N_i)}$

Molecular Weight Characterizations (Scholz 2009)

M_i = molecular weight of species with length i

N_i = number of species (moles) with length i

A fifth parameter, called the polydispersity, is derived from the ratio of M_W to M_N. The polydispersity describes the width of the distribution and is similar to the standard deviation from statistics. A narrow distribution is observed when the polydispersity is close to one. A polydispersity greater than two corresponds to a broad molecular weight distribution (Allcock and others 2003, p 11). Instances of each case are seen below in Figure 4a and b.

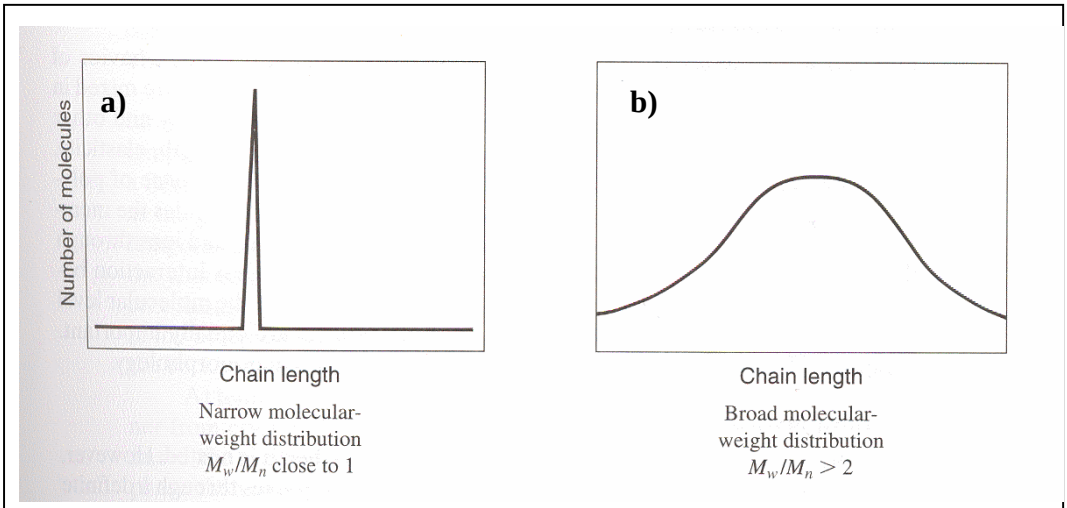

Figure 4: Polydispersity

Source: Allcock and others 2003, p 11

In a sense, polydispersity serves as an indicator of purity within a sample: a very narrow distribution means that most of the molecules in the sample have nearly identical molecular weight. This indicates that the polymerization method utilized is highly controlled. The shape of the molecular weight distribution can be used to identify the polymerization technique. Even more importantly, however, the distribution can be used to "determine the physical properties of polymer mixtures" (Chen and others 1995, p 1).

Influence of Polydispersity on Sample Properties

Both the average molecular weight and the molecular weight distribution strongly impact the properties of the polymer sample. Polymers with broad distributions have some chains that are shorter and some chains that are longer than the average chain length. The shorter chains act as plasticizers and make the whole sample softer. Also, polymers with broad distributions have lower solidification temperatures and are more difficult to crystallize than polymers with narrow distributions (Allcock and others 2003).

The average molecular weight also affects properties of the sample. For example, in my PEG samples, the 1000 Da sample was waxy; the 2000 Da sample was flaky; and the samples greater than 5000 Da were fine powders. Figure 5, at the top of the next page, shows photographs of each of these samples.

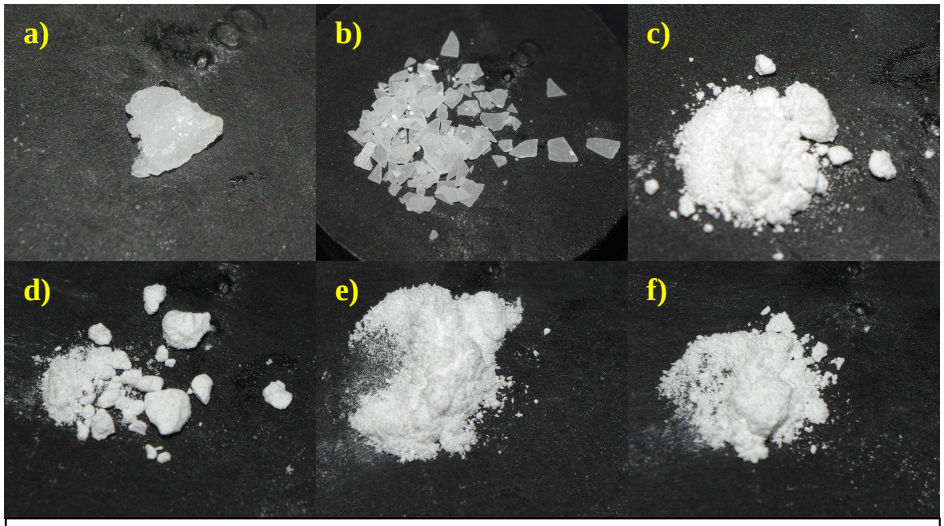

Figure 5: Poly(ethylene glycol) Samples
a) 1,000 Da - waxy **b) 2,000 Da - flakes**
c) 5,000 Da – powder **d) 10,000 Da – powder**
e) 20,000 Da – powder **f) 30,000 Da – powder**

Source: Photos by Author

Poly(ethylene glycol) (PEG)

PEG is a polyether synthesized by a cationic ring-opening polymerization of ethylene oxide. This polymerization method is highly controllable and may be used to generate very narrow molecular weight distributions. One danger is that ethylene oxide is an epoxide ring, and opening such rings sometimes causes explosions because of the rapid, exothermic ring-opening reaction during initialization (Allcock and others 2003).

PEG has many uses medically and industrially. PEG is soluble in both water and organic solvents and has been shown to successfully conceal proteins from the body's natural immune response. This property has led to investigations for the use of PEG in drug delivery (Harris 1992). A solution of PEG 3500 with several salts is prescribed for use to clear the bowels prior to a colonoscopy (FDA 2010). PEG is also used a dye and ink carrier in printing applications. It is especially useful because it physisorbs on metal and plastic surfaces. In the biomedical industry, this is important because PEG coated surfaces can prevent non-specific binding of proteins and DNA (Jang and others 2009). PEG is also used in a variety of other applications including resin preparation, antidusting in agricultural chemicals, low volatility and low toxicity soaps and cleaners, cosmetics, toothpaste, wood working, food packaging, the release of elastomers from molds, and in textiles as a softener and antistatic agent (Chemicalland21.com 2008).

Section 1: Instrumental Techniques Used

For each sample of PEG, I conducted measurements using diffusion ordered nuclear magnetic resonance spectroscopy (DOSY-NMR), T1 and T2 relaxation, matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), and gel permeation chromatography (GPC).

Diffusion-Ordered Spectroscopy (DOSY), T1, and T2

NMR spectroscopy is primarily used for structural determination; however, recent advances have made possible the use of NMR for quantitative calculations. All measurements were made using a 500 MHz Varian NMR spectrometer, pictured in Figure 6 at right. For this project, I conducted diffusion (DOSY) and relaxation (T1 and T2) measurements.

Figure 6: Varian 500 MHz NMR in the UAH High Field NMR Lab

Source: Photo by Author

Theory

Nuclear magnetic resonance (NMR) spectroscopy is fundamentally rooted in understanding the magnetic properties of atomic nuclei and associated electrons. From quantum mechanical principles, certain nuclei are characterized by a spin which creates a magnetic moment vector. In a sample, these nuclei move and rotate and interact with each other randomly. In an NMR experiment, a very large external magnet is used to apply a magnetic field to the sample. As a result, all of the magnetic moments of the nuclei align to this field. Then, a second magnetic field is applied to push the magnetic moments into a perpendicular alignment. The second field is then turned off and the magnetic moments relax to their initial position. This relaxation results in the release of measurable energy which may be converted into valuable information depending on the experiment of interest (Lambert and others 1998; Vogler 2009).

The T1 and T2 experiments are relaxation measurements. Relaxation, simply put, is the process by which a system returns to equilibrium. Both T1 and T2 relaxation are time dependent processes that may be mathematically defined by an exponential decay function. T1 relaxation is known as spin-lattice or longitudinal relaxation and is characterized by the loss of energy to the surroundings (the solvent) as heat. T2 relaxation is know as spin-spin or transverse relaxation and refers to the loss of energy by the interactions between spins of different nuclei. T2 relaxation is always less than T1 relaxation (Vogler 2009).

Diffusion-ordered spectroscopy (DOSY) is an example of a pulsed field gradient stimulated echo experiment. Such experiments incorporate a series of magnetic pulses of varying intensity and duration. In the DOSY experiment, the NMR signal is attenuated

by increasing the gradient strength. In other words, the gradient strength increases, the NMR signal diminishes. The gradient strength is then converted to the diffusion constant using an inverse Laplace transform. In a DOSY plot, the diffusion constant is plotted on the vertical axis versus the chemical shift of the NMR spectrum (Jerschow and Muller 1998). In solution, molecules are in constant motion. Large molecule move more slowly than small molecules. Therefore, larger molecules are characterized by smaller diffusion coefficients (Vogler 2010).

The data for all three of these measurements produces an arrayed data set. That is, each measurement produces many spectra. The trend in the spectra is then used to compute the parameter of interest: T1 time, T2 time, or diffusion coefficient. These calculations all incorporate the use of best fit exponential curves (MestRe Nova 2010).

Procedure

Dr. Bernhard Vogler of the UAH Chemistry Department instructed me in the VNMRj software procedures to collect the NMR data. Each sample was prepared by dissolving the polymer in deuterated chloroform in an NMR tube which was then placed in the magnet. The DOSY, T1, and T2 measurements were queued to run sequentially overnight.

First, a ^{1}H (proton) NMR spectrum was obtained for the sample. This spectrum was optimized using window adjustment, phasing, drift correction, and calfa commands. The spectrum was then copied from experiment one to experiment two and three to set up the measurement queue. The DOSY measurement was conducted in experiment one; the T1 measurement was conducted in experiment two; the T2 measurement was conducted in experiment three.

DOSY

1. Diffusion spectra were obtained using the “Doneshot” protocol.
2. The gzlvl1 command was used to set up the measurement such that the final spectrum had approximately ten percent intensity of the initial spectrum.
3. The parameters were then set up with a relaxation time of 25 seconds between scans, 16 scans, a gradient length of 0.005 seconds, a gradient delay of 0.15 seconds, and 25 increments. The initial and final values for the gradient strength were determined for each sample using the gzlvl1 parameters.
4. The measurement was then allowed to run.
5. After the measurement was complete, the collected data was analyzed using the MestRe Nova software package.
    - The data was loaded into MestRe Nova and analysis was done using both the Bayesian transform and the arrayed data set methods.
    - These methods produced the diffusion coefficient which was then used to calculate the molecular weight of the sample.

T1 Relaxation

1. The T1 spectra were obtained using the “Inversion Recovery” protocol.

2. The parameters were set to a minimum of 0.2 seconds, a maximum of 5 seconds, and a time of 4 hours.
3. The measurement was then allowed to run.
4. The data was interpreted with the MestRe Nova software package using the arrayed data set method and the resulting T1 time was used to calculate the molecular weight of the sample.

T2 Relaxation

1. The T2 spectra were obtained using the "T2" protocol.
2. The parameters were set to a minimum of 0.2 seconds, a maximum of 5 seconds, and a time of 4 hours.
3. The measurement was then allowed to run.
4. The data was interpreted with the MestRe Nova software package using the arrayed data set method and the resulting T2 time was used to calculate the molecular weight of the sample.

Matrix-Assisted Laser Desorption Ionization (MALDI)

The MALDI measurements for this project were conducted at Serina Therapeutics, Inc with the assistance of Rebecca Weimer. The MALDI instrument that was used is pictured in Figure 7 at the right.

Figure 7: MALDI MS at Serina Therapeutics, Inc

Source: Photo by Author

Theory

By definition, mass spectrometry "is a technique for studying the masses of atoms or molecules or fragments of molecules," according to the *Quantitative Chemical Analysis* textbook (Harris 2007, p 474). In general, gaseous species are generated from condensed (solid or liquid) phases and then ionized. The ions, charged particles, are separated according to their mass-to-charge (m/z) ratio which is then plotted against signal intensity to generate the mass spectrum (Harris 2007). Methods of ionization include electron ionization, chemical ionization, spray ionization, and desorption ionization. Electron and chemical ionization only work for volatile samples whereas desorption ionization may be used with solids and liquids. Desorption ionization is especially useful for high molecular weight compounds, like polymers, because such compounds are very difficult to volatilize (Lambert and others 1998).

MALDI is a specific type of mass spectrometry that incorporates desorption ionization. Desorption ionization is generally achieved by depositing large amounts of energy into the sample in very short times. In MALDI, this is accomplished using a rapid pulse laser. The sample is adsorbed onto a matrix which is a material that strongly absorbs provided energy. For example, a MALDI matrix absorbs energy at wavelengths near the wavelength of the laser that is used. The matrix then transfers energy to the sample

resulting in ionization. This process is depicted in Figure 8 at the right. According *Organic Structural Spectroscopy*, "The ideal matrix for [desorption ionization] should be a material that strongly absorbs the energy provided, contributes few ions to the mass spectrum, interacts with the analyte to produce ions from ionic or neutral compounds, and effectively transfers energy to the ionized analyte to cause its release into vacuum" (Lambert and others 1998).

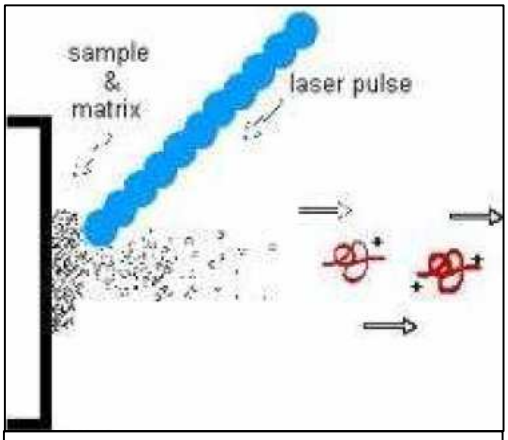

Figure 8: Schematic of MALDI Process

Source: Vogler 2009.

After the sample is ionized, the particles must be separated by the m/z ratio and analyzed. For MALDI, this is typically accomplished in a time-of-flight analyzer. In Figure Y, the vertical portion of the mass spectrometer is the time-of-flight chamber. "[The] ions are accelerated through [an electric] potential and are then allowed to 'drift' down a tube to a detector," as explained in *Spectrometric Identification of Organic Compounds* (Silverstein 2005, p12). Ions of different mass will have different velocities—larger ions will move slower while smaller ions will move faster. Time-of-flight spectrometers require ions to enter the drift tube at the same time and position; therefore, they are especially useful in conjunction with pulsed techniques such as MALDI. Time-of-flight instruments have a nearly unlimited mass range and very high sensitivity (Silverstein 2005). The diagram in Figure 9, at the right, shows the path of an ion in a time of flight instrument.

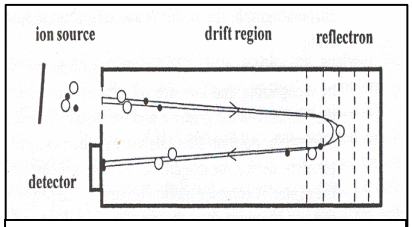

Figure 9: Time of Flight Mass Analyzer Diagram

Source: Lambert and others 1998, p 379

Traditional mass spectrometry techniques are not especially useful for polymers because of the high molecular weights. Conventional methods typically result in multiple ionizations which result in overlapping peaks and spectra that cannot be interpreted as seen in Figure 10a, below, for a 3,500 molecular weight PEG sample (Vogler 2009). By contrast, MALDI allows for single ionization because of the interaction between the sample and the matrix. The MALDI spectrum of my 30,000 molecular weight PEG sample may be seen in Figure 10b (Weimer 2010). This spectrum, which has a molecular

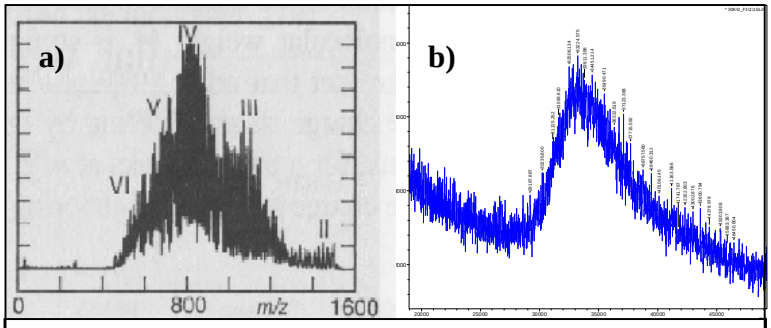

Figure 10: Polymer Mass Spectra
a) PEG 3,500 Da Source: Vogler 2009
b) PEG 30,000 Da (MALDI) Source: Weimer 2010

weight about ten times greater than the other spectrum, is much clearer. MALDI has been used to obtain spectra of samples with molecular weights up to approximately half a million daltons (Allcock and others 2003, p 432).

Procedure

The MALDI measurements of my PEG samples were conducted by Rebecca Weimer at Serina Therapeutics, Inc.

1. The first step was to adsorb the sample onto the matrix. The polymer was dissolved in acetonitrile. A separate solution of sodium iodide and α-cyano-4-hydroxycinnamic acid (HCCA) in acetonitrile. The HCCA composed the matrix while the sodium iodide was included to help initiate ionization. The matrix solution was then mixed with each polymer sample.
2. Five samples of each polymer-matrix solution were then deposited on the sampling array (see Figure 11 at right). The sampling array was placed under vacuum to evaporate the acetonitrile leaving behind the polymer adsorbed onto the matrix.
   - Row 1 – 1,000 Da PEG
   - Row 2 – 2,000 Da PEG
   - Row 3 – 5,000 Da PEG
   - Row 4 – 10,000 Da PEG
   - Row 5 – 20,000 Da PEG
   - Row 6 – 30,000 Da PEG

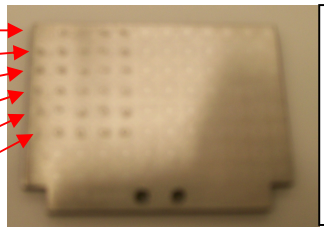

Figure 11: Sampling Array

Source: Photo by Author

3. The sampling array was then placed in the spectrometer.
4. Using a high resolution camera above the sampling plate, the computer was used to position the laser above the first cell. The laser pulses were controlled using the computer interface.
   - Each pulse generated a spectrum and several spectra were added together to generate the final spectrum for each polymer. This was done to increase the signal-to-noise ratio: for each additional spectrum, the signal-to-noise ratio increases by a factor of $\sqrt{n}$, where n is the number of spectra added (Harris 2007).
   - With each subsequent pulse, some of the matrix was blasted away exposing more of the sample which resulted in better spectra. Occasionally, some of the sample was also blasted away which did not improve the spectra.
   - This was repeated for all six of the PEG samples.
5. After all of the spectra were obtained, the files were transferred to a separate program which was used to analyze them and obtain the molecular weight parameters.

Gel Permeation Chromatography (GPC)

The GPC measurements were conducted using the GPC in Dr. Carmen Scholz's lab in the UAH Material Science Building. The GPC is pictured in Figure 12 at the right. Tracy Armstrong, one of Dr. Scholz's graduate students, assisted me with these measurements.

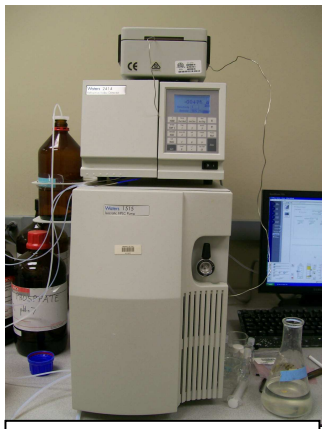

Figure 12: GPC in Dr. Carmen Scholz's lab

Source: Photo by Author

Theory

Gel permeation chromatography (GPC) is also known as size-exclusion chromatography (SEC). Typically GPC is used to describe measurements conducted on polymer samples while SEC is used to describe measurements on large biomolecules. The basis of this technique is to separate molecules according to their size. A GPC consists of a column packed with fine bead-like particles. Each of these particles is permeated by pores of a specific diameter which act like tunnels through the particle. Large molecules cannot fit into these pores so they maneuver around the particles. Smaller molecules, on the other hand, can enter the pores. Since the small molecules must then navigate through the "tunnels" they are delayed. Therefore, large molecules will pass through the column faster and elute first followed by the smaller molecules (Allcock and others 2003). Figure 13, below, depicts the separation process. In the resulting chromatogram, large molecules will contribute to peaks at the left while small molecules will be found at the right of the plot.

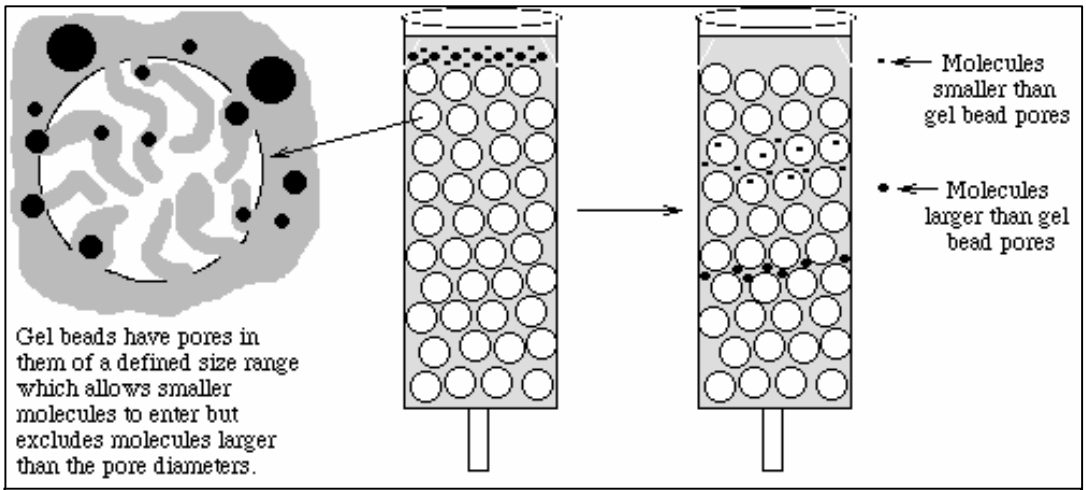

Figure 13: GPC Separation

Source: Google Images

GPC "is essentially a process for the fractionation of polymers according to their size and, therefore, according to their molecular weight. The molecular weight as such cannot be determined directly, but only after calibration of the system in terms of elution time"

(Allcock and others 2003, p 479). To restate this, GPC simply separates polymers by size but cannot be used to directly calculate the molecular weight of the sample. The molecular weight is approximated by comparing the measured elution time to the elution time of standard samples of known molecular weight. This is a valid method because compounds with similar molecular weights should have similar retention times (Scholz 2009).

Procedure

Tracy Armstrong, a graduate student in Dr. Carmen Scholz's lab, assisted me with setting up and taking the GPC measurement.

1. The elution solvent, dimethylformamide (DMF) with a small concentration of lithium bromide, was prepared from stock DMF and filtered to remove any small solids.
    - GPC is very sensitive and will detect almost anything present in the solvent or sample.
    - Lithium bromide was added to break down the secondary structure of the PEG samples. The secondary structure of the polymer refers to its overall three-dimensional shape. The lithium bromide broke down this structure so that the polymer was mostly linear.
2. The GPC pumps and detector were purged with the fresh DMF solution to remove impurities from any previous solvents or leftover samples.
3. The column was allowed to equilibrate overnight to achieve a 50°C temperature and allow the DMF solution to flush the column and stabilize the baseline.
4. The next day, the solvent was degassed with nitrogen to displace oxygen which is a reactive gas. Nitrogen, on the other hand, is inert.
5. The injection sample was prepared by adding approximately five milligrams of each PEG sample to the same test tube. The final mass was forty milligrams. One milliliter of DMF was added to dissolve the polymers.
6. 250 microliters of the PEG sample were injected onto the column and the measurement was allowed to run by an isocratic (single solvent) method with a flow rate of one milliliter DMF per minute.

Section 2: Results and Analysis

Both the NMR and MALDI experiments were very successful and the results are presented below. The GPC experiment, however, did not succeed due to an instrumental error which will be discussed below.

The MALDI and NMR spectra are included at the end of this report after the references list. The spectra are grouped by sample; that is, all of the 1,000 Da PEG spectra are together followed by all of the 2,000 Da PEG spectra, and so on. The spectra are ordered as follows: MALDI, DOSY, DOSY Transform, T1, and T2.

NMR Data and Analysis

The NMR data was collected using the VNMRj software which is used to operate the instrument. Analysis was carried out using the MestRe Nova software published by Mestrelab Research, a chemistry software company. The diffusion coefficients were extracted by fitting the exponential decay function, B*exp(-x*F), to the curve generated by the peak intensities. The F parameter corresponds to the diffusion coefficient. The T1 and T2 times were obtained by fitting the equation, B+F*exp(-x*G), to the corresponding data sets. The actual values for T1 and T2 are the inverses of the G parameter. The parameters and corresponding values are given below in Table 1.

Table 1: NMR Results

	DOSY		T1				T2			
Sample	**B**	**F**	**B**	**F**	**G**	**T1**	**B**	**F**	**G**	**T2**
1000	39050.7	2.476e-6	368275	-400830	0.520	1.923	10.105	22107.9	1.186	0.843
2000	19379.0	1.875e-6	166386	-180946	0.481	2.079	13.191	9293.52	1.150	0.870
5000	23552.7	1.774e-6	187281	-205766	0.642	1.558	-26.107	10173.6	1.426	0.701
10000	35129.6	8.115e-7	1.013e6	-1.101e6	0.485	2.062	52.746	55712.1	1.194	0.838
20000	20964.7	8.235e-7	1.611e6	-1.750e6	0.458	2.183	15.820	86744.1	1.136	0.880
30000	25280.8	2.892e-7	1.315e6	-1.414e6	0.418	2.392	275.019	73468.9	1.052	0.951

Mathematica 6.0, from Wolfram Research, Inc, was used to plot the diffusion constant versus molecular weight and the corresponding natural log plot. Similar plots were also generated for the T1 and T2 data and the six plots may be seen below.

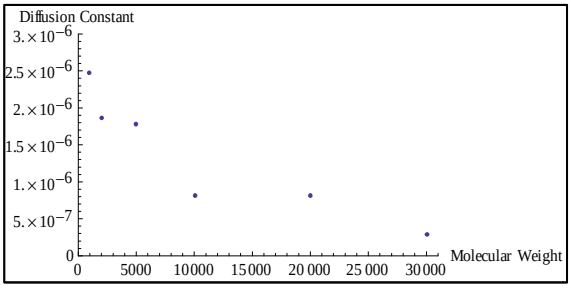

Figure 14: Diffusion vs. Molecular Weight

Source: Generated Using *Mathematica 6.0*

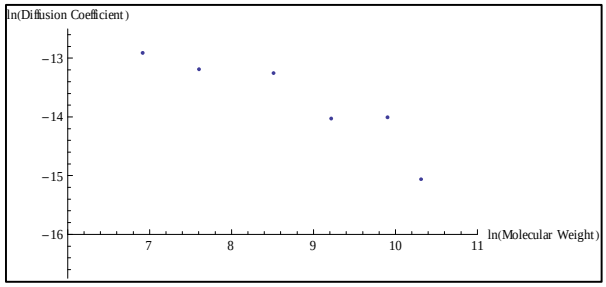

Figure 15: ln(Diffusion) vs. ln(Molecular Weight)

Source: Generated Using *Mathematica 6.0*

These plots show that, overall, the diffusion coefficient decreases as molecular weight increases. The exception is PEG 20,000 which had a diffusion coefficient greater that PEG 10,000. Also, in the logarithmic plot, the trend should have been linear. The deviations from the trendline occur at PEG 5,000 and PEG 20,000.

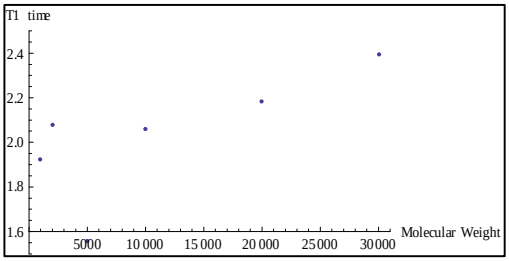

Figure 16: T1 vs. Molecular Weight

Source: Generated Using *Mathematica 6.0*

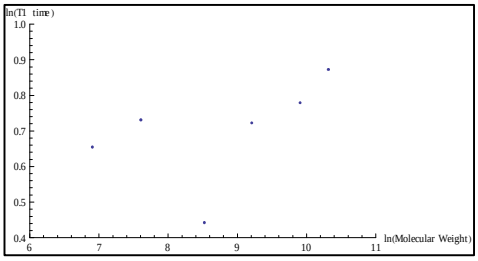

Figure 17: ln(T1) vs. ln(Molecular Weight)

Source: Generated Using *Mathematica 6.0*

In the T1 data, the PEG 2,000 and PEG 5,000 data points are outliers from the linear trend. The overall trend, as expected, is that T1 increases with increasing molecular weight.

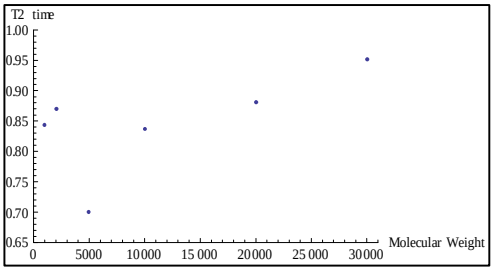

Figure 18: T2 vs. Molecular Weight

Source: Generated Using *Mathematica 6.0*

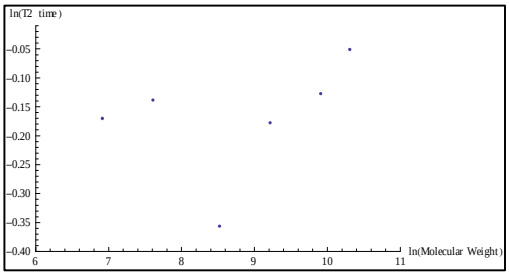

Figure 19: ln(T2) vs. ln(Molecular Weight)

Source: Generated Using *Mathematica 6.0*

In the T2 data, the three low molecular weight PEG samples—PEG 1,000, PEG 2,000, and PEG 5,000—are outliers from the linear trend. The high molecular weight samples have a very strong linear correlation. As expected, the general trend is that the T2 time increases with increasing molecular weight.

MALDI Data and Analysis

The MALDI data was collected using the Bruker instrument and software at Serina and analyzed using the polymer analysis extension package. The data collection and analysis was done by Rebecca Weimer. The analysis package automatically calculated the M_W, M_N, and polydispersity for each sample. The results are presented on the next page in Table 2.

Table 2: MALDI Results

Sample	M_W	M_N	Polydispersity
1000	1075.73	1035.08	1.03928
2000	2105.8	2066.8	1.01887
5000	5854.61	5816.45	1.00656
10000	11120.1	11036.9	1.00753
20000	22713.8	22527.4	1.00827
30000	36147.8	35627.3	1.01461

The polydispersity values are all less than 1.04 suggesting that all of the samples are nearly monodisperse. There was some variation between the label molecular weight and the measured molecular of PEG 5,000 and PEG 30,000. For each sample, the M_W was slightly greater than the M_N. From Figure 3 on page 3, this is expected based on the definition of the two parameters.

GPC Discussion

The GPC measurement was conducted on the instrument in Dr. Carmen Scholz's lab with the assistance of Tracy Armstrong. Unfortunately, this measurement was unsuccessful. All six samples were placed in the injection mixture. The expected result, given in Figure 20 below, is that the peaks should have separated in order from largest to smallest molecular weight: PEG 30,000 → PEG 20,000 → PEG 10,000 → PEG 5,000 → PEG 2,000 → PEG 1,000. However, all of the peaks eluted simultaneously at approximately eight minutes. Also, there was very low pressure on the column despite the high flow rate.

One possible explanation is that the flow rate was too high. As a result, all of the PEG samples were pushed out of the column without entering any pores so they could not separate. However, this is unlikely because of the low pressure. A high flow rate should cause a high pressure. The low pressure, therefore, suggests a faulty column. All of the samples moved through simultaneously meaning that the small molecules did not become trapped in any pores. Therefore, there must have been a problem with the pores which indicates a problem with the column.

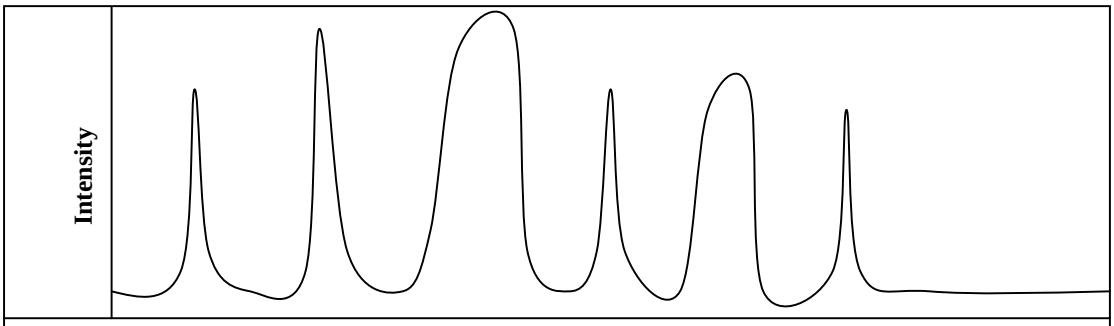

Figure 20: Expected GPC Results **Source: Generated by Author**

Section 3: Conclusions and Future Action

Of the three measurements I investigated in this experiment, only MALDI provides a direct measurement of the molecular weight of the sample. DOSY and GPC are indirect methods.

Molecular Weight Calculations

Indirect methods can only give a molecular weight "measurement" when the results are compared to those of known samples. This is done by building calibration curves from monodisperse standard samples. For GPC, the molecular weight is plotted against retention time (Allcock and others 2003). For DOSY, the molecular weight is plotted against the diffusion coefficient. A best fit line through the data points is then computed. When a measurement is conducted on an unknown, the resulting retention time, for GPC, or diffusion coefficient, for DOSY, is substituted into the equation of the best fit line. Solving the equation yields the molecular weight of the sample (Auge and others 2009). This may also be done for the T1 and T2 times. The best fit lines for the NMR data, as computed using *Mathematica 6.0*, are:

- Diffusion: D = (2.08e-6)-(6.50e-11)MW
- T1: T1 = (1.83) + (0.0000177) MW
- T2: T2 = (0.80) + (4.54e-6) MW
- ln(Diffusion): ln(D) = (-8.96)-(0.55) ln(MW)
- ln(T1): ln(T1) = (0.22)+(0.055) ln(MW)
- ln(T2): ln(T2) = (-0.41)+(0.028) ln(MW)

Determination of Molecular Weight Distributions

However, as described in the introduction, polymers do not have a discrete molecular weight; they have a molecular weight distribution. In GPC, the polydispersity is indicated by the width of the peaks in the chromatogram (Allcock and others 2003). In DOSY, on the other hand, the molecular weight distribution is obtained by running multiple measurements on the same sample and on different concentrations of the same sample. "The diffusion coefficient varies considerably with the concentration of the diffusate" resulting in slightly different diffusion coefficients after each measurement (Li and others 2008, p 1). The molecular weight distribution function may be produced by fitting the data points with cubic splines (Chen and others 1995). Also, the continuous molecular weight distribution is seen in the DOSY spectrum by the spread of the diffusion signal as seen in Figure 21 (Morris and Johnson 1993).

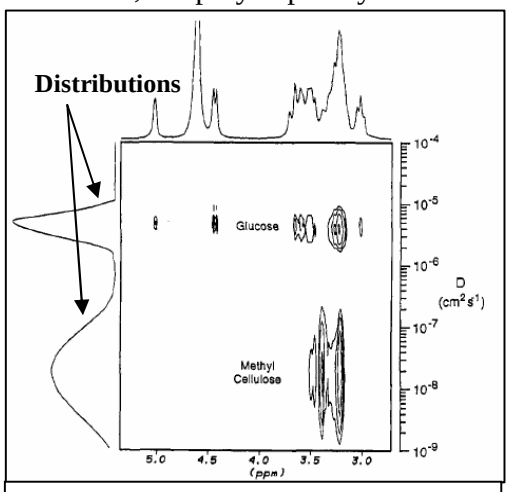

Figure 21: Polydispersity in DOSY Spectrum

Source: Morris and Johnson 1993, p 8

Conclusions

In conclusion, the MALDI measurement was the only experiment that gave actual results for the molecular weight of the PEG samples. The results confirmed that the samples were nearly monodisperse. The measured molecular weights for the PEG 5,000 and PEG 30,000 samples were higher than the label molecular weights.

The NMR measurements provided the groundwork for building a calibration curve which could be used for subsequent measurements. Overall the results matched the expected trends. The diffusion constants decreased with increasing molecular weight, and the T1 and T2 times both increased with increasing molecular weight.

Unfortunately, the GPC measurement was unsuccessful, most likely because of a bad column.

Future Actions

First, I would like to rerun the GPC measurement on another instrument or with a different column to test my hypothesis that the error was in the instrument. I would also like to run the GPC measurement on the individual samples rather than the mixture.

The MALDI measurement gave very strong data. I would be interested in comparing these results to mass spectra obtained from other ionization techniques such as electron ionization, spray ionization, or chemical ionization.

In the NMR, I would be curious to run a measurement on an unknown PEG sample. I would then compare this measurement to the calibration curve that I generated during this project to compute the molecular weight of the unknown. I would also like to measure the polydispersity by running experiments with different concentrations of the same sample.

I would also like to try to run a DOSY measurement on a solution composed of a mixture of the PEG samples I investigated. The purpose of this test would be to test how well the DOSY measurement can resolve the spectra. That is, I would be looking at how sensitive the DOSY procedure is to see if it can really separate these samples by size.

It would be interesting, at some point, to also run experiments on the samples using some of the techniques described in the supplemental section that follows.

Lastly, Dr. Winston Hedges of Hexcel Corporation in Decatur provided several polystyrene samples. I would like to do this project again using those standards in place of the PEG samples.

Supplemental: Other Techniques

In this experiment, I investigated three techniques to determine the molecular weight of polymers: GPC, MALDI, and NMR. There are many other techniques available to the polymer chemist. These techniques are generally classified as either absolute or secondary methods of molecular weight determination.

Absolute Techniques

According to Allcock, "absolute methods give values that provide a direct estimate of the molecular weight" (and others 2003, p 395). MALDI is an example of an absolute method. Other absolute techniques include end-group analysis, colligative properties, osmotic pressure measurement, light scattering, and ultracentrifugation. Generally, these techniques are time consuming, expensive, and have limited accuracy (Allcock and others 2003; Scholz 2009).

End-Group Analysis

The basis of this method is to determine the ratio of end groups to repeat units. For example, the PEG I studied was actually mPEG meaning that it was methoxy-terminated. The end group, therefore, is a methoxy group whereas the middle units are ethylene glycol. The number of end groups is then compared to the number of chains and used to calculate the number of moles of chains. The number-average molecular weight is then obtained by taking the weight of the sample divided by the number of moles present (Allcock and others 2003). End-group analysis is only effective when the end group is distinctive, meaning it must be measurable. Also, end-group analysis is most effective for low molecular weight polymers because the end group is drowned out by the signal from the repeat units in high molecular weight polymers (Scholz 2009).

Colligative Properties

In a solution, a solute (polymer) lowers the chemical potential of the solvent. As a result, the properties of the solvent are affected. These properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. These properties are mathematically related to the molecular weight by the concentration of the polymer and a solvent parameter. The magnitude of the effect is inversely proportional to the number-average molecular weight which may be computed directly. However, the changes in freezing point, boiling point, and vapor pressure are often very small such that they are below the limits of accurate measurement (Allcock and others 2003).

Osmometry

Osmotic pressure, unlike the other colligative properties, is a valid means of measuring average molecular weight of polymers. An osmometer is a two-chamber instrument with

a semipermeable membrane separating the chambers. The membrane is designed so that only small solvent molecules and move across it; polymers are too large. The polymer solution is placed in one chamber while pure solvent is placed in the second. To establish equilibrium, solvent moves across the membrane to mix with the polymer solution. The movement of solvent increase the pressure in the chamber with the polymer solution and this increase is measurable. To determine the average molecular weight, the experiment is run with several concentrations of the polymer solution. The concentration is then plotted against the osmotic pressure divided by concentration. The molecular weight is extracted by finding the limit as concentration approaches zero and inverting this result. The accuracy of osmometry depends heavily on the membrane. It must be small enough so that polymer can pass through. Also, it must be of a material that will not be dissolved by the solvent (Allcock and others 2003; Scholz 2009).

Light Scattering

In dynamic light scattering, a beam of monochromatic light (a laser) is shone into a solution of polymer. When the light strikes a polymer, it is scattered. A detector is used to measure the intensity of scattered light at angles from approximately 30° to 150° from the sample. As with osmometry, this experiment is conducted for several concentrations of the polymer solution. The angles and concentration may then be used to extract the weight-average molecular weight of the sample. This is a very accurate and informative method. In addition to molecular weight, the resulting data also gives information about the interaction between the polymer and the solvent and the radius of a polymer chain. However, it is very time consuming because the sample must be filtered numerous times to remove dirt or dust particles that may scatter the light beam (Allcock and others 2003; Scholz 2009).

Ultracentrifugation

Ultracentrifugation is typically applied to biomacromolecules like proteins and nucleic acids rather than synthetic polymers. In this method, a centrifuge is used to generate a gravitational force that pulls polymer chains to the bottom of a tube. Diffusion of polymers, however, creates a concentration gradient. The largest chains are present at the bottom of the tube while the smaller chains diffuse upward and may be found on top of the larger chains. The ratio of these concentrations may be measured optically using the change in refractive index. This ratio may then be used to compute the weight-average molecular weight. This method, however, is not very accurate, and the calculated molecular weights deviate significantly from those measured by other methods. Also, polymer molecules diffuse very slowly so very long times are needed to establish the concentration gradient equilibrium (Allcock and others 2003).

Secondary Methods

Allcock defines secondary molecular weight determination methods as techniques which "yield comparisons between the molecular weights of different polymers, and must be calibrated by reference to a system that has been studied by one of the absolute

approaches" (and others 2003, p 395). In my project, GPC and NMR are both examples of secondary methods. Other secondary techniques include solution viscosity, vapor-phase osmometry, and matrix fluorescence photobleaching recovery. These techniques are standardized and fast, but their accuracy depends on the accuracy of the calibration. Generally, these techniques are preferred to study trending over time (Allcock and others 2003; Doucet and others 2006; Scholz 2009).

Viscosimetry

One of Staudinger's principle characteristics for a polymer was that "a dissolved polymer markedly increases the viscosity of a solution relative to that of the pure solvent. This increase in viscosity is caused principally by the unusual size and shape of the dissolved polymer" (Allcock and others 2003, p 452). In solution, polymers rarely assume a straight chain secondary structure but typically form random coils. The viscosimetry measurement is very simple in practice. The solution is placed in a instrument called a viscosimeter which has two reservoirs on either side of a capillary tube. The time required for the solution to pass from the top of the capillary tube to the bottom is measured and the relative viscosity is determined by dividing this time by the time required for pure solvent. Then, the specific viscosity is computed by subtracting one from the relative viscosity. This is done for several concentrations to generate a plot of concentration versus specific viscosity divided by concentration. Extrapolating the best fit line gives the intrinsic viscosity which may be used to calculate the molecular weight of the polymer using the Mark-Houwink equation (Allcock and others 2003; Scholz 2009).

Vapor-Phase Osmometry

In this technique, a drop of solvent and a drop of solution of known weight concentration are placed on two separate thermistors. The resistance between the thermistors is converted to a temperature distance which is displayed as a function of time. This is repeated for several solutions of known molecular weight and a plot of concentration versus change in temperature is used to create a calibration. This method is fast and uses very little polymer sample. However, the molecular weights are determined relative to the calibration standards (Allcock and others 2003).

Matrix Fluorescence Photobleaching Recovery

Matrix fluorescence photobleaching recovery (MFPR) is a technique in which a fluorescent dye is attached to the polymer sample. In this technique, an initial fluorescence measurement is made; then, some of the attached dyes are destroyed by a laser pulse. The tagged polymers diffuse over the matrix redistributing the dyes. Then fluorescence is measured again to see the diffusion which is used to calculate the molecular weight from a calibration. Some of the advantages of this technique are that fluorescence detection is very sensitive, there are no moving parts, very little solvent is required, and change of solvent, pH, or temperature are trivial. The primary disadvantage is that this technique requires calibration of known samples (Doucet and others 2006).

Acknowledgements

I would like to take a moment to recognize and thank all of the individuals who assisted me with this project. Without their help, I do not believe that I would have been able to create this report.

I would like to thank Rebecca Weimer, Tracy Armstrong, and Dr. Bernhard Vogler for their assistance with the MALDI, GPC, and NMR measurements, respectively.

I would also like to thank Dr. Winston Hedges for supplying to polystyrene samples which I will investigate during the rest of this semester to complete the requirements for the chemistry senior research project.

Lastly, I would like to thank my advisors for this project, Dr. Bernhard Vogler and Dr. Carmen Scholz. Dr. Scholz provided much of the theoretical background for understanding polymers and Dr. Vogler assisted with literature research, measurements, and data analysis.

Many thanks again to all who helped me complete this project.

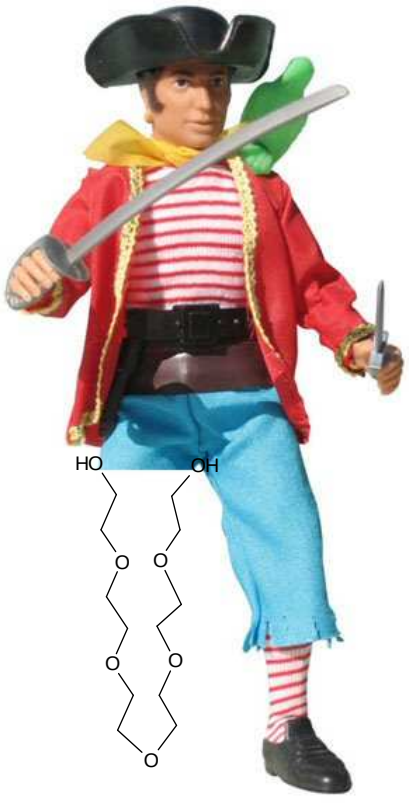

Figure 22: PEG-leg Pirate

Source: Pirate from Google Images, Overall Design by Author

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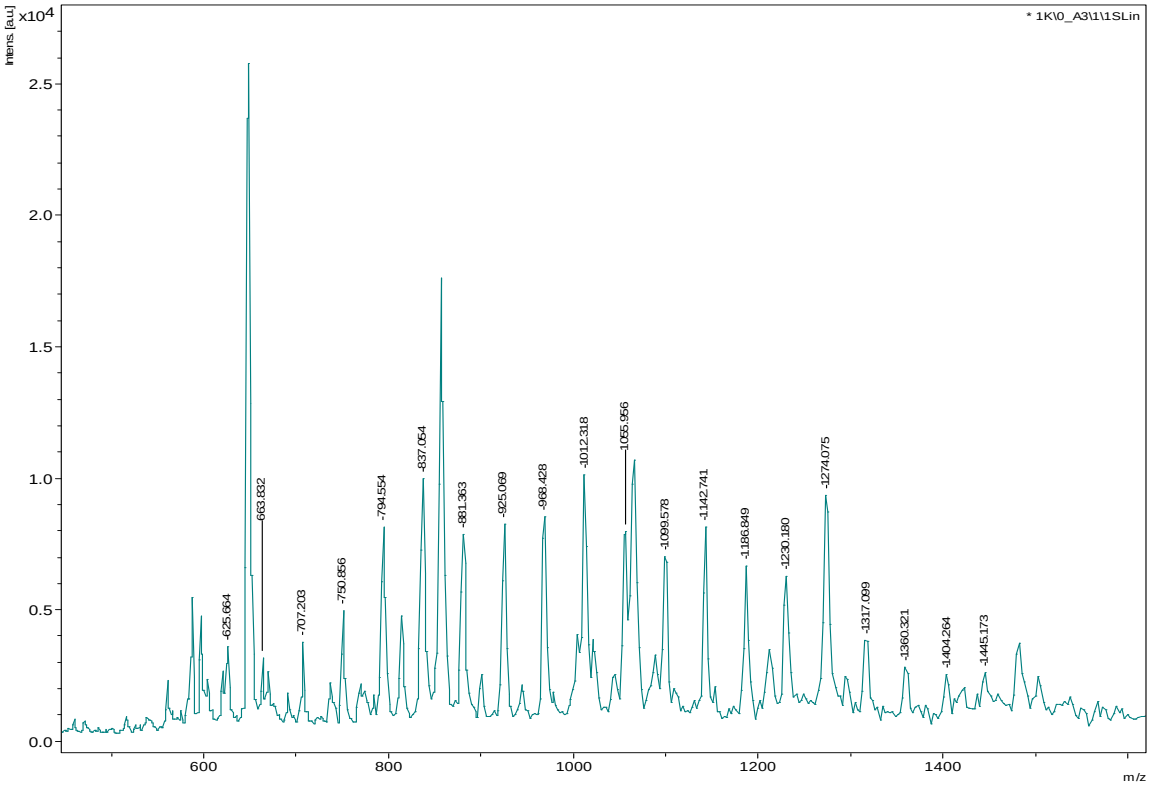
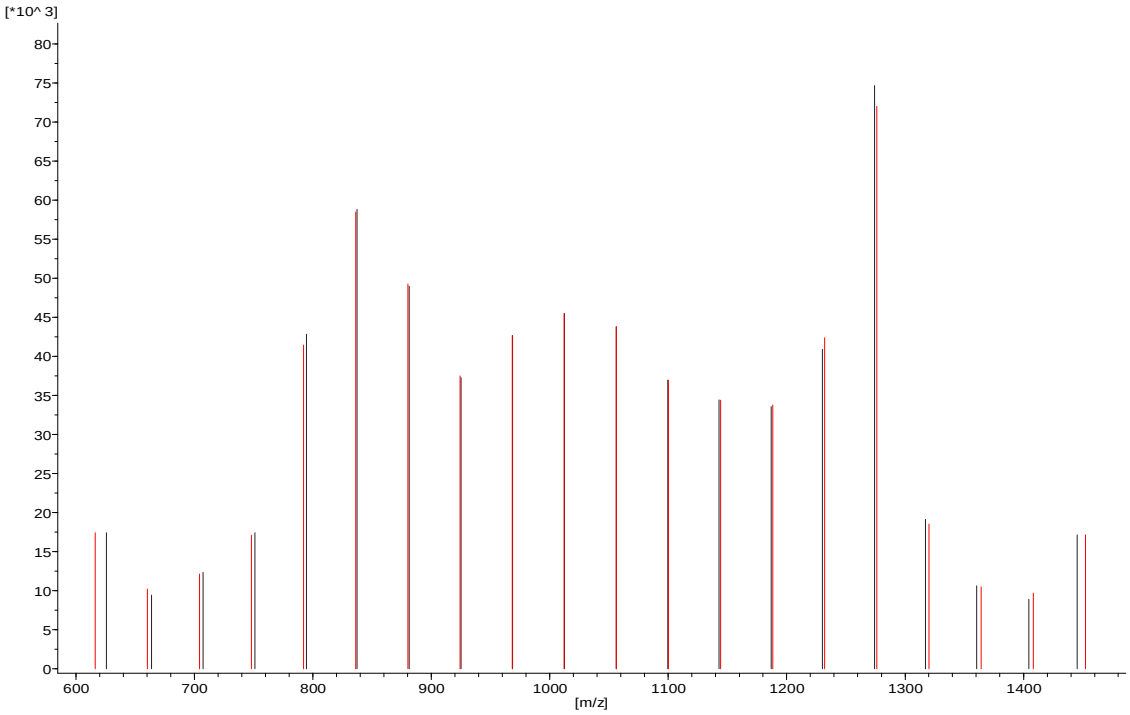
Vogler 1K





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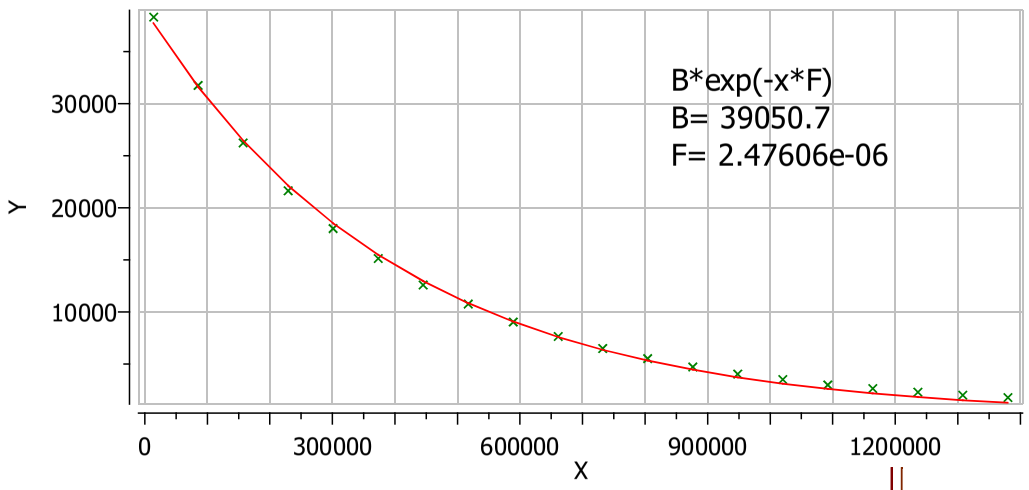
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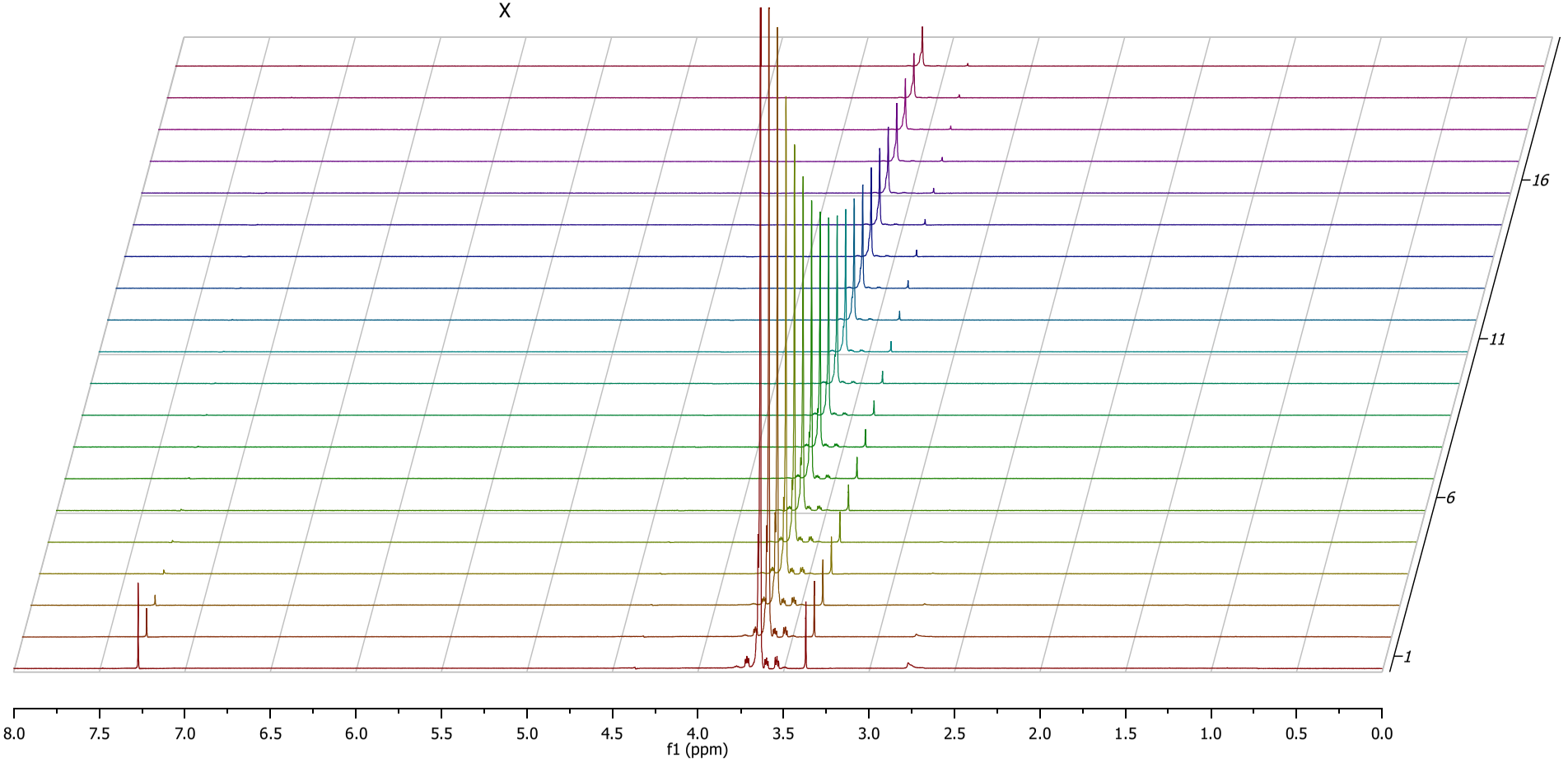
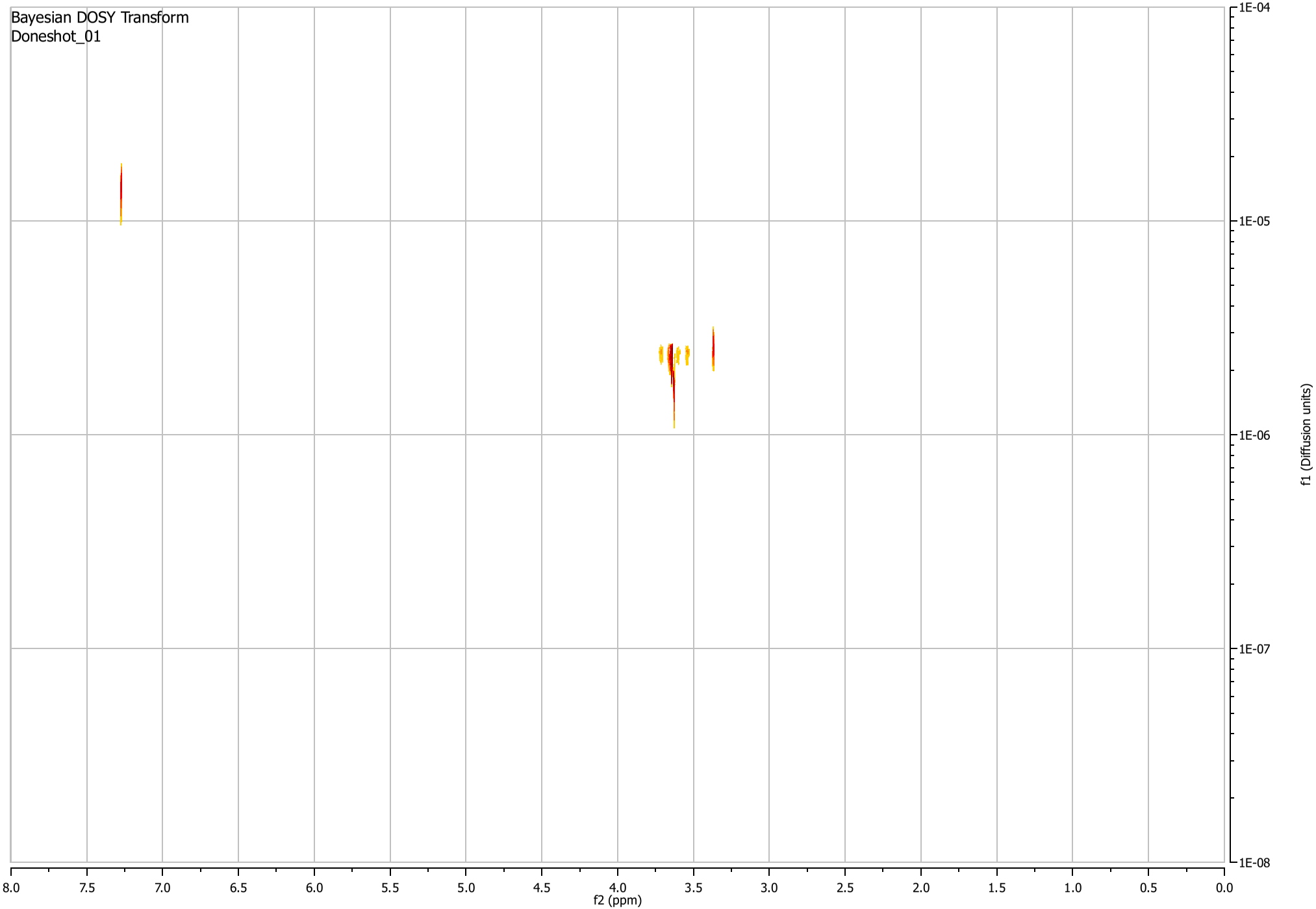
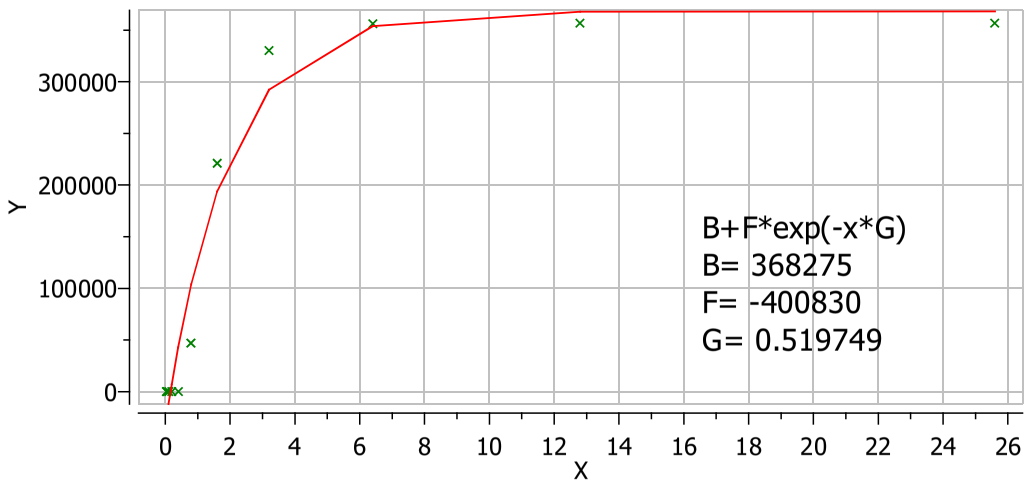
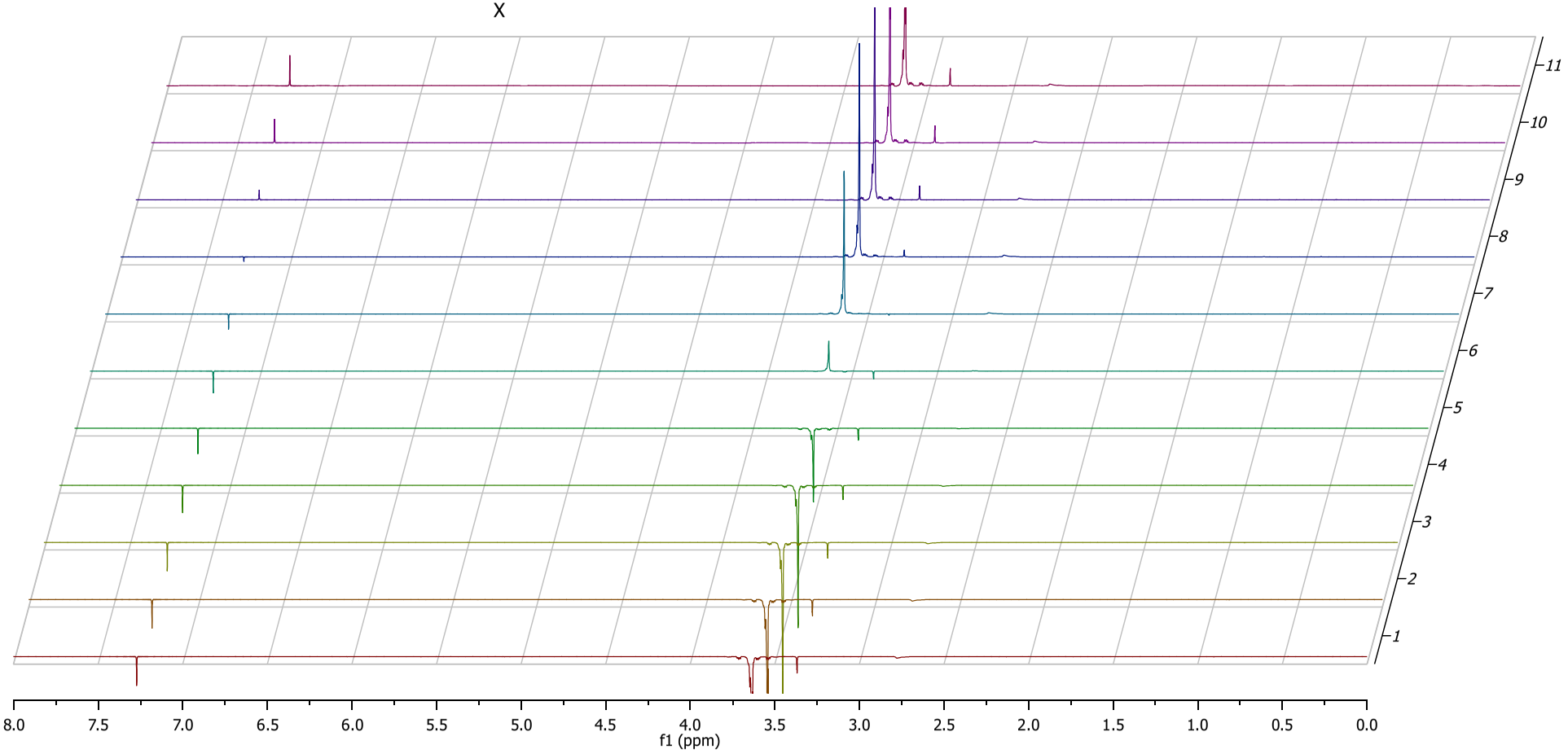
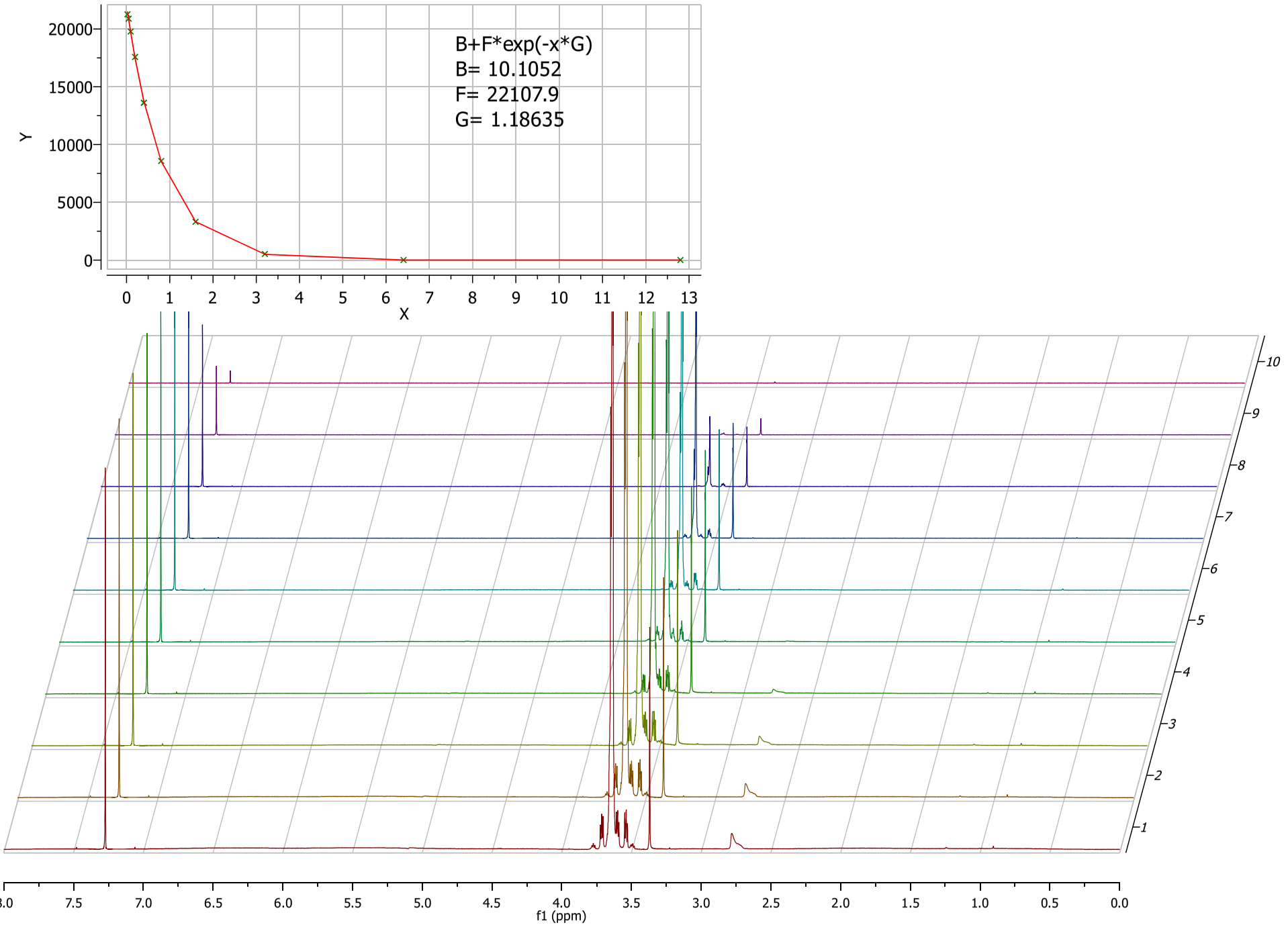
1200000
X


16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

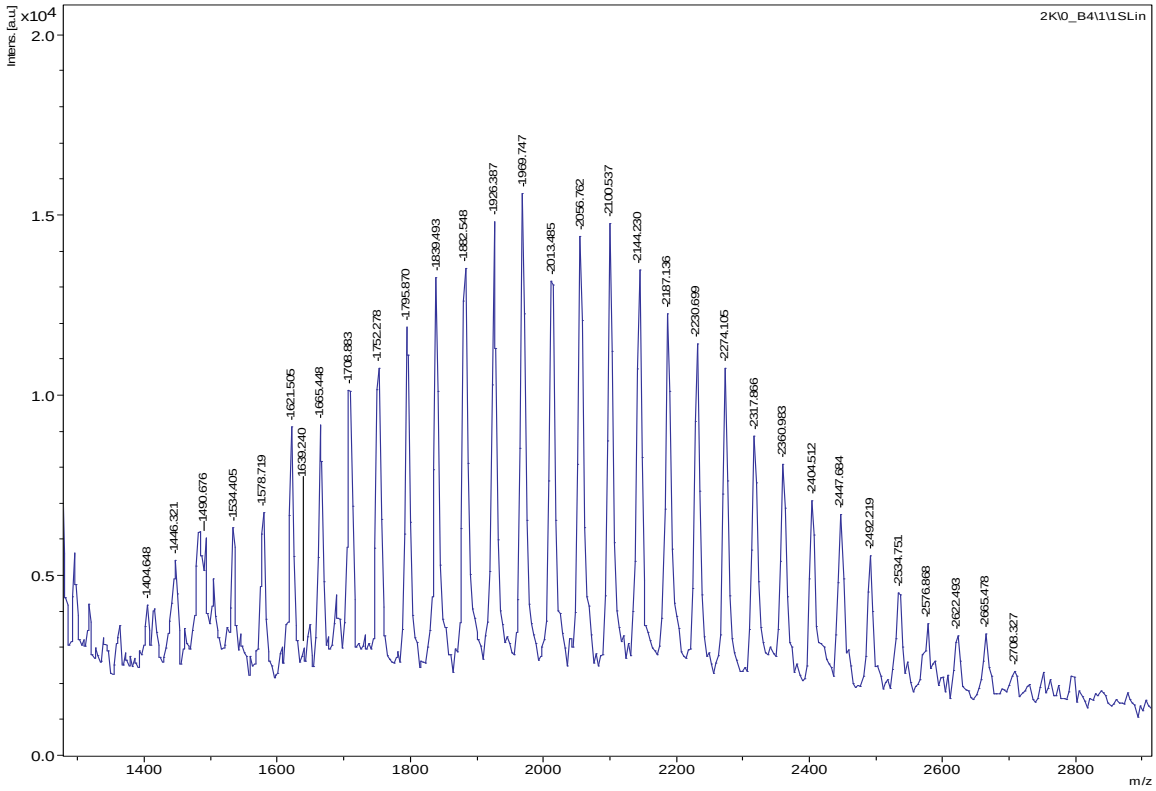

Bayesian DOSY Transform
Doneshot_01
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

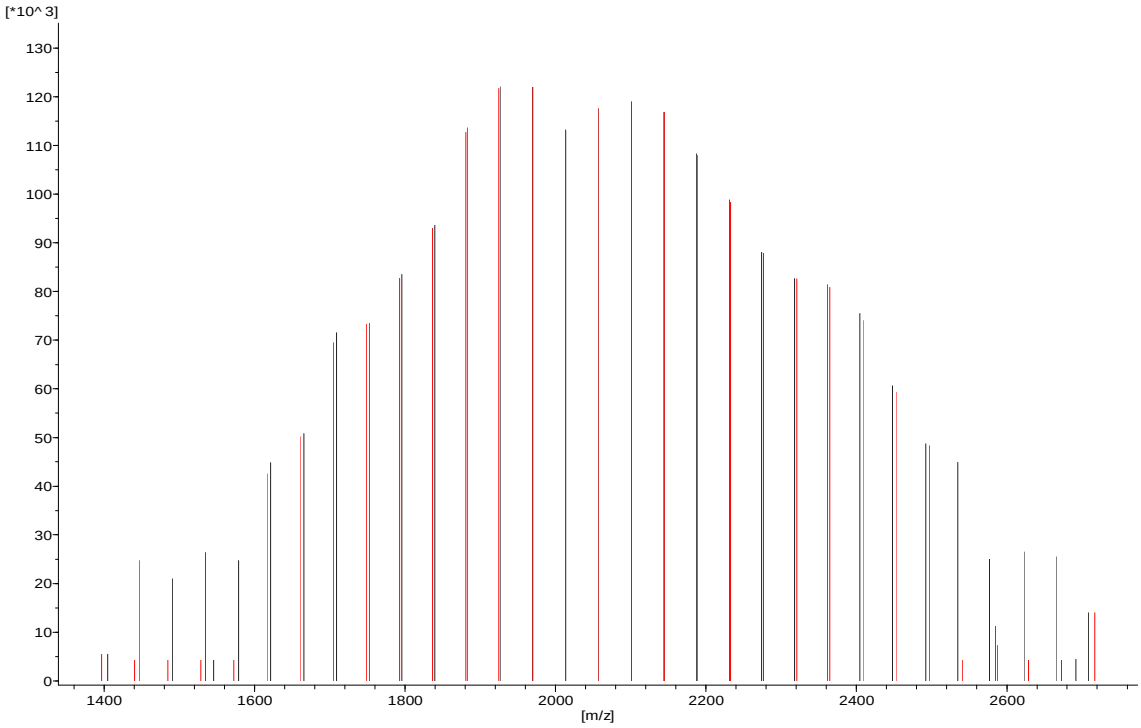

B+F*exp(-x*G)
B= 368275
F= -400830
G= 0.519749
Y
X
300000
200000
100000
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26


11
10
9
8
7
6
5
4
3
2
1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

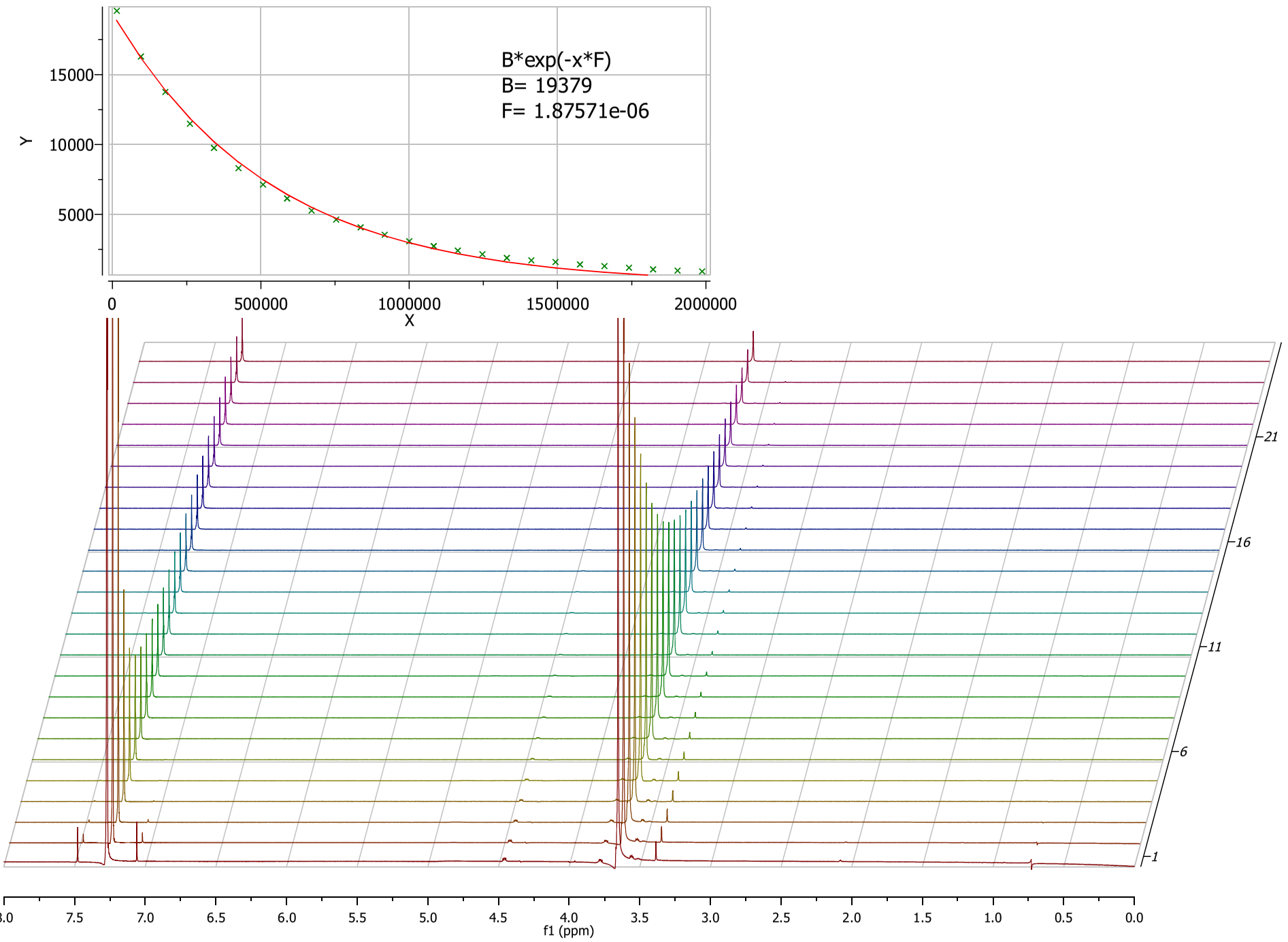

B+F*exp(-x*G)
B= 10.1052
F= 22107.9
G= 1.18635
Y
X
f1 (ppm)

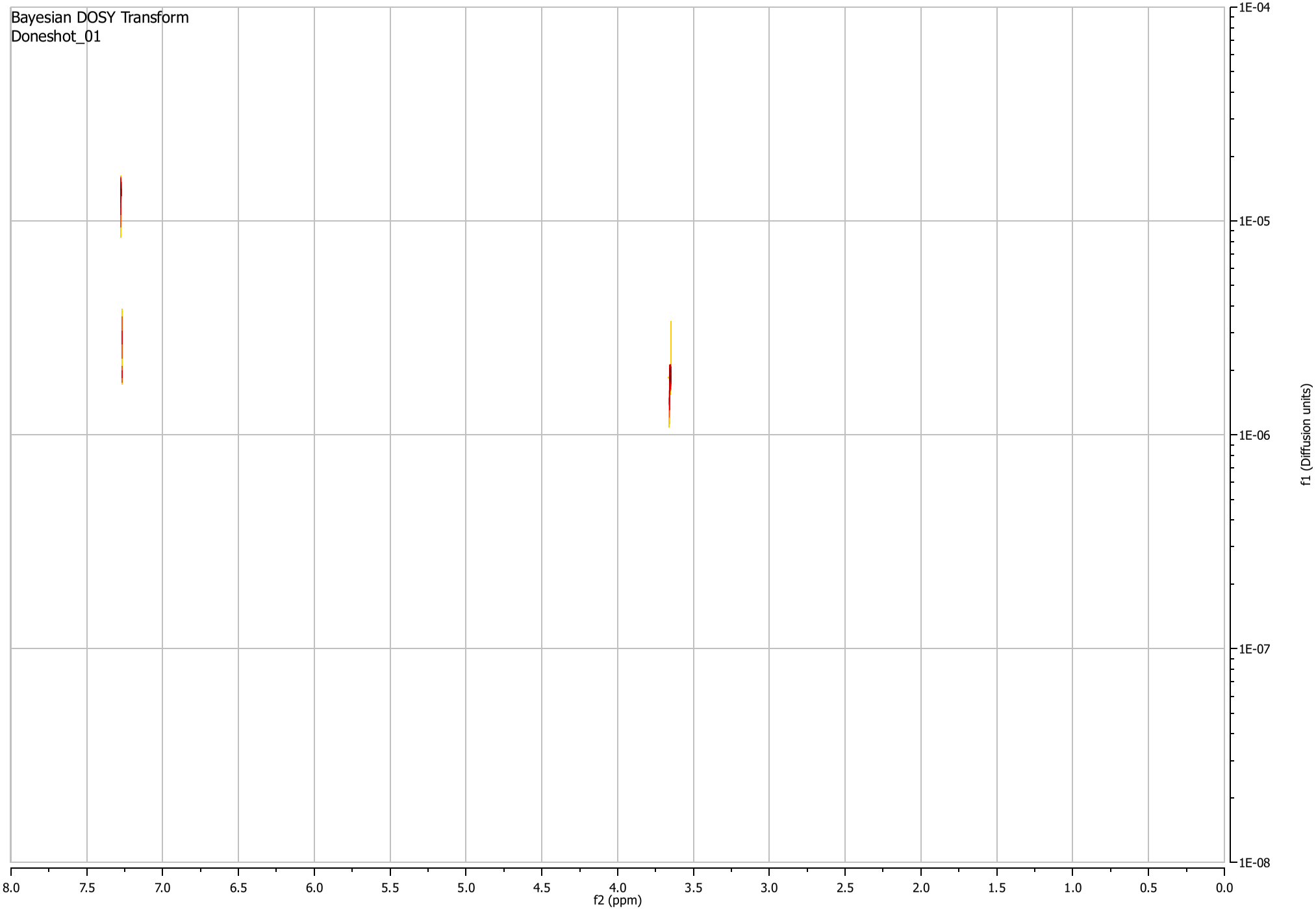
Vogler 2K

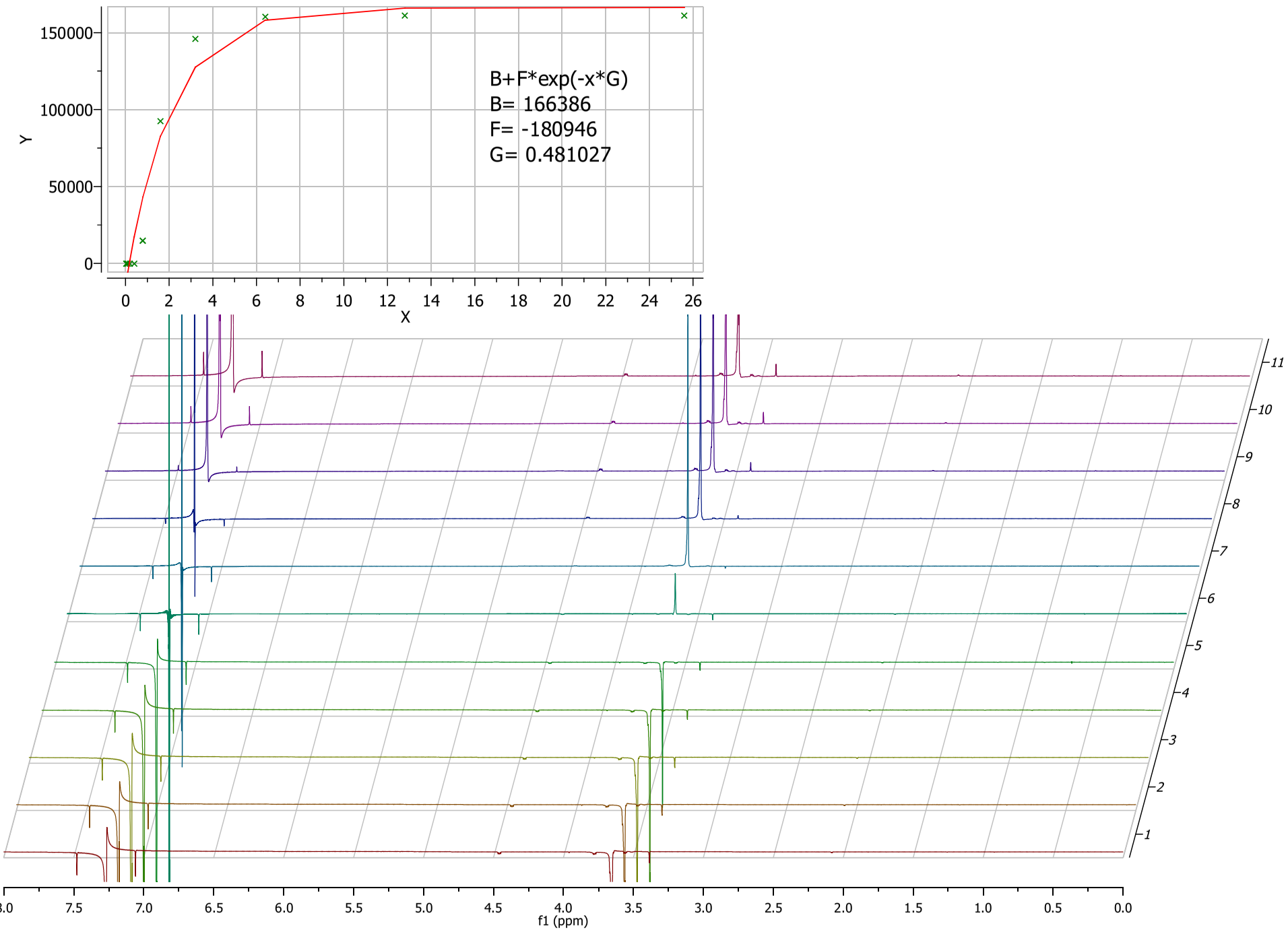


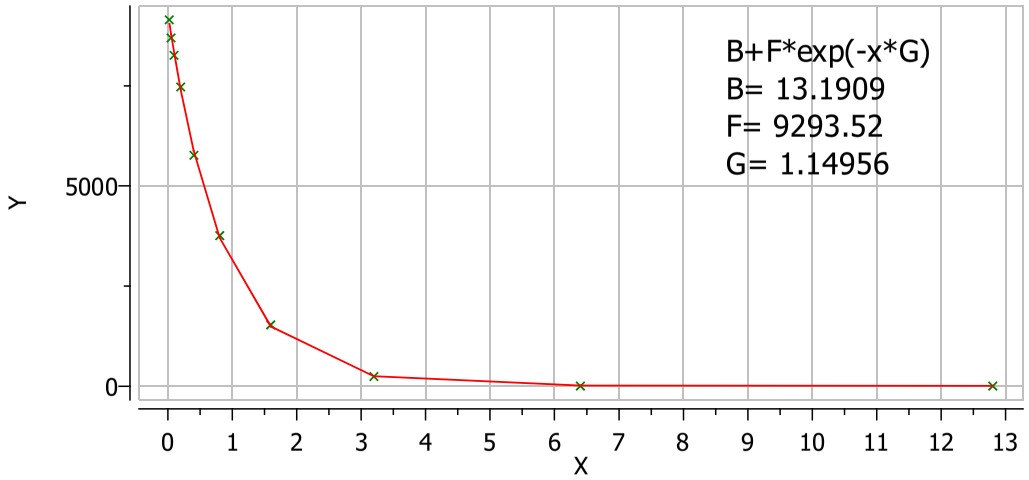


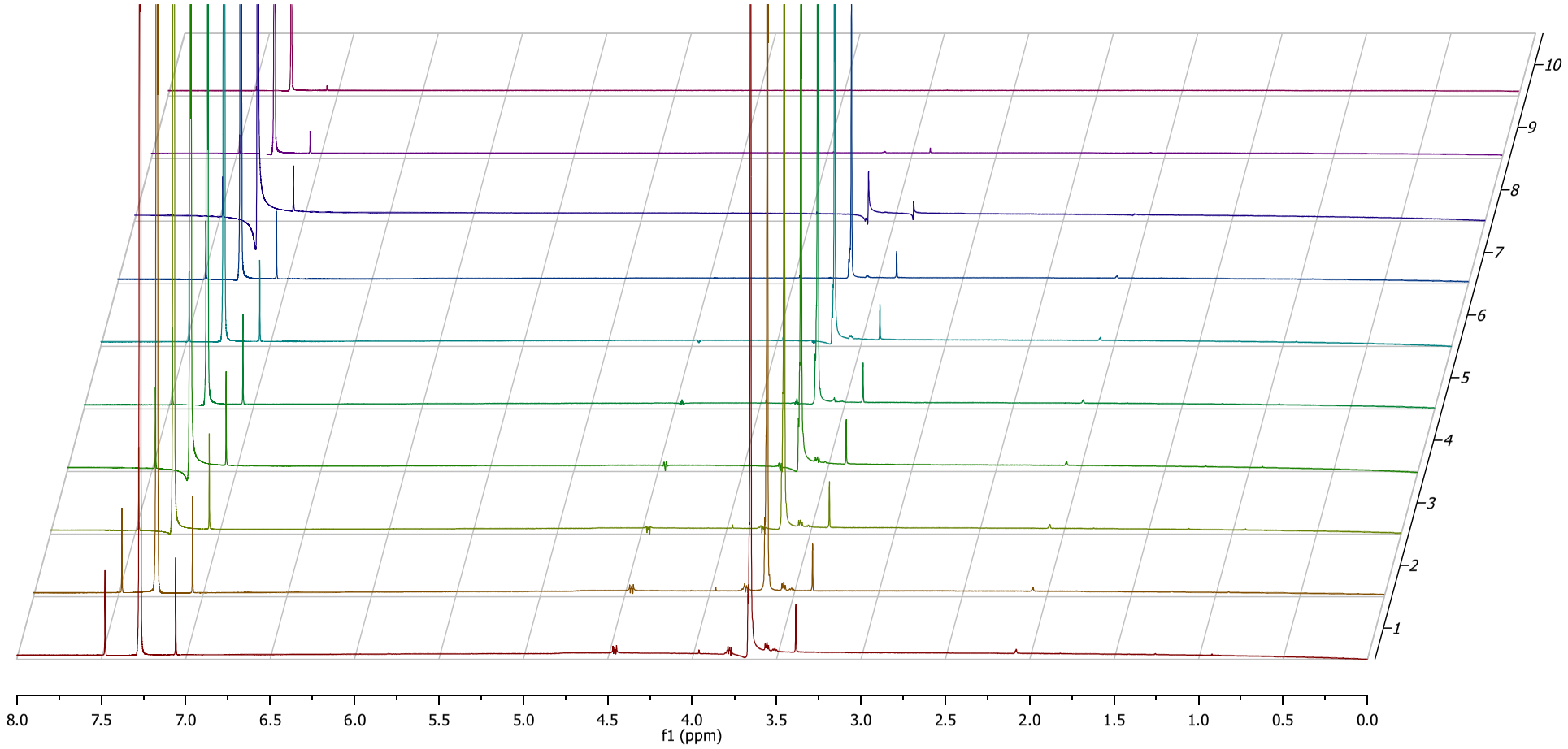
n	ser.	rep.unit	resid.	Mn	Mw	pd	DP	% Int.
1	1	44	32.615	2066.8	2105.8	1.01887	46.9728	99.3


B*exp(-x*F)
B= 19379
F= 1.87571e-06
Y
15000
10000
5000
0
500000
1000000
1500000
2000000
X
21
16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

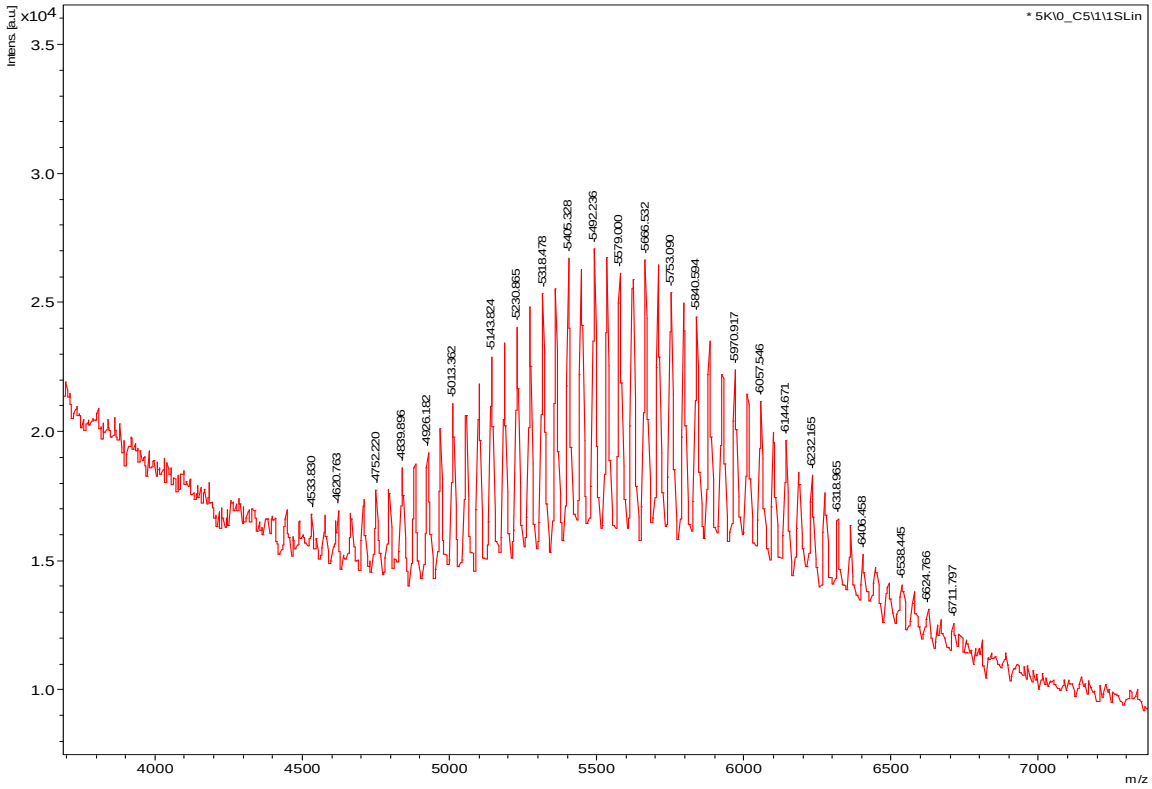

Bayesian DOSY Transform
Doneshot_01
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

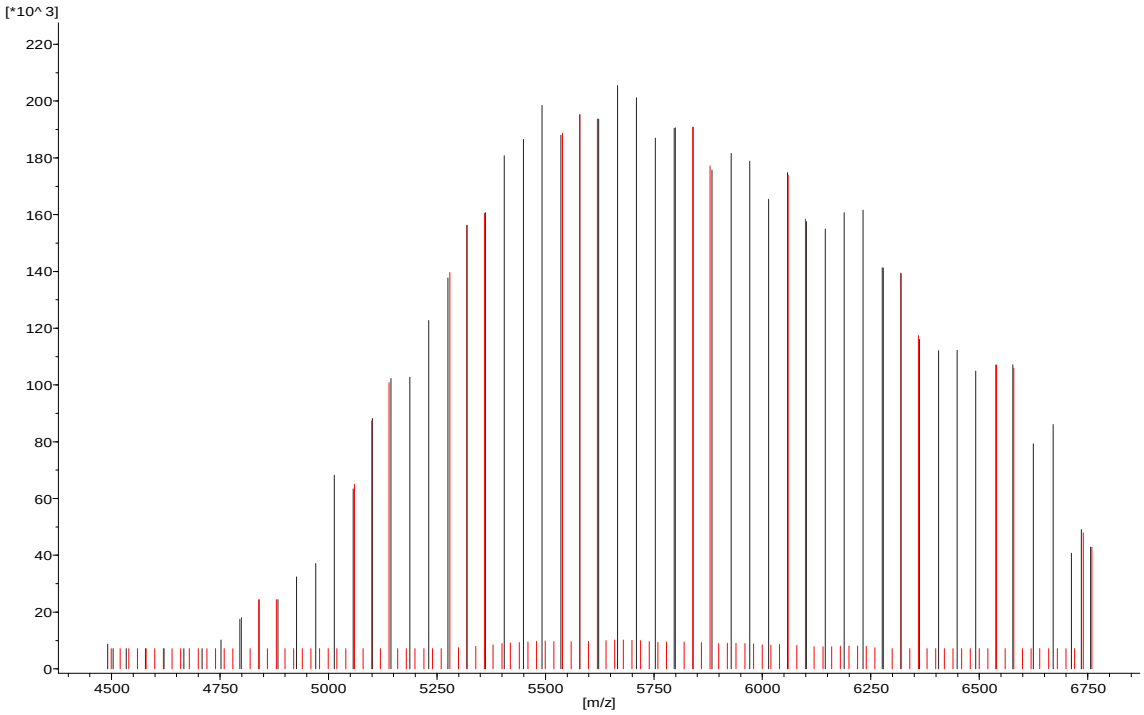

B+F*exp(-x*G)
B= 166386
F= -180946
G= 0.481027
Y
X
f1 (ppm)


B+F*exp(-x*G)
B= 13.1909
F= 9293.52
G= 1.14956
Y
5000
0
X
0 1 2 3 4 5 6 7 8 9 10 11 12 13

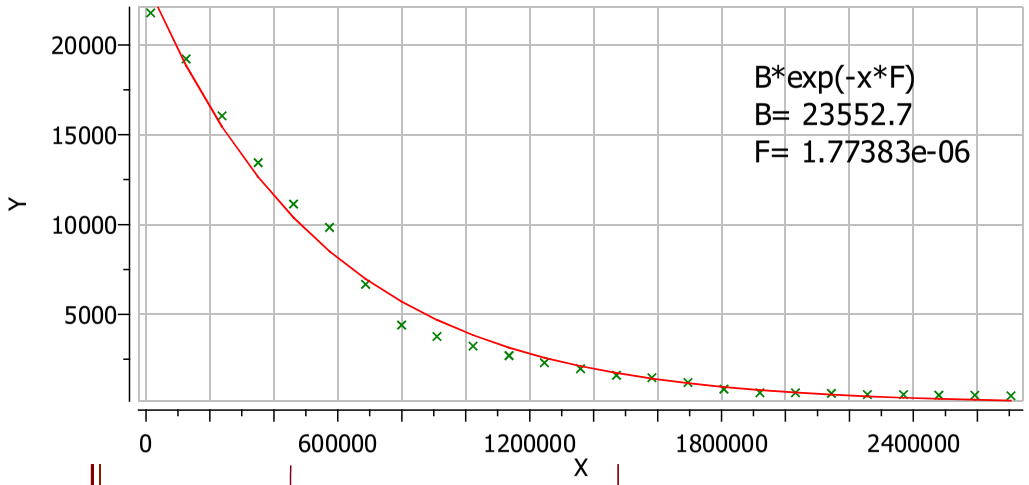

10
9
8
7
6
5
4
3
2
1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

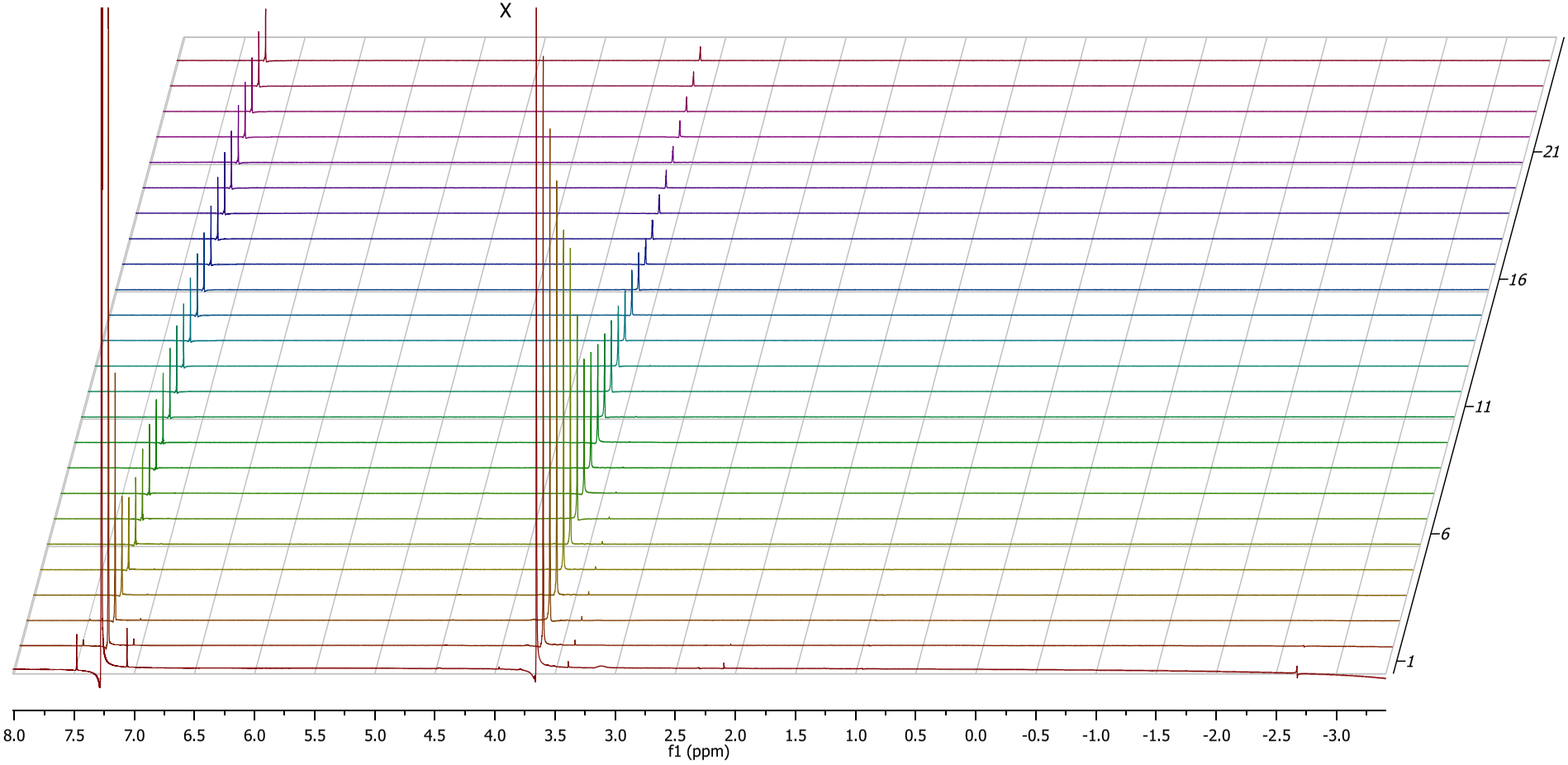
Vogler 5K

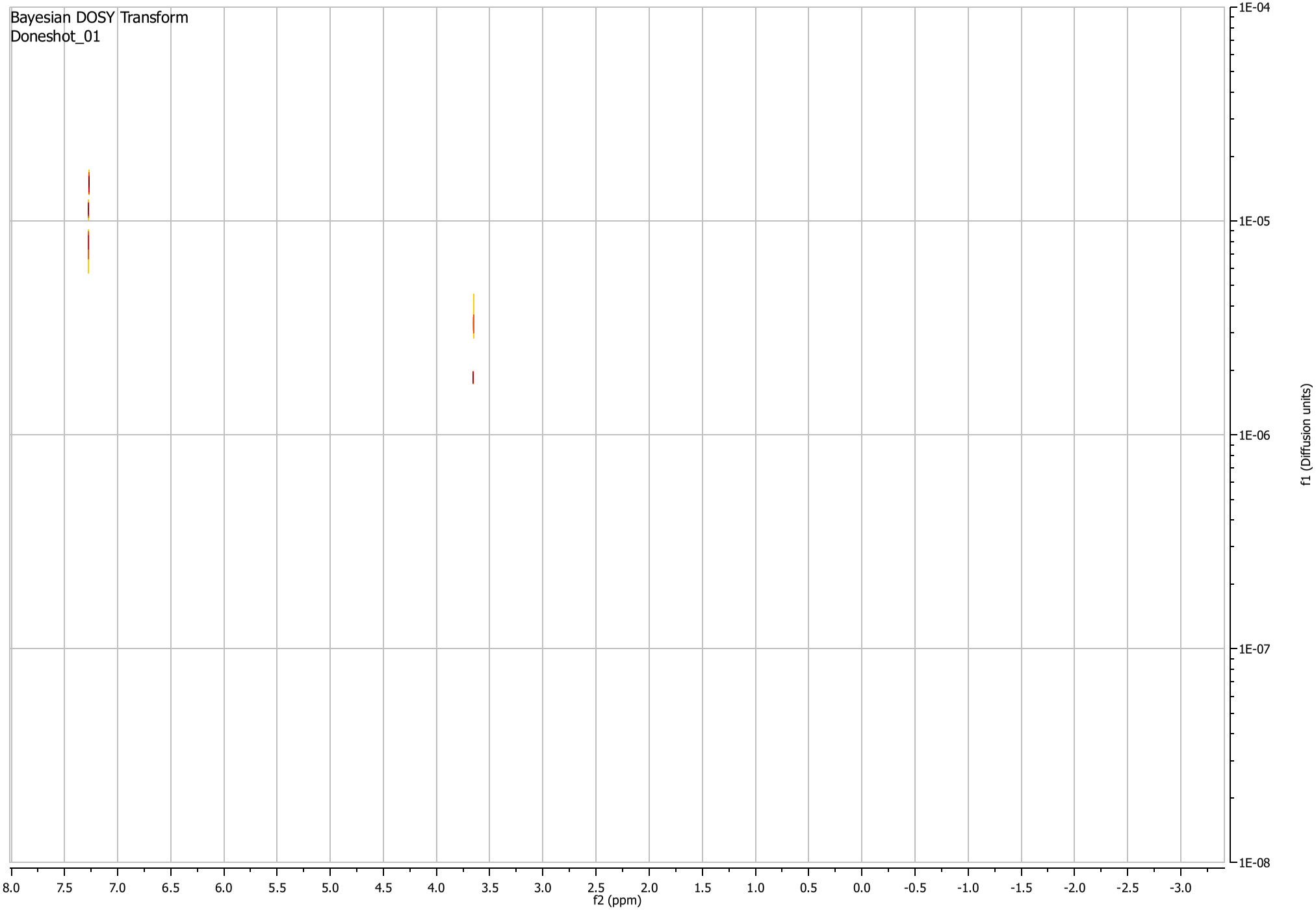


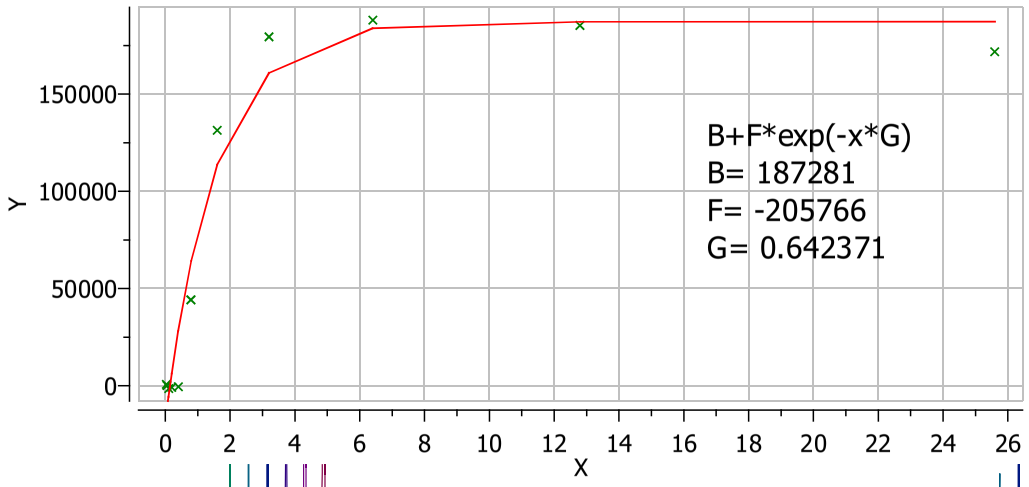


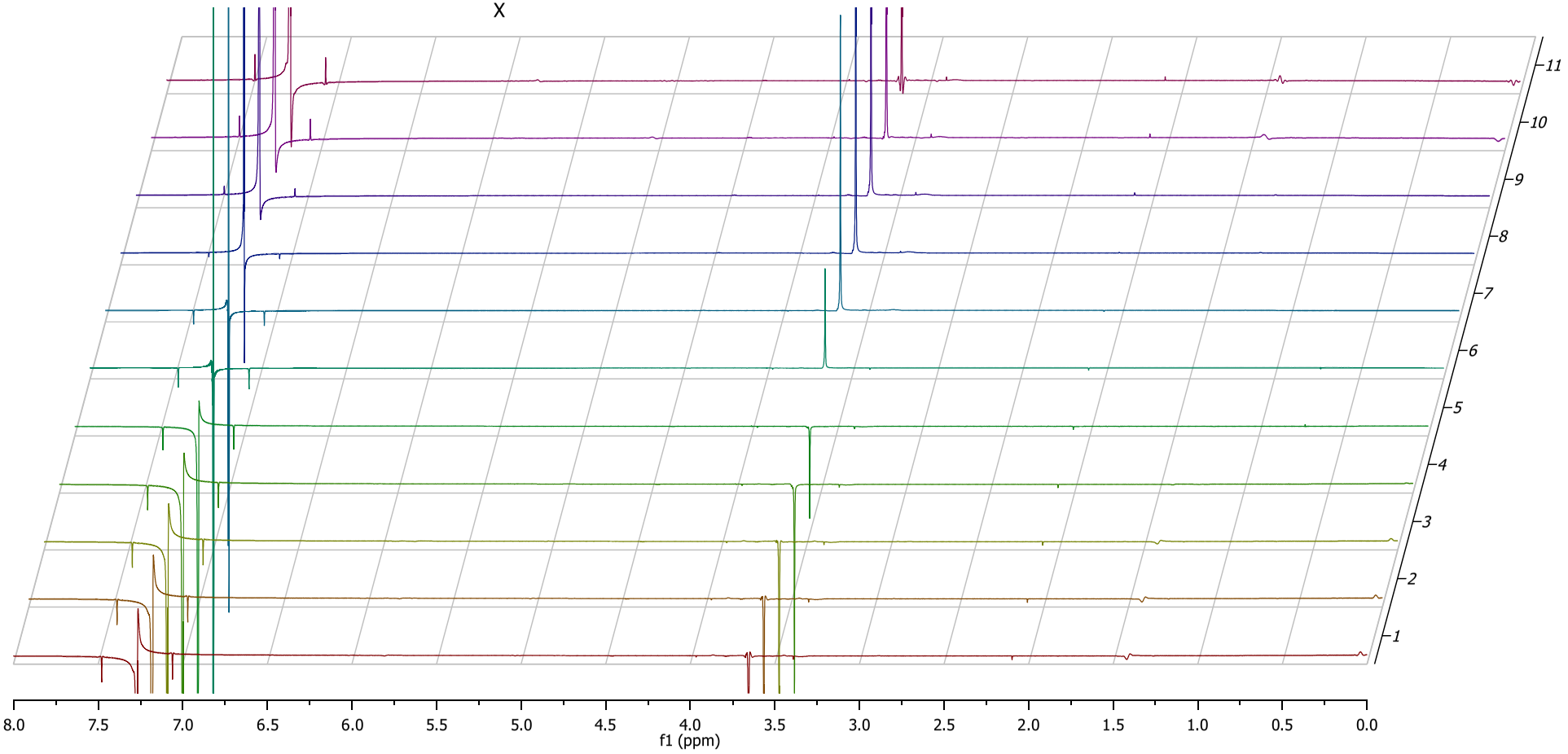
n	ser.	rep.unit	resid.	Mn	Mw	pd	DP	% Int.
1	1	20	19.4239	5816.45	5854.61	1.00656	290.822	100

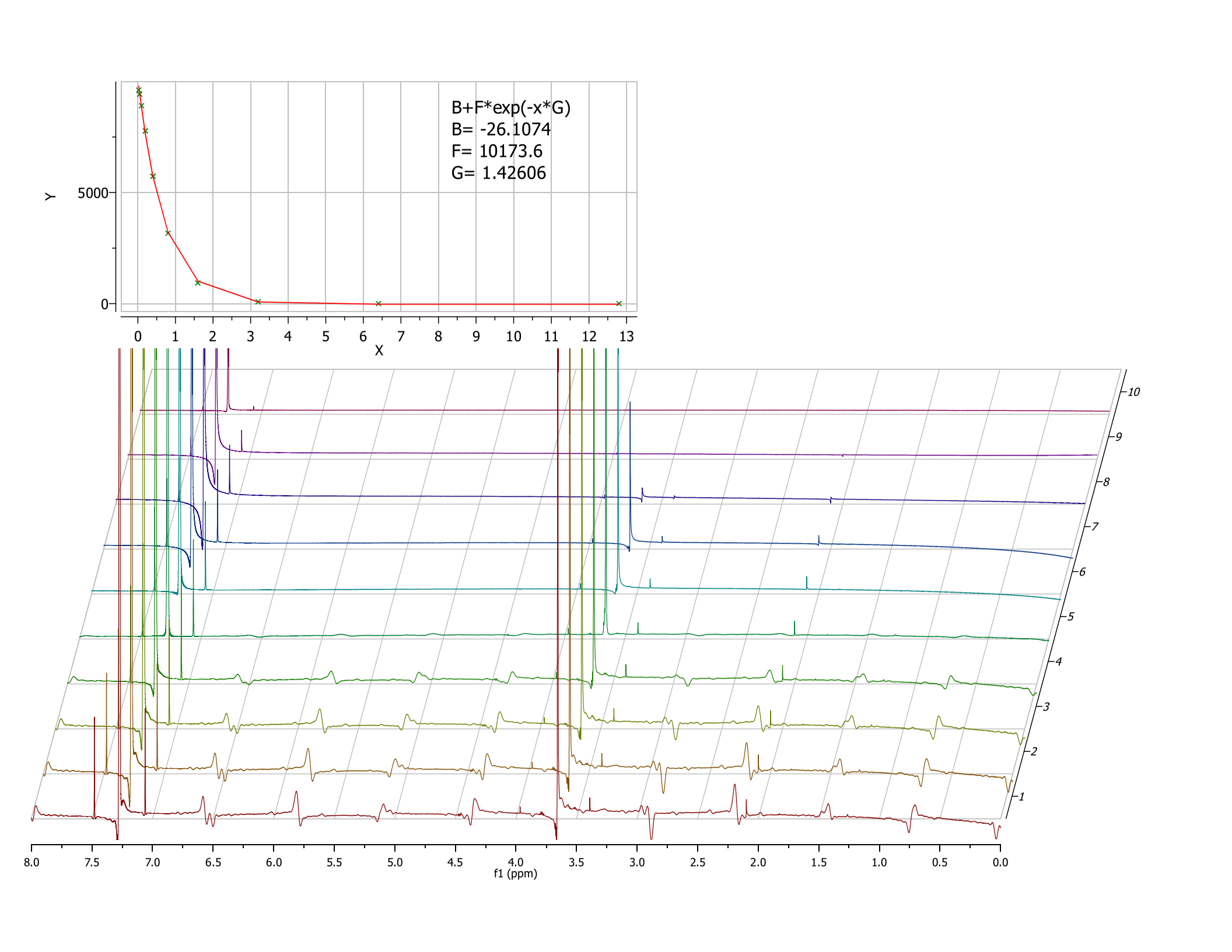

B*exp(-x*F)
B= 23552.7
F= 1.77383e-06
20000
15000
10000
5000
Y
0
600000
1200000
1800000
2400000
X


21
16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f1 (ppm)

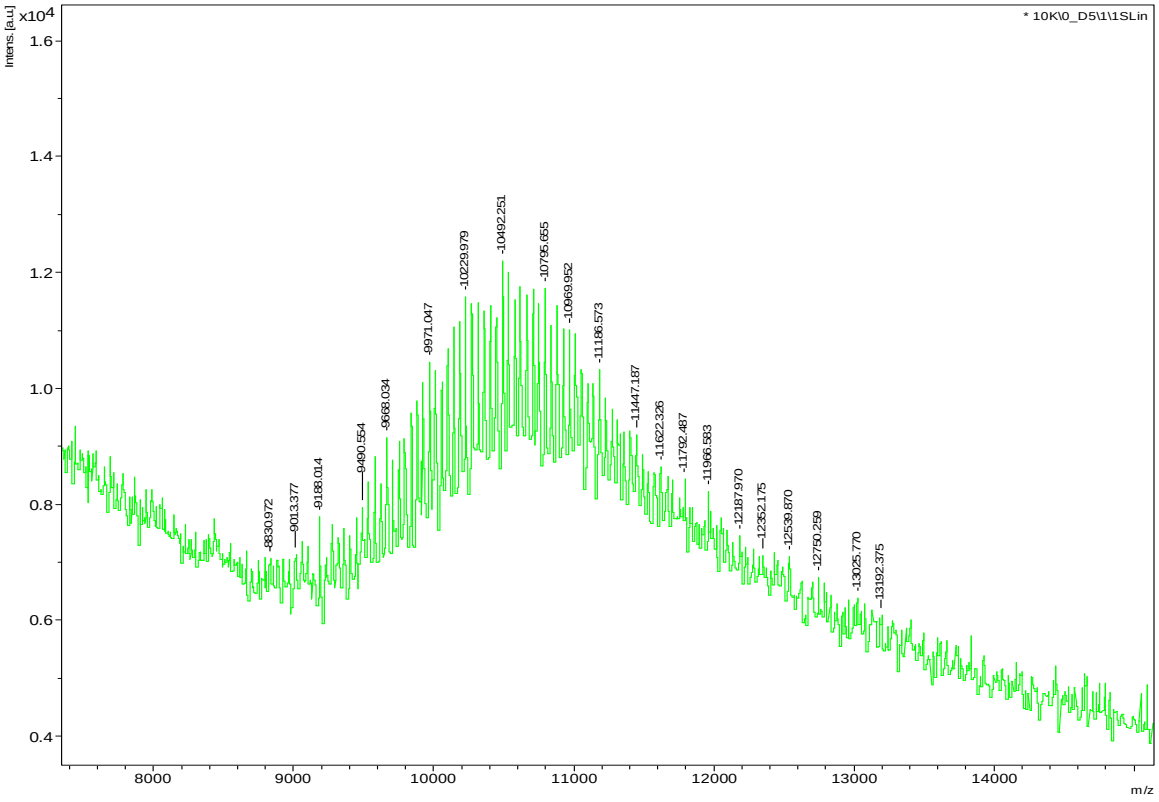

Bayesian DOSY Transform
Doneshot_01
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f2 (ppm)

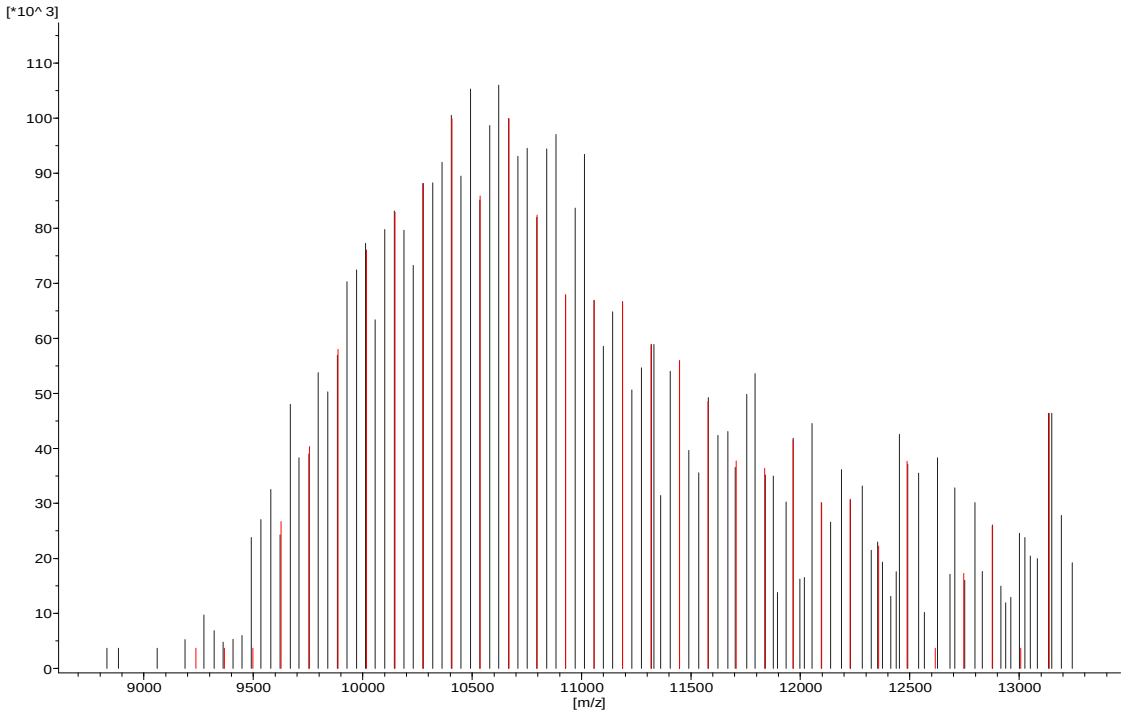

B+F*exp(-x*G)
B= 187281
F= -205766
G= 0.642371
Y
X
150000
100000
50000
0
0
2
4
6
8
10
12
14
16
18
20
22
24
26


11
10
9
8
7
6
5
4
3
2
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

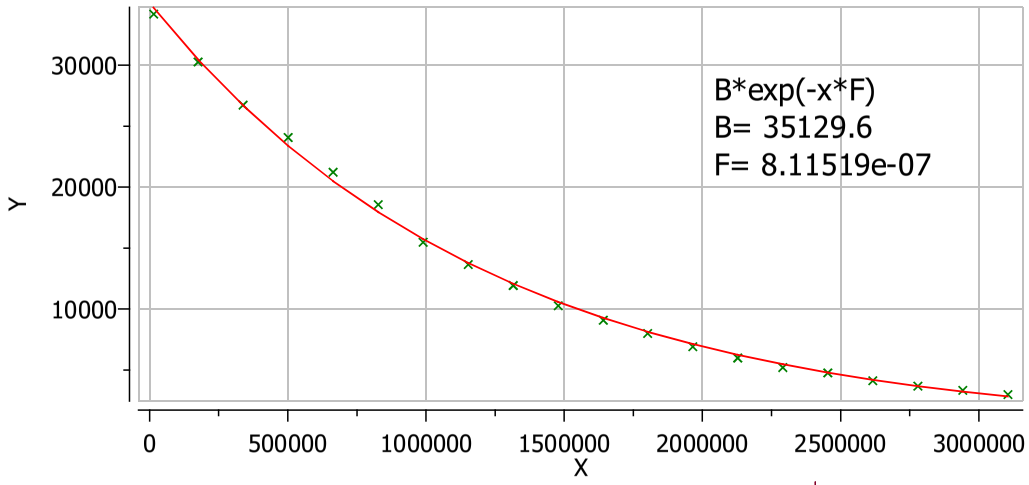

B+F*exp(-x*G)
B= -26.1074
F= 10173.6
G= 1.42606
Y
5000
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13
X
10
9
8
7
6
5
4
3
2
1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

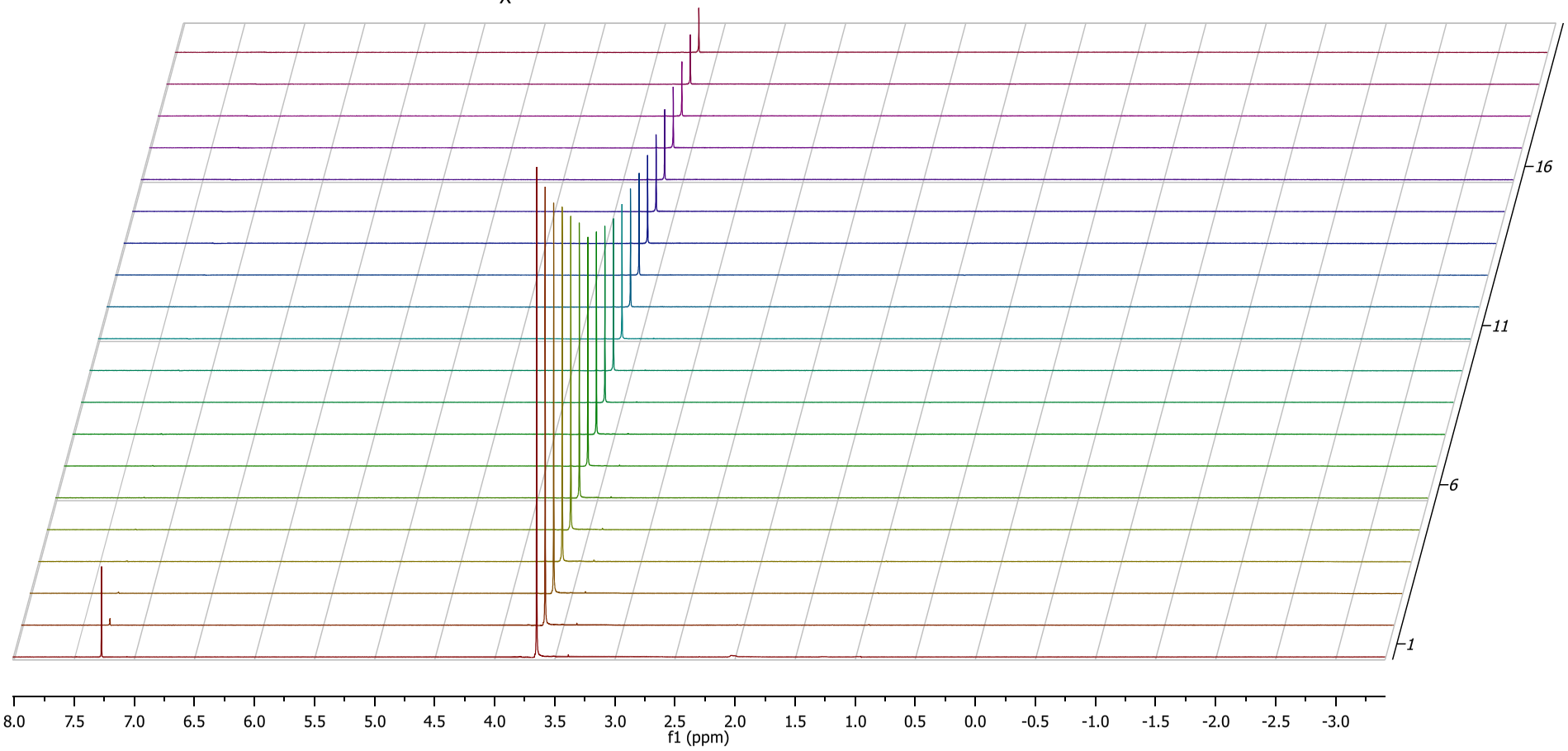
Vogler 10K

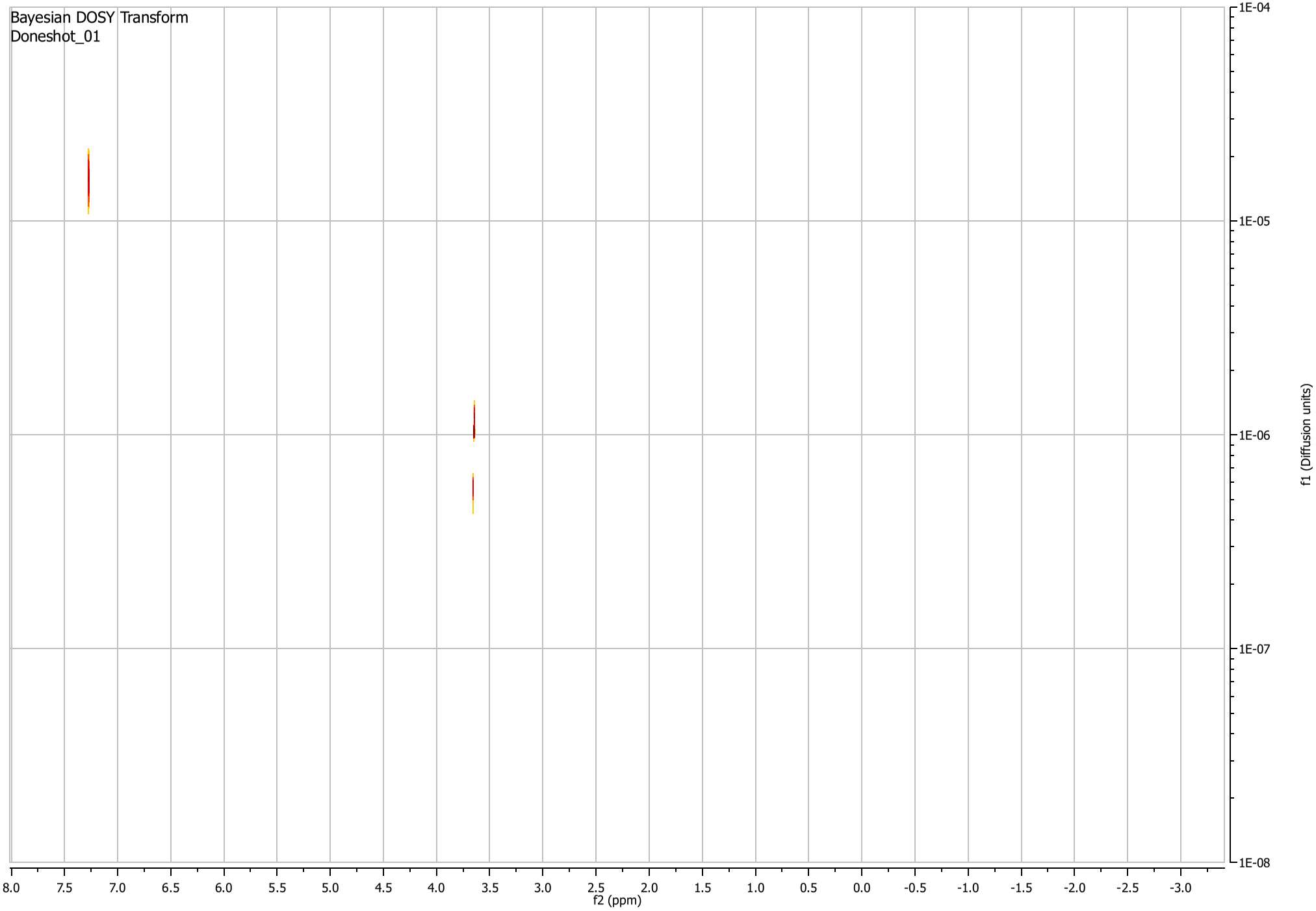


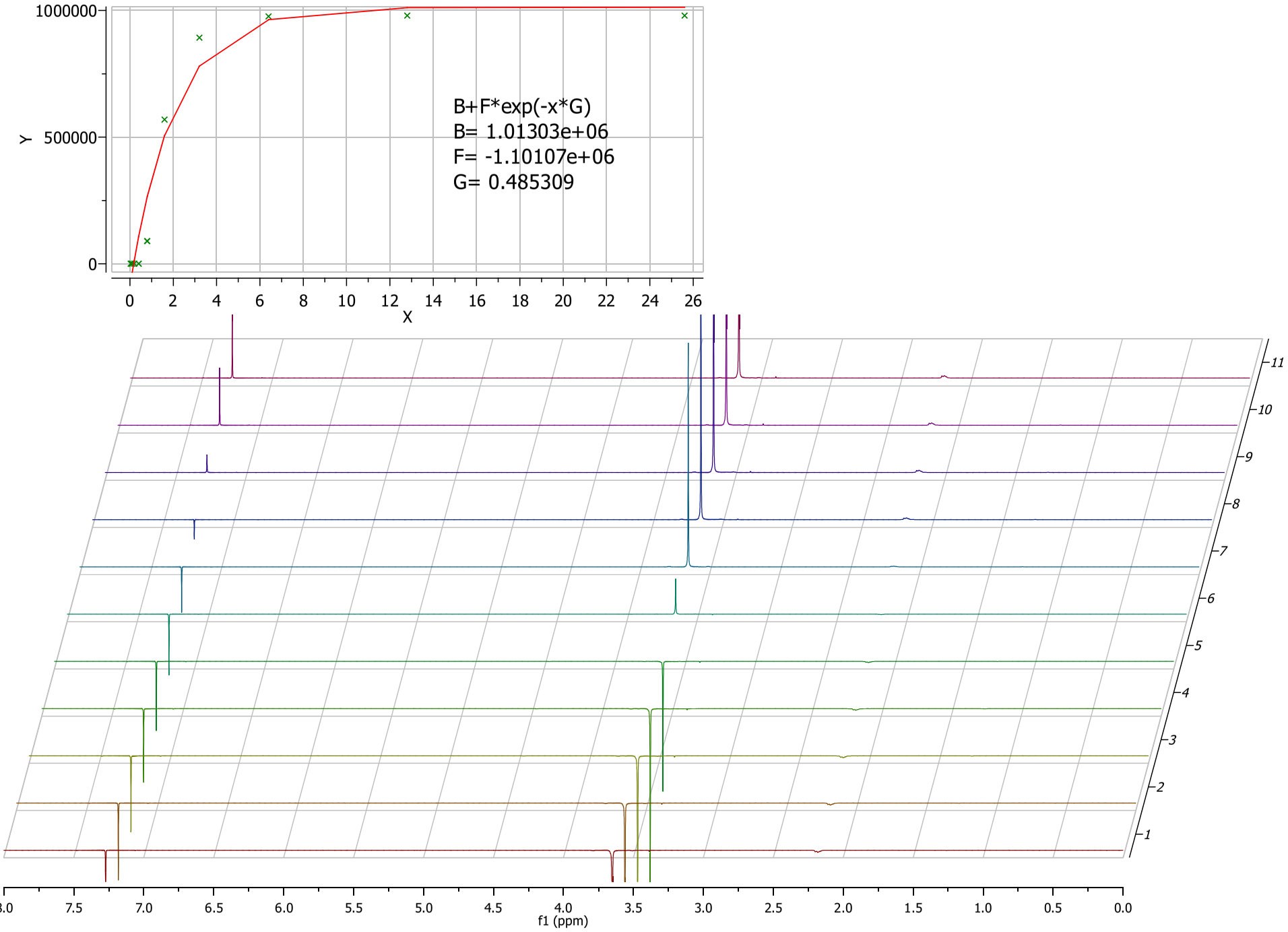


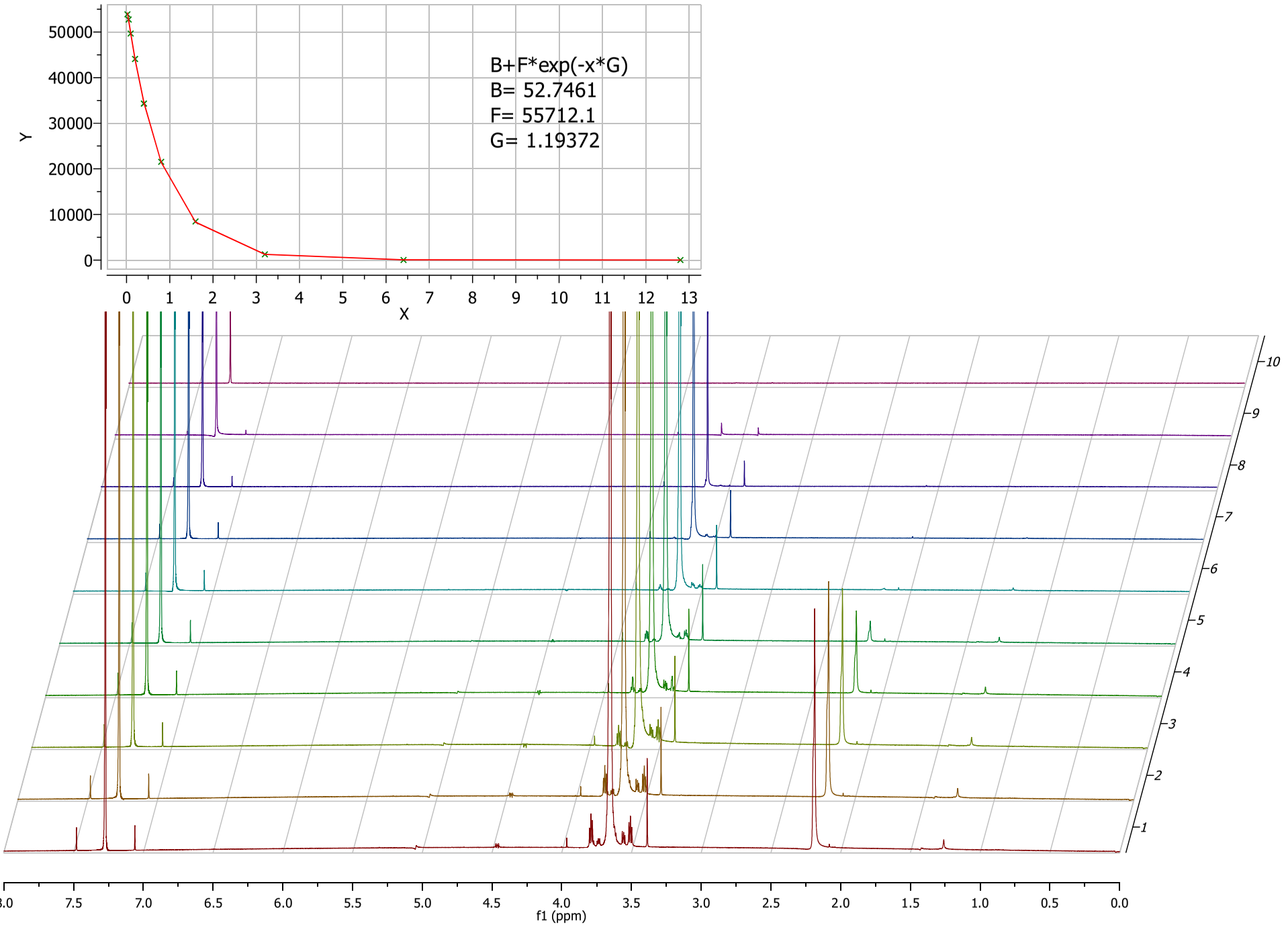
n	ser.	rep.unit	resid.	Mn	Mw	pd	DP	% Int.
1	1	129.994	7.49412	11036.9	11120.1	1.00753	84.9033	32.3


B*exp(-x*F)
B= 35129.6
F= 8.11519e-07
30000
20000
10000
Y
0
500000
1000000
1500000
2000000
2500000
3000000
X

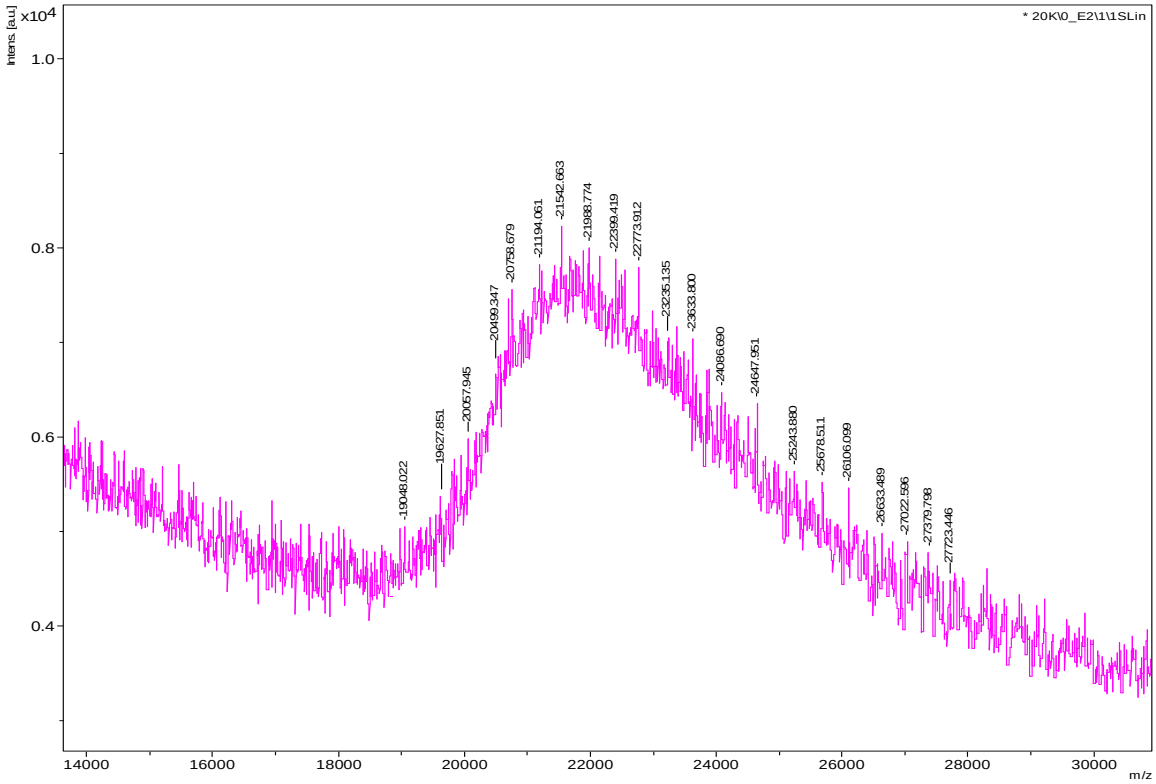

16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f1 (ppm)

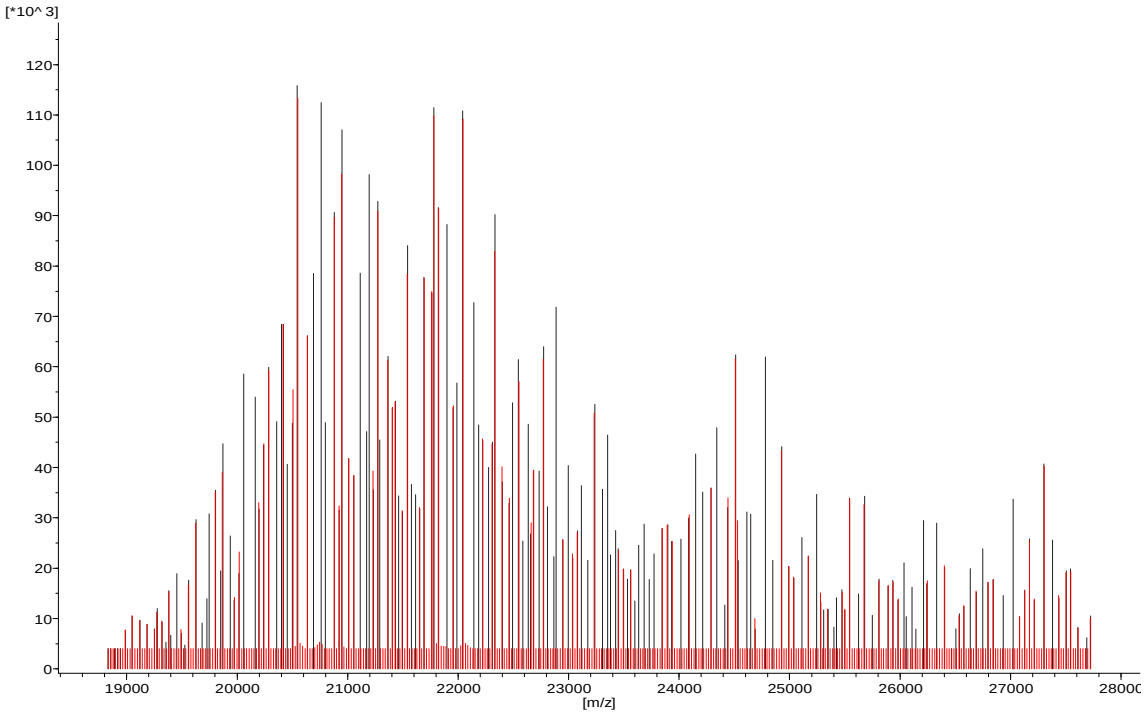

Bayesian DOSY Transform
Doneshot_01
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
f2 (ppm)


1000000
500000
0
Y
0 2 4 6 8 10 12 14 16 18 20 22 24 26
X
B+F*exp(-x*G)
B= 1.01303e+06
F= -1.10107e+06
G= 0.485309
11
10
9
8
7
6
5
4
3
2
1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

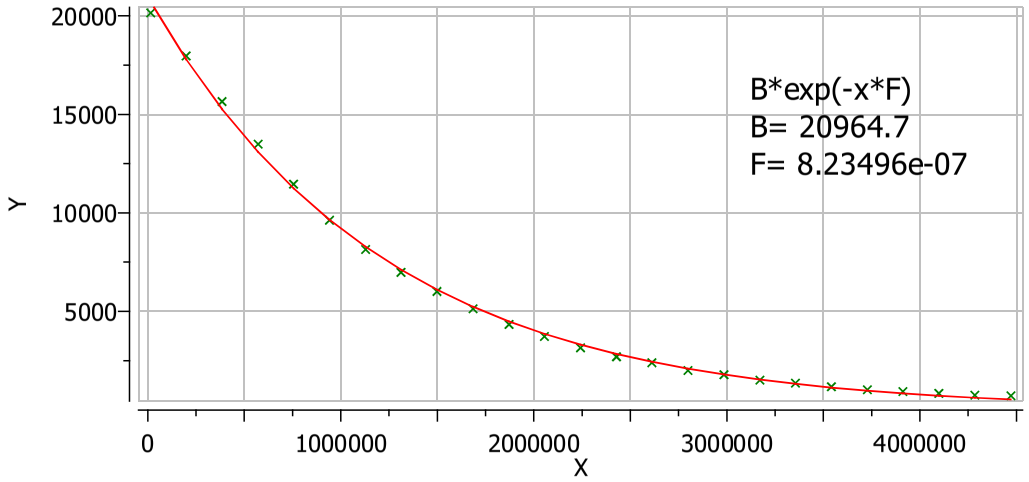

B+F*exp(-x*G)
B= 52.7461
F= 55712.1
G= 1.19372
Y
X
f1 (ppm)

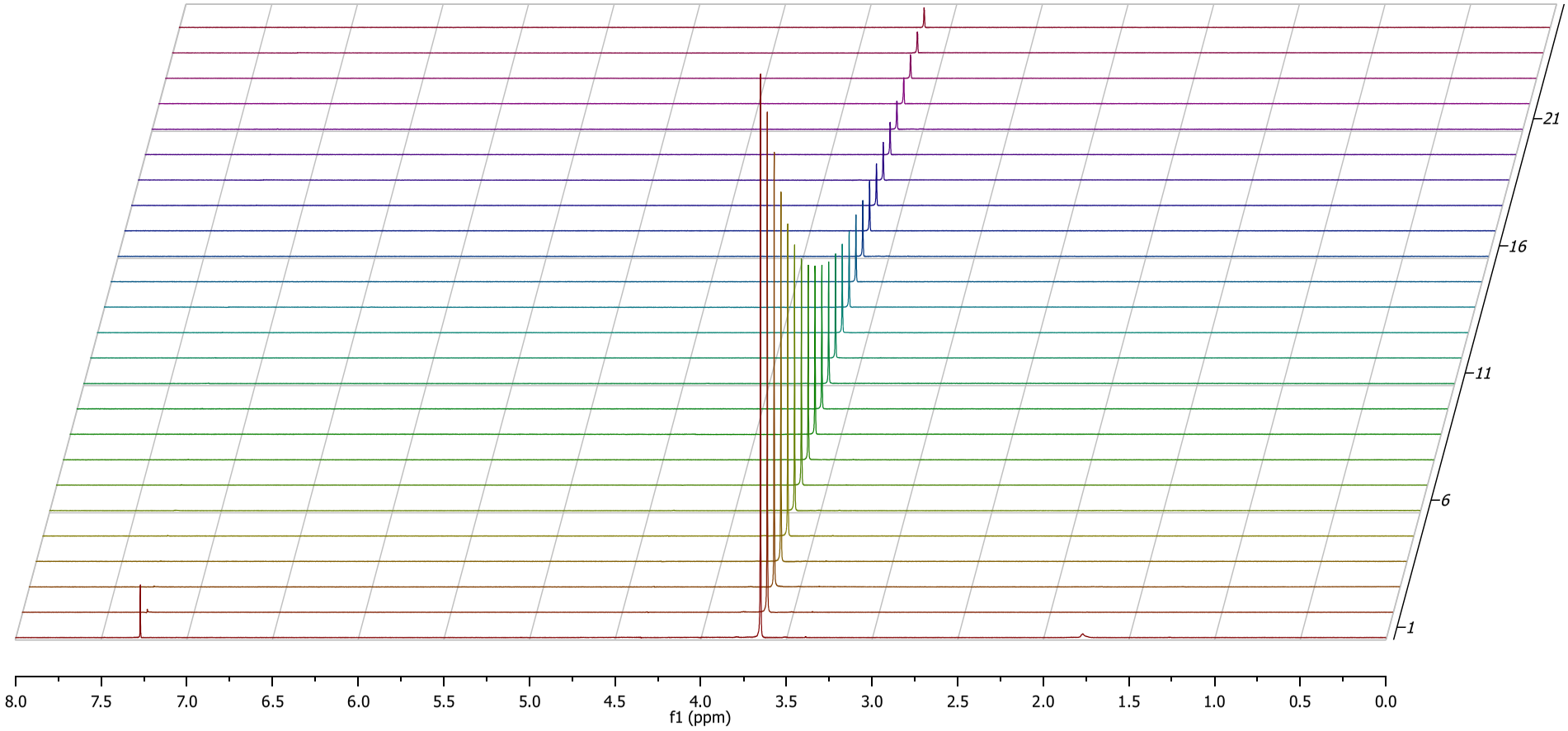
Vogler 20K

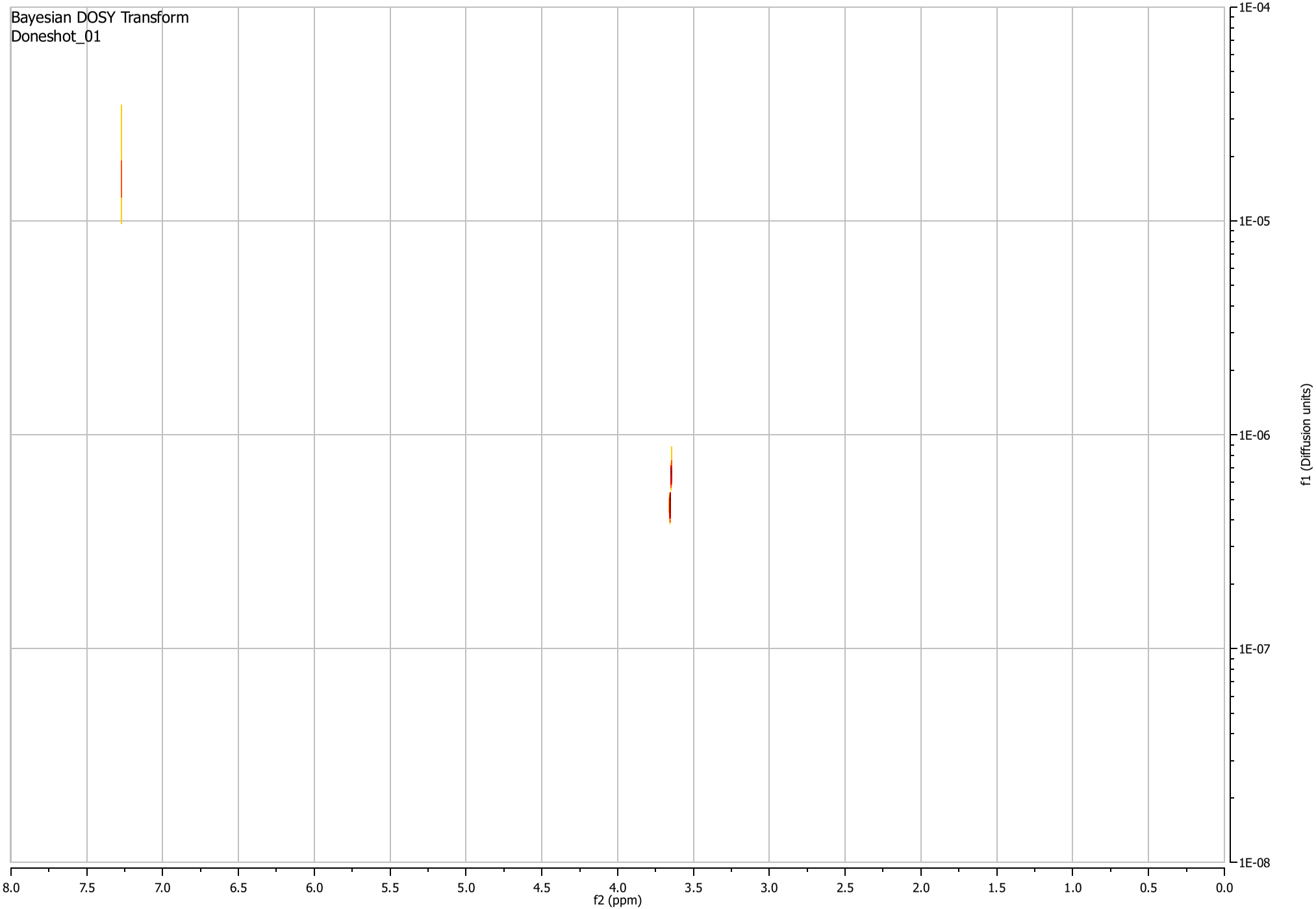


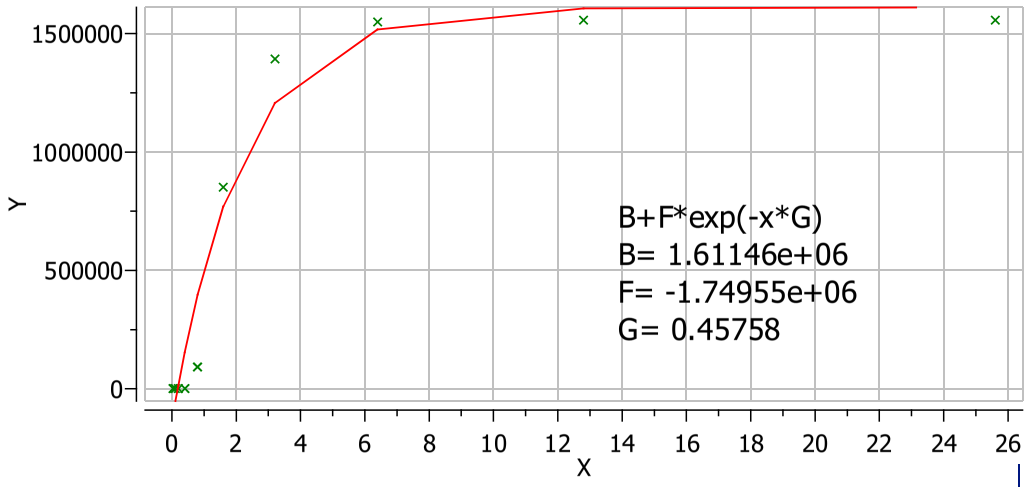


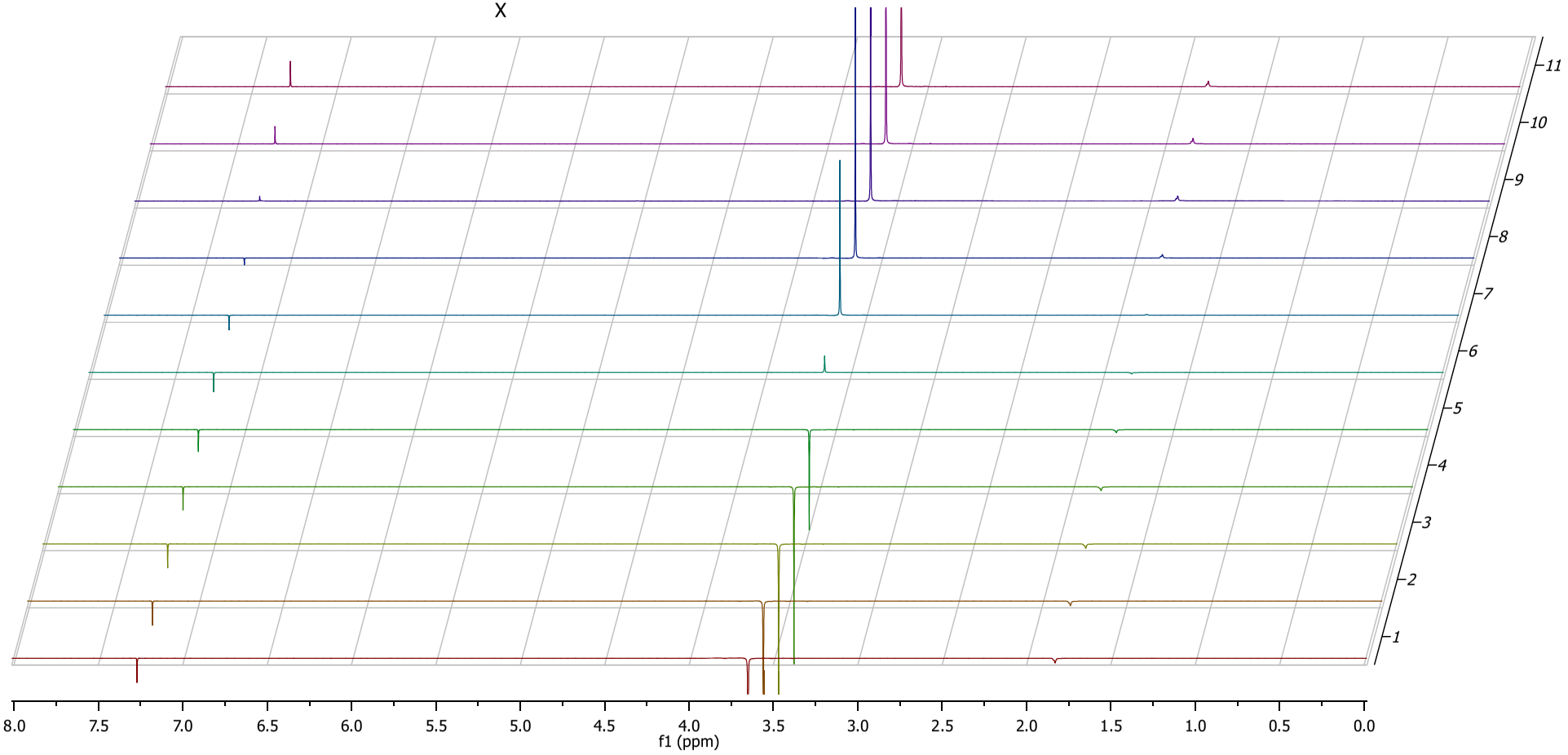
n	ser.	rep.unit	resid.	Mn	Mw	pd	DP	% Int.
1	1	22	21.7068	22527.4	22713.8	1.00827	1023.97	100

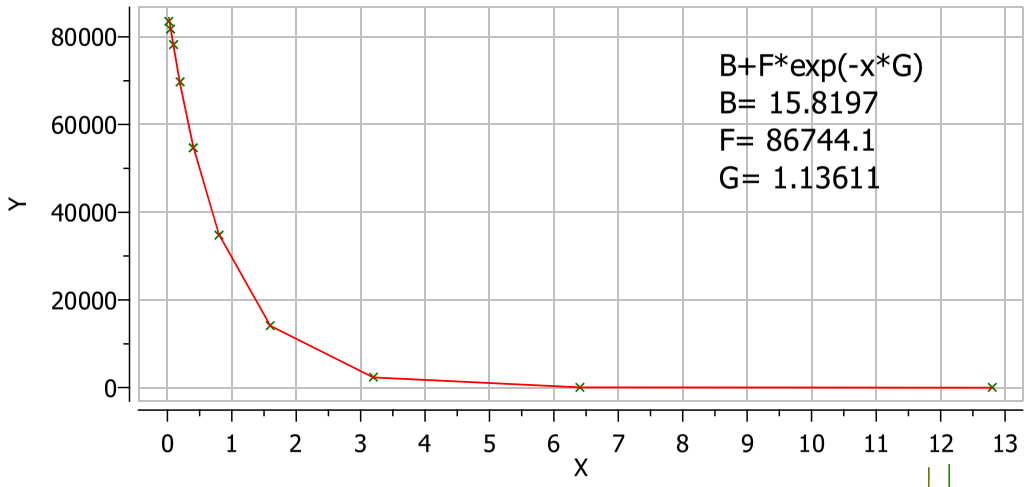

B*exp(-x*F)
B= 20964.7
F= 8.23496e-07
Y
X
20000
15000
10000
5000
0
1000000
2000000
3000000
4000000

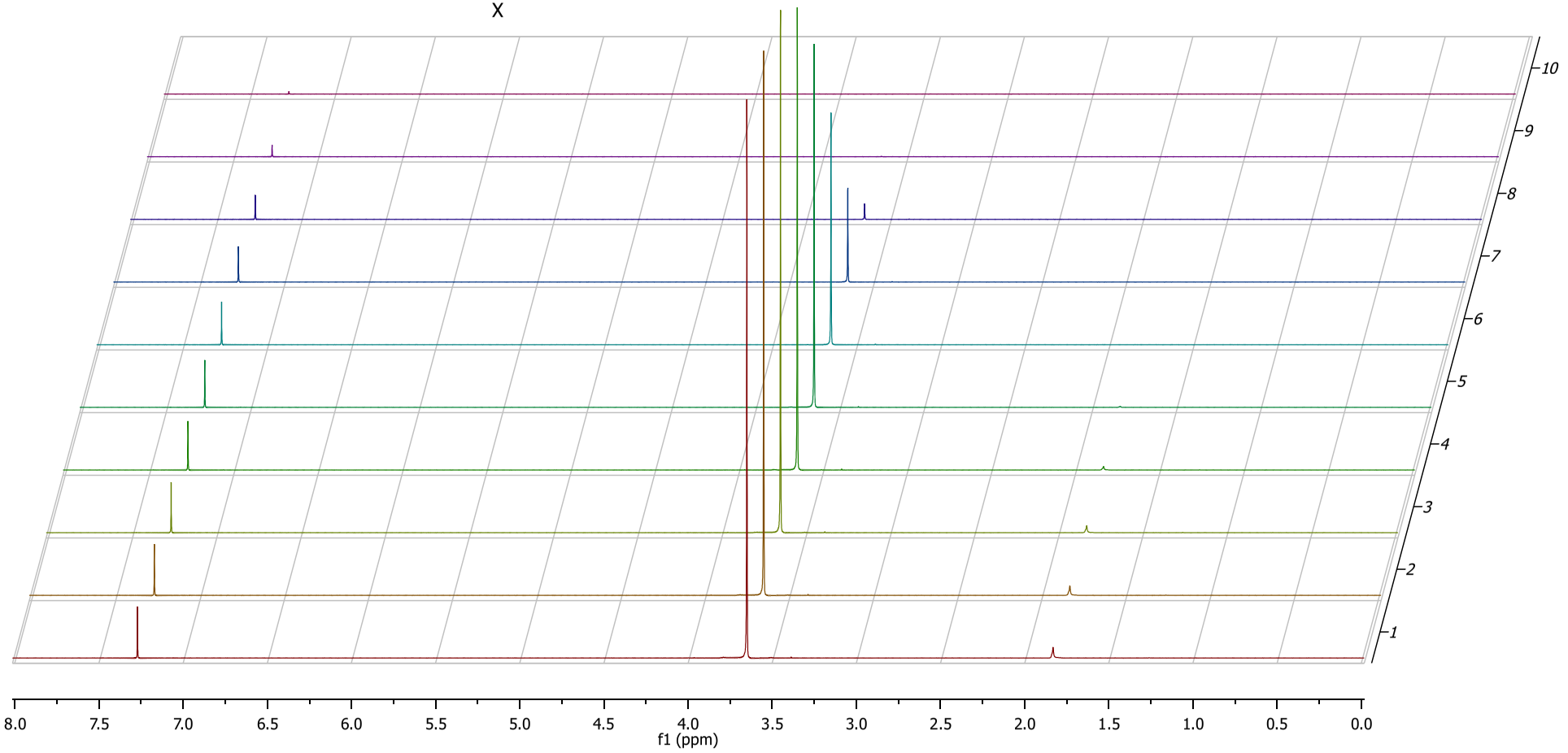

21
16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Bayesian DOSY Transform
Doneshot_01
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

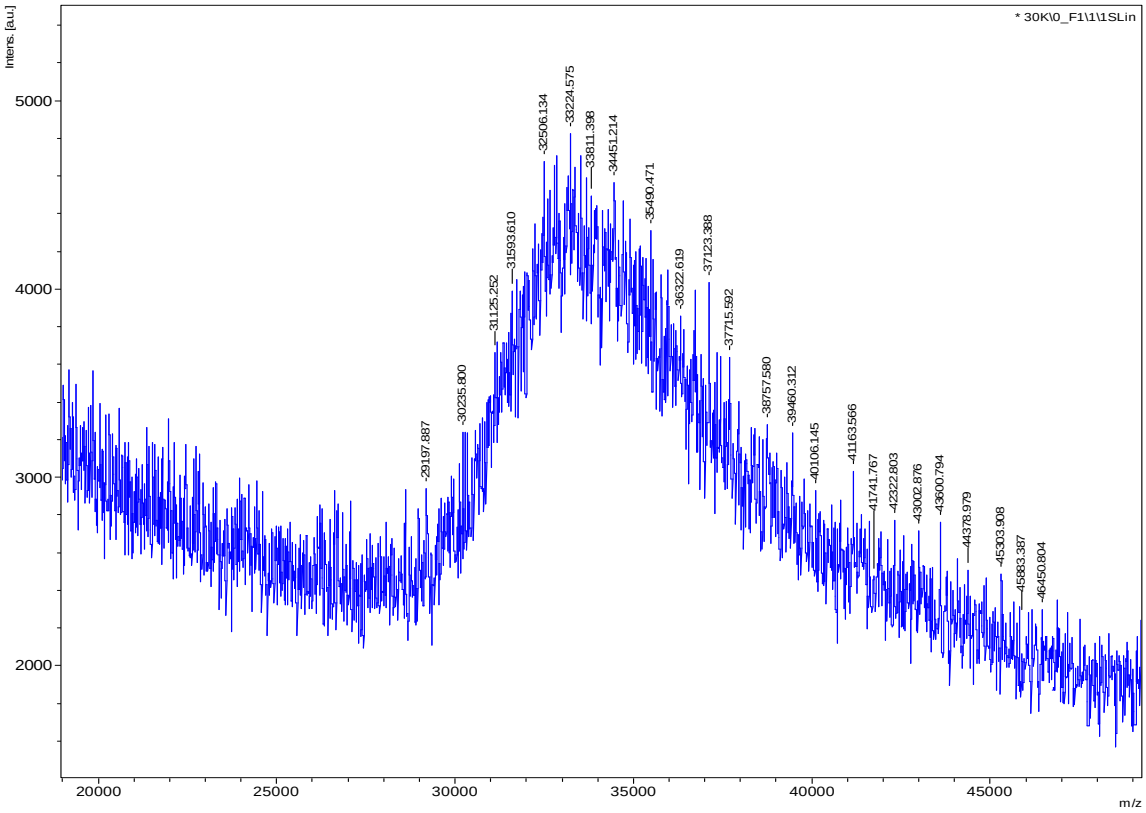

B+F*exp(-x*G)
B= 1.61146e+06
F= -1.74955e+06
G= 0.45758
Y
X

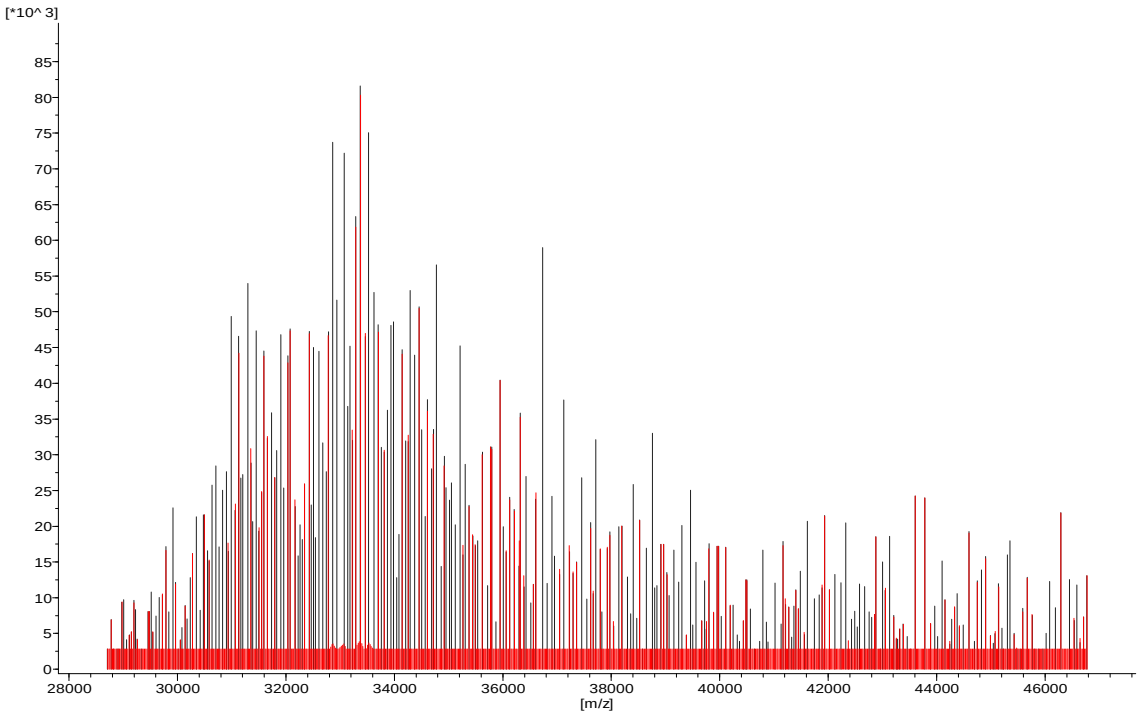

f1 (ppm)


B+F*exp(-x*G)
B= 15.8197
F= 86744.1
G= 1.13611
Y
X
80000
60000
40000
20000
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13

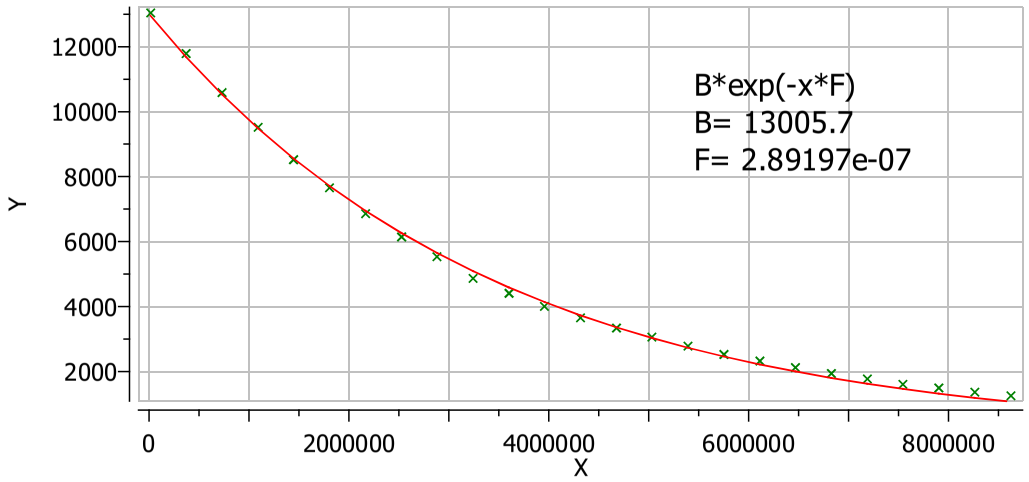

10
9
8
7
6
5
4
3
2
1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

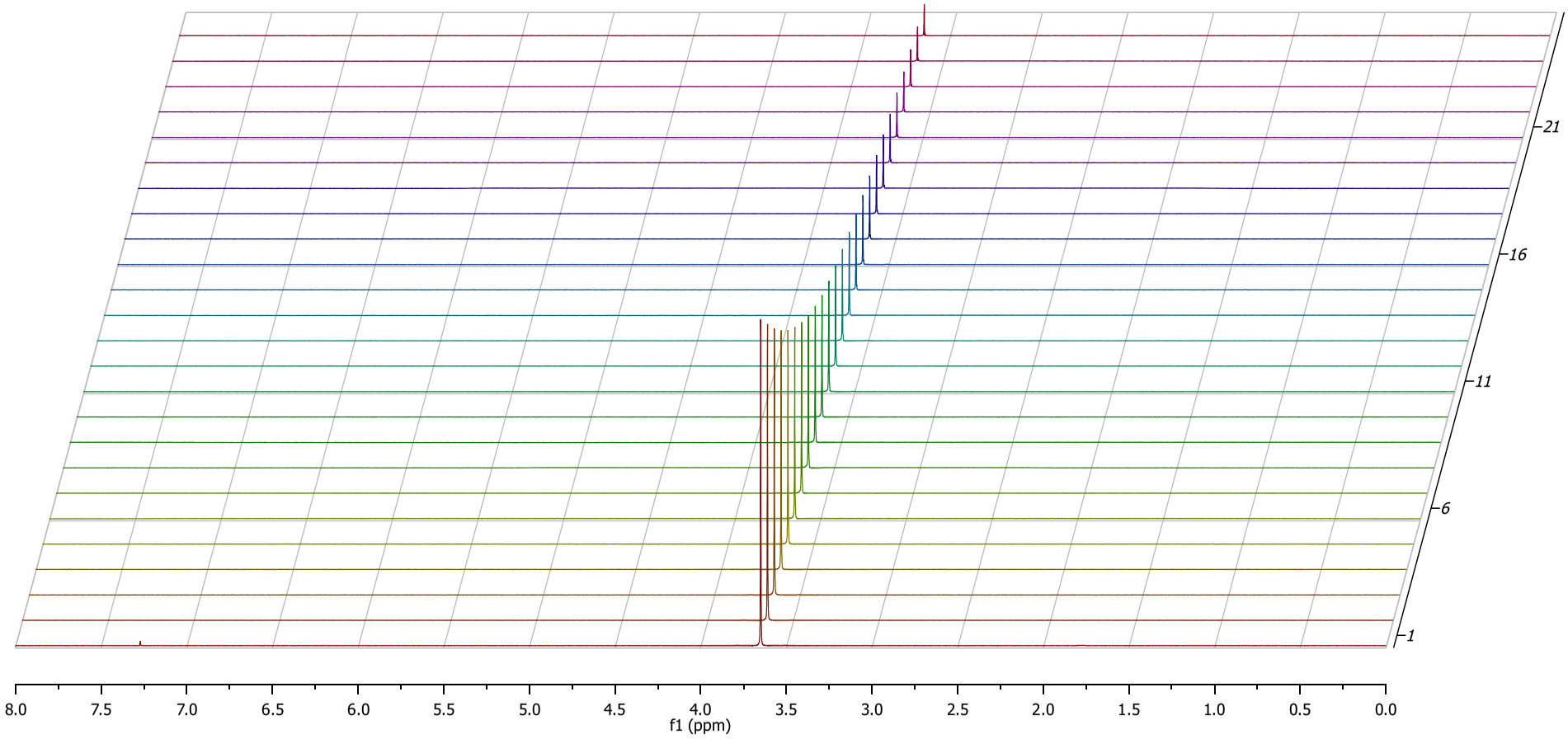
Vogler 30K

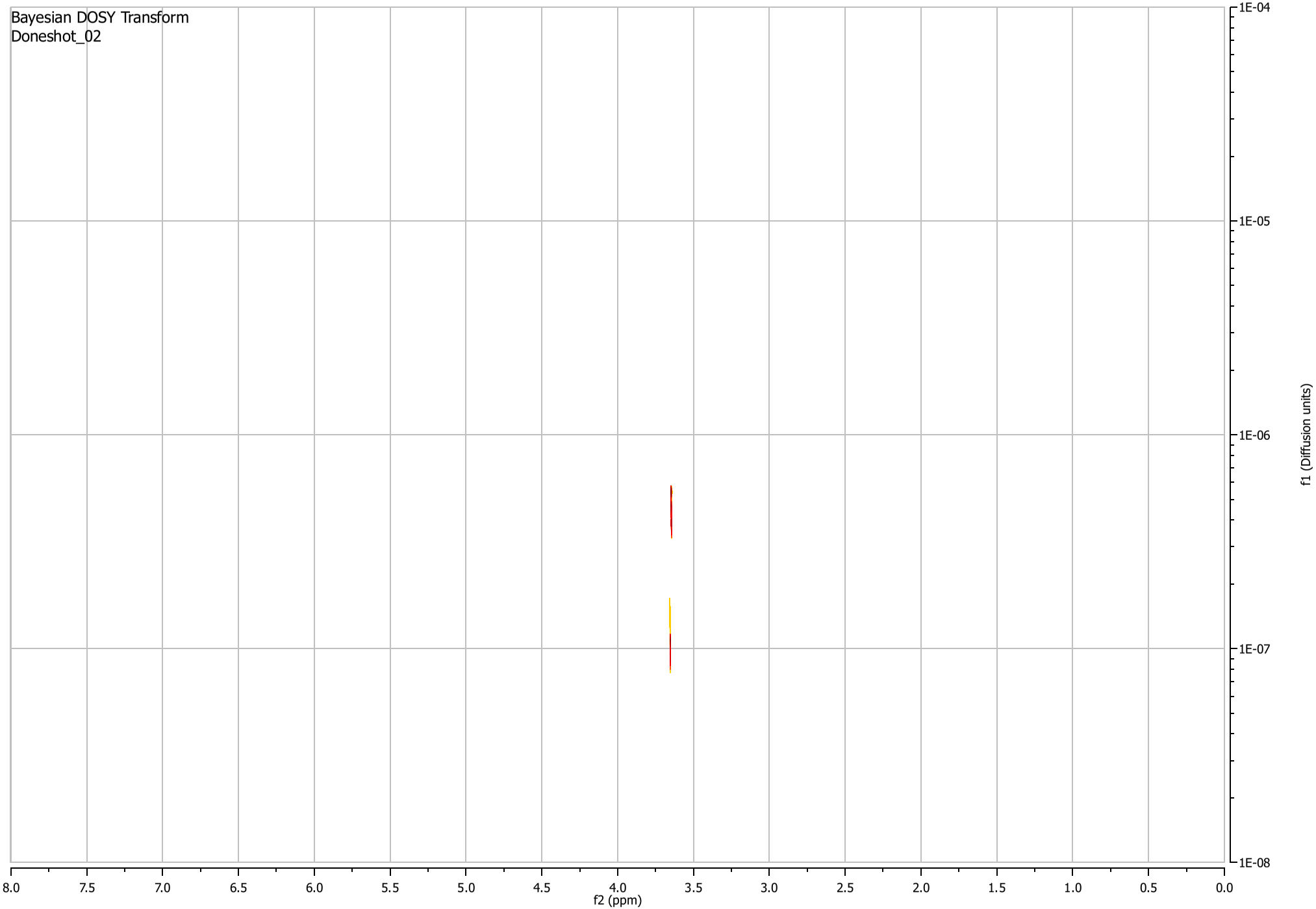


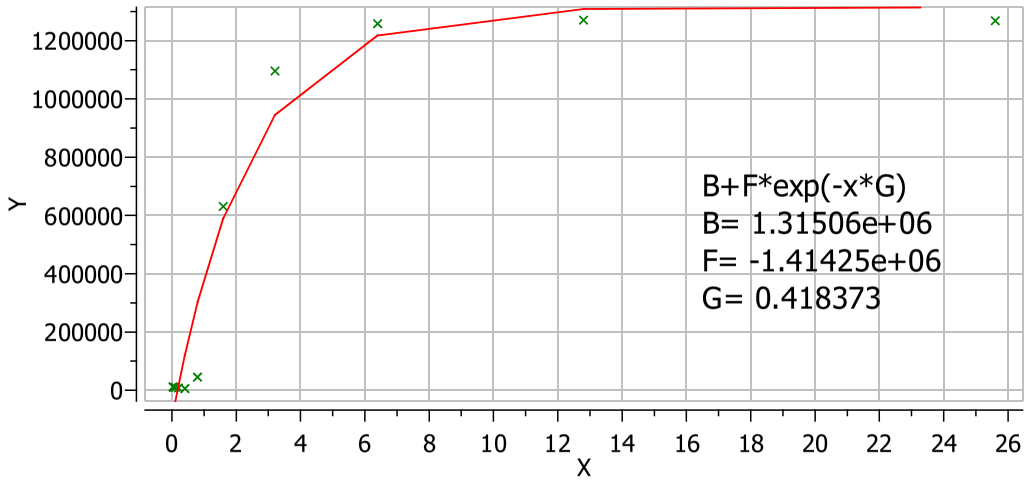


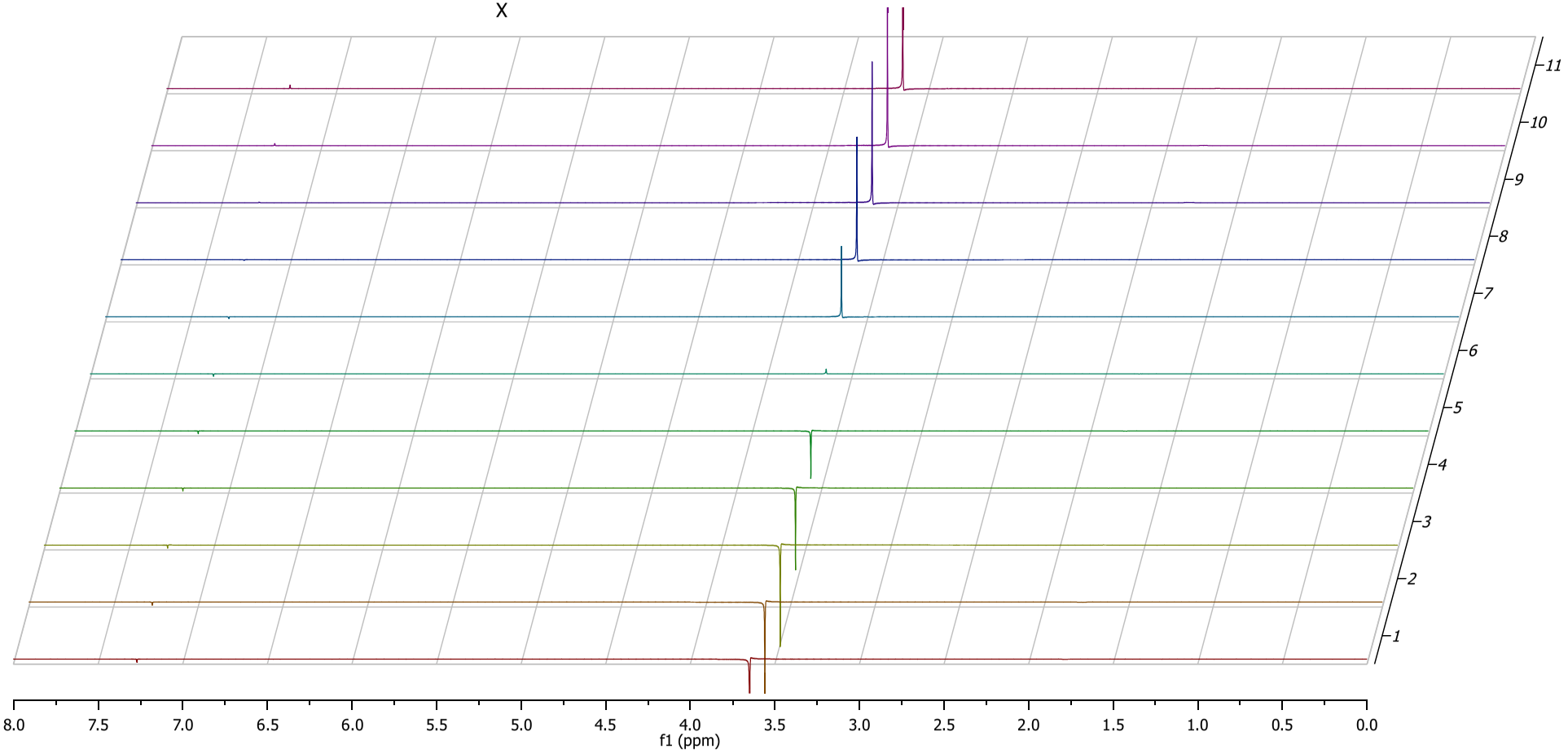
n	ser.	rep.unit	resid.	Mn	Mw	pd	DP	% Int.
1	1	22	21.8822	35627.3	36147.8	1.01461	1619.42	100

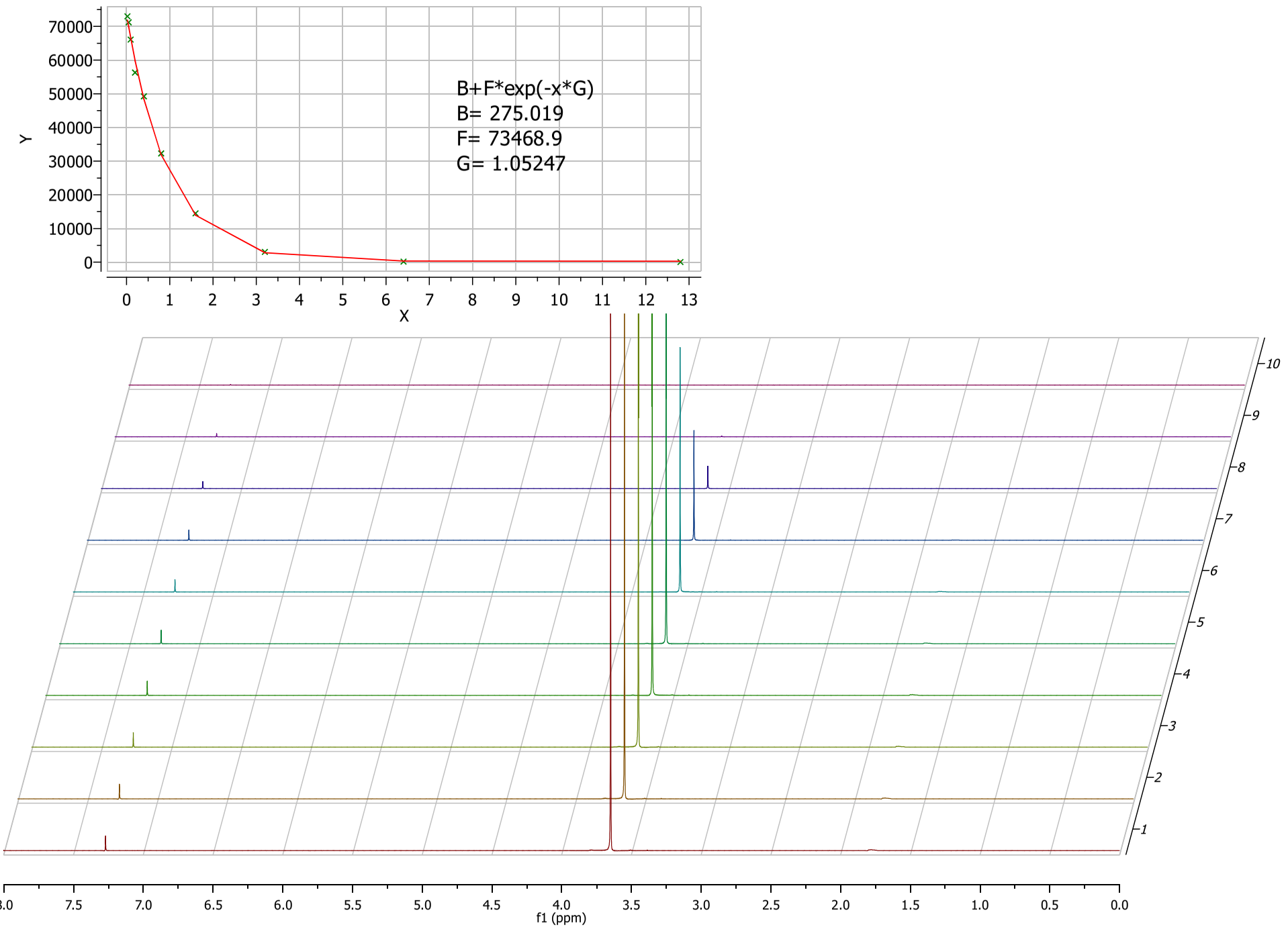

B*exp(-x*F)
B= 13005.7
F= 2.89197e-07
12000
10000
8000
6000
4000
2000
Y
0
2000000
4000000
6000000
8000000
X


21
16
11
6
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Bayesian DOSY Transform
Doneshot_02
1E-04
1E-05
1E-06
1E-07
1E-08
f1 (Diffusion units)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


B+F*exp(-x*G)
B= 1.31506e+06
F= -1.41425e+06
G= 0.418373
Y
X


f1 (ppm)


B+F*exp(-x*G)
B= 275.019
F= 73468.9
G= 1.05247
Y
X
f1 (ppm)