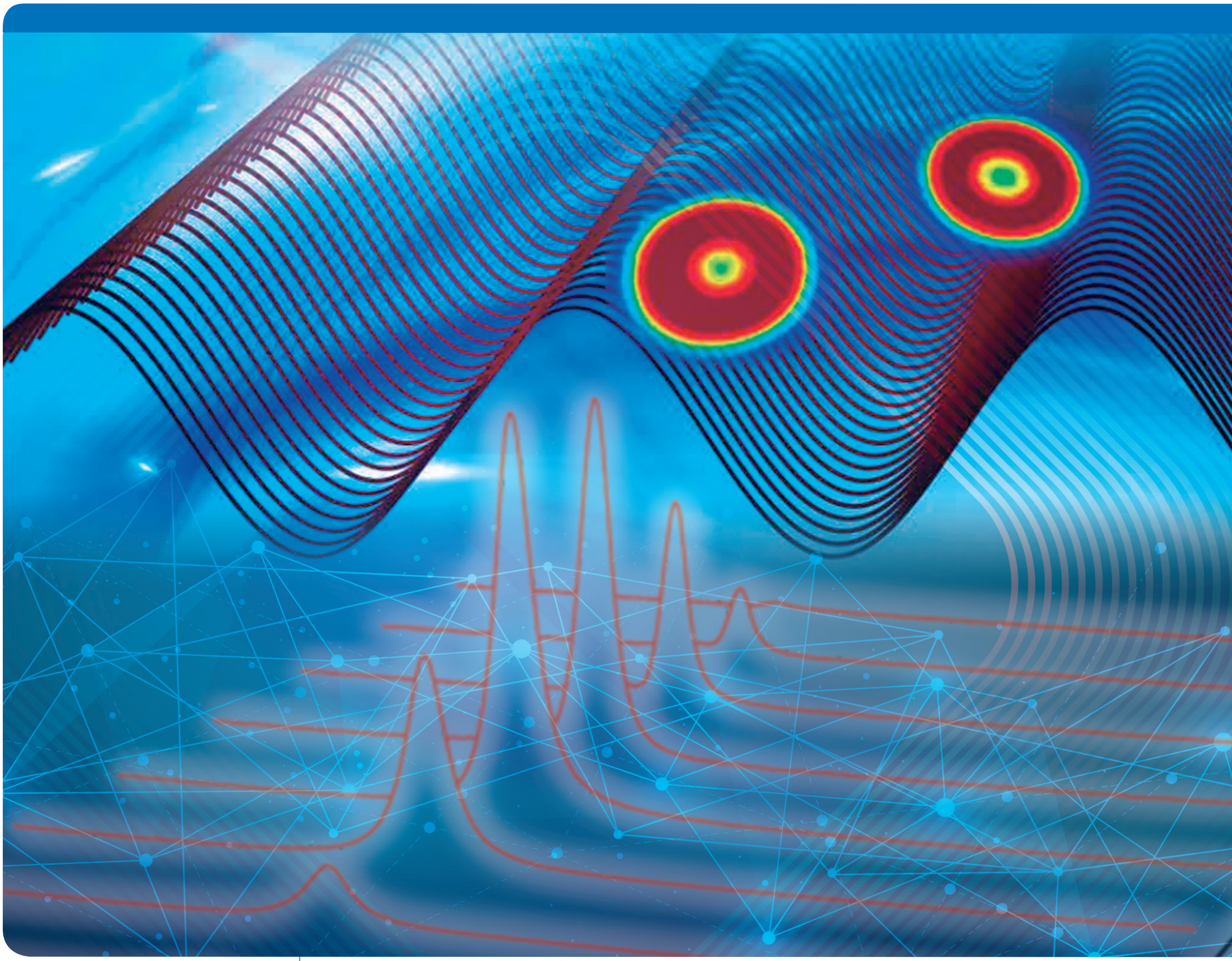


Rapid Scan – EPR

- A new era in sensitivity and time resolution

Innovation with Integrity

EPR

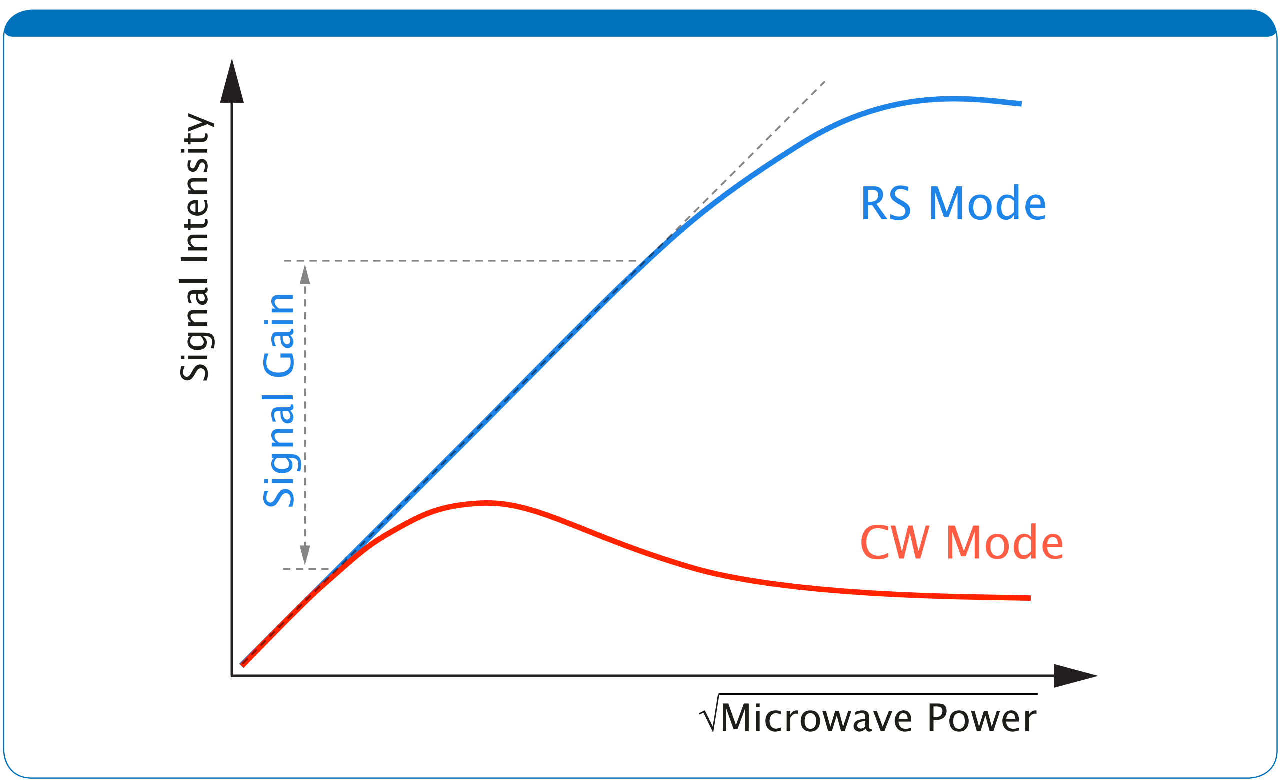
Rapid Scan EPR

Rapid Scan Electron Paramagnetic Resonance (RS-EPR) Spectroscopy is the next big step in EPR. RS-EPR is a revolutionary technique that opens new possibilities not previously available with conventional CW-EPR. With an increase in the signal to noise ratio and a decrease in the acquisition time, RS-EPR can probe very low concentrations and very fast reactions.

Rapid Scan EPR

- Direct detection
- Absorption line shape
- Scan rate up to 10 MG/sec
- Sweep width ≤ 200 G + segments
- Acquisition time per scan down to 10's of µs

- With field scan times as low as 10 microseconds, the full EPR spectrum of short lived species can be observed and the changes can be followed with unprecedented time resolution.
- Later onset of signal saturation allows higher microwave powers to be used. The increase in signal due to the higher power leads to the improvement in signal to noise.



EPR signal amplitude vs square root of power. In CW Mode the signal saturates at much lower powers than in RS Mode.

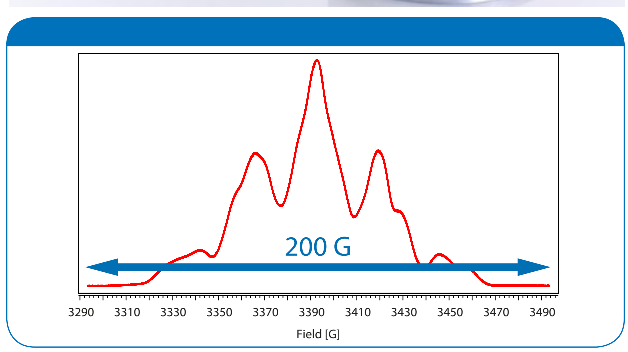
The Rapid Scan components :

1. Driver
2. Acquisition Unit
3. Resonator
4. MW Frontend with I/Q Detector
5. Coils
6. Water cooler for coils
7. Capacitor unit

Rapid Scan Coils

Scan field homogeneity	± 0.15% over cylinder Ø 4 mm, length 15 mm
Max scan rate	10 MG/s
Scan frequency range:	
Sinusoidal resonant scan	10, 20, 30, 50, 100 kHz
Triangular non-resonant scan	5-30 kHz
Max scan width :	
Sinusoidal scan	200 G @ ≤20 kHz 40 G @ 100 kHz
Triangular scan	60 G @ 5 kHz 10 G @ 30 kHz
Cooling	water
Mounting kit	easy to remove/insert coils

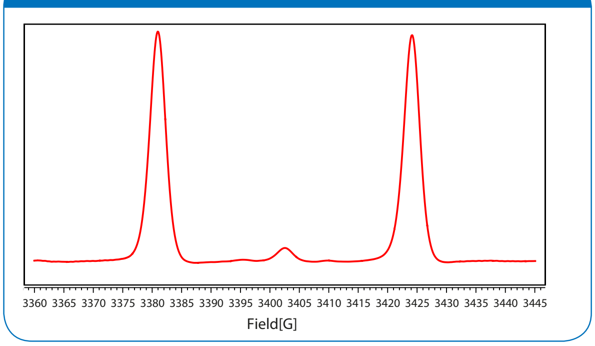
The RS coil capacitor circuit is a completely automated unit featuring both non-resonant and resonant modes with full software control of the capacitor switching. With the dedicated mounting kit, the RS coils are easily removed and reinserted into the magnet. The coils are water cooled with a maximum temperature of 40 °C while keeping the resonator sample space at an operational temperature of 18-22 °C.



Irradiated alanine measured with sinusoidal scan at 20 kHz.

Rapid Scan Resonator

Resonance frequency	9.5 GHz (empty resonator)
Q_L-value	500-6000 (at critical coupling)
Max sample access	Ø 8 mm
Automated matching	yes
Protection	Quartz sleeve insert
Variable temperature compatibility	Liquid nitrogen, helium and cryogen free



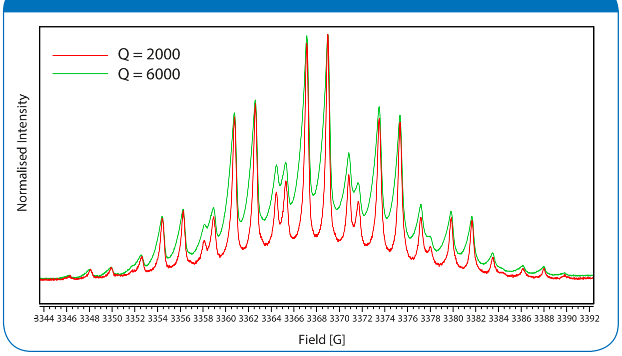
Rapid Scan for P doped Si measured at 5 K with 20 kHz sweep frequency, 126 G sweep width and scan rate of 5.0 MG/s.

The Rapid Scan resonator is completely transparent to the rapid scan field and fully compatible with both the helium and nitrogen variable temperature systems.

Phosphorus-doped silicon at room temperature is a conducting material and requires temperatures lower than 20 K to become resistive. Such low temperatures for CW-EPR on this material require low MW power due to the ease of saturation. RS-EPR benefits from the shift of saturation to higher MW powers resulting in an improved signal-to-noise under this conditions.

Adjusting the Bandwidth

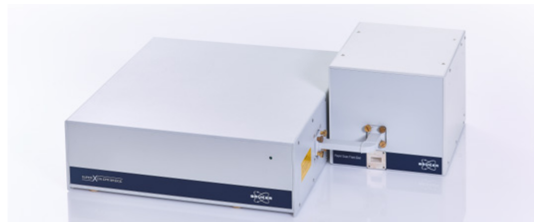
The Q-factor is an important parameter for sensitivity and bandwidth in EPR. Furthermore, in RS-EPR it also has an impact on the line shape. To account for this the Rapid Scan resonator has a variable Q with critical coupling over the full range.
The variation of linewidth with Q-factor is shown in the spectrum of the PNT sample with a Q of 6000 vs. 2000, where the linewidth resolution is higher at the lower Q.



PNT measured with sinusoidal scan at 20 kHz , microwave power of 20 dB and scan width of 70 G.
Peak-to-peak line width after 100 mG pseudo modulation (not shown): 180 mG (Q = 2000), 260 mG (Q = 6000).

Rapid Scan MW Front End and Acquisition Unit

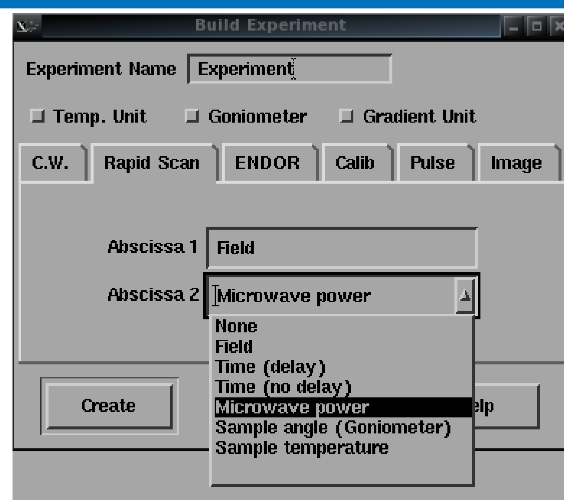
The Front End connects the resonator to the microwave bridge comprising the microwave I/Q detector and signal amplification.
The Acquisition Unit features a 14 bit 500 MS/s digitizer to record the I/Q RS signal.



Receiver	Quadrature
Bandwidth	> 100 MHz
Video gain	0-48 dB
Frequency lock	Automated

Experimental Flexibility

RS-EPR accessory is fully integrated into Xepr for control, acquisition and display covering the full range of experiments.



Rapid Scan Driver

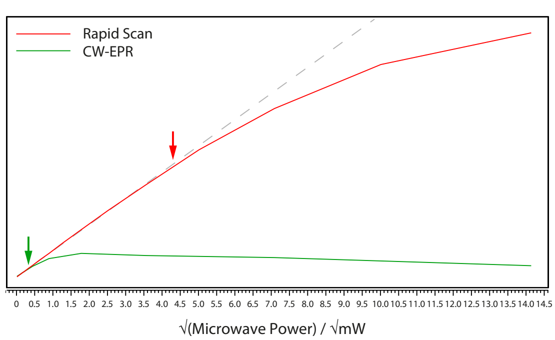
The RS Driver provides both a sinusoidal and a triangular waveforms with user selectable frequencies for resonant mode (sinusoidal) and non-resonant mode (triangular). The driver contains a power stage to drive the RS coils with scan widths up to 200 G.

Scan frequency range:	
Sinusoidal resonant	5 - 150 kHz
Triangular non-resonant	5 - 30 kHz
Outputs	trigger scan waveform coil current waveform driver output voltage
Inputs	scan waveform
Cooling	air

Increasing sensitivity by overcoming saturation limits

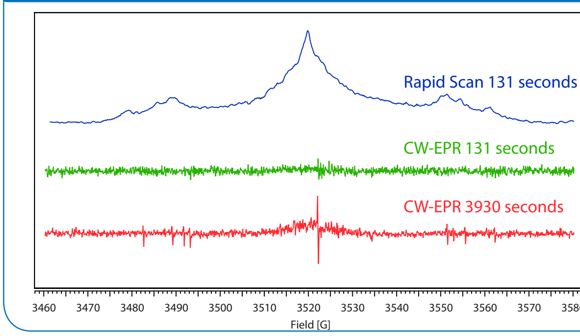
Single nitrogen substitution (P1) centers in diamond require very low microwave powers to obtain the correct CW-EPR spectrum. This in turn leads to very low signal amplitudes, thus long acquisition times. In RS-EPR, the saturation is shifted to higher powers leading to an increase in signal to noise and a decrease in measurement time. For 131 seconds acquisition time, the diamond spectrum is clearly visible in RS-EPR while no clear spectrum is present in the CW-EPR spectrum. Only after 3930 seconds is the diamond spectrum obtained in CW-EPR with reasonable signal to noise.

For a typical organic radical like irradiated alanine, the shift in saturation leads directly to an increase in signal-to-noise. In irradiated alanine, the saturation power is shifted from 0.2 mW in CW-EPR to 20 mW in RS-EPR. This gives an increase in signal-to-noise by a factor of 16 for the same acquisition time.



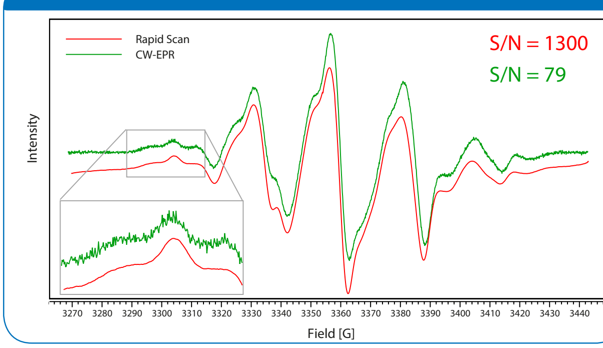
Saturation curves for irradiated alanine under RS-EPR conditions (red) and CW-EPR conditions (green). Arrows indicate the non-saturating powers where the spectra were recorded.

P1 center in Diamond



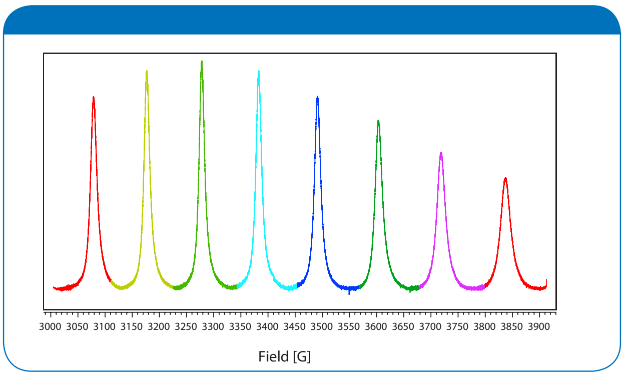
Single nitrogen substitution center (P1) in diamond.
Rapid Scan: P= 0.2 mW , Scan Freq. = 20 kHz, Scan Width = 120 G (7.5 MG/s)
CW-EPR: P = 0.2 uW , Modulation Amplitude = 0.1 G

Irradiated Alanine 0.3 kGy

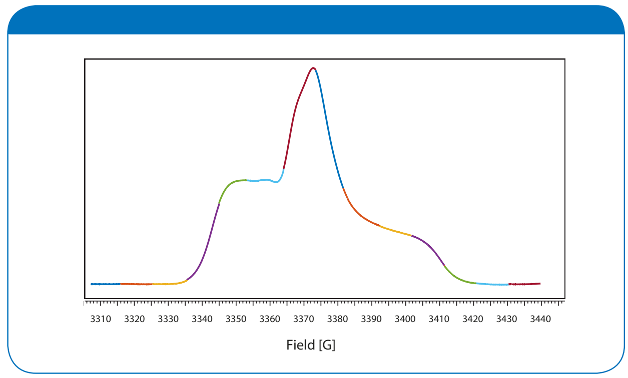


Irradiated Alanine (0.3 kGy) with 21 s scan time
Rapid Scan: P= 20 mW , Psuedo Modulation = 5 G
CW-EPR on EMXplus: P = 0.2 mW , Modulation Amplitude = 5 G

Rapid Scan Field Stepping
No limitation on spectrum width



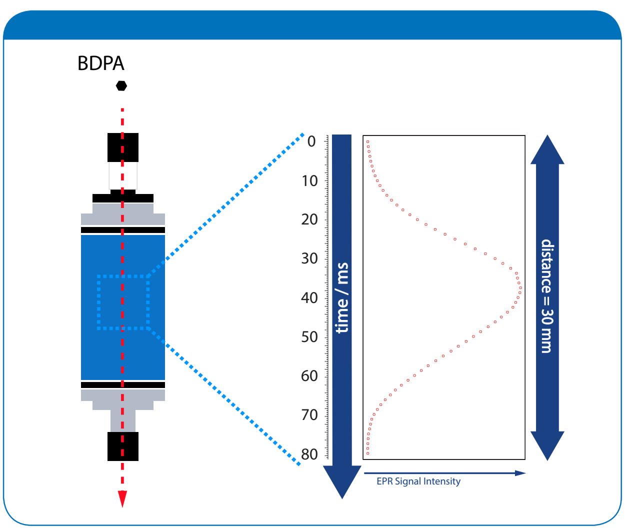
Vanadyl acetylacetonate in solution. 8 field segments of 150 G at 3 s per segment. Sinusoidal Mode with Scan Frequency of 20 kHz.

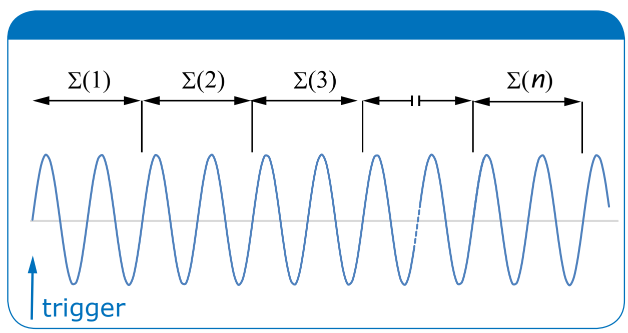


Nitroxide radical solid. 14 field segments of 26 G at 6.5 s per segment. Triangular Mode with Scan Frequency of 10 kHz.

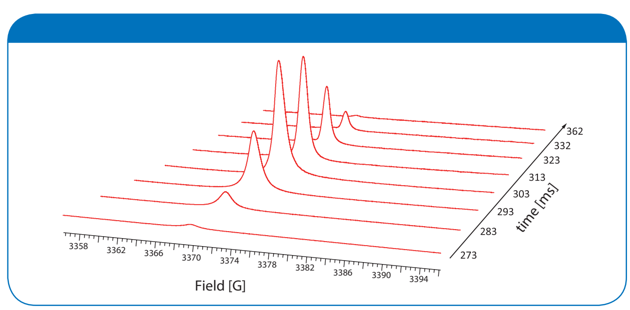
For cases where the EPR spectra are greater than the maximum RS scan width, a field stepping experiment is provided to acquire the full EPR spectrum in segments.

New window in time resolution
Checking gravity: Free fall of BDPA





The time resolution in the non-delay experiment is defined by the scan frequency and the number of cycles accumulated per time point.



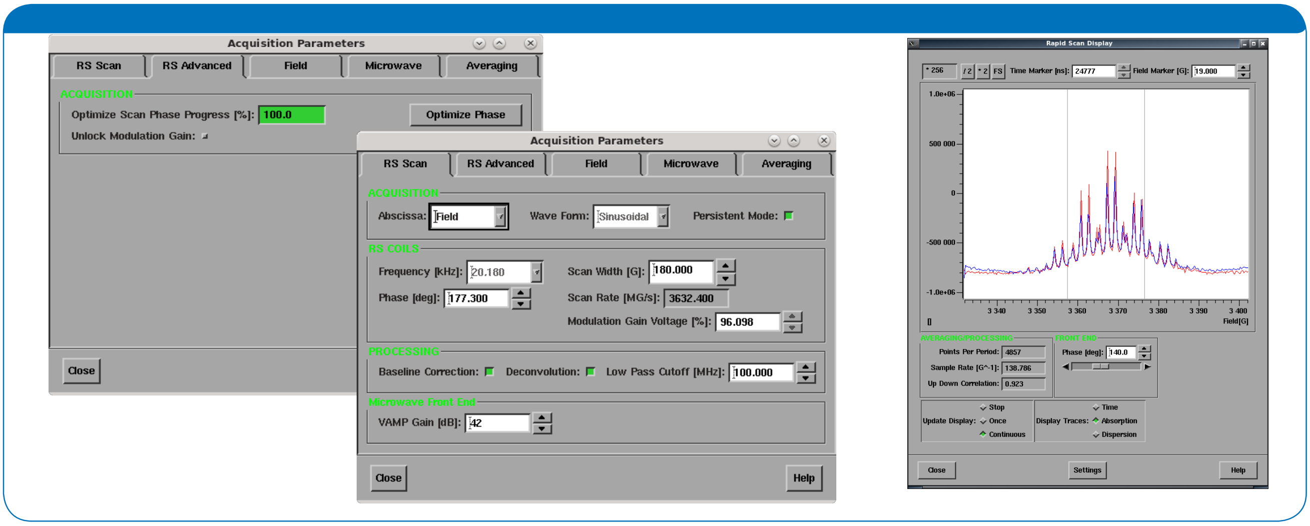
Selected time slices during free fall.
Scan Freq.: 20 kHz, Scan Width: 38 G, Time Window: 80 ms, Time Resolution: 1.25 ms

The free fall of a BDPA sample was followed by Rapid Scan measurement with a time resolution of 1.25 ms (25 accumulations). The falling sample was observed for a time of 80 ms, covering the distance of 30 mm. Distance (d) travelled by an object falling for time (t = 80 ms):

$$d = \frac{1}{2} g \cdot t^2;\ g = 9.81\ \mathrm{m\ s^2},\ d = 32.4\ \mathrm{mm}$$

Acquisition and Control Software

- Real time display of time-domain data.
- On the fly spectrum reconstruction.
- Software controlled waveform and frequency change.



Rapid Scan Accessory

- X-Band
- Compatible with 10 inch magnet ER073
- Available for
  - EMXplus
  - ELEXSYS

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