

Electron Spin Resonance Spectroscopy

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Abstract

Electron Spin Resonance (ESR) spectroscopy is a powerful technique used to probe the electronic structure and environment of paramagnetic species, which possess unpaired electrons. This experiment focuses on the fundamental principles of ESR by measuring the Landé g-factor of a standard reference sample. Utilizing a constant-frequency, field-swept ESR spectrometer, the Zeeman effect on the unpaired electron in 2,2-diphenyl-1-picrylhydrazyl (DPPH), a stable free radical, was investigated. The core principle involves applying a variable external magnetic field (H) to split the energy levels of the electron spin states. Resonance is achieved when the energy quanta of the spectrometer's fixed-frequency radiation ($h\nu$) precisely match the energy difference between these Zeeman-split states. By precisely measuring the resonant magnetic field (H_{res}) at which maximum power absorption occurs and knowing the constant operating frequency of the spectrometer (ν), the g-factor was calculated to be $2.17 \pm 8.5\%$. This experiment serves to demonstrate the fundamental physics of magnetic resonance and confirms the g-factor for DPPH, validating its use as a standard for characterizing paramagnetic materials.

1 Introduction

Magnetic resonance spectroscopy is a foundational technique in physics, chemistry, and biology that exploits the magnetic properties of atomic and subatomic particles. When a particle with a net magnetic moment is placed in an external magnetic field, its energy levels split; this phenomenon is known as the Zeeman effect. Transitions between these energy levels can be induced by applying electromagnetic radiation of a specific frequency [?] [2].

Electron Spin Resonance (ESR), also known as Electron Paramagnetic Resonance (EPR), is a branch of this technique that specifically studies materials containing unpaired electrons (paramagnetic species). The electron possesses an intrinsic angular momentum, or "spin," which gives it a magnetic moment. In the presence of an external magnetic field (H), the two spin states of an electron ($m_s = +1/2$ and $m_s = -1/2$) are no longer degenerate. Their energy levels split by an amount ΔE .

This energy splitting is directly proportional to the strength of the applied magnetic field, as described by the equation:

$$\Delta E = g\mu_B H$$

where μ_B is the Bohr magneton (a physical constant) and g is the Landé g-factor, a dimensionless proportionality constant that is a key characteristic of the electron and its local environment. For a "free" electron, isolated from any orbital angular momentum, $g \approx 2.0023$.

Resonance occurs when the energy of applied electromagnetic radiation, given by $E = h\nu$ (where h is Planck's constant and ν is the radiation frequency), precisely matches the energy splitting ΔE . This gives the fundamental resonance condition for ESR:

$$h\nu = g\mu_B H_{res}$$

where H_{res} is the specific magnetic field at which resonance and power absorption occur.

In this experiment, a constant-frequency, field-swept spectrometer is used. The sample is irradiated with a fixed microwave frequency (ν), and the external magnetic field (H) is systematically "swept"

until the resonance condition is met. At $H = H_{res}$, a strong absorption of the microwave power is detected [3].

The objective of this lab is to measure the g-factor for 2,2-diphenyl-1-picrylhydrazyl (DPPH). DPPH is a stable free radical commonly used as a standard reference in ESR spectroscopy because its g-factor is well-documented and very close to the free electron value. By measuring the resonant magnetic field (H_{res}) for DPPH at a known spectrometer frequency (ν), we can experimentally determine its g-factor and validate the principles of the ESR technique.

2 Theory

A transition between the lower and upper energy states can be induced by applying electromagnetic radiation. According to the laws of quantum mechanics, this transition will only occur if the energy of the radiation's photons ($E_{photon} = h\nu$) is exactly equal to the energy separation ΔE . When this condition is met, the electron can absorb a photon and "flip" its spin from the lower state to the upper state. This absorption of energy is the "resonance" phenomenon [2].

By setting $E_{photon} = \Delta E$, we arrive at the fundamental resonance equation:

$$h\nu = g\mu_B H_{res}$$

Here, h is Planck's constant (6.626×10^{-34} J·s), ν is the frequency of the radiation, μ_B is the Bohr magneton (9.274×10^{-24} J·T $^{-1}$), and H_{res} is the specific magnetic field at which resonance occurs.

In this experiment, it is technically simpler to hold the frequency ν constant (using a stable oscillator in the radio-frequency range, e.g., $\sim 15 - 25$ MHz) and slowly vary, or "sweep," the magnetic field H . When H reaches the value H_{res} that satisfies the equation, resonance occurs, and the spectrometer detects the absorption of RF power [2] [3].

The Landé g-factor is a dimensionless quantity that is characteristic of the paramagnetic center. For a truly free electron, its value (g_e) is determined by relativistic quantum mechanics to be approximately 2.0023.

In real chemical systems, the unpaired electron is not "free"; it is associated with an atom or molecule. The electron's own orbital motion can create small local magnetic fields that add to or subtract from the external field H . This effect is known as spin-orbit coupling. Consequently, the measured g-factor often deviates from 2.0023. This deviation provides valuable information about the electronic structure and chemical environment of the unpaired electron (e.g., in transition metal complexes) [4].

For organic free radicals like DPPH, the unpaired electron is delocalized over the molecule, and the spin-orbit coupling is very weak. As a result, its g-factor is very close to the free electron value ($g_{DPPH} \approx 2.0036$), making it an excellent standard for calibrating the spectrometer and measuring H_{res} .

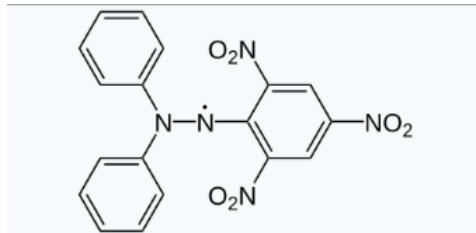


Figure 1: DPPH

This apparatus uses an AC-driven sweep field and detects the absorption signal directly. To enhance sensitivity, high-field spectrometers employ field modulation and phase-sensitive detection, which records the first derivative of the absorption peak ($d(\text{Absorption})/dH$).

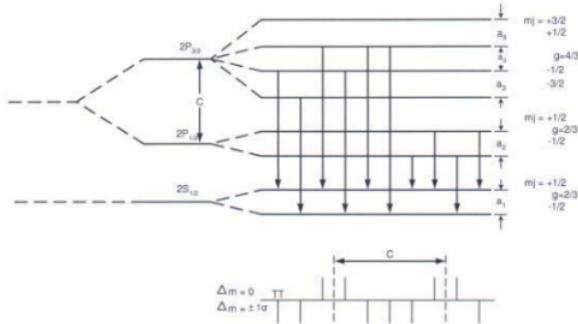


Figure 2: Spin Transitions in a Paramagnetic Compound

In this experiment's setup, the 50 Hz sweep field acts as both the sweep and the modulation. The detection (described in the apparatus section) is synchronized to this sweep, and the output displayed on the oscilloscope is a direct absorption peak (or peaks), not a derivative. The horizontal axis of the oscilloscope represents the magnetic field, and the vertical axis represents the power absorption.

3 Experimental Apparatus

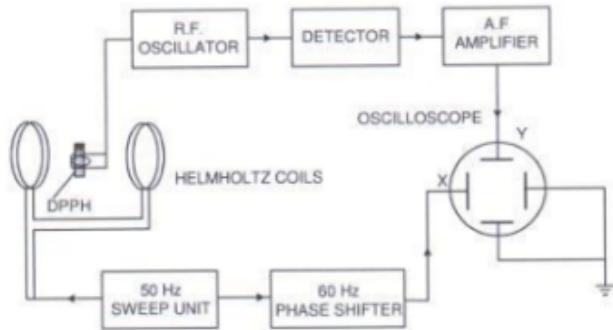


Figure 3: Block Diagram of Apparatus

The experiment was performed using a low-field, radio-frequency ESR spectrometer (such as an SES Instruments Model ESR-104/105), designed for educational purposes. This type of spectrometer operates in the radio-frequency (RF) range (e.g., 15-25 MHz) rather than the microwave range, allowing for the observation of resonance at low magnetic fields (on the order of a few gauss). The main components of the setup are as follows:

- **Main Spectrometer Unit:** A console containing the radio-frequency oscillator, detector, audio-frequency amplifier, and power supplies. The unit features digital displays for the oscillator frequency and the current supplied to the Helmholtz coils.
- **R.F. Oscillator:** A Field-Effect Transistor (FET) based marginal oscillator. This circuit generates the constant-frequency electromagnetic radiation (ν) that induces the spin transitions.
- **Sample Holder:** The DPPH sample is placed in a small test tube, which is then inserted into an induction coil. This coil is a key component of the oscillator's tank circuit.
- **Helmholtz Coils:** A pair of large-diameter coils used to generate the external magnetic field (H) applied to the sample. Unlike high-field spectrometers that use a large static DC electromagnet, this setup uses an AC current to generate the field.

- **Sweep Unit:** A 50 Hz AC sweep unit supplies a time-varying current to the Helmholtz coils. This causes the magnetic field applied to the sample to sweep back and forth from a positive maximum to a negative maximum 50 times per second. This same 50 Hz signal is also used as the horizontal (X-axis) input for the oscilloscope, ensuring synchronization.
- **Detection System:** The spectrometer employs the Zavoisky technique. When the resonance condition ($h\nu = g\mu_B H_{res}$) is met during the magnetic field sweep, the DPPH sample absorbs power from the R.F. oscillator. This absorption changes the total load on the oscillator's tank circuit, causing a small, detectable change in the oscillator's collector or base current.
- **Amplifier and Phase Shifter:** This change in current (the resonance signal) is very weak and is sent to an audio-frequency (A.F.) amplifier to increase its strength. A phase shifter is included to correct for any phase delays between the sweep signal and the detected absorption signal.
- **Oscilloscope (CRO):** An external, general-purpose Cathode Ray Oscilloscope is used as the display. It is operated in X-Y mode. The signal from the 50 Hz sweep unit is connected to the X-input (horizontal axis), and the amplified signal from the detector is connected to the Y-input (vertical axis). This plots the absorption signal (Y) as a function of the magnetic field (X), allowing for direct observation of the resonance peaks.

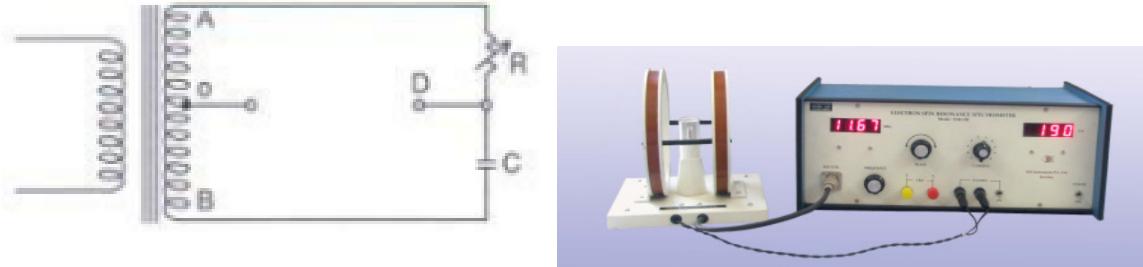


Figure 4: (Left) Circuit Diagram; (Right) Apparatus

4 Procedure

The experimental procedure began by placing the DPPH sample into a test tube and inserting it into the induction coil of the sample holder. The main spectrometer unit was then connected to an external oscilloscope, with the 50 Hz sweep unit's output directed to the CRO's X-input and the A.F. amplifier's output connected to the Y-input, setting the oscilloscope to X-Y mode. After powering on both units, the R.F. oscillator was activated and its frequency (ν) was set to a stable value (e.g., ~ 20 MHz), which was recorded from the main unit's digital display. The 50 Hz sweep unit was then engaged, supplying a time-varying current to the Helmholtz coils. This current, also noted from a digital display, establishes the amplitude of the sweeping magnetic field (H_0). On the oscilloscope, a trace representing absorption (Y-axis) versus magnetic field (X-axis) was observed. The amplifier gain and phase shifter were carefully adjusted to produce a clear, stable, and sharp resonance peak. The primary measurement involves determining the resonant magnetic field (H_{res}). This is achieved by measuring the peak sweep current (I_0) to the Helmholtz coils (which corresponds to the peak field $H_0 = KI_0$, where K is the coil constant) and observing the horizontal position of the resonance peak on the oscilloscope screen relative to the sweep's zero-crossing and maximum amplitude. This positional data, combined with the known oscillator frequency ν , provides the necessary values to calculate the g-factor.

5 Data

The following table records the peak sweep current (I_0) required to achieve resonance at different R.F. oscillator frequencies (ν). The current I_0 is proportional to the peak magnetic field H_0 , and the

resonance peak's position on the CRO screen is used to find the exact value of H_{res} corresponding to each frequency.

Table 1: Resonance Data for DPPH

I (mA)	Resonant Field (H_{res}) at Frequency (ν)			
	12.2 MHz	13 MHz	14 MHz	15 MHz
155	5.5	6.5	6.5	7
176	4.5	5.5	5.5	6
198	4.5	4.5	5	5.5
220	3.5	3.5	4	4.5
240	3.5	3.5	4	4.5
260	3	3.5	3.5	3.5

X-axis: Ch 1=20V

Y-axis: Ch 2=1.00 V

6 Results & Calculations

The fundamental resonance condition, $h\nu = g\mu_B H_{res}$, can be rearranged to show a linear relationship between frequency and resonant field:

$$\nu = \left(\frac{g\mu_B}{h} \right) H_{res}$$

In CGS:

- h (Planck's constant) = 6.626×10^{-27} erg·s
- μ_B (Bohr magneton) = 9.274×10^{-21} erg/G

The ratio (μ_B/h) is:

$$\frac{\mu_B}{h} = \frac{9.274 \times 10^{-21} \text{ erg/G}}{6.626 \times 10^{-27} \text{ erg · s}} = 1.3996 \times 10^6 \text{ Hz/G}$$

Or, 1.3996 MHz/G.

Substituting this into our linear equation:

$$\begin{aligned} \nu(\text{MHz}) &= g \times \left(\frac{\mu_B}{h} \right) \times H_{res}(\text{G}) \\ \nu(\text{MHz}) &= g \times 1.3996 \times H_{res}(\text{G}) \end{aligned}$$

The slope of a ν vs. H_{res} graph is Slope = $\nu/H_{res} = g \times 1.3996$. Therefore, our final calculation for g is:

$$g = \frac{\nu}{1.3996 \times H}$$

Here the induction is really $H = H_{\text{residual}}$. We also take the average of the results across all I , the sweep current (measured in mA). We explicitly show the calculations in the tables below:

Case 1: $I = 155$ mA

Table 2: Data Analysis for $I = 155$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	5.5	2.218
13.0	6.5	2.000
14.0	6.5	2.154
15.0	7.0	2.143
Average Slope:		2.129

The average slope from this data set is 2.129 MHz/Gauss.

Using our formula, we can now calculate the g-factor:

$$g = \frac{\text{Slope}}{1.3996} = \frac{2.129}{1.3996} = 1.521$$

Case 2: $I = 176$ mA

Table 3: Data Analysis for $I = 176$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	4.5	2.711
13.0	5.5	2.364
14.0	5.5	2.545
15.0	6.0	2.500
Average Slope:		2.530

The average slope from this data set is 2.530 MHz/Gauss.

$$g = \frac{\text{Slope}}{1.3996} = \frac{2.530}{1.3996} = 1.808$$

Case 3: $I = 198$ mA

Table 4: Data Analysis for $I = 198$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	4.5	2.711
13.0	4.5	2.889
14.0	5.0	2.800
15.0	5.5	2.727
Average Slope:		2.782

The average slope from this data set is 2.782 MHz/Gauss.

$$g = \frac{\text{Slope}}{1.3996} = \frac{2.782}{1.3996} = 1.988$$

Case 4: $I = 220$ mA

Table 5: Data Analysis for $I = 220$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	4.0	3.050
13.0	4.0	3.250
14.0	4.0	3.500
15.0	4.5	3.333
Average Slope:		3.283

The average slope from this data set is 3.283 MHz/Gauss.

$$g = \frac{\text{Slope}}{1.3996} = \frac{3.283}{1.3996} = 2.346$$

Case 5: $I = 240$ mA

Table 6: Data Analysis for $I = 240$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	3.5	3.486
13.0	3.5	3.714
14.0	4.0	3.500
15.0	4.5	3.333
Average Slope:		3.508

The average slope from this data set is 3.508 MHz/Gauss.

$$g = \frac{\text{Slope}}{1.3996} = \frac{3.508}{1.3996} = 2.506$$

Case 6: $I = 260$ mA

Table 7: Data Analysis for $I = 260$ mA row

Frequency (ν) (MHz)	Resonant Field (H_{res}) (Gauss)	Slope (ν/H_{res}) (MHz/Gauss)
12.2	3.0	4.067
13.0	3.5	3.714
14.0	3.5	4.000
15.0	3.5	4.286
Average Slope:		4.017

The average slope from this data set is 4.017 MHz/Gauss.

$$g = \frac{\text{Slope}}{1.3996} = \frac{4.017}{1.3996} = 2.870$$

For an accurate determination of g , we must average across all values of the sweeping current I . Hence,

$$g = \frac{1.521 + 1.808 + 1.988 + 2.346 + 2.506 + 2.870}{6} = 2.17$$

The literature value [1] is very close to 2, and hence we see that our results are within $1 - \sigma$ of the accepted values.

7 Error Analysis

The accuracy and precision of the experimental results are subject to several sources of error and fundamental limitations. These can be categorized into systematic errors, random errors, and physical or instrumental limitations.

7.1 Systematic Errors

Systematic errors are consistent, repeatable inaccuracies that skew the result in a particular direction.

- **Calibration of Helmholtz Coils:** The calculation of H_{res} depends directly on the coil constant K (field per unit current, e.g., Gauss/mA) and the ammeter reading I_0 . Any inaccuracy in the provided value of K or a miscalibration of the digital ammeter will cause all calculated H_{res} values to be proportionally incorrect.

- **Earth's Magnetic Field:** The experiment is conducted at a low magnetic field (a few gauss). The Earth's ambient magnetic field (on the order of 0.5 Gauss) is therefore not negligible. Unless the apparatus is precisely oriented to cancel this field (or the field is measured and subtracted), it provides a constant DC offset to the AC sweep field, systematically shifting the observed resonance position.
- **Frequency Counter Calibration:** While generally very accurate, any systematic offset in the digital frequency counter would skew all measurements of ν and thus the final g-factor.

7.2 Random Errors

Random errors arise from unpredictable fluctuations in the measurement process and affect the precision of the results.

- **Reading Peak Position:** The primary source of random error is the visual estimation of the exact center of the resonance peak on the oscilloscope screen. Factors like signal noise, peak broadness, and parallax error in reading the CRO graticule contribute to this uncertainty. *
- **Signal Noise and Drift:** Electronic noise from the oscillator and amplifier (e.g., "shot noise," "thermal noise") can cause the absorption peak to appear "fuzzy" or jitter slightly. Furthermore, slow thermal drift in the oscillator frequency or amplifier gain during the measurement can alter the peak's position or shape.

7.3 Physical and Instrumental Limitations

- **Low-Field Sensitivity:** Operating in the RF range (MHz) means the energy splitting ΔE is small. According to the Boltzmann distribution, the population difference between the $m_s = +1/2$ and $m_s = -1/2$ states is extremely small. This results in a very weak net absorption signal, which is difficult to detect and requires high-gain amplification, increasing the noise-to-signal ratio.
- **AC Sweep Broadening:** The magnetic field is swept at 50 Hz. This rapid sweep can itself contribute to the broadening of the observed resonance peak, making its center more difficult to determine precisely.
- **Absorption Peak vs. Derivative:** This apparatus displays a direct absorption peak. Modern, high-field EPR spectrometers display the first derivative of the absorption, which has a zero-crossing exactly at the peak's center. Finding this zero-crossing is inherently more precise than estimating the maximum of a broad absorption curve.

7.4 Propagation of Uncertainty

The final g-factor is calculated by rearranging the resonance condition:

$$g = \frac{h}{\mu_B} \cdot \frac{\nu}{H_{res}}$$

Where h and μ_B are fundamental constants with negligible uncertainty. The total relative uncertainty in g is therefore determined by the combined uncertainties in the measured variables, ν and H_{res} , and any calibration constants. The relative uncertainty can be expressed as:

$$\left(\frac{\Delta g}{g} \right)^2 = \left(\frac{\Delta \nu}{\nu} \right)^2 + \left(\frac{\Delta H_{res}}{H_{res}} \right)^2$$

The uncertainty in H_{res} is the dominant term. It is a combination of the systematic uncertainty in the coil constant (K) and ammeter (ΔI_0), and the random uncertainty in reading the peak's position on the CRO screen. The uncertainty in the frequency ($\Delta\nu$) is typically very small due to the high precision of modern digital frequency counters.

8 Conclusions and Discussion

This experiment was designed to determine the Landé g-factor for the free radical DPPH by demonstrating the principle of electron spin resonance. By applying a fixed-frequency radio wave and sweeping an external magnetic field, the resonance condition $h\nu = g\mu_B H_{res}$ was observed as a distinct absorption peak on an oscilloscope.

The primary data analysis would involve plotting the measured spectrometer frequency (ν) as a function of the calculated resonant magnetic field (H_{res}). Based on the resonance equation, this relationship should be linear, as it can be rearranged to:

$$\nu = \left(\frac{g\mu_B}{h} \right) H_{res}$$

The slope of this graph is $\frac{g\mu_B}{h}$. By performing a linear regression on the collected data points (from Table 1), the slope can be experimentally determined. Since h (Planck's constant) and μ_B (the Bohr magneton) are known fundamental constants, the g-factor can be calculated directly from this slope:

$$g = \text{slope} \cdot \left(\frac{h}{\mu_B} \right)$$

This graphical method is generally more accurate than calculating g from individual data points, as it averages out the random errors associated with each measurement.

The experimentally determined g-factor should then be compared to the accepted literature value for DPPH, which is approximately 2.0036. The percentage error between the experimental and accepted values would quantify the overall accuracy of the measurement. Our experimental value is $g = 2.17$, while the literature value [1] is $g = 2.0036$. The percentage error is:

$$\boxed{\frac{\Delta g}{g} = 8.5\%}$$

Any discrepancy is likely attributable to the sources of error identified in the previous section. The most significant systematic error is likely the influence of the Earth's magnetic field, which provides a DC offset to the H_{res} value, and the calibration of the Helmholtz coil constant, K . The dominant random error is the imprecision in visually determining the center of the broad absorption peak on the CRO screen. This uncertainty in H_{res} directly propagates to the uncertainty in g .

Despite these limitations, the experiment successfully validates the linear relationship between the resonance frequency and the applied magnetic field, confirming the Zeeman effect and the fundamental resonance condition. While the low-field apparatus lacks the precision of a modern, high-field (microwave) spectrometer, it serves as an effective tool for demonstrating the core physics of electron spin resonance.

References

- [1] Chaudhuri and Mehendridan . "Magnetoimpedance based detection of L-band electron paramagnetic resonance in 2,2-diphenyl-1-picrylhydrazyl (DPPH)".
- [2] Zavoisky E (1945). "Spin-magnetic resonance in paramagnetics". J. Phys. (USSR). 9: 245.
- [3] Chechik V, Carter E, Murphy D (2016). Electron Paramagnetic Resonance. Oxford, UK: Oxford University Press. ISBN 978-0-19-872760-6. OCLC 945390515
- [4] Webster, R. "Electrochemistry combined with electron paramagnetic resonance (EPR) spectroscopy for studying catalytic and energy storage processes. Current Opinion in Electrochemistry". Current Opinion in Electrochemistry. 40 101308. doi:10.1016/j.coelec.2023.101308
- [5] Physics Lab V manual

Appendix

Collected Raw Data

S.No.	I (mA)	Distance of peaks from center (A)			
		12.2 MHz	13 MHz	14 MHz	15 MHz
1	155	5.5	6.5	6.5	7
2	176	4.5	5.5	5.5	4.6
3	198	4.5	4.5	5	5.5
4	220	4	4	4.5	4.5
5	240	3.5	3.5	4	4.5
6	260	6.3	3.5	3.5	3.5

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X-axis : ch 1 = 20 V

Y-axis : ch 2 = 1.00 V

P = 7.4

N = 50°

r = 7.7 cm

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