

Measuring Fast Relaxing Samples on Current FFC - NMRD Relaxometers

Experimental difficulties and limits



Stanislav Sykora, Gianni M. Ferrante, Alexander Galkin,
Stelar s.r.l. Via E.Fermi, Mede (PV), Italy



Breaking the "barrier" of relaxation rates above 1000 s^{-1} (T_1 shorter than 1 ms) and doing so in a reliable and reproducible way is an experimental feat which would have been impossible even just three years ago. Yet this poster illustrates that the latest FFC instruments make it an affordable reality which lies just slightly beyond the realm of everyday routine. It also shows that with full-range field switching times of 1 ms (corresponding to the current state-of-art) one can in some cases measure reliably relaxation rates R_1 up to 10000 provided that the switching waveforms are perfectly controlled and reproducible. A more quantitative study of the phenomena involved and of possible optimization strategies is now in progress.

Two samples with very different relaxation behaviours (Fig.1) had been used for this preliminary study of phenomena occurring when switching times become close-to or longer-than relaxation times.

Sample I was a 2.1M solution of dysprosium perchlorate in bidistilled water (kindly provided by Dr.L.Helm, University of Lausanne).

Sample II was the commercial Parafilm M (American National Can Co.) which, according to the NASA/MSFC Materials and Processes home page, consists of a wax (~56%) and a polyolefin (the exact composition is a closely guarded secret).

Sample I has a flat ^1H -NMRD profile over the whole explored field range from 5kHz to 20 MHz (^1H Larmor frequency). At 25°C , its mean relaxation rate is $R_1 = 1425 \text{ s}^{-1}$ with an rms. error of 0.7%. It is not easy to measure its profile, despite the fact that the required polarization time is very short making it possible to acquire a large number of raw data in a rather short time. Since the maximum switching rate of our instrument was 24 MHz/ms, we have used switching time $\text{SWT} = 1\text{ms}$, polarization field $\text{BPOL} = 15 \text{ MHz}$ and acquisition field $\text{BACQ} = 9.15\text{MHz}$. This, under all switching conditions, leaves enough spare time for fine field settling. Even with such close-to-optimal settings, and despite excellent S/N ratio, we had to use 64 tau-value blocks and 8 scans for every point to achieve the fitting errors shown in Fig.3.

Two series of measurements have been taken. One was a fully automated run (red disks), while the other was a set of manually optimized, point-by-point measurements (blue disks).

As expected, the point-by-point adjustments reduce the scatter in the profile (Fig.3) but, surprisingly, they do not seem to have much impact on the fitting errors (Fig.2). Another puzzling feature regards the automated measurement which exhibits a slight, but statistically significant field dependence (Fig.3, red disks). The automated measurement gives marginally lower values of R_1 and the deviation tends to become more appreciable at higher relaxation fields (the behaviour is currently being investigated in more detail).

We have complemented the investigation by a very careful measurement of R_2 at 9.15 MHz by means of the classical CPMG sequence. The result, shown in Fig.3, is very comforting since in this particular sample we expect $R_2 = R_1$, barring a possible small discrepancy due either to dissolved O_2 and/or chemical-exchange phenomena. The agreement between the measured R_2 and the optimized series of R_1 measurements is thus absolutely extraordinary.

Sample II behaves in a quite different way since its R_1 varies steeply from 39.9 s^{-1} at 18 MHz to over 6400 s^{-1} at 10 kHz. Despite the fact that it reaches R_1 values four times higher than Sample I, it can be easily measured even using the automated profile-acquisition procedure. The only required precautions consist in setting all switching times to 1ms, the polarization time to a value adequate for whatever is the chosen polarization field and the field slew rate to its maximum allowed value.

We have measured two distinct preparations of Sample II, one subject to no stress and one first stretched and then allowed to mechanically relax. The two profiles (Fig.1) are almost identical with just the slightest difference below 30 kHz. Measurements of both profiles were extremely fast and their fitting errors (Fig.2) were better than for Sample I, despite the number of scans and number of tau-blocks were both halved and, due to worse filling factor, its S/N ratio was about two times lower.

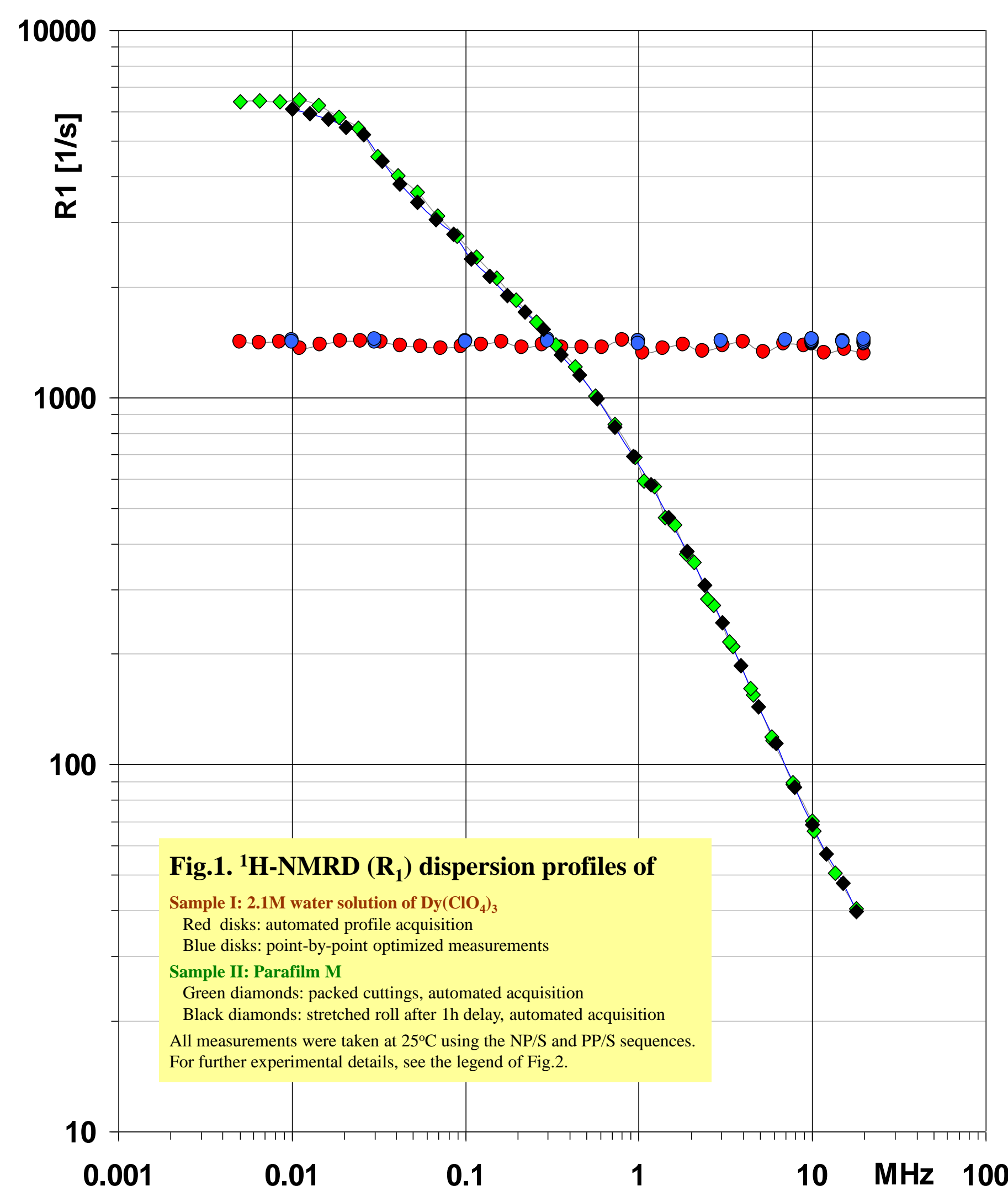


Fig.1. ^1H -NMRD (R_1) dispersion profiles of

Sample I: 2.1M water solution of $\text{Dy}(\text{ClO}_4)_3$
Red disks: automated profile acquisition
Blue disks: point-by-point optimized measurements
Sample II: Parafilm M
Green diamonds: packed cuttings, automated acquisition
Black diamonds: stretched roll after 1h delay, automated acquisition
All measurements were taken at 25°C using the NP/S and PP/S sequences.
For further experimental details, see the legend of Fig.2.

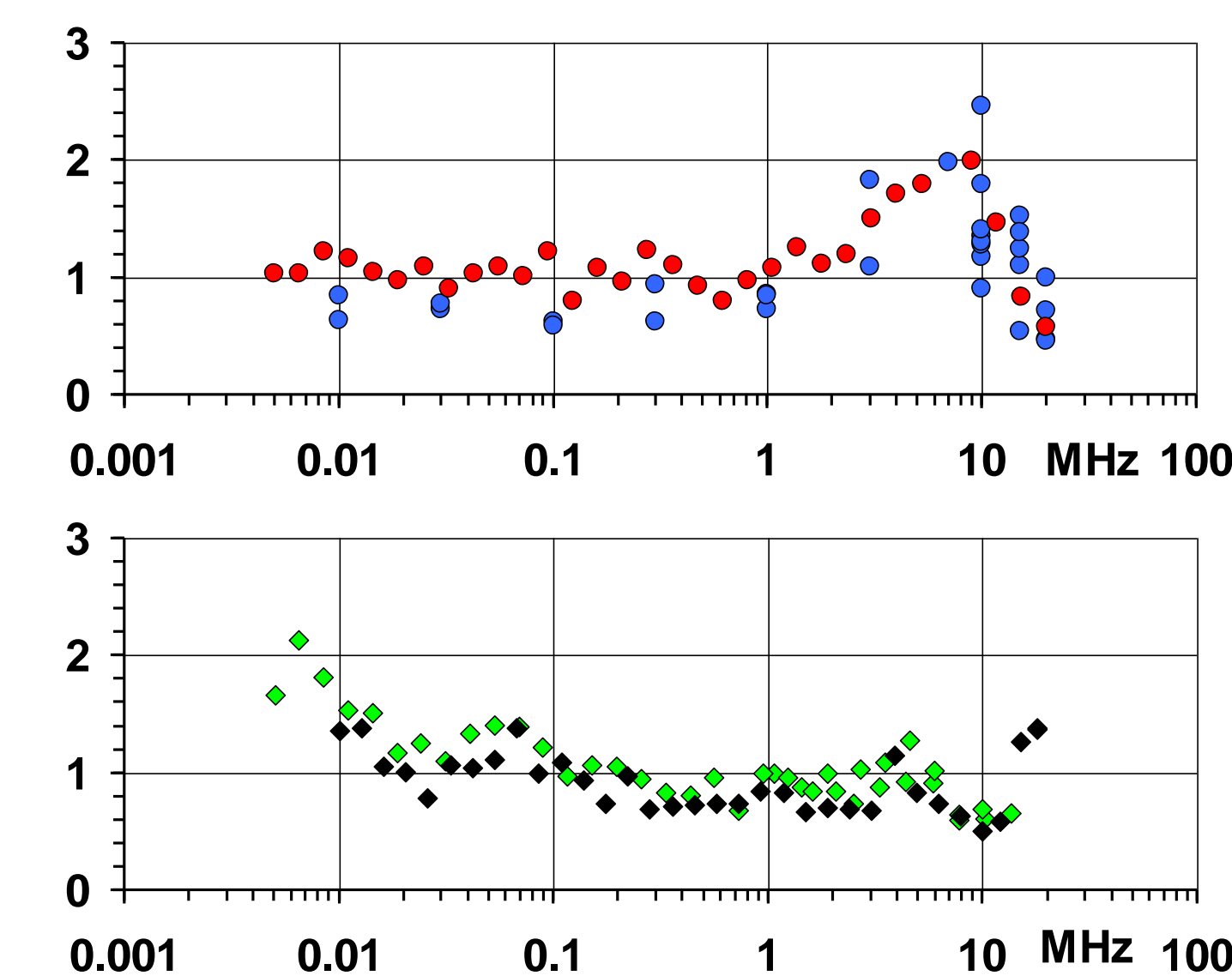


Fig.2. Percentual mono-exponential fitting errors

Sample I (above): Data acquired with 64 tau-value blocks (NBLK) and 8 scans (NS) per point. The polarization field (BPOL) in the PP/S sequence was 15 MHz. The switchover field between the NP/S sequence and the PP/S sequence was 4 MHz.
Sample II (below): Data acquired with: NBLK=32, NS=4, BPOL=10 MHz; other parameters as above.
All automated measurements were carried out using the switching time $\text{SWT}=1\text{ms}$ and the linear field-switching slew rate $\text{SLEW}=24 \text{ MHz/ms}$. In point-by-point, manually adjusted measurements, these two parameters were carefully optimized with a proper switching time calculated separately for every distinct switching interval.
In both samples, statistical analysis of the fitting residues did not reveal even a slightest hint of non-exponentiality. This is a bit surprising in Sample II because of its presumably composite nature (it indicates a very high degree of internal homogeneity and efficient spin diffusion).
In Sample I, individual FID's were completely dominated by field inhomogeneity (T_2^* of about 0.15 ms), while in Sample II they were perceptibly shorter (T_2^* of about 0.10 ms). All data were acquired with $\text{SW}=500 \text{ kHz}$ and $\text{FLTR}=120 \text{ kHz}$. Signal intensities were estimated by taking the average of the first 16 points of each FID.

Analysis

The reason for the difference is best explained using the examples of raw experimental data shown in Figure 4.

A sample with a flat profile and high R_1 relaxes fast during the whole duration of any switching interval. This dampens the differences in the acquired signal due to what happened before acquisition and results in data with possibly very good S/N but little variation of signal intensity S with respect to the delay τ (the upper three curves in Fig.4).

On the other hand, a sample which relaxes really fast only below, let's say, 1 MHz is not subject to the above problem at all during switching intervals which do not involve low field levels. Moreover, even when the switching does involve a very low field, the sample is exposed to it only for a small fraction of the switching time (maybe 10% or less) so that the detrimental damping effect is drastically reduced and the resulting $S(\tau)$ curves have nearly the same range as in much slower-relaxing samples.

Conclusion

From the analysis it is evident that the low-field fraction of the switching waveform is crucial and must be carefully controlled. In general, precise control of the switching waveforms is a sensitive issue when measuring samples with steep R_1 profiles which reach very high relaxation rates at low relaxation fields.

May 23, 2003.

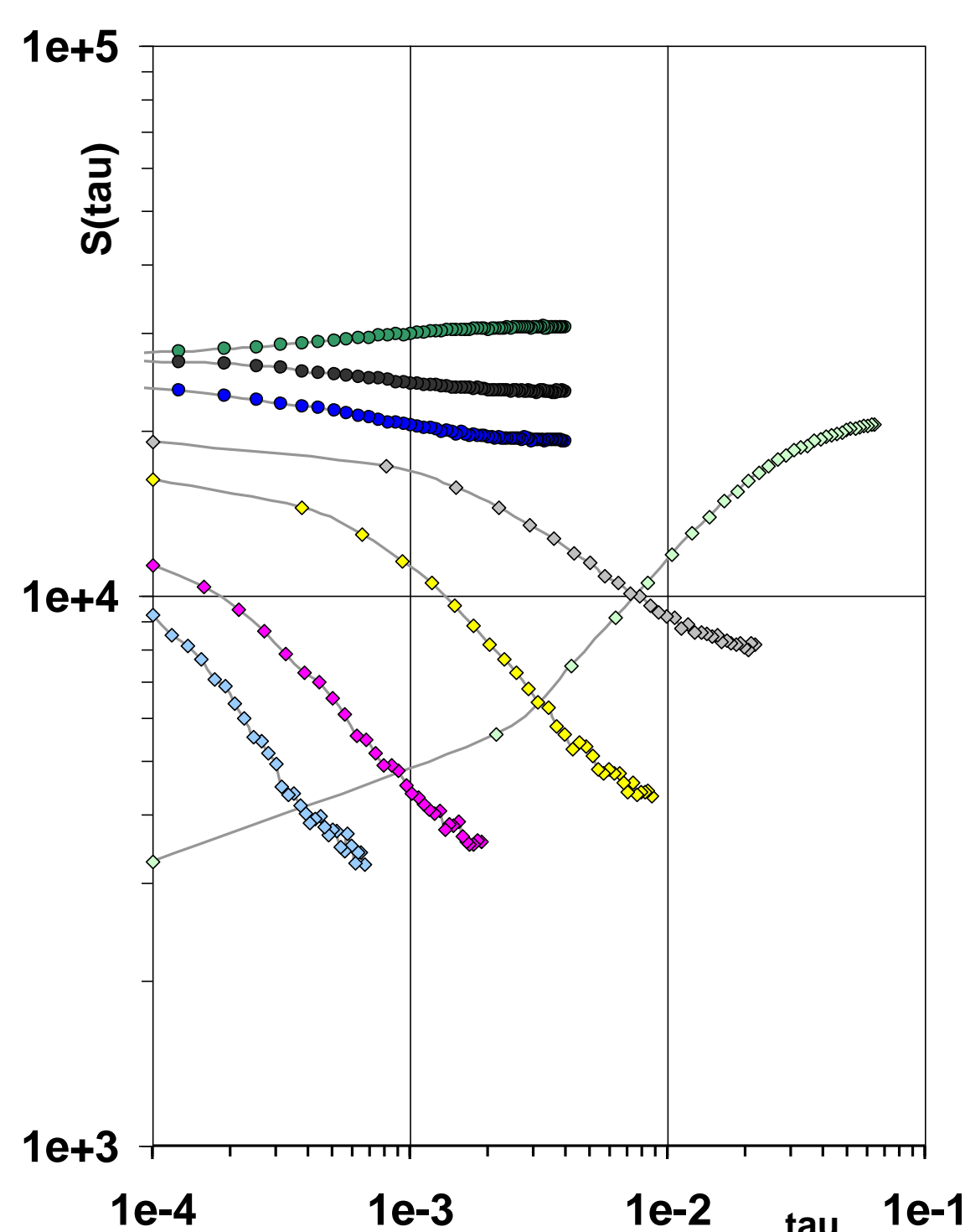


Fig.4. Signal-against-tau curves

Examples of the experimental curves $S(\tau)$ are shown here for both samples at several relaxation-field values. The somewhat uncommon log-log representation is best suited for the point to be made, though it "deforms" the exponential curves.
Sample I: Uppermost three curves (disks) measured at relaxation fields of 10 MHz (green), 3 MHz (black) and 10 kHz (blue). They give a clear idea of the severe "flattening" of the $S(\tau)$ dependence for samples of this type.
Sample II: The remaining five curves (diamonds) measured at 10 MHz (light green), 3 MHz (gray), 1 MHz (yellow), 100 kHz (violet) and 10 kHz (light blue). Despite the signal is less intense at its R_1 at low fields are higher than in Sample I, its $S(\tau)$ curves at all relaxation fields cover a much wider range of values and are therefore much more suited for the R_1 estimates.

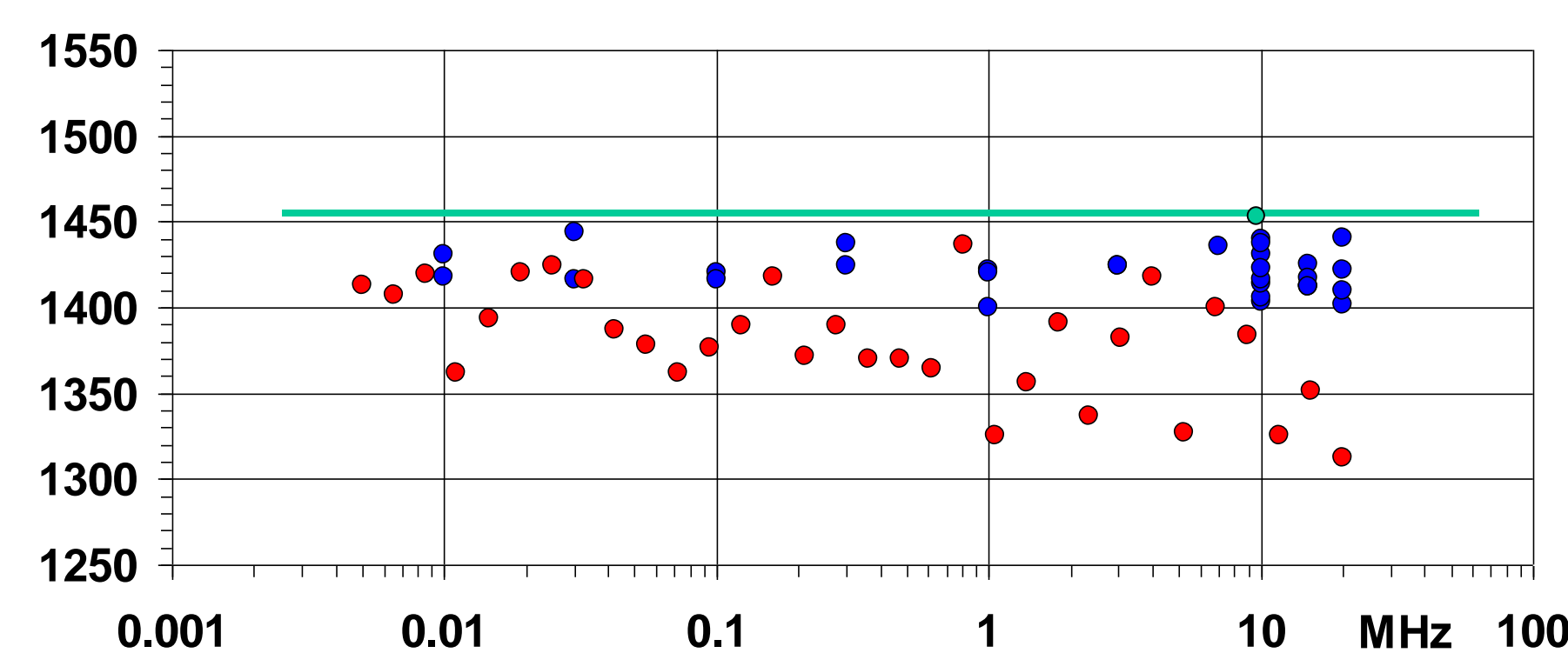


Fig.3. Expansion of the ^1H NMRD profile of Sample I

Red disks: Data acquired using the standard, automated profile.
Blue disks: Data acquired point-by-point, optimizing at each point the field-switching slew rate and switching period durations.
The single green point is the R_2 of the sample, measured at 9.15 MHz by means of the standard LR-CPMG sequence with 256 echoes and echo separation of 0.033 ms. The decay, accumulated over 2048 scans, was perfectly mono-exponential (fitting error 0.12%). The resulting R_2 value was 1455 with a probable error of 2. Since in this sample R_2 is presumed to be independent of the field, the horizontal green bar passing through the measured point represents the sample's presumed R_2 profile.