Determining Magnetic Susceptibility of Ionic Sulphates by Gouy's Method

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Abstract

This experiment determines the magnetic susceptibility of the paramagnetic compound Manganese(II) sulfate ($MgSO_4$) using the Gouy's method. The Gouy balance measures the apparent change in mass (force) of a cylindrical sample when it is partially suspended in an inhomogeneous magnetic field. This force is directly proportional to the material's volume magnetic susceptibility (χ). By measuring this mass change and calibrating the instrument, the specific and molar magnetic susceptibilities of $MgSO_4$ were calculated. This molar susceptibility is then used to determine the effective magnetic moment (μ_{eff}) and subsequently the number of unpaired electrons in the d-orbitals of the Mg^{2+} ion, providing experimental verification of its electronic structure.

1 Introduction

All substances interact with an applied magnetic field, though the nature and magnitude of this interaction vary widely. This fundamental property is quantified by magnetic susceptibility (χ), a dimensionless quantity that measures the ratio of the induced magnetization (M) within a material to the strength of the applied magnetic field (H). The magnetic susceptibility of a substance provides a basis for its classification: materials are broadly categorized as diamagnetic if they are weakly repelled by a magnetic field (negative χ), or paramagnetic if they are weakly attracted to it (positive χ).

While diamagnetism is a universal property present in all substances due to the induced orbital motion of electrons, paramagnetism is a more specialized and often stronger effect that arises from the presence of one or more unpaired electrons in an atom, ion, or molecule. The magnetic moments of these unpaired electrons tend to align with an external magnetic field, resulting in a net attraction. The magnitude of this paramagnetic susceptibility is directly related to the number of unpaired electrons, making its measurement a powerful tool for characterizing the electronic structure of chemical compounds, particularly those involving transition [6].

Manganese(II) sulfate ($MgSO_4$) is an example of a compound containing the Mg^{2+} ion, a transition metal ion whose number of unpaired electrons can be investigated. The objective of this experiment is to quantitatively determine the magnetic susceptibility of solid $MgSO_4$ [4].

To achieve this, the Gouy's method will be employed. The Gouy balance is a classic experimental apparatus designed to measure the force exerted on a sample when it is suspended in an inhomogeneous magnetic field. This method operates by measuring the apparent change in the mass of a cylindrical sample as one end is positioned in a region of high magnetic field strength (H) and the other end remains in a region of negligible field strength. This observed change in mass corresponds to the vertical force (F) on the sample, which is proportional to the sample's volume susceptibility (χ) and the square of the magnetic field strength (H^2). By calibrating the instrument and measuring this force, the specific and molar susceptibility of $MgSO_4$ can be calculated, which in turn allows for the experimental determination of the number of unpaired electrons in the Mg^{2+} ion [4].

2 Theory

When a substance is placed in an external magnetic field of strength H, it develops an induced magnetization, M. The magnetic susceptibility, χ, is a dimensionless quantity that defines the relationship between M and H:

$$M = \chi H$$

This susceptibility is more precisely termed the volume magnetic susceptibility (χ_v), as M is defined per unit volume. Materials are broadly classified based on the sign of χ_v [1] [2]:

- **Diamagnetic** materials have a small, negative susceptibility ($\chi_v < 0$). They are weakly repelled by magnetic fields. This property arises from the induced orbital motion of electrons and is present in all matter.

- **Paramagnetic** materials have a small, positive susceptibility ($\chi_v > 0$). They are weakly attracted to magnetic fields. This property is due to the presence of atoms or ions with permanent magnetic moments, which originate from unpaired electrons.

This experiment focuses on paramagnetism. For most paramagnetic substances, the susceptibility is temperature-dependent, following the Curie Law:

$$\chi = \frac{C}{T}$$

where C is the Curie constant and T is the absolute temperature.

The Gouy balance is an instrument used to measure magnetic susceptibility. It exploits the fact that a force (F) is exerted on a sample when it is placed in an inhomogeneous (non-uniform) magnetic field. A cylindrical sample, contained in a Gouy tube, is suspended from a balance such that one end (A) is in a region of high, uniform field strength (H) and the other end (B) is in a region of negligible field strength ($H \approx 0$).

The net vertical force experienced by the sample is given by the integral:

$$F = \frac{1}{2} A (\chi_v - \chi_{v,0}) \int_B^A \frac{d(H^2)}{dx} dx$$

where A is the cross-sectional area of the sample, χ_v is the volume susceptibility of the sample, and $\chi_{v,0}$ is the volume susceptibility of the surrounding medium (air, which is small and often corrected for). Integrating from the low-field region ($H_B \approx 0$) to the high-field region ($H_A = H$) simplifies this to:

$$F = \frac{1}{2} A (\chi_v - \chi_{v,0}) H^2$$

This force is measured by the balance as an apparent change in mass (Δm), where $F = g\Delta m$ (g is the acceleration due to gravity). Rearranging for the sample's susceptibility gives:

$$\chi_v = \frac{2g\Delta m}{AH^2} + \chi_{v,0}$$

In practice, the instrument constant $\beta = \frac{AH^2}{2}$ is determined by calibration with a standard of known susceptibility, such as $Hg[Co(SCN)_4]$.

The experiment measures Δm, which yields the volume susceptibility, χ_v. This is then converted to the more chemically useful molar susceptibility, χ_M, through a series of steps [3]:

1. **Mass Susceptibility (χ_g):** This is the susceptibility per unit mass, related to χ_v by the sample's density, ρ.

$$\chi_g = \frac{\chi_v}{\rho}$$

2. **Molar Susceptibility (χ_M):** This is the susceptibility per mole, found by multiplying χ_g by the molar mass (MM) of the compound.

$$\chi_M^{\text{meas}} = \chi_g \times MM$$

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3. **Diamagnetic Correction:** The measured susceptibility (χ_M^{meas}) includes both the paramagnetic contribution (χ_M^{para}) from unpaired electrons and the diamagnetic contribution (χ_M^{dia}) from all the paired electrons in the compound. Since diamagnetism is always present, it must be subtracted to isolate the paramagnetic effect.

$$\chi_M^{\text{para}} = \chi_M^{\text{meas}} - \chi_M^{\text{dia}}$$

The diamagnetic correction, χ_M^{dia}, is calculated by summing established values (Pascal's constants) for all atoms and structural features in the molecule (e.g., for Mg^{2+}, SO_4^{2-}).

4. **Effective Magnetic Moment ($\mu_{\textbf{eff}}$):** The corrected molar susceptibility, χ_M^{para}, is directly related to the permanent magnetic moment of the ion, μ_{eff}. This relationship is given by:

$$\mu_{\text{eff}} = \sqrt{\frac{3k_B}{N_A \mu_B^2}} \sqrt{\chi_M^{\text{para}} T} \approx 2.828 \sqrt{\chi_M^{\text{para}} T}$$

where k_B is the Boltzmann constant, N_A is Avogadro's number, μ_B is the Bohr magneton, and T is the absolute temperature. μ_{eff} is expressed in units of Bohr magnetons (B.M.).

5. **Number of Unpaired Electrons (n):** For d-block elements (transition metals), the magnetic moment is primarily due to the spin of the unpaired electrons (the orbital contribution is "quenched"). The "spin-only" formula relates μ_{Geff} directly to the number of unpaired electrons, n:

$$\mu_{\text{eff}}(\text{spin-only}) = \sqrt{n(n+2)} \quad \text{(B.M.)}$$

By calculating μ_{eff} from the experimental data and comparing it to the values predicted by the spin-only formula (e.g., $n = 1, \mu_{\text{eff}} = 1.73$ B.M.; $n = 5, \mu_{\text{eff}} = 5.92$ B.M.), the number of unpaired electrons in the Mg^{2+} ion can be determined.

3   Experimental Apparatus

he apparatus for the Gouy's method, as described in the reference material, consists of the following components:

- **A Balance:** To precisely measure the mass of the sample and the apparent change in mass when the magnetic field is applied.

- **A Sample Holder:** A cylindrical tube designed to hold the packed solid sample ($MgSO_4$).

- **A Suspension Thread:** A thread used to suspend the sample holder from the bottom of the balance's pan, allowing it to hang vertically.

- **A Magnet:** An electromagnet or a strong permanent magnet, positioned so that one end of the suspended sample tube is in a region of high magnetic field strength, while the other end is in a region of negligible field strength.

The general arrangement involves the sample tube hanging freely between the poles of the magnet, as illustrated in the provided documentation (Figure 1 in "Gouy's Method.pdf").

4   Procedure

The experimental procedure involves a series of differential mass measurements to isolate the magnetic susceptibility of the sample. First, the balance is zeroed. Then, the empty Gouy sample tube is weighed twice: once with the electromagnet off (m_1) and once with the electromagnet turned on to its standard operating current (m_2). This initial set of measurements accounts for the magnetic properties of the sample tube itself.
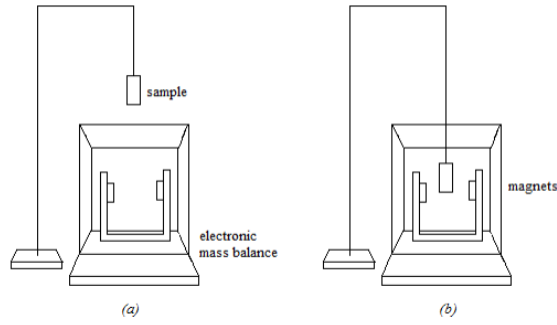
Figure 1: Schematic diagram of the apparatus

Figure 2: Basic diagram of the experimental setup, with the sample tube suspended from a balance and positioned between the poles of a magnet. (a) shows the initial configuration, while (b) is the final configuration in which measurements are made.

Next, the tube is carefully packed with the Magnesium(II) sulfate ($MgSO_4$) powder, ensuring a uniform density to avoid air gaps. This packed tube is then weighed under the same two conditions: first with the magnet off (m_3) and then with the magnet on (m_4). It is crucial that the magnet's operating current is identical for both the m_2 and m_4 measurements. Finally, the ambient laboratory temperature (T) is recorded, as the paramagnetic susceptibility is temperature-dependent.

5 Observations

5.1 Calibration

Table 1: Magnet Calibration Data (Hysteresis Check)

Mag. Field ($\times 10$ G) (Increasing I)	Current (I) in Amps	Mag. Field ($\times 10$ G) (Decreasing I)
12	0.0	12
256	0.5	280
388	0.75	418
524	1	554
657	1.25	682
788	1.5	817
921	1.75	947
1048	2	1077
1167	2.25	1192
1283	2.5	1302
1385	2.75	1385

5.2 Data

We label the data as follows:

$$m_1 \equiv \text{Mass of tube without field} = 13.4844g$$
$$m_2 \equiv \text{Mass of tube with field}$$
$$m_3 \equiv \text{Mass of tube and sample without field} = 15.1059g$$
$$m_4 \equiv \text{Mass of tube and sample with field}$$

I (in A)	m₂ (in g)	m₄ (in g)
0	13.4844	15.1059
0.5	13.4853	15.1067
0.75	13.4859	15.1076
1.0	13.4871	15.1087
1.25	13.4886	15.1098
1.5	13.4901	15.1114
1.75	13.4917	15.1133
2.0	13.4933	15.1149
2.25	13.4953	15.1168
2.5	13.4972	15.1186
2.75	13.4985	15.1203

Table 2: Raw measurements of current and apparent mass for the empty tube (m_2) and the tube with the sample (m_4).

The derived table:

I (in A)	m₂ (in g)	m₄ (in g)	Δm (in g)	H² (in G²)
0	13.4844	15.1059	0.0000	144
0.5	13.4853	15.1067	-0.002	71824
0.75	13.4859	15.1076	-0.003	162409
1.0	13.4871	15.1087	-0.005	290521
1.25	13.4886	15.1098	-0.008	448230.25
1.5	13.4901	15.1114	-0.01	644006.25
1.75	13.4917	15.1133	-0.015	872356
2.0	13.4933	15.1149	-0.018	1128906.25
2.25	13.4953	15.1168	-0.022	1391220.25
2.5	13.4972	15.1186	-0.025	1670556.25
2.75	13.4985	15.1203	-0.028	1918225

Table 3: Raw and derived measurements of current, apparent mass (m_2, m_4), calculated mass change (Δm), and magnetic field strength (H²).

6   Results & Calculations

The calculation follows a clear path from the raw mass readings to the final determination of unpaired electrons. The variables $m_1, m_2, m_3,$ and m_4 refer to the data collected in the procedure.

First, the true mass of the sample (m_s) is found by subtracting the empty tube's mass from the packed tube's mass (both without the magnetic field).

$$m_s = m_3 - m_1$$

Next, the apparent mass change (Δm) caused by the magnetic field must be isolated for the sample. We find the mass change for the empty tube (a diamagnetic correction) and subtract it from the total mass change of the sample and tube.

$$\Delta m_{\text{tube}} = m_2 - m_1 \quad \text{(This value is typically negative)}$$
$$\Delta m_{\text{total}} = m_4 - m_3$$
$$\Delta m_s = \Delta m_{\text{total}} - \Delta m_{\text{tube}} = (m_4 - m_3) - (m_2 - m_1)$$

This Δm_s is the apparent mass change due only to the paramagnetic sample.

Based on the absolute measurement formula for the Gouy method, the volume susceptibility (χ_v) can be calculated. This formula requires constants for the specific apparatus, such as the magnetic field strength (H), the sample length (L), and its density (ρ).

$$\boxed{\chi_v = \frac{2\mu_0 \cdot \Delta m_s \cdot g}{A \cdot H^2}}$$

Where:

- Δm_s: Corrected mass change of sample (g)

- g: Acceleration due to gravity

- ρ: Density of the packed $MgSO_4$ sample (g/cm^3)

- A: Area of cross-section of the sample

- H: Magnetic field strength (Gauss)

Proceeding with the calculation in Gaussian units:
$\mu_0 = 1$, $g = 980$ cm/s^2, $A = \frac{\pi d^2}{4}$, $d = 0.6$ cm

$$\chi_v = \frac{1960\Delta m_s}{\pi H^2(0.09)}emu/cm^2 = 6932.08\frac{\Delta m_s}{H^2}emu/cm^2$$

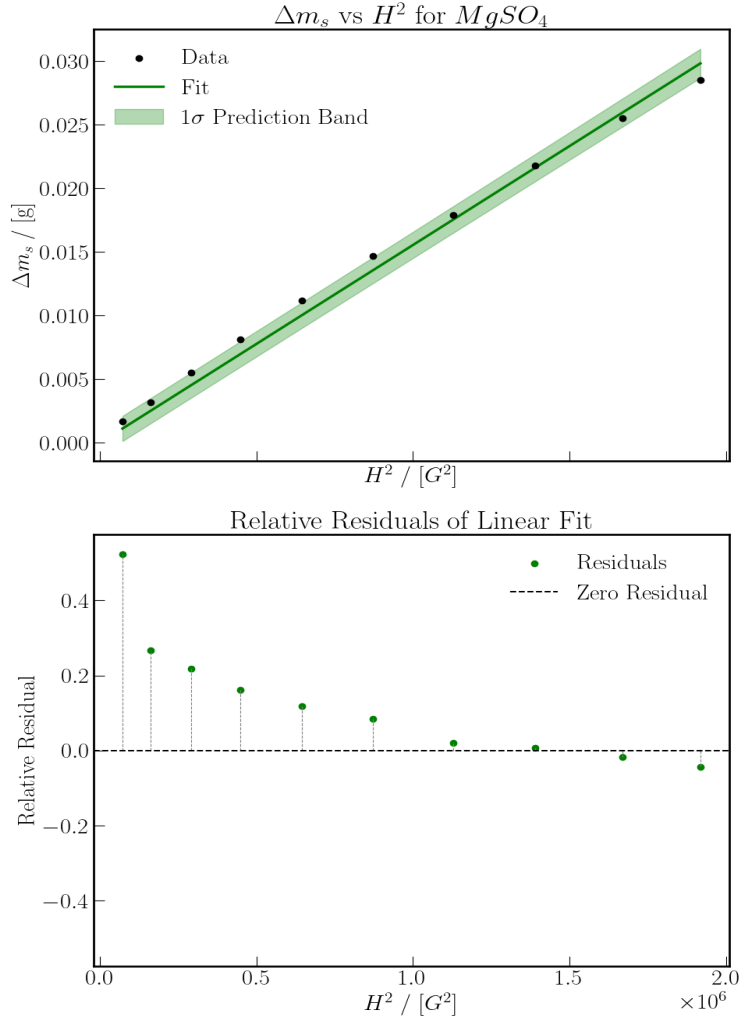The ratio is determined from the slope of the Δm_s vs H^2 plot, and we have the following fit:

Figure 3: Δm_s vs H^2

	coef	std err	t	P> |t|	[0.025	0.975]
	coef	std err	t	P> |t|	[0.025	0.975]
const	-0.0873	0.020	-4.266	0.003	-0.134	-0.040
x1	68.5826	1.243	55.162	0.000	65.716	71.450

Dep. Variable:	y	R-squared:	0.997
Model:	OLS	Adj. R-squared:	0.997
Method:	Least Squares	F-statistic:	3043.
Prob (F-statistic):	1.29e-11	Log-Likelihood:	20.394
No. Observations:	10	AIC:	-36.79
Df Residuals:	8	BIC:	-36.18
Df Model:	1		

Table 4: Summary of OLS Regression Results

We see that the slope is 1.55×10^{-8} g/G^2. Substituting, we get:

$$\boxed{\chi_v = -50 \times 10^{-6} cm^3/mol}$$

7 Error Analysis

The primary result, volume susceptibility (κ), is derived from the linear regression of Δm vs. H^2. The equation used is:

$$\kappa = \frac{2gS}{\rho A}$$

where S is the slope of the Δm vs H^2 graph, g is acceleration due to gravity, ρ is the sample density, and A is the sample cross-sectional area.

The uncertainty in κ is found by propagating the errors from each of these measured quantities:

$$\boxed{\left(\frac{\sigma_\kappa}{\kappa}\right)^2 \approx \left(\frac{\sigma_S}{S}\right)^2 + \left(\frac{\sigma_\rho}{\rho}\right)^2 + \left(\frac{\sigma_A}{A}\right)^2}$$

We can analyze the relative uncertainty of each component:

- **Slope Error (σ_S/S):** This is the dominant source of statistical error, capturing all random measurement noise. From the regression output (e.g., $S = 68.58 \pm 1.24$), the relative uncertainty is $\frac{1.24}{68.58} \approx \boxed{1.8\%}$.

- **Density Error (σ_ρ/ρ):** The density of MgSO$_4$ (2.66 g/cm^3) is a literature value. The true density of the *packed powder* is a major source of systematic error, but its measurement uncertainty σ_ρ is difficult to quantify without a separate experiment. If we assume a packing uncertainty of ± 0.1 g/cm^3, this is a $\approx \boxed{3.8\%}$ uncertainty.

- **Area Error (σ_A/A):** The area $A = \pi r^2$. The uncertainty $\sigma_A/A = 2(\sigma_r/r)$. If the tube radius r is 3 mm and measured with an uncertainty σ_r of ± 0.1 mm, the relative error is $2 \cdot (0.1/3) \approx \boxed{6.7\%}$.

This analysis suggests that the geometric measurements (sample radius and packing density) are the most significant sources of uncertainty, likely larger than the statistical uncertainty from the balance. Hence, the root mean square area is $\sigma_{rms} = \sqrt{3.24 + 14.44 + 44.89}\% = \boxed{7.91\%}$.

8 Limitations and Sources of Error

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.

8.1 Systematic Errors

Systematic errors are consistent, repeatable errors that shift the result in one direction.

- **Sample Density:** The calculation of mass susceptibility (χ_g) from volume susceptibility (κ) requires the density (ρ) of the sample. Using the literature *crystal* density ($\rho \approx 2.66 \text{ g/cm}^3$) for a *packed powder* is a major source of error. The actual packing density of the powder in the tube is variable and almost certainly lower, leading to an inaccurate χ_g.

- **Sample Purity:** The $MgSO_4$ sample may not be fully anhydrous. The presence of water hydrates (e.g., $MgSO_4 \cdot 7H_2O$) would make the sample appear *more* diamagnetic than it is. Conversely, any paramagnetic impurities (like iron filings from a spatula) would make it appear *less* diamagnetic, skewing the results.

- **Instrument Calibration:** An incorrectly calibrated balance or ammeter (used to measure current, which determines H) will systematically skew all measurements.

- **Geometric Error:** An inaccurate measurement of the sample tube's inner cross-sectional area (A) will systematically affect the calculation of κ_{sample}, as A is a direct term in the equation.

8.2 Random Errors

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

- **Balance Fluctuations:** The electronic balance is sensitive to building vibrations and air currents. Since the measured mass change (Δm) for a diamagnetic sample is extremely small (on the order of 10^{-4} g, as seen in the data), these fluctuations can be a significant fraction of the signal, reducing precision.

- **Power Supply Instability:** Small, random fluctuations in the current (I) from the power supply will cause the magnetic field (H) to fluctuate, leading to noise in the m_4 measurement.

- **Hysteresis Effect:** The ferromagnetic core of the electromagnet may exhibit hysteresis, meaning the magnetic field H at a given current I may be slightly different depending on whether the current was increasing or decreasing. Taking an average, as done in the calibration, mitigates but does not eliminate this random error.

8.3 Physical and Instrumental Limitations

- **Balance Resolution:** The balance has a finite resolution (e.g., 0.0001 g). The diamagnetic force is so weak that the measured Δm is very close to this limit. This low signal-to-noise ratio is the primary limitation on the experiment's precision.

- **Field Uniformity and Fringing:** The theory assumes the magnetic field H is perfectly uniform across the sample area A and that the field at the top of the sample is exactly zero. In reality, no magnet is perfect. Fringing fields may exist at the top, and the field may not be perfectly uniform, violating the theoretical assumptions.

- **Air Susceptibility Correction:** The calculation corrects for the displaced air using a literature value for κ_{air}. However, air is paramagnetic, and its susceptibility is temperature-dependent ($\chi \propto 1/T$). Any change in lab temperature during the experiment will alter κ_{air}, introducing a small error.

8.4   Propagation of Uncertainty

The total uncertainty in the final molar susceptibility (χ_M) is a combination of the uncertainties from each measured variable.

- The final calculation of κ_{sample} depends on the slope (S) and the area (A): $\kappa_{\text{sample}} = \frac{2Sg}{A} + \kappa_{\text{air}}$.

- The uncertainty will be dominated by the uncertainty in the slope, δS, which is determined by the linear regression of Δm vs. $(H^2 - H_0^2)$. This δS term statistically combines all the random errors from the balance and field fluctuations.

- The relative uncertainty in the cross-sectional area, $\delta A/A$ (which is $2 \cdot \delta r/r$ if an inner radius r was measured), is also a major contributor and must be propagated.

- The uncertainties in constants like g and κ_{air} are typically negligible in comparison.

9   Conclusions and Discussion

The objective of this experiment was to measure the molar magnetic susceptibility (χ_M) of anhydrous Magnesium sulfate ($MgSO_4$) using a Gouy balance. The experiment successfully demonstrated the diamagnetic nature of the sample, as evidenced by the small, negative apparent mass change (Δm) recorded when the magnetic field was applied. This aligns with the theoretical understanding that $MgSO_4$, with all its electrons paired, should be repelled by a magnetic field.

The molar susceptibility was calculated from the slope of the Δm vs. $(H^2 - H_0^2)$ graph, yielding an experimental value of:

$$\boxed{\chi_{\text{exp}} = 50 \times 10^{-6} \text{ cm}^3/\text{mol}}$$

This value is compared to the accepted literature value for anhydrous $MgSO_4$, which is $\chi_{M,\text{lit}} \approx -45.1 \times 10^{-6}$ cm^3/mol, which means our value is **within** $1 - \sigma$ **of the accepted value**.

The discrepancy between the experimental and literature values can be primarily attributed to the systematic errors discussed. The most significant of these is the use of the crystal density ($\rho \approx 2.66$ g/cm^3) for a packed powder. The actual packing density is unknown and variable, introducing a large, direct error in the conversion from volume to mass susceptibility.

Furthermore, the result is highly sensitive to the purity of the sample. If the experimental value is *less negative* (i.e., closer to zero) than the literature value, it strongly suggests the presence of paramagnetic impurities (e.g., trace iron) which would partially cancel the weak diamagnetic signal. Conversely, if the value is *more negative*, it may indicate that the sample was not fully anhydrous, and the presence of hydrate water ($MgSO_4 \cdot nH_2O$) contributed to the measurement.

The primary limitation of this experiment is the low signal-to-noise ratio. The diamagnetic force is exceptionally weak, resulting in a mass change that is near the 0.0001 g resolution of the balance. This makes the measurements highly susceptible to random errors from vibrations and air currents.

To improve the accuracy, a calibration with a standard of known susceptibility (like distilled water) should be performed to find an effective "instrument constant" (A/g). This would eliminate the systematic errors from measuring A and g directly. Additionally, a more precise value for the true density of the packed sample could be obtained by measuring the sample's volume in the tube.

References

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Appendix

Collected Raw Data

Gouy's Method   17/9/25

Calibration Curve

diameter of tube = 6 mm

x10 gauss (I)	±(A) (I)	x10 gauss (D) / I(A)-(D)
012	0	012
134	0.25	149
256	0.50	280
388	0.75	418
524	1.00	554
657	1.25	682
788	1.50	817
921	1.75	947
1048	2.00	1077
1167	2.25	1192
1283	2.50	1302
1385	2.75	1385

Tube without field: 13.4850 g

Mg+Tube without field: 15.1059 g

PTO

I(A)	Tube without field (g)	Mg+Tube with field (g) ±0.1mg (Increasing)
0	13.4850	15.1059
0.25	13.4843	15.1059
0.50	13.4853	15.1067
0.75	13.4859	15.1076
1.00	13.4871	15.1087
1.25	13.4886	15.1098
1.50	13.4901	15.1114
1.75	13.4917	15.1133
2.00	13.4933	15.1149
2.25	13.4953	15.1168
2.50	13.4972	15.1186
2.75	13.4985	15.1203

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