The EPR Spectrometer

Microwave band	Frequency/ GHz
S	3.0
X	9.5
K	23
Q	35
W	95

X-Band spectrometer Bruker

https://www.weizmann.ac.il/chemphys/EPR_group/x-band-95-ghz-pulsed-epr-

EPR Course

Series of EPR Lectures given by Prof. Daniella Goldfarb, recorded by the Australia and New Zealand Society for Magnetic resonance at the EPR Workshop in 2014.

https://www.weizmann.ac.il/chemphys/EPR_group/epr-course

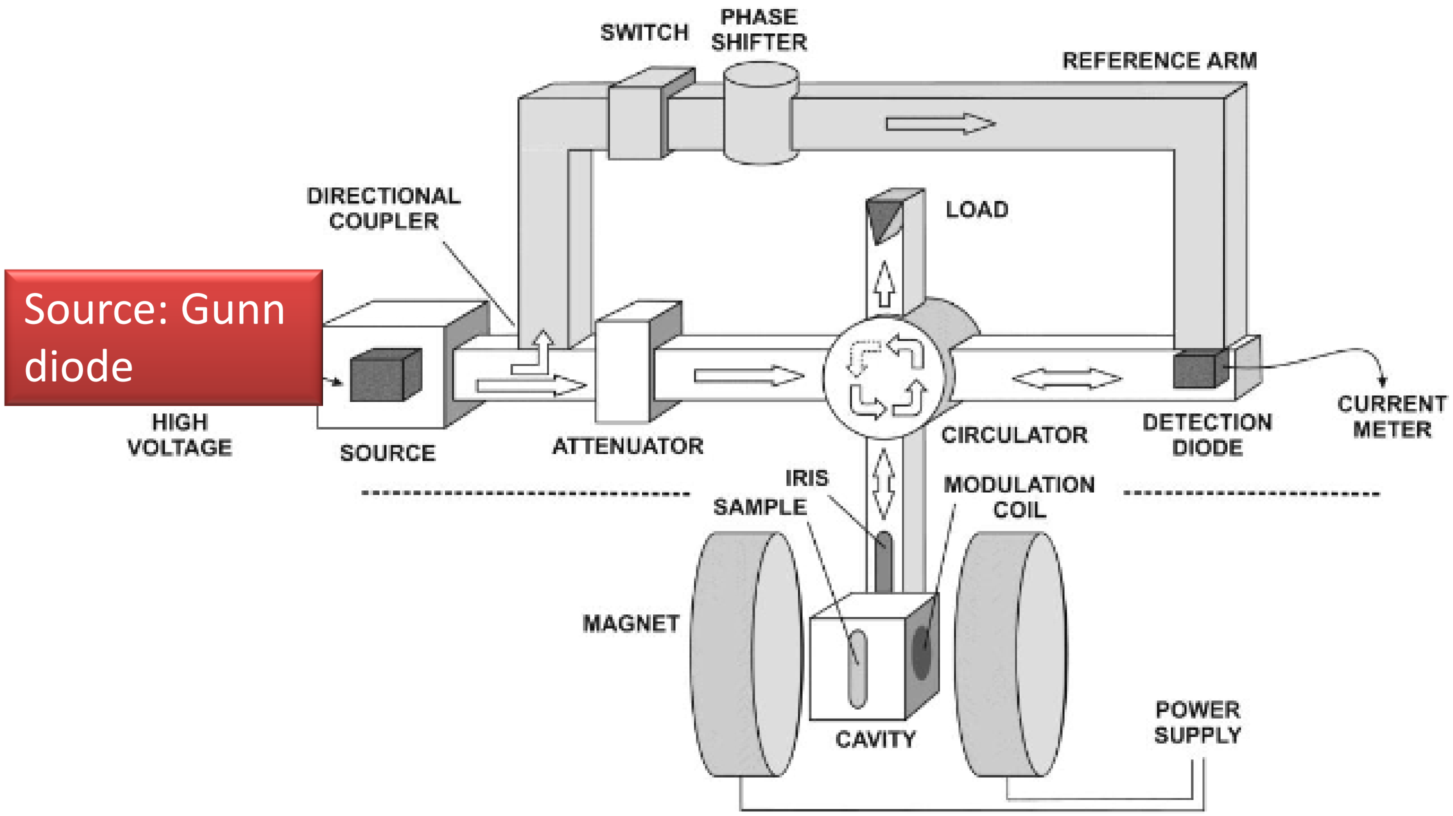


Fig. 2: Flow of the microwaves in the EPR spectrometer (Adapted from Hagen, W.R. (2009) *Biomolecular EPR Spectroscopy*).

The parts above the dashed lines are all hidden inside the Microwave Bridge box.

https://www.auburn.edu/~duinedu/epr/2_pracaspects.pdf

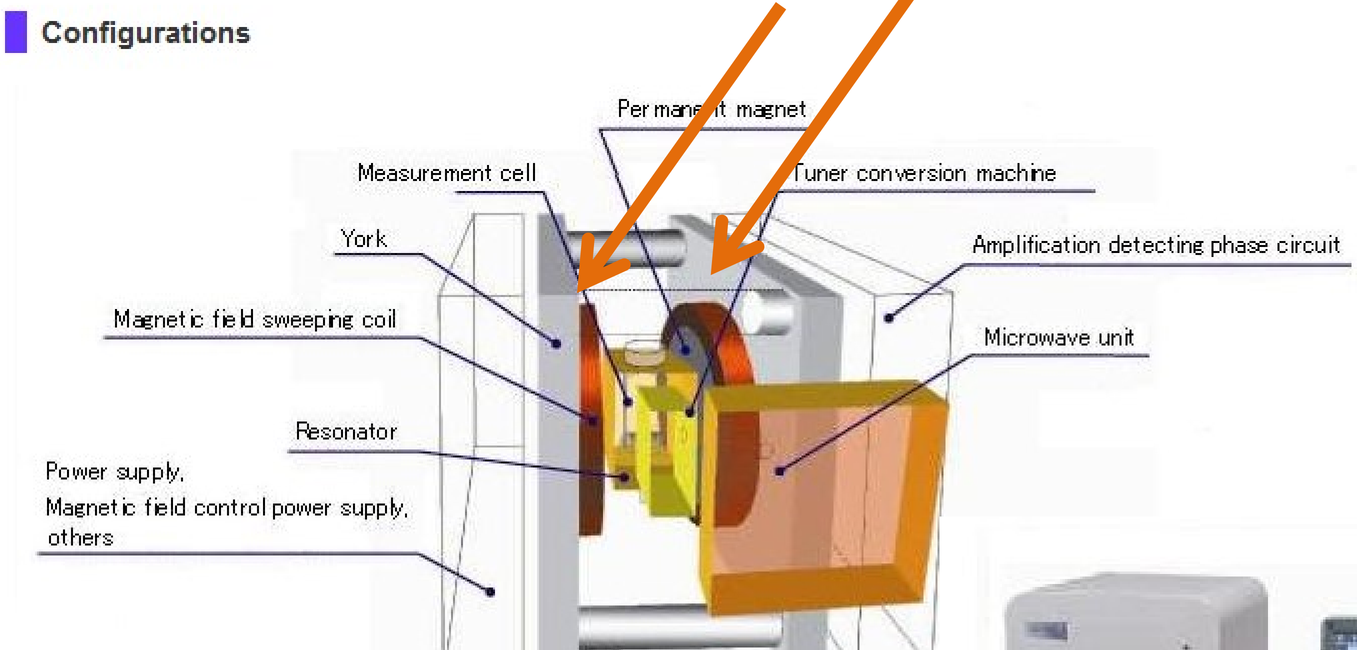
Magnet

A free e- resonate at the X-band in a field of 3400 G.
Higher fields are required for lower g.
A versatile X band EPR spectrometer has an **electromagnet** that can be scanned from 0 to 6000 G
Contrary to NMR fine tuning of the field, or shimming, is not required.

Bechtop EPR: Bruker EMX Nano

No prior EPR experience needed
Video how-to guide
Startup kit
Superior sensitivity and stability
Accurate results
Ease to use software

https://www.bruker.com/products/mr/epr/emxnano/technical-details.html rare earths permanent magnet



http://www.keycom.co.jp/eproducts/esr/esr04/page.html

Desktop EPR

weight 27 Kg

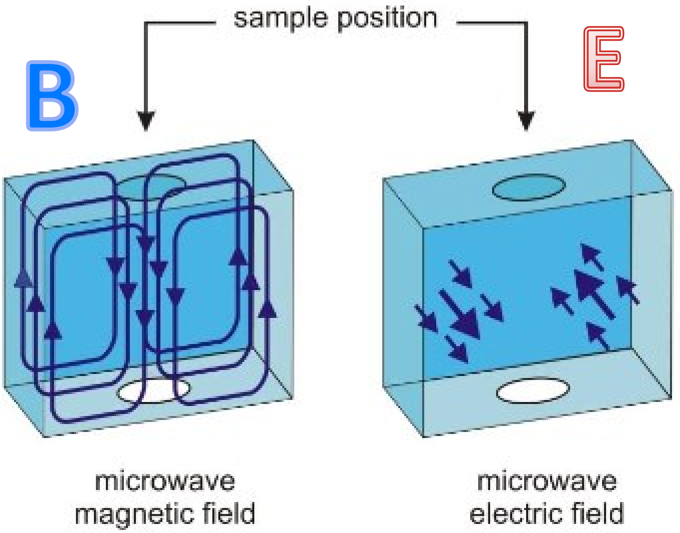
microESR: The Portable ESR Spectrometer

micro ESR Bruker

The microESR is a small, portable research grade instrument. The spectrometer has a mass of only **10 kg** and a 30.5 x 30.5 x 30.5 cm^3 foot print. It can easily fit in a fume hood or glove box, or be transported to the field. It requires no special installation or regular maintenance.

Operating Frequency: X-Band
Continuous Wave
Field Sweep Range: 500 G centered at g=2
Spectrum simulation and fitting
Easily run samples at liquid nitrogen temperature

Microwave Cavity



A microwave cavity is a metal box with a rectangular or cylindrical shape which resonates with microwaves

Standing electromagnetic waves have their electric and magnetic field components exactly out of phase where the B is maximum, the E is minimum and vice versa. The place where the sample is situated has a minimum E and maximum B.

https://www.auburn.edu/~duinedu/epr/2_pracaspects.pdf

The quality of the cavity system is defined through the unloaded **quality factor Q_0** of the microwave cavity.

$$Q_0 = \frac{v_{res.}}{\Delta v}.$$

Effectively Q_0 is found by measuring the position of the resonance frequency $\nu_{res.}$ and the width $\Delta\nu$ of the absorption signal at half it's height

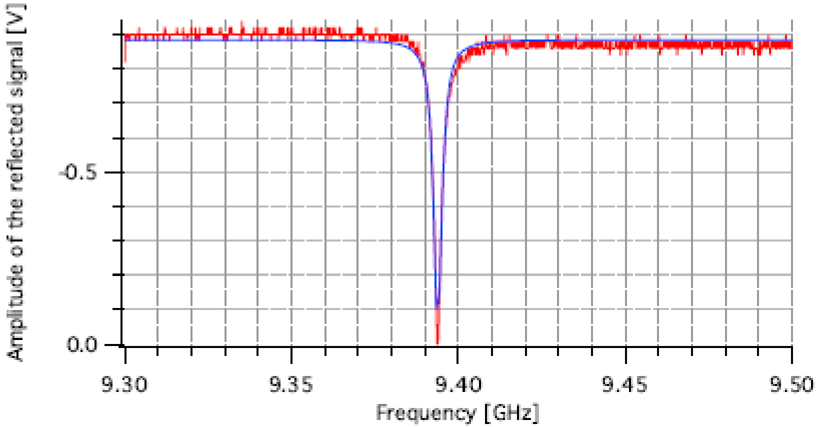
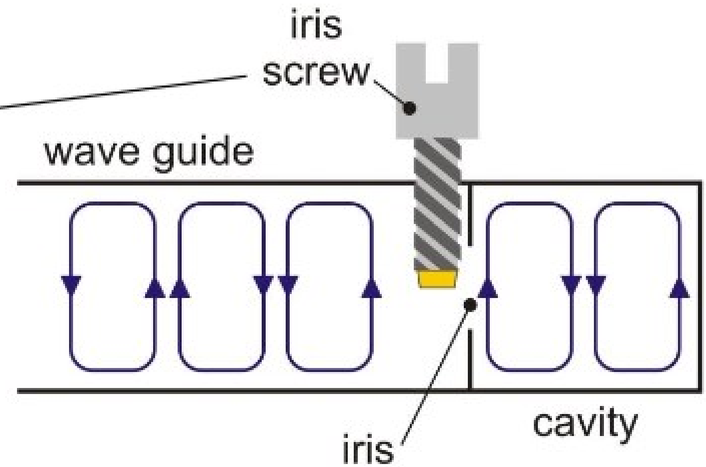


Figure 3: Reflected signal for a MW frequency scan to find the resonance position of the cavity.

The 'dip' is the result of the loss of reflected waves at the resonance frequency of the cavity.

Iris

Vincent van Gogh, May 1890



wave guide: metal tube of rectangular cross-section

Turning the iris screw causes the iris to become larger and smaller.

Only at one position is the cavity **critically coupled**.

This position will be different, however, with different samples and different temperatures.

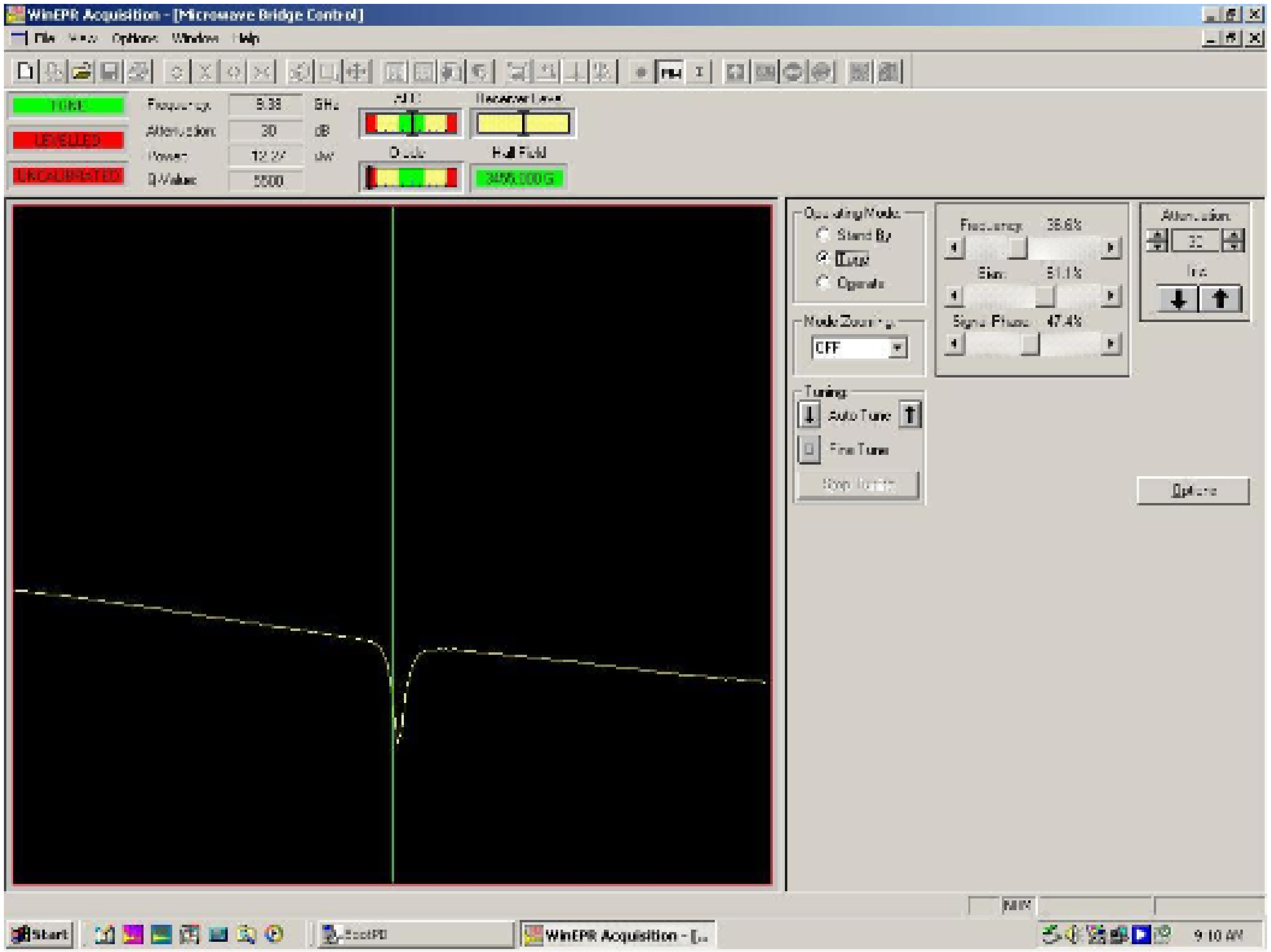


Fig. 6: Screen shot of the EPR computer during the tuning process.

The basic set-up consists of an electro-magnet for B_0 and a MW generator (once klystron, now **Gunn diodes**)

The MW are guided through w**ave-guides** (metallic, hollow tubes), which allow only single modes.

To optimise the EPR absorption, a resonator (**cavity**) is used. The MW are guided into the resonator where they are reflected from the walls, forming a standing wave. The MW reflected out of the cavity is detected with e.g. a **shottky-diode**.

The dimensions of the cavity therefore have to be adjusted, such that at a certain MW frequency no signal is reflected out of the chamber anymore. Figure 3 shows the reflected signal of the cavity for a frequency sweep. The resonance frequency, where no MW is reflected out of the chamber anymore is visible as the dip in that scan. The adjustment process to find this resonance frequency of the cavity is called matching and tuning.

For the EPR spectrum of a sample in the matched and tuned cavity, the MW frequency is kept constant, while **B_0 is swept**.

The sample absorbs MW energy at the field corresponding to the resonance condition

The **absorption** changes the cavity impedance and therefore the couplingcondition of the cavity. As the cavity at B_0 resonance (hv) is now no longer critically coupled, **MW is reflected out of the cavity**. However, this absorption induced reflection-signal is very small.

Therefore, we measure the derivative signal with a Lock-In detector by additional B-field variation coils which induce a sinusoidal field parallel to B_0.

Detection

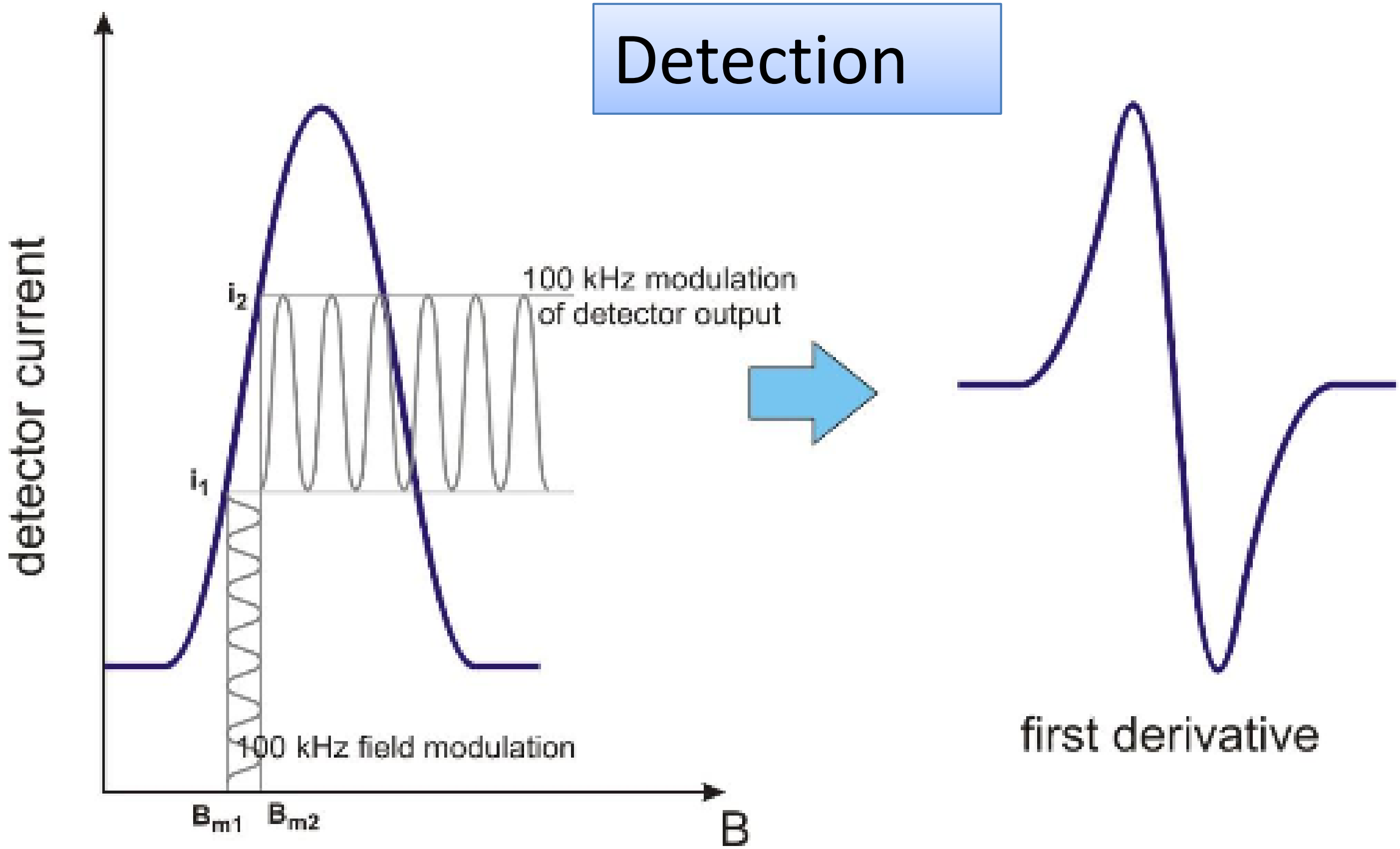


Fig. 8: Schematic representation of phase sensitive detection. As the main field is scanned slowly through the EPR line, a small additional oscillating magnetic field, B_m, is applied in the same direction as the main field B. B_m is commonly at 100 kHz. As B_m increases from the value B_{m1} to B_{m2}, the crystal detector output increases from i_1 to i_2. If the magnitude of B_m is small relative to line width, the detector current oscillating at 100 kHz has a peak-to-peak value that approximates the slope of the absorption curve. Consequently, the output of the 100 kHz phase-sensitive detector is the derivative of the absorption curve. Adapted from Eaton, Eaton, Barr and Weber (2010).

The EPR Spectrum

There are two parameters associated with the phase sensitive detection: **modulation amplitude**,
and
modulation frequency.
These parameters have to be chosen wisely.
With more magnetic field modulation, the intensity of the detected EPR signals increases; however, if the modulation amplitude is too large (larger than the linewidths of the EPR signal), the detected EPR signal broadens and becomes distorted

For measurements at X -band frequency, the modulation frequency is normally set to 100 kHz.

microwave power level

The EPR signal intensity grows as the square root of the microwave power in the absence of saturation effects. When saturation sets in, the signals broaden and become weaker. Several microwave power levels should be tried to find the optimal microwave power.
Also the gain can be varied

The EPR Spectrum
basic features

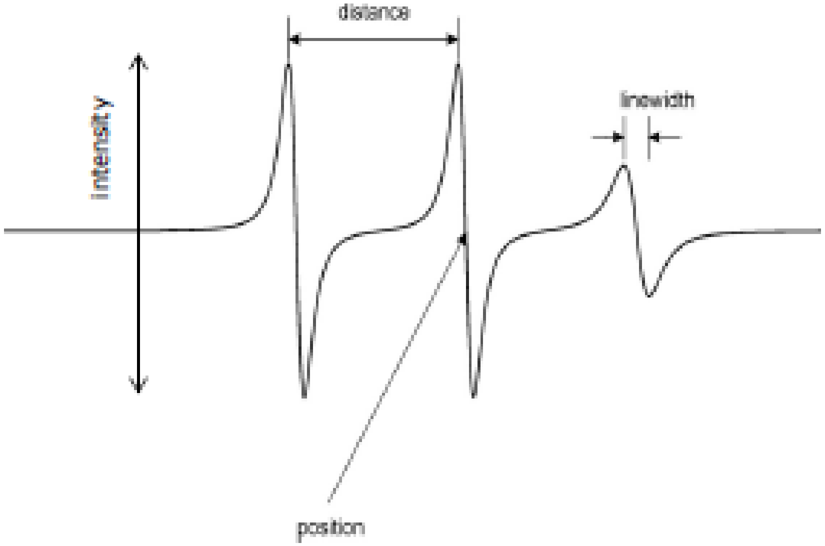
- Detection: First derivative

Fingerprinting

- Position in Field
- Splittings
- Lineshape and Width

Quantification

- Intensity changes
- Shape changes



SpinCount

quantitative EPR at your finger tip