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# RF technique and Electron-Paramagnetic Resonance (EPR)

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# 1 Theoretical Background

## 1.1 EPR

Electron paramagnetic resonance (EPR), also known as electron spin resonance, is a spectroscopy method used to study materials with unpaired electrons. These paramagnetic substances are placed in a magnetic field and radiated with microwaves (GHz-range). Through EPR spectroscopy we can gain information about the substance's structure and it's dynamics. EPR is quite similar to nuclear magnetic resonance (NMR); however NMR deals with nonzero spin nuclei instead of unpaired electrons.

## 1.2 Zeeman effect

An electron is a charged particle which spins around it's axis. Upon applying an external field to a paramagnetic substance, the electron's spin of the unpaired electrons can align either parallel or antiparallel to the direction of the applied magnetic field, resulting in a spin states of  $m_s = \pm \frac{1}{2}$ . These alignments correspond with different energies and therefore lift the degeneracy of the electron spin states. The energy difference between those levels is given by:

$$\Delta E = g\mu_B B$$

where  $B$  is the external magnetic field,  $\mu_B$  the Bohr magneton and  $g$  the g-factor. The g-factor is also known as the Landé factor and gives a relation between the magnetic moment and the angular momentum of an electron system. For a free electron  $g = 2.0023$ .

The electron's spin and it's charge create a magnetic moment for the electron. The splitting of energy levels due to a magnetic field interacting with the magnetic moment of the electron is known as the Zeeman effect. A diagram showing the Zeeman splitting is shown below.

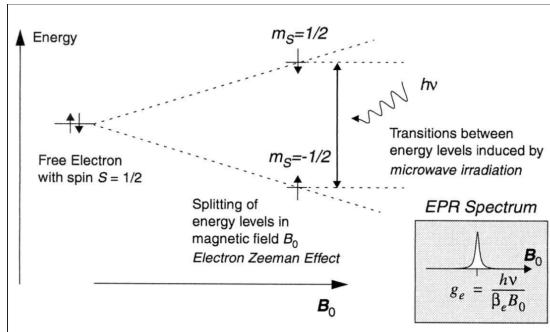


Figure 1: Zeeman Splitting [6]

## 1.3 Resonance Condition

Electrons can change in between energy levels through absorption and emission of photons, given that they posses an energy of  $\Delta E$ . This results in the resonance condition

$$\Delta E = h\nu_0 = g\mu_B B \quad (1)$$

which is the fundamental equation for EPR.

## 1.4 EPR spectrum

Typically, to obtain an EPR spectrum, the microwave frequency is kept constant and the external magnetic field is varied until the resonance condition is met. The typical EPR spectrum is the first derivative of an absorption peak. The derivative signal can be positive or negative. This is irrelevant to the interpretation since one is simply the mirror image of the other.

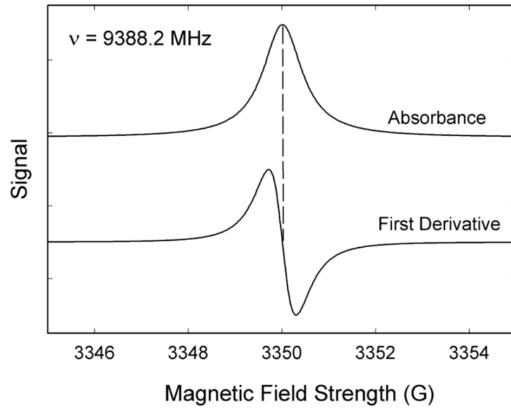


Figure 2: EPR spectrum [7]

## 1.5 RF techniques

For EPR measurements radiation in GHz range is used. For the purpose of this experiment, it is advise to know about important RF techniques. In the following we will discuss two of the most important techniques, frequency modulation and frequency mixing, in more detail.

### 1.5.1 Frequency modulation

Modulation is a RF technique in which a periodic waveform is modified using another waveform. Through frequency modulation a given RF "carrier" signal (sine wave) can be varied in frequency, depending on the "modulation" signal. This technique can come in useful when trying to separate a RF signal from other RF signals in the spectrum. It's most common use is in radio-broadcasting, so we can listen to a specific radio station without interference from the other signals in the whole RF spectrum.

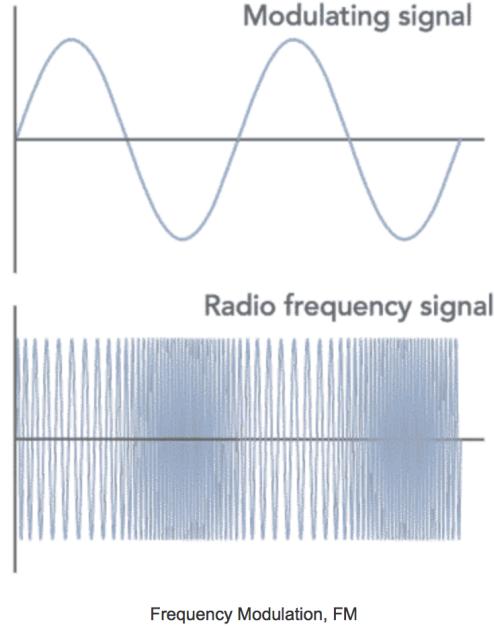


Figure 3: Frequency modulation [5]

### 1.5.2 Frequency mixing

Mixing is a RF technique in which multiple signals are mixed together to form an additional signal. For example if signals at frequencies of  $f_1$  and  $f_2$  enter a mixer, then additional signals at frequencies of  $(f_1 + f_2)$  and  $(f_1 - f_2)$  appear at the output.

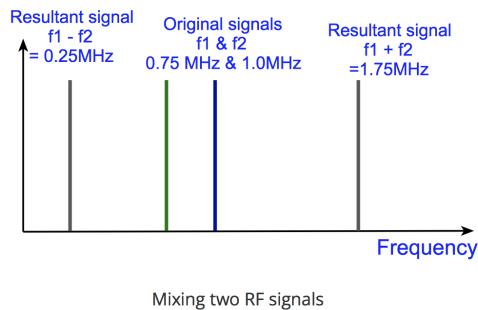
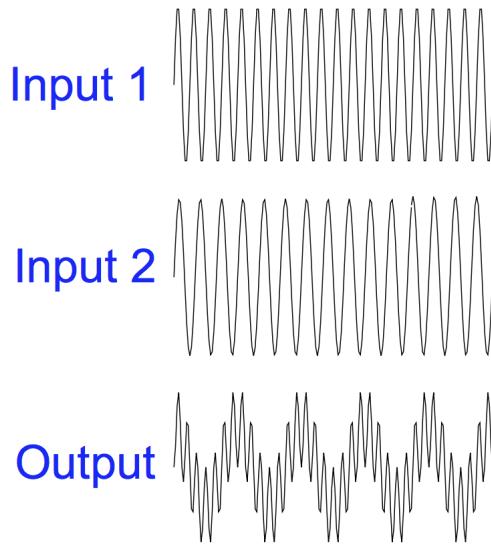


Figure 4: Frequency mixing [4]

The input signals can be modelled by sine waves. The immediate output level depends on the multiplication of the immediate levels of signal A and signal B. The output waveform takes a more complicated shape if all the points along the curves are multiplied. A schematic is shown below:



Mixing or multiplying two signals together

Figure 5: Signal mixing [4]

## 1.6 Materials

EPR measurements focus on substances such as:

- free radicals in solid state materials, liquids or gases
- paramagnetic transition metal ions

In this experiment we used DPPH and Ultramarine in different concentrations as samples. They are described further in the following.

### 1.6.1 DPPH

Diphenyl-Picryl-Hydrazyl (DPPH) is a common used material for EPR measurements. It is a crystalline powder of dark color and has an unpaired electron. Its g-factor is  $g = 2.0036$ , which is pretty close to the g-factor of an electron.

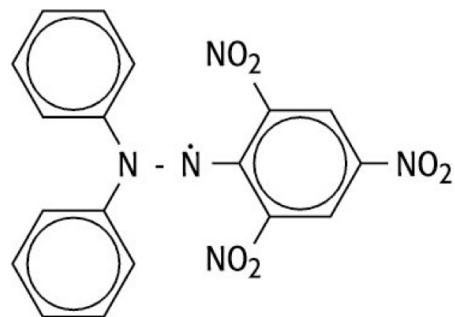


Figure 6: Structural formula of DPPH [1]

### 1.6.2 Ultramarine

Ultramarine (UM) is another commonly used substances for EPR measurements due to it's strong paramagnetic characteristics. The paramagnetism arises from the sulfur radicals, whose structure is largely unknown. The chemical formula of ultramarine is  $Na_{8-10}A_{16}Si_6O_{24}S_{2-4}$ . It's g-factor is  $g = 2.0290$  and therefore differs strongly from  $g = 2.0023$ , the g-factor of an electron.

## 2 Experimental set-up / Methodology

In an EPR measurement the absorption of microwaves in different samples for a slowly varying magnetic field is measured. The microwave frequency is usually kept constant and the external magnetic field is swept. Important elements of an EPR set-up and their workings are described below.

### 2.1 Microwave bridge

The microwave bridge is responsible for the generation of microwaves and the detection of the EPR signal. It can be seen in more detail in figure 7. The set-up consists of a klystron, an attenuator, a circulator and the sample cavity resonator. The klystron is a vacuum tube that is responsible for creating the microwaves. In this experiment, a X-band frequency range was used. The microwaves then travel into an attenuator where the microwave power is adjusted. The attenuated microwave power is then guided through the circulator into the sample cavity, which is surrounded by a pair of Helmholtz coils. The resonant sample cavity acts as a tuned circuit. It has a very high Q ( $\approx 5000$ ), where Q is defined as follows:

$$Q = \frac{\omega \cdot \text{Energy stored}}{\text{Power dissipated in cavity}}$$

At the sample resonance, the impedance of the cavity changes and consequently a signal is reflected. The circulator directs that reflected energy back to a detector.

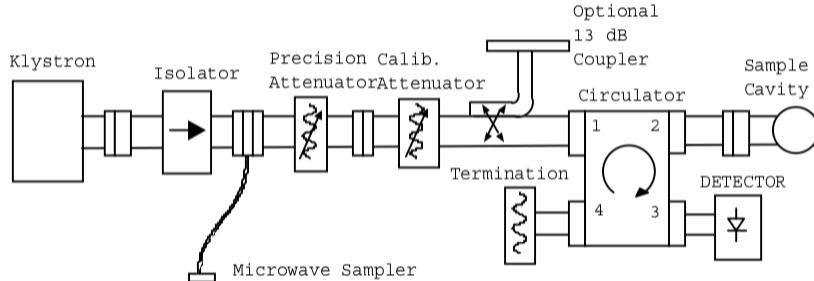


Figure 7: Schematics of a microwave bridge taken from [2]

### 2.2 Magnet system

The sample is placed at the position of the highest magnetic field  $B_1$  and perpendicular polarized to the main field direction,  $B_0$ . As the field  $B_1$  is linearly polarised, it can therefore be represented by the sum of two fields rotating in opposite directions. One of the field components is therefore rotating in the same direction as the precessing spins. This means it will be in resonance and may cause transitions. The other component is rotating in the opposite direction, which is out of phase and does not affect the spin system.

### 2.3 Magnetic field sweep and field modulation system

As mentioned before, the microwave frequency is kept constant and the external magnetic field is swept through the resonance condition. The sweep gives a resonance if the fixed cavity fre-

quency corresponds to the splitting of the energy levels. In order to amplify the EPR signal, a high frequency modulated magnetic field is superimposed on top of the slow swept magnetic field. Additionally, this eliminates most of the noise and enhances spectral resolution. The improvements arise from the sample responding to the modulated magnetic field and the amplitude of the signal changes as a result. It now corresponds to the difference in absorbed energy in the resonator cavity. The noise is filtered out of the measured signal as the phase and frequency of the signal is known.

The high frequency modulation is applied using small coils, which are placed on each side of the cavity walls along the axis of the static field. Typically a frequency of 100 kHz is used.

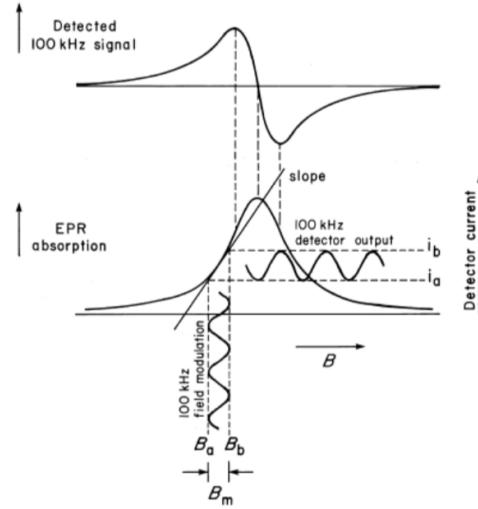


Figure 8: Result of field modulation with 100 kHz [2]

It is best to keep the modulation amplitude smaller than the resonance line width. This results in the detected 100 kHz signal being proportional to the slope of the absorption curve. Therefore, at resonance (corresponding to the zero curve) the 100 kHz component at the detector is zero. Similar, the maximum slope occurs at the inflection point where the output signal is also maximum. The polarity of the output signal of the phase-sensitive detector is determined by the sign of the slope. Therefore, for small modulation amplitudes, the output signal approaches the first derivative of the absorption signal. If higher modulation amplitudes which are closer to the value of the line width are used the line shapes get distorted.

## 2.4 Low-Noise Block

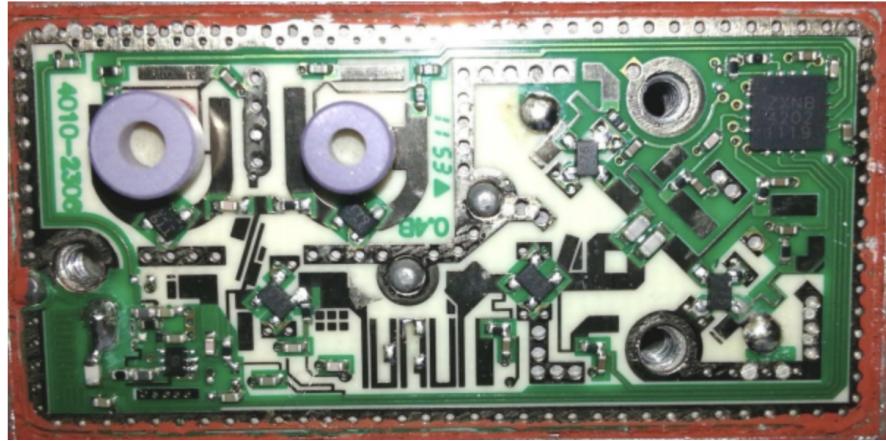


Figure 9: Picture of a Low-noise-block taken from [2]

The low-noise block (LNB) also known as modified low-noise block down converter is used for the EPR measurements on the DPPH and ultramarin samples. Typically, a LNB is a combination of a frequency mixer, local oscillators and a down converter. It usually also includes a low-noise amplifier which amplifies a low-power signal while keeping approximately the same signal-to-noise ratio.

A picture of the LNB used is given above in figure 9. Here, the two violet ring cylinders that can be seen in figure 9 are two local oscillators (LO). The two LOs each generate a frequency. One LO generates a frequency of 9.75 GHz, the other of 10.6 GHz. The two frequencies are mixed by a mixer, producing the sum and difference frequencies of the two local oscillators. Only the signal at the difference frequency is considered. The resulting frequency is then put through a down converter. Because of the down converter the frequency is shifted and therefore only ranges around 800 MHz at the output. The samples are applied to the dielectric resonator with the 10.6 GHz frequency, which in figure 9 is the smaller violet ring cylinder on the right. Now, the dispersion signals can be measured.

### 3 Task 1

#### Frequency mixing and modulation

One frequency was set to 2MHz, while the other frequency was varied around a low frequency value. The behaviour was then observed and documented below.

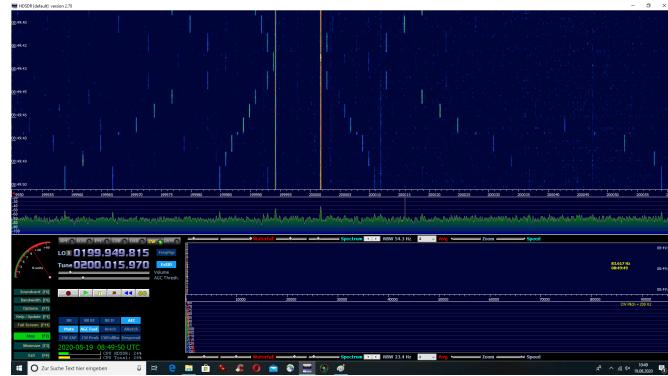


Figure 10: Screenshot of the Software

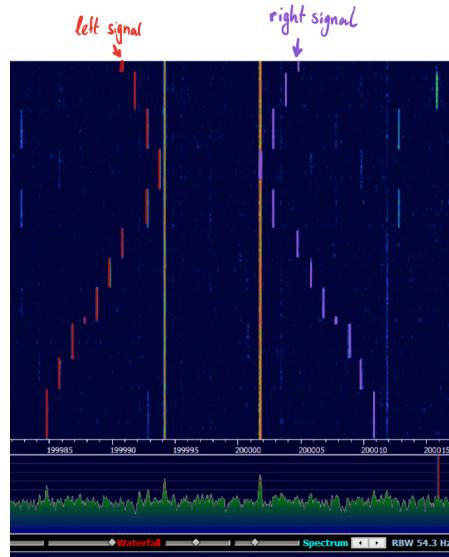


Figure 11: Figure 10 zoomed in and signals marked

In the following the discussion of the picture will focus on two of the signals only, The red colored signal will be referred to as "left signal", the purple colored signal as "right signal". It can be seen that varying the second frequency changes the locations of the additional appearing signals. One of those signal should appear at  $(f_1 + f_2)$ , the other one at  $(f_1 - f_2)$ . When the second frequency was turned down, the left signal shifts towards the right. Turning the second frequency back up, the signal's location shifted back towards the left. The right signal showed

opposite behaviour. Therefore the conclusion of the left signal being the one corresponding to  $(f_1 + f_2)$  can be drawn. Similarly the right signal corresponds to  $(f_1 - f_2)$ .

In Figure 9 one can observe additional signals, exhibiting similar behaviour as described above. This is due to the fact that in frequency mixing, signals of integer combinations of the two provided signals can appear, e.g.  $(f_1 + 2f_2)$ .

The two major straight lines in the center appear already if only the 2MHz frequency is turned on.

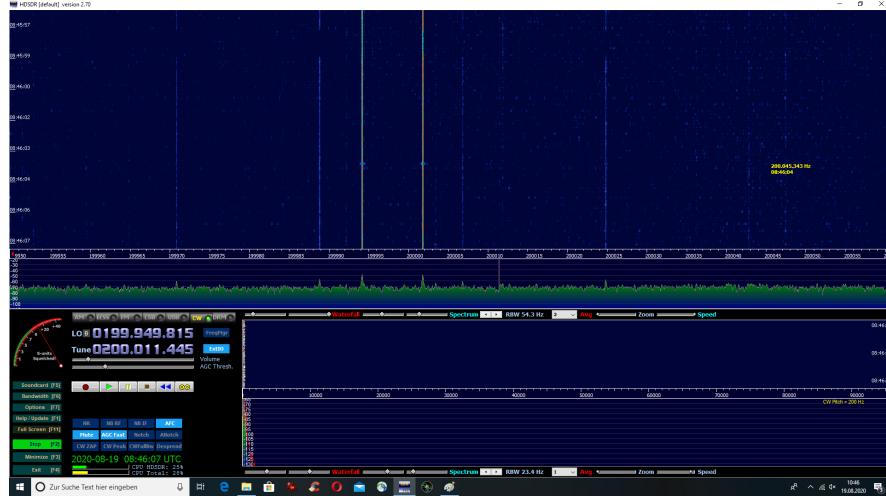


Figure 12: 2MHz signal

One of the lines correspond to the frequency provided, the other lines may appear due to some internal frequency overlaps.

## 4 Task 4

*Determination of the resonance frequency and recording of the dispersion curves of different DPPH samples*

In this task we were provided with two DPPH samples of different weights. The dispersion curve of the different samples were taken and the resonance frequency determined. For each substances a screenshot directly taken from the software and a graph was included. The resonance magnetic field was marked with a dashed red line. For the graph, data was extracted from the screenshot using WebPlotDigitizer.

#### 4.1 $1\mu g$

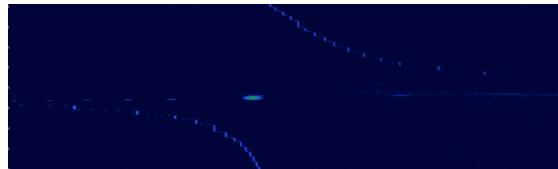


Figure 13: Screenshot from Software: DPPH  $1\mu g$

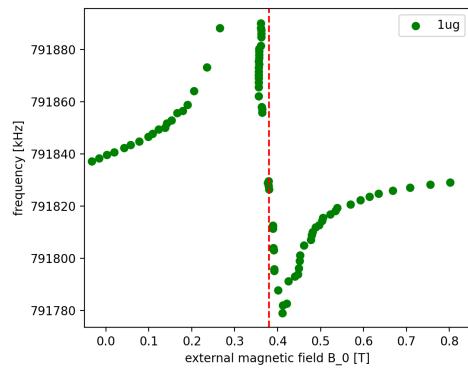


Figure 14: DPPH  $1\mu g$

The resonance occurs at  $B = 0.380$  T. The corresponding frequency is  $\nu = 791827$  kHz.

#### 4.2 $10\mu g$

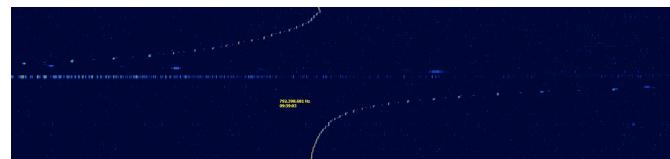


Figure 15: Screenshot from Software: DPPH  $10\mu g$

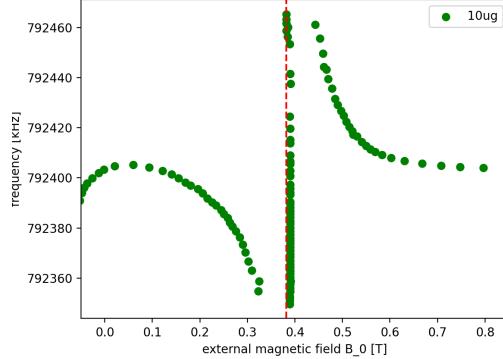


Figure 16: DPPH 10 $\mu g$

The resonance occurs at  $B = 0.385$  T. The corresponding frequency is  $\nu = 792410$  kHz.

### 4.3 The g-factor

Solving the resonance condition (given in equation 1) for g gives:

$$g = \frac{h\nu_0}{\mu_B B}$$

where h is the Planck's constant,  $\mu_B$  is the Bohr magneton, B the magnetic field at resonance and  $\nu_0 = 10.6$  GHz.

Using this formula the g-values were calculated using the experimental data for DPPH 1 $\mu g$  and 10 $\mu g$ . The results were then compared to the theoretical value.

DPPH	g-factor (calculated)	Theoretical value	Absolute Error	Relative Error
1 $\mu g$	1.9930	2.0036	-0.0106	-0.5%
10 $\mu g$	1.9671	2.0036	-0.0365	-1.8%

Table 1: g-factor of DPPH

The 10  $\mu g$  sample results in a larger error for the g-value compared to the 1 $\mu g$  sample. For a measurement to result in an even smaller error, a less concentrated sample may provide a g-factor more consistent with the theory. Using a frequency of 10.6GHz and using the theoretical g-factor value of  $g=2.0036$ , the expected resonance magnetic is field is  $B = \frac{h\nu}{\mu_B g} = 0.377$  T. The more DPPH is present the higher the frequency  $\nu$  and the corresponding resonance magnetic field as can be seen in figure 17. This means in our absorption spectrum, we obtain a higher amplitude for more material present.

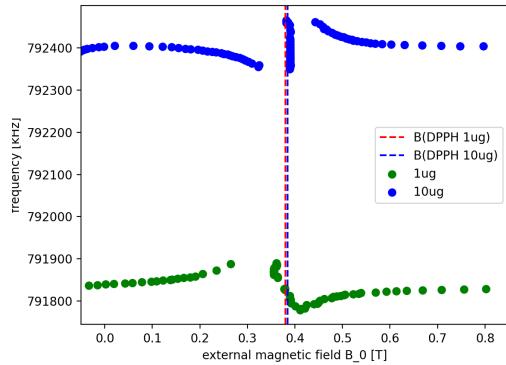


Figure 17: all DPPH samples

## 5 Task 5

*Determination of the resonance frequency and recording of the dispersion curves of different Ultramarine (UM) samples*

In this task we were provided with four different UM samples, each with different dilution levels. The dispersion curve of the different samples were taken and the resonance frequency determined.

### 5.1 Undiluted

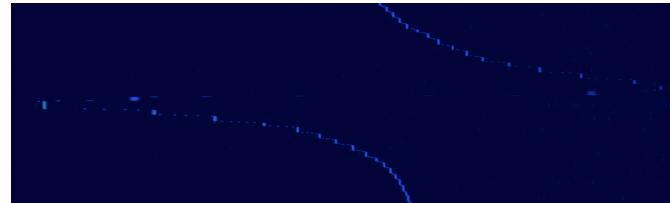


Figure 18: Screenshot from Software: UM undiluted

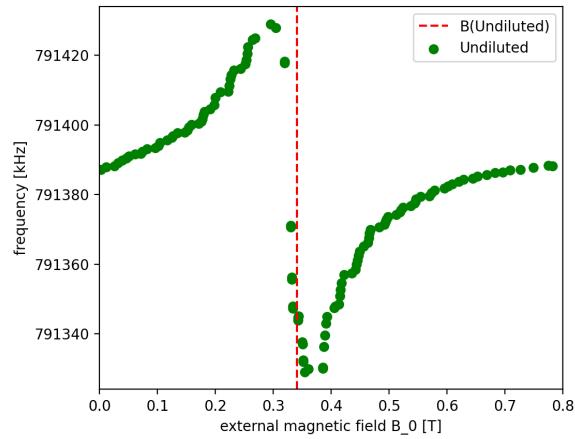


Figure 19: UM undiluted

The resonance occurs at  $B = 0.341\text{ T}$ . The corresponding frequency is  $\nu = 791378\text{ kHz}$ .

## 5.2 1:10

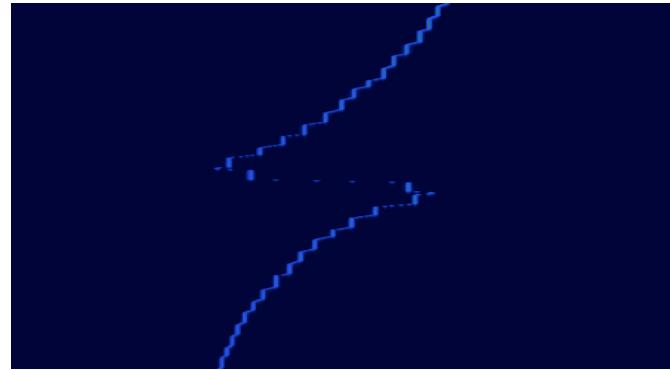


Figure 20: Screenshot from Software: UM 1:10

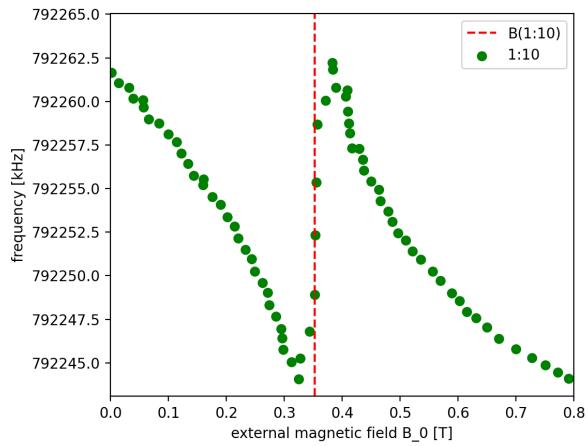


Figure 21: UM 1:10

The resonance occurs at  $B = 0.353$  T. The corresponding frequency is  $\nu = 792252$  kHz.

### 5.3 1:100

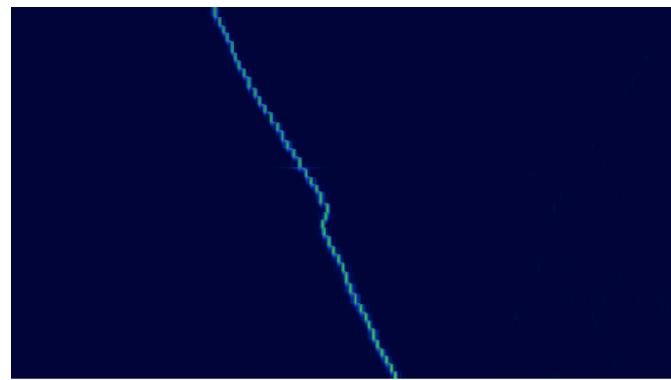


Figure 22: Screenshot from Software: UM 1:100

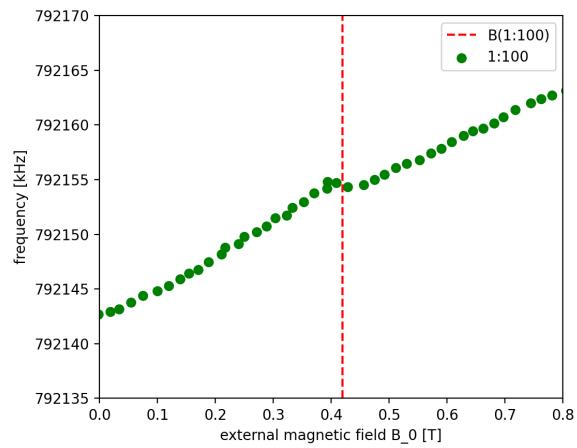


Figure 23: UM 1:100

The resonance occurs at  $B = 0.419$  T. The corresponding frequency is  $\nu = 792154$  kHz.

#### 5.4 1:1000

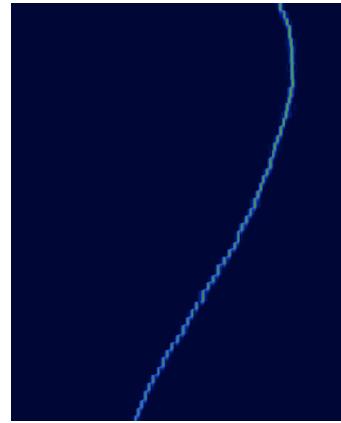


Figure 24: Screenshot from Software: UM 1:1000

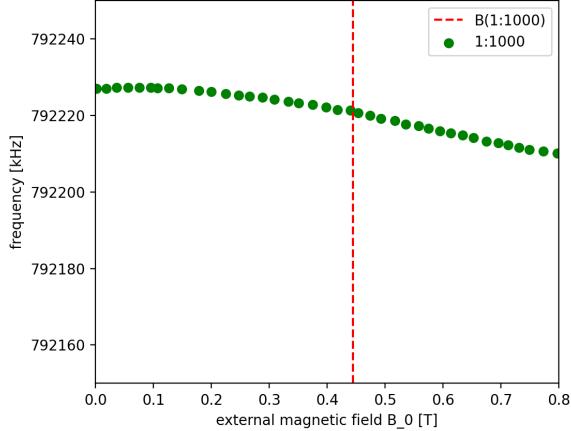


Figure 25: UM 1:1000

The resonance occurs at  $B = 0.440 \text{ T}$ . The corresponding frequency is  $\nu = 792221 \text{ kHz}$ .

## 5.5 The g-factor

Again the resonance condition (equation 1) and the resonance frequency of  $\nu_0 = 10.6 \text{ GHz}$  were used to calculate the g-factor.

UM	g-factor (calculated)	Theoretical value	Absolute Error	Relative Error
undiluted	2.2209	2.0290	0.1919	9.5%
1:10	2.1455	2.0290	0.1165	5.7%
1:100	1.8075	2.0290	-0.2215	-10.9%
1:1000	1.7213	2.0290	-0.3077	-15.2%

Table 2: g-factor of UM

Generally the more diluted the sample, the bigger the g-factor varies from the theoretical value. While the 1:10 diluted UM sample gives an error for the g-factor of approximately 5.7%, the 1:100 diluted UM gives an error of only 10.9%. The 1:1000 diluted UM samples gives the highest error. The graphs of the undiluted and the 1:10 diluted sample clearly portray the typical derivative of a peak shape. Additionally, they give the least errors when calculating the g-factor. Therefore the hyper-fine structure of the sample can be observed more easily the more undiluted the sample is. The amplitude of the absorption peak generally increases with more ultramarine present. The frequency  $\nu$  generally increases with a more diluted sample, with exception of the UM 1:10 sample showing the highest value for  $\nu$ . This can be seen in figure 26. It is important to mention here, that EPR is a very sensitive measurement, hence all the signal can be very easily affected from the surrounding environment.

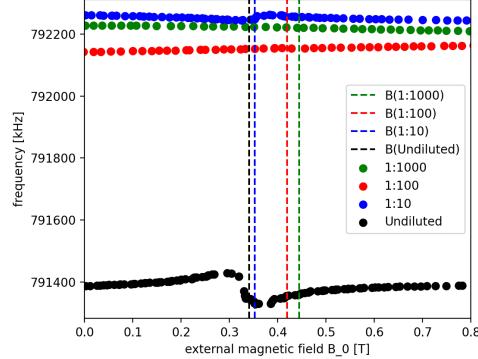


Figure 26: All UM samples

The resonance magnetic field also increases with a more diluted sample. Using a frequency of 10.6 GHz and using the theoretical g-factor value of  $g=2.0290$ , the expected resonance magnetic field is  $B = \frac{h\nu_0}{\mu_B g} = 0.373$  T.

## References

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