



Measurements of Diffusion rates in liquids, using the Lab-Tools Mk3 NMR Spectrometer.

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<http://www.lab-tools.com/instrumentation/>

Having measured some 1D imaging profiles in the natural 1D magnetic gradient that had been found, by NMR profiling, in the gap of an old horseshoe magnet (probably intended for use with Klystrons), the next question was to determine if this gradient was adequate for diffusion measurements in liquids ?

The decay of the NMR magnetization, following excitation by a $\pi/2$ RF pulse, is typically exponential. However, if diffusion is taking place, the logarithm of the decay of the excitation does not follow a straight line, but a cubic curve, as determined by H. C. Torrey [1].

Bloch Equations with Diffusion Terms*

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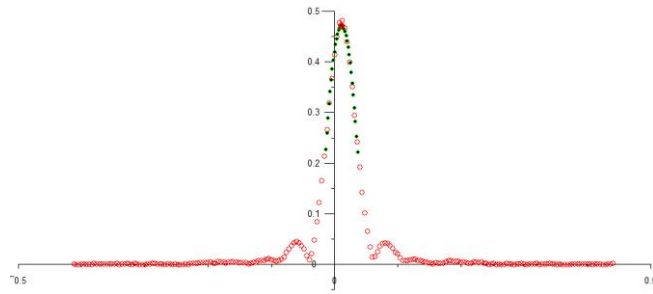
$$A = \exp(-1/3 D \gamma^2 G^2 t^3)$$

where, D is the diffusion constant of the liquid, γ is the Gyromagnetic ratio of the active NMR nucleus – usually Protons, for which $\gamma = 2.67512 \text{ rad}\cdot\text{s}^{-1}\cdot\text{T}$, and G is the magnetic field gradient in which the diffusion is taking place.

The diffusion “constant” changes significantly with temperature, so this needs to be recorded or controlled for each measurement; for water a convenient source of fitted values as a function of temperature is the website in reference [2]. For instance this suggests $D_{\text{water}20\text{C}} = 2.0204 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1} @20\text{C}$; $D_{\text{water}25\text{C}} = 2.2952 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1} @25\text{C}$.

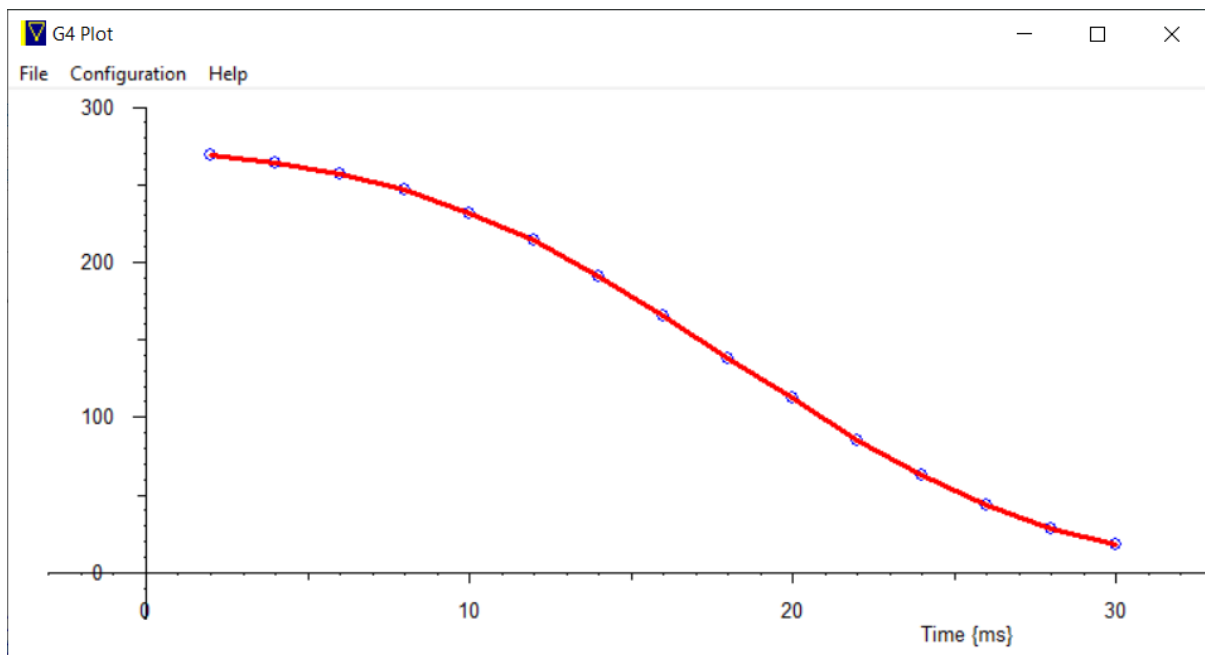
Now the diffusion can be measured in one measurement using a CPMG echo train; however then the t^3 behaviour is only observed during the inter-pulse time, and the amplitudes of the echoes follow an exponential decay. We wish to see the t^3 behaviour explicitly, so we can un-ambiguously determine if we are indeed measuring diffusion in this low magnetic gradient.

Thus we make a series of measurements with a simple $\pi/2 - \tau - \pi - \tau - \text{echo}$ sequence, using the T_2 sequence menu options on the Lab-Tools Mk3 NMR Spectrometer. This then steps through a suitable range of τ values, each time measuring the averaged resultant echo amplitude. A polynomial fit to the echo peak is used, solving the polynomial to obtain a best-fit height.

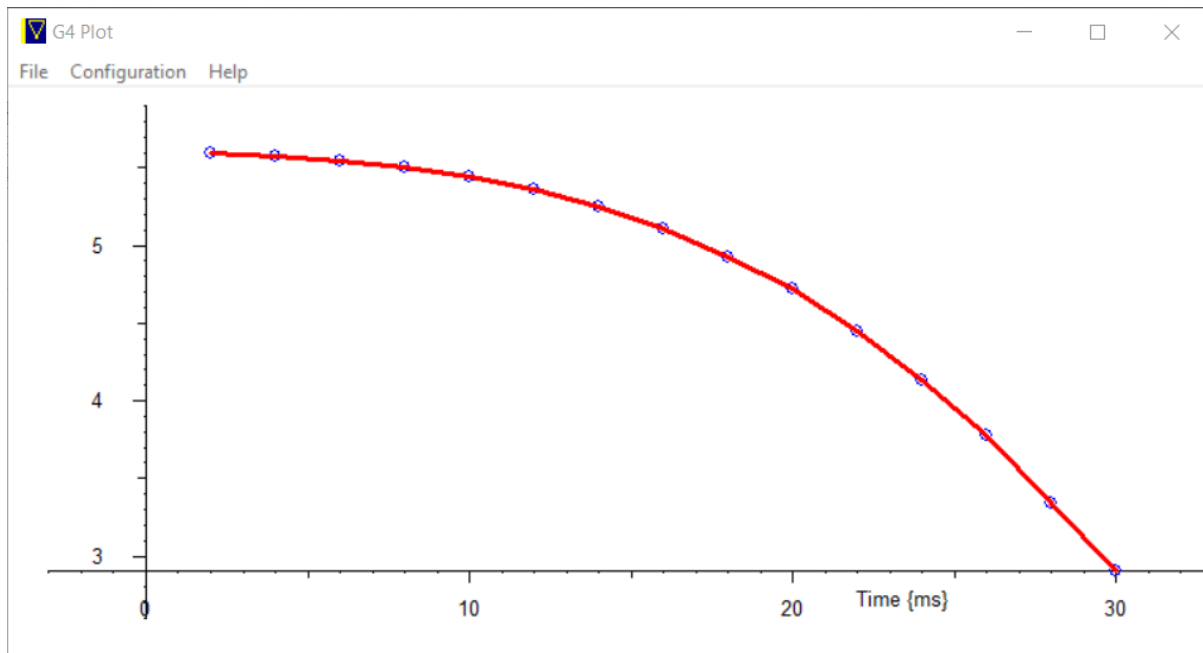


The program then fits and determines (in this case) the best-fit Diffusion constant, using the recorded value for the magnetic gradient.

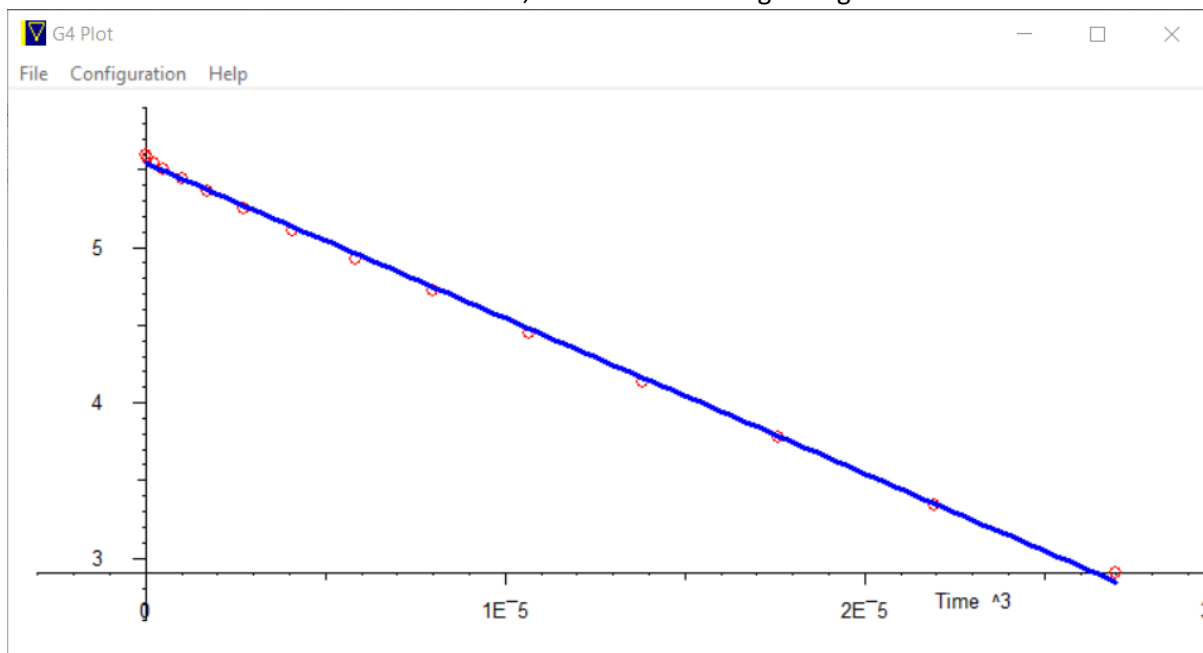
With a preliminary experiment on water at 18.4 C, for the raw measurement, we obtain :



If we take the natural logarithm, we clearly obtain a cubic fall-off of signal intensity with increased time :



It is most convenient to plot this against t^3 , then we obtain a fairly convincing straight line fit, that we can use to obtain the diffusion constant, if we know the magnetic gradient :



When the magnet was profiled, we obtained measured gradients for in-plane of $64.328 \text{ mT}\cdot\text{m}^{-1}$, and transversely of $7.893 \text{ mT}\cdot\text{m}^{-1}$. We can not just use the in-plane 1D gradient, as diffusion in the bulk liquid is a 3D phenomenon. The 1D value would give a diffusion constant of $1.0128 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, whereas reference [2] suggests that at 18.4C $D_{\text{water}18.4\text{C}} = 1.9368 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$.

So we turn this around, and insert the predicted value for $D_{\text{water}18.4\text{C}}$, to calculate the measured gradient in this magnet.

The following afternoon a series of diffusion measurements were made on organic liquids, preceded and followed by further measurements on water, for calibration. These suggested a calculated 3D gradient of $36.09 \text{ mT}\cdot\text{m}^{-1}$, which was used for the organic liquids measurements.

Measurements were then made on cyclohexane, acetone, glycerol, acetone, dodecane, hexadecane and tetradecane.

However these measurements should just be considered as guidelines, rather than calibrated values, as they were made rapidly in a simple test probe, primarily to see what the spectrometer capabilities were.

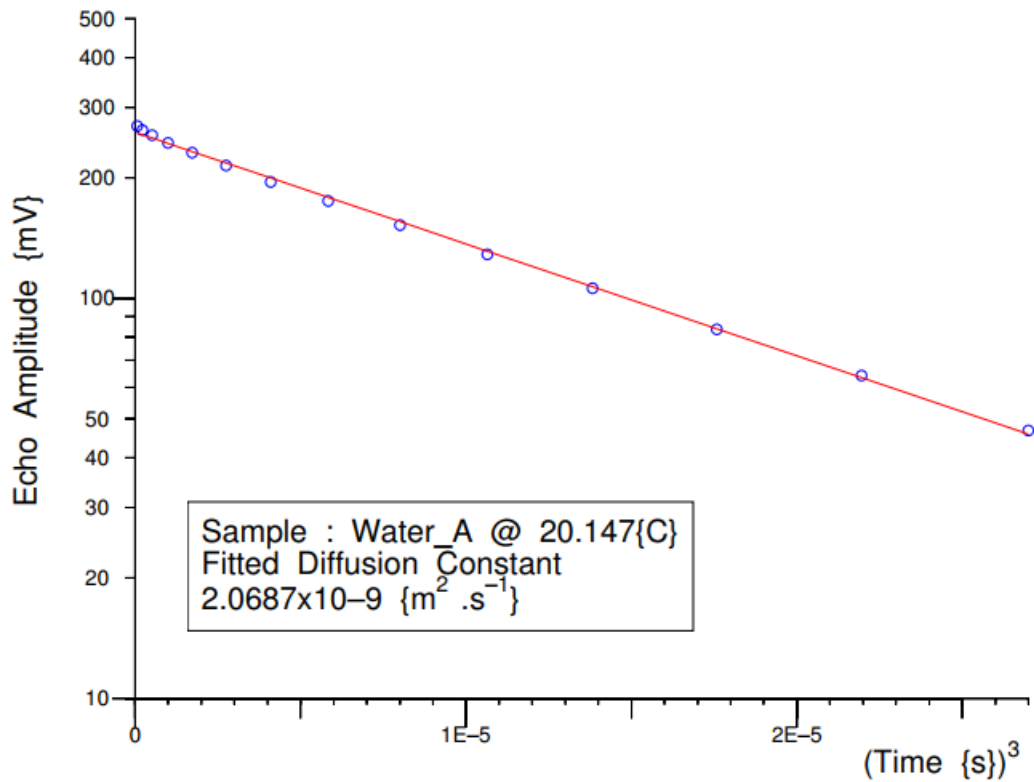
The sample temperature was measured using a thermocouple, and averaged for each reading. Each echo point was averaged 10 times, and this allowed time for the sample temperature to be averaged as well. For easy comparison of the the results, a simple protocol was followed for all the automated measurements, of incrementing the τ time (echo time 2τ) from 1 ms to 15 ms, and recording the averaged echo amplitude and averaged temperature; here is a typical example; this is water data :

	1	2	3	4
1	Tau (ms)	T time (ms)	Ampl (mV)	T Sample (C)
2	1	2	275.099	20.027
3	2	4	270.104	20.036
4	3	6	263.657	20.045
5	4	8	255.621	20.0835
6	5	10	244.485	20.122
7	6	12	231.042	20.128
8	7	14	214.618	20.1505
9	8	16	195.611	20.1765
10	9	18	175.291	20.176
11	10	20	152.294	20.184
12	11	22	128.71	20.191
13	12	24	105.952	20.1925
14	13	26	83.7064	20.209
15	14	28	64.0935	20.2315
16	15	30	46.807	20.253

At the en of the measurement, the spectrometer calculates the diffusion constant, and then plots the natural logarithm of the amplitude vs time³.

Thus we obtain a reasonable value for the diffusion of water :

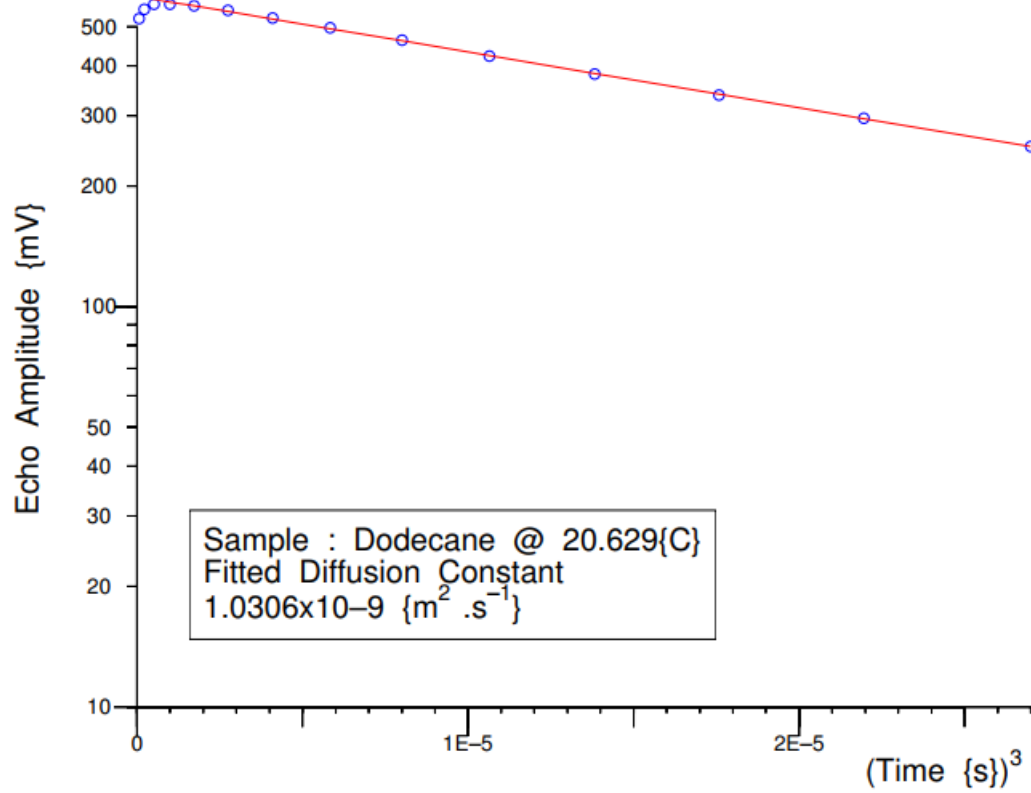
Diffusion graph vs. Time³



Not all the data sets are as clean as this; they will be discussed here as examples of possible problems :

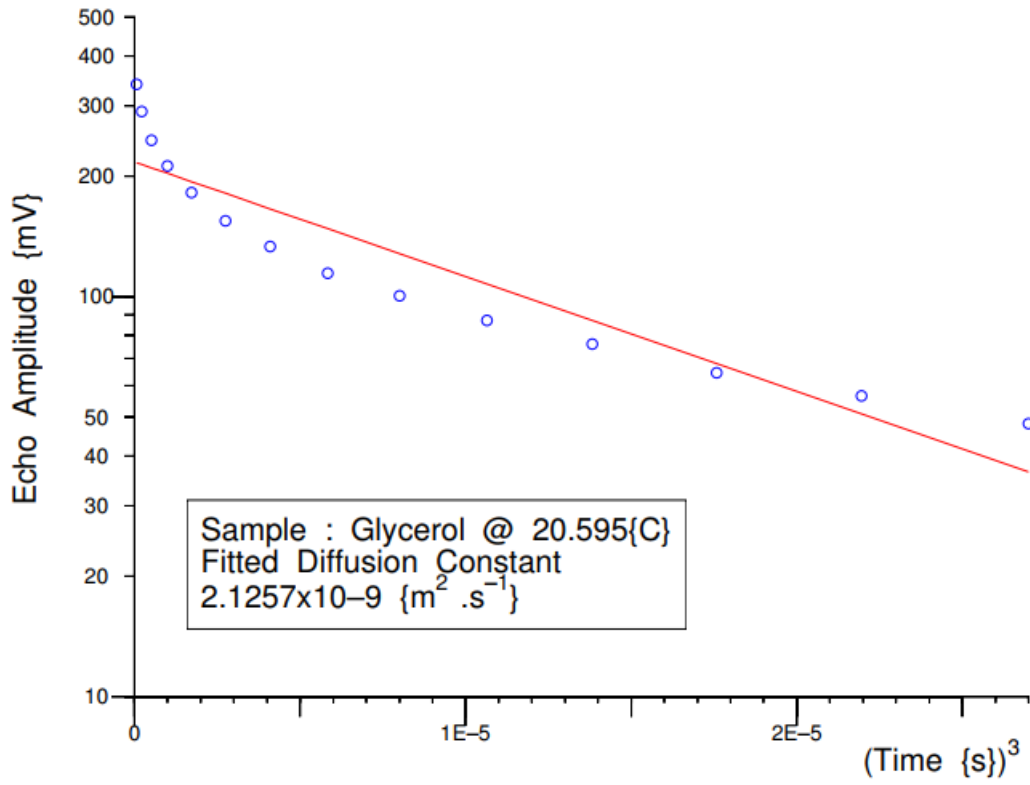
The dodecane measurement was probably made with too short a minimum repeat time – for larger τ times more data has to be transferred from the Field Programmable Gate Array to the desktop (just in the current measurement configuration, this is not an invariant) and then the repeat time increases and the signal slightly rises. However there is little problem in determining the diffusion time. The simple solution is just to set the correct repeat time.

Diffusion graph vs. Time³

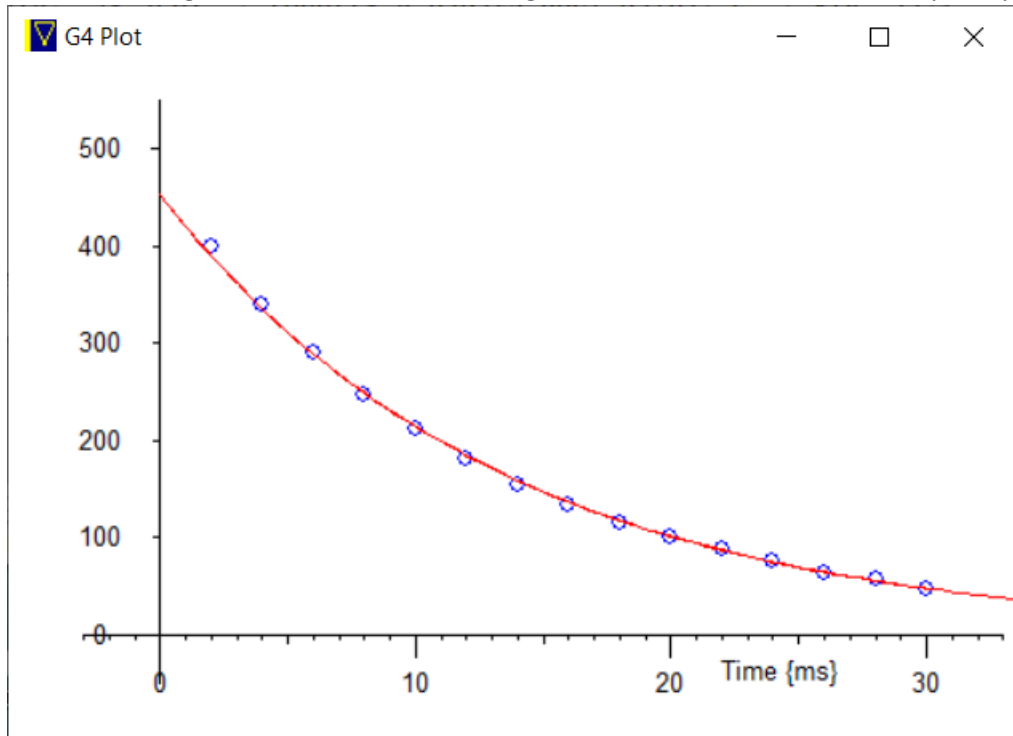


For the Glycerol sample, however the diffusion measurement failed; the glycerol could be expected to have slow diffusion, however this sample was clearly not of high purity and showed a very short T_2 decay time that dominated the NMR relaxation :

Diffusion graph vs. Time³



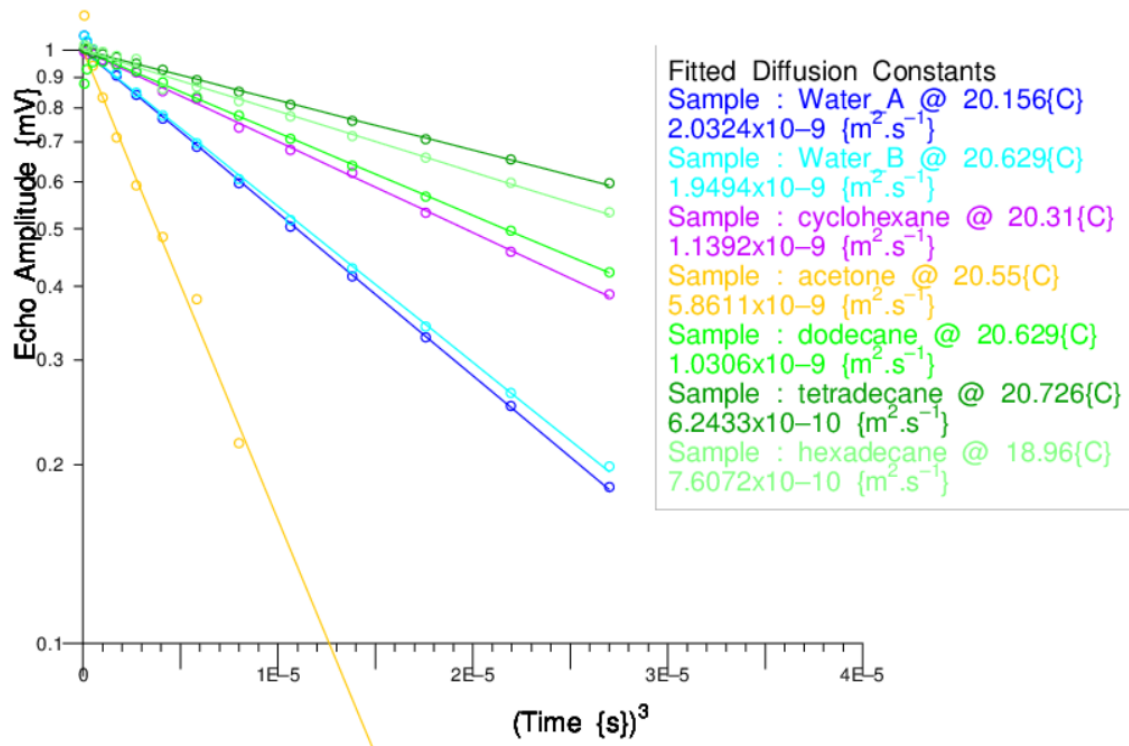
The fitted straight diffusion value is meaningless, as we can see if we do a simple exponential fit :



We obtain a T_2 of 13.3 ms.

However in the main the rest of the diffusion results are believable :

Normalised Diffusion graphs vs. Time³



It is planned to build a simple but robustly located new probe, with added limited temperature control, able to do such measurements with higher repeatability at chosen temperatures. However it is hoped that this script may be useful to others, and as a way of further demonstrating the capabilities of the Lab-Tools Mk3 NMR Spectrometer.

[1] Bloch Equations with Diffusion Terms. H. C. Torrey
Phys. Rev. 104, 563 – Published 1 November 1956

[2] Diffusion Coefficients of Water. Olaf Dietrich, Munich, Germany:
<https://dtrx.de/od/diff/>