

EPR INVESTIGATIONS OF DPPH AND MANGANESE CHLORIDE

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ABSTRACT

Findings on EPR spectroscopy applied to DPPH and Manganese Chloride matched the initial hypothesis in line with the currently accepted theories on Electron Spin Resonance (ESR). The spectrometer instrumentation and apparatus in the experiment was intricate, The Varian E-3 X-band spectrometer was used. The g-values were calculated with a simplified formula that included the variables of Electromagnetic wave frequency, scalar constant and the center field. Some differences and minor anomalies were observed when comparing the expected theoretical values with the experimental values obtained, however, the final experimental values were quite similar to that of the theoretical g-values, thus proving the experiment a success.

I. INTRODUCTION

Electron Spin Resonance (ESR), or Electron Paramagnetic Resonance (EPR) are techniques of spectroscopy that use the technology of electromagnetism to determine the presence of free radicals, ions or molecules with unpaired electrons present. This can further be analyzed to identify information on the paramagnetic ions and their interactions with other ions and substances, as well as their oxidation and spin states. EPR spectrometers have many industrial uses such as in medicine, materials science, pharmacology, environmental science and cell biology. For example, EPR spectroscopy is often used to identify impurities in pharmaceutical products that might have free radicals that steal ions from the molecules of the product, thus changing its ionic configuration and chemical properties, free radicals are often considered impurities.

To conduct EPR spectroscopy, a well-calibrated spectrometer is required. This involves an electromagnet, that generates the external magnetic field, which is the key environmental factor that allows the interaction between electromagnetic waves (microwaves), produced through the microwave bridge, interacting with the paramagnetic ions present. This is where the Zeeman effect occurs, where the spectrum line splits into 2 different energy states of the paramagnetic material due to the presence of the magnetic field. The same is visually represented below:

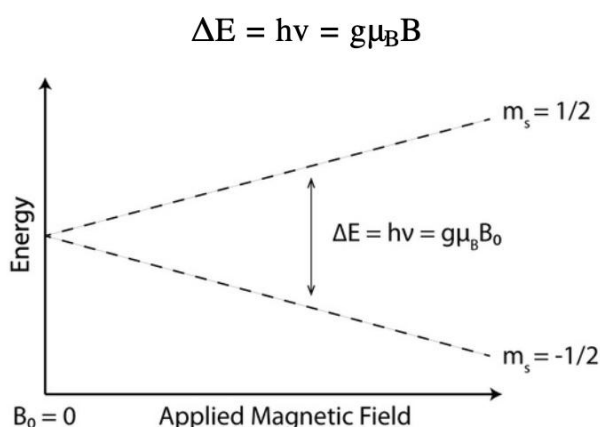


Figure 1: Energy levels for an electron spin ($M_S = \pm 1/2$) in an applied magnetic field B.

The above figure displays the direct correlation between energy levels and magnetic field strength. The presence of the magnetic field around the paramagnetic ions leads to them splitting into 2 possible degenerate (m_s) energy levels: +0.5 or -0.5.

The Electron Spin Resonance phenomenon occurs when an unpaired electron on the lower energy level ($m_s = -0.5$) absorbs electromagnetic radiation and transitions into a higher $m_s = +0.5$ under certain conditions, which are as follows in the equation provided:

$$h\nu = \Delta E = g\mu_B B_0$$

This equation is known as the Electron Paramagnetic Resonance condition.

The values used in the equations are as follows:

h represents the Planck Constant, which can be multiplied to the frequency of a wave to determine its energy.

ν is the frequency of the microwave radiation that is absorbed by the unpaired electron.

ΔE represents the total change in energy; while g is the g -factor, which characterizes the magnetic moment and angular momentum of the electron.

The final part of the equation also involves μ_B which is the Bohr Magnetron at $9.27 \times 10^{-24} \text{J/T}$, defining the magnetic moment of a single electron, and the B refers to the applied magnetic field.

The EPR spectrometer detects minute changes in the electron's energy levels and state transitions. This enables it to determine the g values (g -factors). In this paper, the G factor is the dependent variable, as the microwave frequency is controlled, and the magnetic field is the independent variable. In the following sections of this paper, the spectrometer is used to determine the g values of Manganese Chloride (MnCl_2) and DPPH, at the end a comparison between the theoretical g values and obtained g values will be drawn.

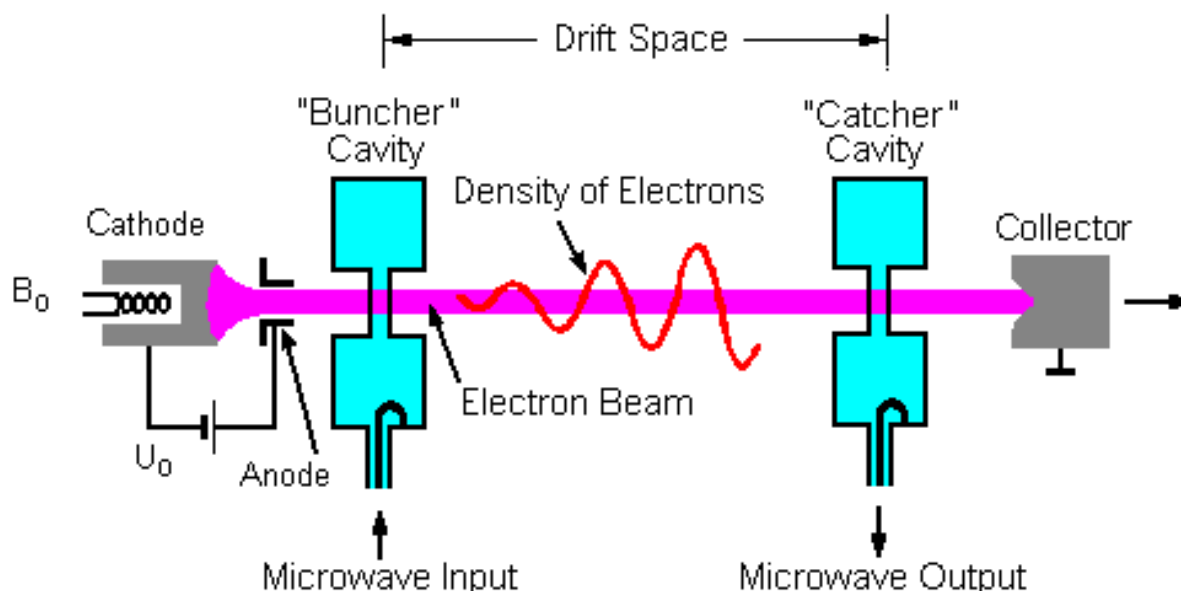
II. THEORY

Basic EPR Theory:

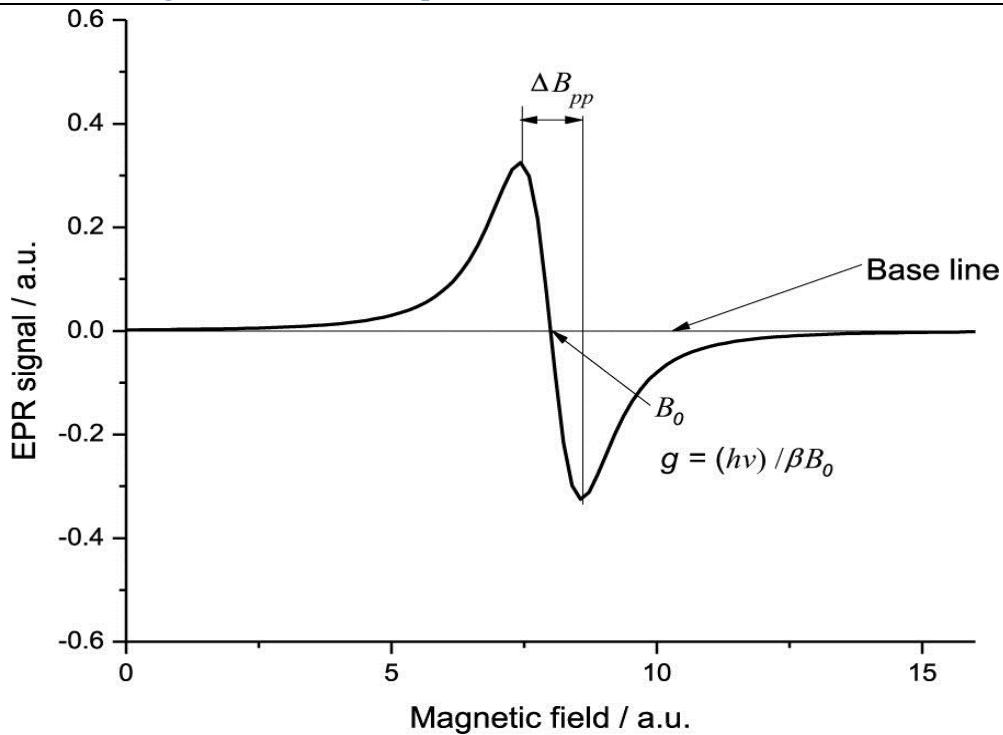
For Electron Paramagnetic Resonance to work, the sample being tested, in the case of this paper being that of DPPH, diphenyl picrylhydrazyl and Manganese Chloride, MnCl_2 have to be tested by exposing them to both a magnetic field and an electromagnetic radiation.

By placing the sample in the magnetic field, any unpaired electron achieves one of the possible energy levels as explained before, shown in the diagram explain the Zeeman effect. When further exposed to electromagnetic radiation, the switch between the energy states can be detected to check for the presence of such unpaired electrons.

A Klystron, a linear beam vacuum tube that produces electromagnetic radiation at a constant frequency is used to expose the samples to microwave radiation as shown below:



Once the magnetic field allows the unpaired electron to achieve its M_s energy state, and the microwave radiation enables to electron to absorb the energy to switch energy states, this change in energy is detected in the microwave power spectrum, which can be represented by a curve, known as the Electron Paramagnetic Resonance (EPR) line:



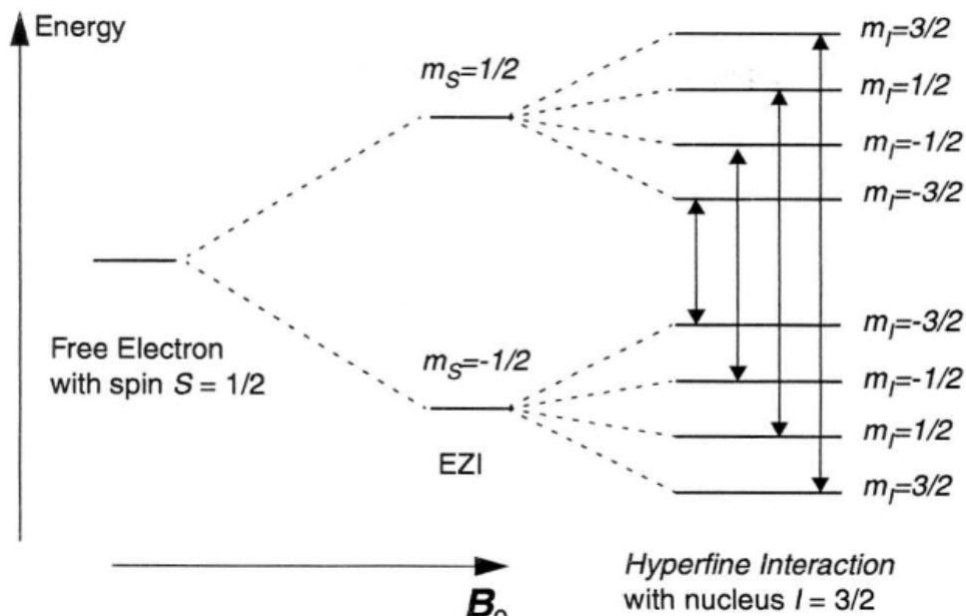
Using the reading, the g factor can be determined using the EPR condition simplified to:

$$g = 0.71449 \frac{v(\text{Ghz})}{B(\text{kG})}$$

Once determined, the g factor can be compared to the theoretical value of the g factor being 2.00232 of unpaired or free electron. If the experimental value is similar to this, one can confirm the presence of a free radical. If the value deviates, there are no free electrons in the sample.

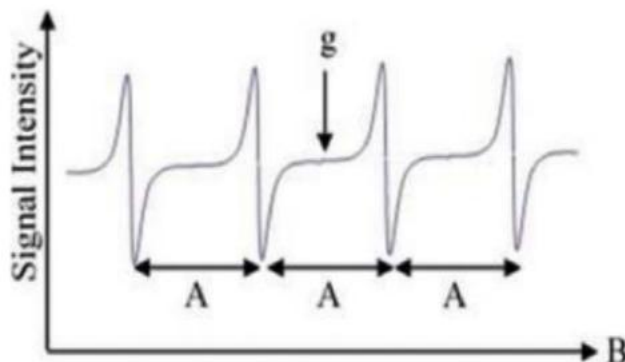
Hyperfine Interaction

The Manganese Chloride sample involves the hyperfine interaction of electrons in order to determine a signal on the spectrometer. This Technique is slightly different to the one involving the Zeeman effect. In many cases, ions of elements from the transitions series have a nucleus that has spin which interacts with the spin of the electron in its orbital, this results in the hyperfine structure to occur. This leads to the peaks in the ESR to be split; this is called hyperfine splitting. The spin energy states can split with the selection rule: $m_s + 1$ Or $m_s = 0$. The number of EPR lines is determined with the formula: $2I + 1$ where I refer to the spin of the nucleus.



This is an example of what the energy states look like in hyperfine interaction.

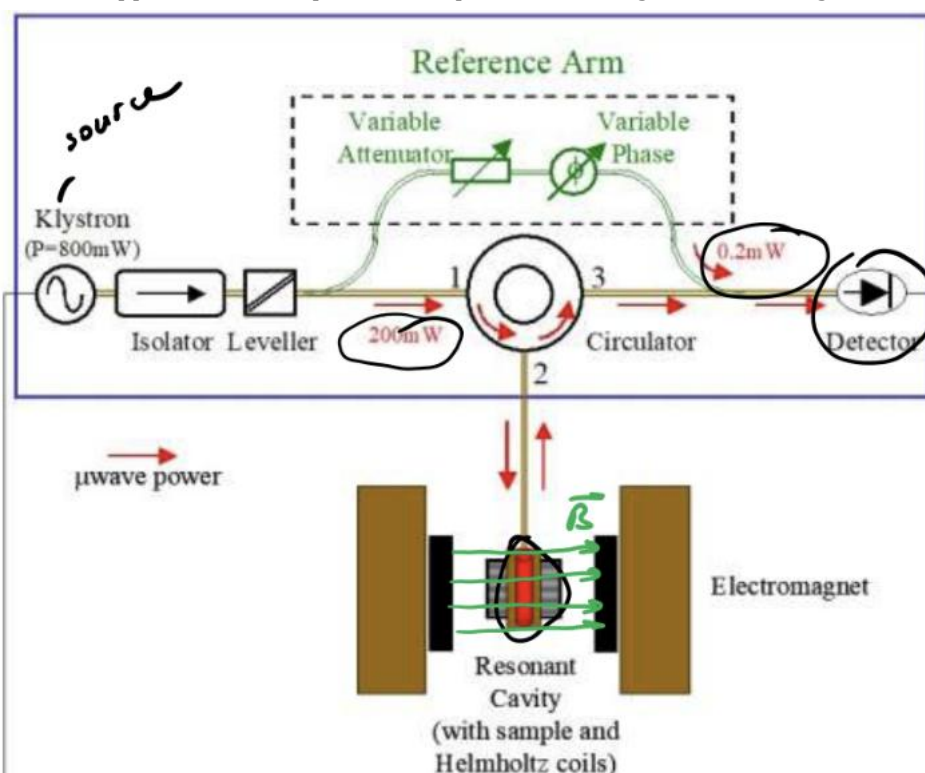
A hyperfine EPR line reading would look as shown below, where A refers to the hyperfine constant:



A typical hyper-fine spectrum of a species with $I = 3/2$

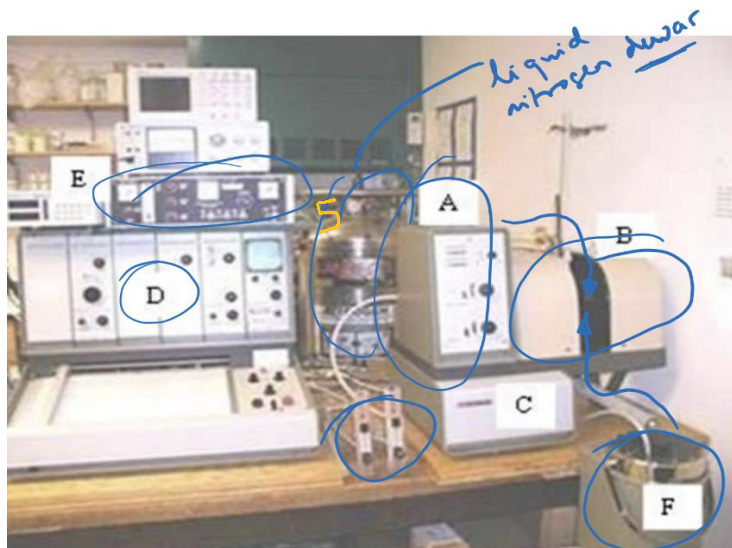
III. EXPERIMENTAL PROCEDURE

As mentioned before, DPPH and $MnCl_2$ samples will be tested on the Varian E-3 X band spectrometer that uses a liquid nitrogen flow cryostat. The picture below explains how the EPR line is detected as the microwave bridge in the box. Exposes the sample to microwave radiation while detecting changes in energy signals through the reference arm. All this happens as the sample is also exposed to the magnetic field using the electromagnet.



In order to set up the instrumentation, which in this case involves the Varian E-3 spectrometer, as shown in the image below, one must place the sample of DPPH or $MnCl_2$ in the slot of the spectrometer at B, in the electromagnet, as shown below. The Microwave Bridge at A can now be set to TUNE and can be calibrated. Once this is done, the spectrometer considers the current signal value as the signal baseline, where if any changes to the signal value are made, it will now reflect on the graph. In order to begin the scan, the spectrometer is set to OPERATE. The DPPH spectra was expected to come out close to symmetrical, as this helps confirm that the sample is off DPPH. The Varian E-3 spectrometer operates in between the frequencies of 8.5GHz to 12GHz and temperatures of 80 K to 293K. The experiment is conducted at room temperature for DPPH and 104K for $MnCl_2$ as the colder the sample is, the sharper the signal derivative would be. Both the experiments were recorded on

an X band spectrometer. Once the samples were scanned, the spectra obtained were observed, marked, analyzed and g value was calculated as shown in the segment below.



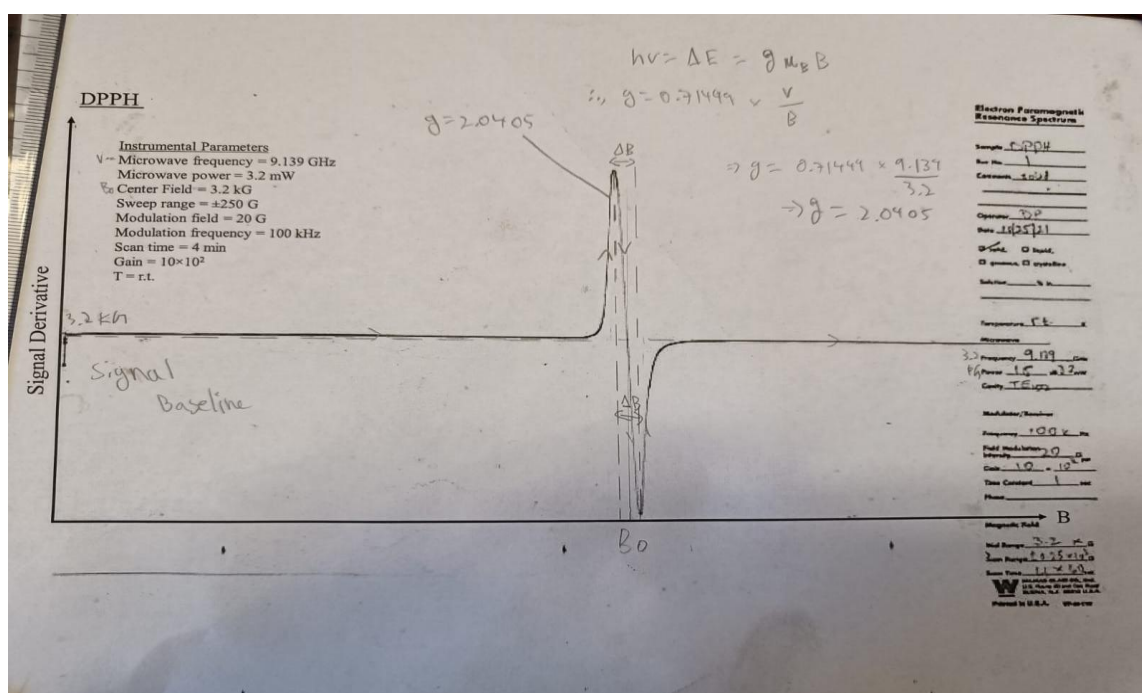
Varian E-3 Spectrometer at Prof. Doros Petasis' lab in Allegheny

Key for parts of the spectrometer:

- A) Microwave Bridge
- B) Electromagnet
- C) Magnet power supply
- D) Control Console
- E) Temperature controller
- F) Liquid Nitrogen Cryostat

IV. OBSERVATIONS AND ANALYSIS

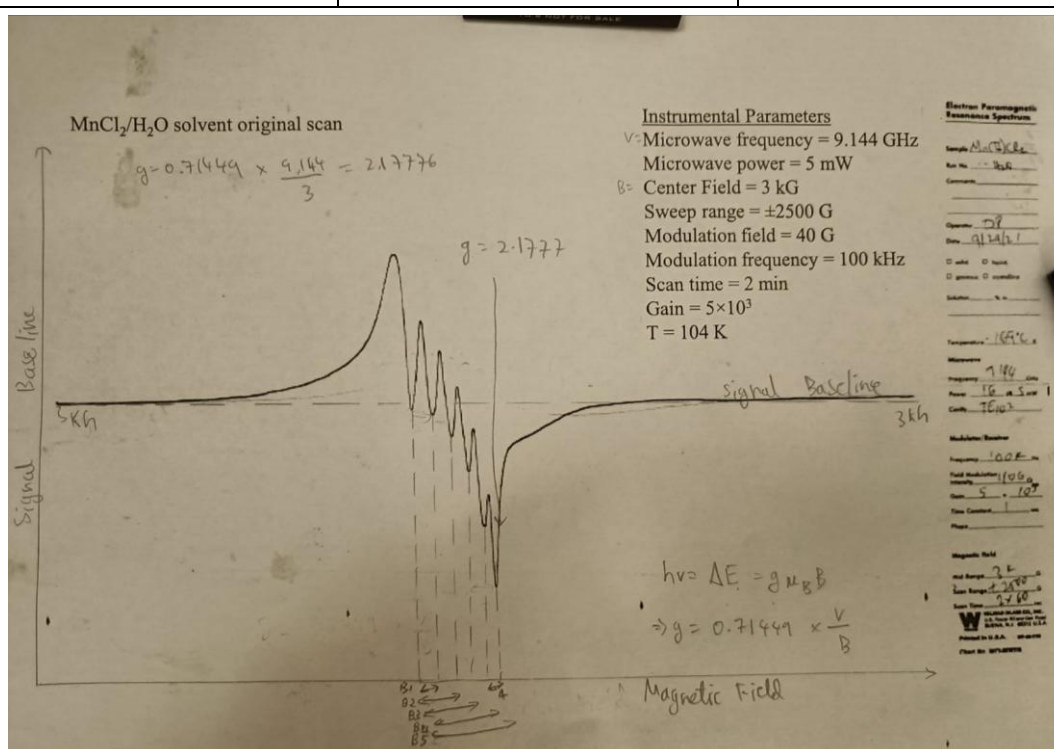
Using the simplified equation of the Electron Paramagnetic Spectrum Equation, for the samples, the values of ν (frequency of Electromagnetic wave) in GHz and B(Centerfield) in kG (Gauss, being the unit for magnetic flux) was used to calculate the g value for both the samples. The calculations are shown in the markings and analysis of the scans below.



For the DPPH sample as shown above, the theoretical value is 2.0036, and the value calculated from the experiment is 2.0405, which is close enough to the theoretical value to consider the scan on the DPPH sample a success and one can confirm that the sample scanned contained DPPH.

For the MnCl₂ sample, the Manganese Chloride was dissolved in water, H₂O, as also shown in the scan. A is marked as the hyperfine constant, where A is the hyperfine constant, the constant difference between B1 and B2, as marked in the graph. After calculation, the Experimental g value for MnCl₂ was 2.1777. When compared to the expected g value of 2.0023, the experimental g value deviates slightly from the expected one, however, it is close enough to consider it a MnCl₂ sample.

	Expected Value	Obtained Value
DPPH	2.0036	2.0405
MnCl ₂	2.0023	2.1777



V. CONCLUSION

In conclusion, the experiment on the samples of DPPH and MnCl₂ was a success as the values determined post analysis of the EPR spectra from both samples, and calculation using the simplified EPR condition equation, gave experimental values of the g factor close to that of the one theoretically mentioned, which explained that the DPPH sample had resemblance to characteristics of a free radical.

Manganese Chloride (MnCl₂) too provided a g value close enough to be considered similar to the g value of the electron. Therefore, this experiment can be considered a success. EPR spectroscopy is a very technical, complicated yet precise and useful technique with many applications in the real-world industries and many more in research.

ACKNOWLEDGEMENTS

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VI. REFERENCES

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