

Microscale Determination of Magnetic Susceptibility¹

In this experiment you will determine the magnetic susceptibility, and from it the magnetic moment, of your previously prepared hexammine chromium(III) nitrate or another compound you have prepared. If you have insufficient product for a suitable sample, you may be supplied with a sample of another compound.

Introduction

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 $+1/2$ or $-1/2$. 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 experience a repulsion for the applied field. The repulsion arises from circulation of the electrons caused by the applied field, resulting in an induced magnetic field in opposition. 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. However, 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. 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

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

with a certain number of unpaired electrons can be estimated from the spin-only magnetic moment, μ_s , which disregards orbital contributions:

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

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

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

Thus, for a d^1 configuration, such as Ti^{3+} , we obtain $\mu_s = [1(1 + 2)]^{1/2} = \sqrt{3} = 1.73$. The units of the magnetic moment are Bohr magnetons (BM). Actual magnetic moments tend to be somewhat larger than the spin-only values obtained from either equation (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 and can suggest its oxidation state or mode of bonding.

Experimental Determination of Magnetic Moments

Magnetic moments are not measured directly. Instead, they are calculated from the measured *magnetic susceptibility*, χ . Over the years there have been a number of techniques used to determine magnetic susceptibilities of transition metal complexes. These include the Gouy method, the Faraday method, and the NMR method. Of these, only the Faraday and NMR techniques are suitable for microscale samples of 50 mg or less. In 1974, D. F. Evans² of Imperial College, London, developed a new type of magnetic susceptibility balance suitable for semi-microscale samples, which is commercially available from Johnson Matthey. The Evans balance employs the Gouy method in a device that is compact, lightweight, and self-contained. 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

²D. F. Evans, *J. Phys. E; Sci. Instr.*, **1974**, 7, 247.

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 general expression for the mass magnetic susceptibility is

$$\chi_g = \frac{L}{m} \left[C(R - R_o) + \chi_v' A \right] \quad (3)$$

where χ_g = mass magnetic susceptibility

L = sample length in centimeters

m = sample mass in grams

C = balance calibration constant (different for each balance; printed on the back of the instrument) (Calculated in this experiment using a calibration standard.)

R = reading from the digital display when the sample (in the sample tube) is in place in the balance

R_o = reading from the digital display when the empty sample tube is in place 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 is usually ignored with solid samples, so equation (3) can be rewritten as

$$\chi_g = \frac{CL(R - R_o)}{m \times 10^9} \quad (4)$$

Equation (4) gives the mass magnetic susceptibility 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 $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$.

Calculation of Magnetic Moment from Magnetic Susceptibility

The *molar magnetic susceptibility*, χ_M , is obtained from the mass magnetic susceptibility by multiplying by the molecular weight of the sample in units of g/mol; i.e.,

$$\chi_M = M\chi_g \quad (5)$$

The units of χ_M are $\text{erg}\cdot\text{G}^{-2}$. This experimentally obtained value of χ_M includes both paramagnetic and diamagnetic contributions, which we may identify as χ_A and χ_d , 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.³ We are interested in the paramagnetic molar susceptibility, which can be obtained by removing the diamagnetic contributions from χ_M . Thus we may write

$$\chi_A = \chi_M - \sum \chi_d \quad (6)$$

Values of χ_A (sometimes called the corrected magnetic susceptibility, χ_M^{corr}) are inherently positive, while those of χ_d are inherently negative. Thus, for a paramagnetic substance, it must be that $\chi_A > \chi_M$.

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

The value of the effective magnetic moment, μ_{eff} , can be determined from χ_A by the *Curie Law* equation where k is the Boltzmann constant, T is the absolute temperature (K), N is Avogadro's number, and β is the Bohr magneton. If the appropriate constants are substituted, equation (7) becomes

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

³A table of Pascal's constants can be found in the Appendix. Other values may be found in P. F. Selwood, *Magnetochemistry*, 2nd ed., Wiley (Interscience), N.Y., 1956. An updated tabulation of values has been given by G. A. Bain and J. F. Berry, *J. Chem. Educ.*, **2008**, 85, 532.

Experimental Procedure (Evans/Johnson Matthey Balance)

The first measurement will be made with 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 equation (4). The procedure is then repeated with the $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$, and the experimentally determined value of C for the balance system is used to calculate the magnetic susceptibility of the sample. Other compounds used or provided by your instructor will be treated identically to $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$.

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 (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 rezeroed before each measurement.

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.

4. 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: If necessary, use a mortar and pestle to grind the sample into a fine powder before attempting to fill the sample tube.

5. Rezero 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 $\times 10$, rezero, and multiply the reading by 10.

Note: A critical part of the technique is correctly packing the well-powdered solid in the sample tube. 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.

6. Using a thermometer placed or suspended near the instrument, determine the temperature to 0.1°C .
7. Using equation (4), calculate the instrument constant C (reference standard) or the mass susceptibility (sample) from your recorded values of L , R_o , R , m , and (for the sample) C . You will need the value of T for the calculation of μ from the Curie Law, equation (8).
8. 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 disposable pipette with a fine tip (Pasteur pipette).

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, $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ or the compound you used. 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 the metal ions in both the standard and the sample, assuming an octahedral ligand field in both cases. Write out the crystal field splitting diagrams and indicate the expected distribution of electrons between the t_{2g} and e_g orbital levels using "line and arrow" notation.
4. Calculate the expected spin-only magnetic moments for high-spin octahedral ions Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , and Fe^{3+} . Repeat the calculation for low-spin Mn^{3+} and Fe^{3+} .

Appendix
Diamagnetic Correction Constants (Pascal's Constants)*

Cations	$-10^6\chi_a$	Anions	$-10^6\chi_a$	Molecules	$-10^6\chi_a$
Li ⁺	1	F ⁻	9	H ₂ O	13
Na ⁺	7	Cl ⁻	23	NH ₃	16
K ⁺	15	Br ⁻	34	en	47
Rb ⁺	22	I ⁻	50	py	49
Cs ⁺	33	CH ₃ CO ₂ ⁻	29	PPh ₃	167
NH ₄ ⁺	13	C ₆ H ₅ CO ₂ ⁻	71		
Mg ²⁺	4	CN ⁻	13		
Ca ²⁺	9	CNO ⁻	23		
Sr ²⁺	16	CNS ⁻	34		
Ba ²⁺	26	ClO ₄ ⁻	32		
Cu ⁺	15	CO ₃ ²⁻	28		
Ag ⁺	27	C ₂ O ₄ ²⁻	28		
Zn ²⁺	13	HCO ₂ ⁻	17		
Cd ²⁺	20	NO ₃ ⁻	19		
Hg ²⁺	36	O ²⁻	6		
Tl ⁺	36	OH ⁻	11		
Pb ²⁺	32	S ²⁻	28		
core**	13	SO ₄ ²⁻	38		
		S ₂ O ₃ ²⁻	46		
		acac ⁻	55		

*All values are $-10^6\chi_a$ in cgs units. Example: for Li⁺, $\chi_a = -1 \times 10^{-6} \text{ erg}\cdot\text{G}^{-2} \text{ mol}^{-1}$.
 Abbreviations: acac⁻ = acetylacetonate; en = ethylenediamine; PPh₃ = triphenylphosphine; py = pyridine. Values of Bain and Berry (cf. ref. 3) may be used instead of these values.

**Core electrons of first-row transition metal ions.