

Microscale Determination of Magnetic Susceptibility¹

Electrons have a magnetic moment that can be aligned either with or in opposition to an applied magnetic field, depending on whether the spin magnetic quantum number, m_s , is $+\frac{1}{2}$ or $-\frac{1}{2}$. For an atom or ion with only paired electrons, the individual electron contributions to the overall spin magnetic quantum number, M_s , cancel one another, giving a zero net value of the overall spin quantum number; i.e., $S = 0$. Such a species is said to be *diamagnetic*. If a diamagnetic material is placed between the poles of a strong magnet it will display repulsion for the applied field. This repulsion arises from an induced response caused by the applied field. Suppose the sample is suspended between the poles of the magnet and is connected to the pan of an analytical balance. This is the experimental arrangement of a *Gouy balance*. As a result of the induced diamagnetic repulsion, the sample will *appear* to weigh less in the magnetic field, compared to its true weight outside the field. When removed from the applied field, the sample has no residual magnetic moment, and its apparent weight will be its true weight.

If the sample contains one or more unpaired electrons, the overall spin quantum number will be greater than zero; i.e., $S > 0$. Such a species is said to be *paramagnetic*. If a paramagnetic species is placed between the poles of a strong magnet it will experience an attraction for the field, due to the alignment of the permanent paramagnetic moment with the applied field. If the sample is weighed with a Gouy balance, it will *appear* to be heavier in the magnetic field, compared to its true weight outside the field. With the exception of monatomic hydrogen, all atoms or ions with unpaired electrons also have paired electrons. In an applied field, these paired electrons and their associated induced diamagnetic moment slightly mitigate the paramagnetic attraction for the applied field. Nonetheless, the paramagnetic moment is always stronger than the opposing diamagnetic moment, so the net effect is an attraction for the field. Thus, whenever we refer to a substance as paramagnetic, owing to an electronic configuration having unpaired electrons, we must realize that there is also a subtractive diamagnetic contribution to the overall magnetic moment of the sample.

Transition metals, by definition, have at least one oxidation state with an incompletely filled *d* or *f* subshell and are consequently paramagnetic in such states. The *magnetic moment*, μ , results from both the spin and orbital contributions of these unpaired electrons. The presence of coordinated ligands around the metal ion quenches the orbital contribution to greater or lesser degree, making the spin contribution most important. As an approximation, the expected magnetic moment for an ion with a certain number of unpaired electrons can be estimated from the spin-only magnetic moment, μ_s , which disregards orbital contributions using equation 1:

$$\mu_s = g\sqrt{S(S+1)} \quad (\text{eqn. 1})$$

In equation (1), g is the gyromagnetic ratio ($g = 2.00023$) and $S = n(\frac{1}{2})$, where n is the number of unpaired electrons in the configuration. Substituting $g = 2$ and $S = n(\frac{1}{2})$ into eqn. 1, we can calculate the spin-only moment in terms of the number of unpaired electrons from equation 2:

$$\mu_s = \sqrt{n(n+2)} \quad (\text{eqn. 2})$$

¹ Adapted in part from Z. Szafran, R. M. Pike, and M. M. Singh, *Microscale Inorganic Chemistry*, John Wiley & Sons, N.Y., 1991, pp. 49-57.

Thus, for a d^1 configuration, such as Ti^{3+} , we obtain $\mu_s = [1(1 + 2)]^{1/2} = \sqrt{3} = 1.73$ BM (the units of the magnetic moment are Bohr magnetons). Actual magnetic moments tend to be somewhat larger than the spin-only values obtained from either equations (1) or (2), owing to incomplete quenching of the orbital contribution. Nonetheless, the experimentally obtained value of the *effective magnetic moment*, μ_{eff} , taken as approximately the spin-only value, often serves as a practical means of determining the number of unpaired electrons on the transition metal in a complex. This, in turn, gives information about the spin state of the metal (high vs. low spin) and can even suggest its oxidation state or mode of bonding.

Experimental Determination of Magnetic Moments

In this experiment you will determine the *magnetic susceptibility*, χ , and from it the magnetic moment, μ , of your previously prepared $\text{Mn}(\text{acac})_3$ complex. Magnetic moments are not measured directly. Instead, they are calculated from the experimentally determined *magnetic susceptibility*, χ . A number of techniques exist to observe magnetic susceptibilities of transition metal complexes. These include the Gouy balance method, the Faraday method, NMR and Evans microbalance. The Gouy balance is not suitable for microscale experiments, however, the Evans balance employs the Gouy method in a device that is compact, lightweight, self-contained and capable of observing microscale magnetic susceptibilities. It does not require a separate magnet or power supply, and is therefore portable. The instrument has a digital readout that provides quick and accurate readings, with sensitivity matching traditional apparatus. It can be used with solids, liquids, and solutions. As such, the Evans balance is ideal for our purposes.

In the Gouy method, as previously noted, the balance measures the apparent change in the weight of the sample created by the sum of the diamagnetic repulsion and paramagnetic attraction for the applied field. The Evans balance uses the same principle, but instead of measuring the force that the magnet exerts on the sample, it measures the equal and opposite force the sample exerts on a suspended permanent magnet. The Evans balance determines this force by measuring the change in current required to keep a set of suspended permanent magnets in balance when their fields interact with the sample. The magnets are on one end of a balance beam, and when interacting with the sample change the position of the beam. This change is registered by a pair of photodiodes set on opposite sides of the balance beam's equilibrium position. The diodes send signals to an amplifier that in turn supplies current to a coil that will exactly cancel the interaction force. A digital voltmeter, connected across a precision resistor in series with the coil, measures the current directly. This current is displayed on the digital readout. The sample's magnetic susceptibility per gram is called the *mass magnetic susceptibility*, χ_g . For the Evans balance, the expression for the mass magnetic susceptibility is given by equation 3:

$$\chi_g = \frac{L[C(R-R_0) + \chi_v' A]}{m} \quad (\text{eqn. 3})$$

where χ_g = mass magnetic susceptibility

L = sample length in centimeters

m = sample mass in grams

C = balance calibration constant

R = reading from the digital display when the sample and tube are in the balance

R_0 = reading from the digital display when the empty sample tube is in the balance

χ_v' = volume susceptibility of air ($0.029 \times 10^{-6} \text{ erg} \cdot \text{G}^{-2} \text{ cm}^{-3}$)

A = cross-sectional area of the sample

The volume susceptibility of air can be ignored with solid samples, so eqn. 3 can be rewritten as

$$\chi_g = \frac{CL(R-R_0)}{m \times 10^9} \quad (\text{eqn. 4})$$

which gives χ_g in the cgs-units of $\text{erg}\cdot\text{G}^{-2}\text{cm}^{-3}$ (where G is Gauss). The calibration standards usually employed in magnetic susceptibility measurements are $\text{Hg}[\text{Co}(\text{SCN})_4]$ or $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$, which have χ_g values of 1.644×10^{-5} and $1.104 \times 10^{-5} \text{ erg}\cdot\text{G}^{-2}\text{cm}^{-3}$, respectively. A preferred method to evaluate C in equation (4) is to perform the experiment with one of these calibration standards employing the appropriate value of χ_g . In order to avoid the use of a mercury compound we will use the $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ standard available in the laboratory.

Calculation of Magnetic Moment from Magnetic Susceptibility

The *molar magnetic susceptibility*, χ_M , is obtained from the mass magnetic susceptibility, χ_g , by multiplying by the molecular weight of the sample in units of g mol^{-1} ; i.e.,

$$\chi_M = M \chi_g \quad (\text{eqn. 5})$$

The units of χ_M are $\text{erg}\cdot\text{G}^{-2}$. The experimentally obtained value of χ_M includes both paramagnetic and diamagnetic contributions, which we may identify as χ_A and χ_α , respectively. All sources of paired electrons (e.g., ligands, counter ions, core electrons on the paramagnetic species) contribute to the diamagnetic portion of the overall susceptibility. In 1910, Pascal observed that these contributions were approximately additive and consistent from sample to sample. Consequently, the diamagnetic contribution to the observed molar susceptibility can be estimated as the sum of constants (called Pascal's constants) for each diamagnetic species in the sample.² As we are only interested in the paramagnetic molar susceptibility, we can remove the diamagnetic contributions from χ_M using the relationship:

$$\chi_A = \chi_M - \sum \chi_\alpha \quad (\text{eqn. 6})$$

Values of χ_A (sometimes called the corrected magnetic susceptibility, χ_M^{corr}) are inherently positive, while those of χ_α are inherently negative. Thus, for a paramagnetic substance, it must be that $\chi_A > \chi_M$. The value of the effective magnetic moment, μ_{eff} , can be determined from χ_A by the *Curie Law* shown in equation 7 where k is the Boltzmann constant, T is the absolute temperature (K), N is Avogadro's number, and β is the Bohr magneton.

$$\mu_{\text{eff}} = \sqrt{\frac{3kT \chi_A}{N\beta^2}} \quad (\text{eqn. 7})$$

If the appropriate constants are substituted, eqn. 7 can be simplified as shown in eqn. 8

$$\mu_{\text{eff}} = 2.828\sqrt{T \chi_A} \quad (\text{eqn. 8})$$

² An updated tabulation of Pascal's constants has been summarized by G. A. Bain and J. F. Berry, *J. Chem. Educ.*, **2008**, 85, 532.

Experimental Procedure

The first measurement will be to measure the calibration standard $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ in order to obtain a value of C , the instrument constant in eqn. 4 (the original C value following production is printed on the rear of the instrument). The procedure is then repeated with the $\text{Mn}(\text{acac})_3$ sample and the experimentally determined value of C for the balance system is used to calculate its magnetic susceptibility.

1. Turn the RANGE knob on the balance to $\times 1$ and allow the balance to warm up for 30 min.
2. Adjust the ZERO knob until the display reads 000. The zero should be readjusted if the range is changed.

Note: The zero knob on the balance has a range of 10 turns. It is best to operate the balance in the middle of this range. This can be accomplished by turning the knob 5 turns from one end and then, ignoring the bubble level, adjusting the back legs of the balance until the digital display reads about zero. Once this is done at the beginning of the laboratory, all further adjustments can be made with the knob on the front of the instrument.

3. Place an empty tube of known weight (use the analytical balance) into the tube guide on top of the instrument and take the reading R_o .

Note: The instrument can drift over short periods of time and should be re-zeroed before each measurement.

4. On the $\times 1$ setting the digital display should fluctuate by no more than ± 1 . However, when you record R or R_o take a "visual average" of this fluctuation and use this as your reading.
5. Carefully fill the sample tube with the solid so that the height will be at least 1.5 cm after packing. A lesser amount will not give a stable reading of R . Gently tap the bottom of the tube on a hard surface (**not the table the balance is on**) to pack the sample. When it is well packed, measure the sample length in centimeters to obtain the value of L . Then, obtain the mass of the sample in grams.

Note: A critical part of the technique is correctly packing the well-powdered solid in the sample tube. If necessary, use a mortar and pestle to grind the sample into a fine powder. The sample consistency must be of a fine powder so that it may be densely packed to avoid any contribution from the volume susceptibility of air.

6. Re-zero the instrument, place the packed sample tube into the tube guide, and take the reading R . A negative reading indicates a diamagnetic sample. If the reading is off-scale, change the RANGE knob to $\times 10$, re-zero, and multiply the reading by 10.

Note: To be sure you have the true value of R after the first reading, repeatedly tap the bottom of the tube firmly but gently on a hard surface for about 30 - 60 seconds. Then, take another reading of R . Continue this until you have three values that agree within ± 1 . Also, during the tapping process ensure that the solid forms an even surface in the tube and is not sloped to one side.

7. Using a thermometer placed or suspended near the instrument, determine the temperature to $\pm 0.1^\circ\text{C}$.

8. Using eqn. 4, where $\chi_g = 1.104 \times 10^{-5} \text{ erg} \cdot \text{G}^{-2} \text{ cm}^{-3}$ for $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$, calculate the instrument constant C from your recorded values of L , R_o , R and m for $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$.
9. Remove the sample from the tube by inverting it and gently tapping it on a piece of weighing paper on a hard surface. Do not tap too hard, since the glass lip can be easily broken. After the tube is empty, rinse with an appropriate solvent from a fine tip disposable Pasteur pipette.
10. Again using eqn. 4, calculate the mass susceptibility χ_g of $\text{Mn}(\text{acac})_3$ from the determined value of C and your recorded values of L , R_o , R and m . You will also need the value of T for the calculation of μ from the Curie Law (eqn. 8).
11. Repeat step 9 above to clean all sample tubes.

Laboratory Report

1. Show all calculations for C , the instrument constant determined from measurements on $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$.
2. Show all calculations leading to your value of μ_{eff} of the metal complex sample, $\text{Mn}(\text{acac})_3$. How well does your value agree with the expected value for the sample?
3. Write out the electron configurations in the form $t_{2g}^x e_g^y$ for both the nickel and manganese metal ions in the standard and the sample, assuming an ideal octahedral ligand field in both cases. Draw a schematic of the crystal field splitting diagrams and indicate the expected distribution of electrons between the t_{2g} and e_g orbital levels for both cases.
4. What other oxidation states of manganese are common? Calculate their expected spin-only magnetic moments for both high- and low-spin cases.
5. Calculate the expected spin-only magnetic moments for high-spin octahedral ions Ti^{3+} , V^{3+} , Cr^{3+} , Fe^{3+} and Co^{3+} . Repeat the calculation for low-spin Fe^{2+} and Co^{2+} .