5 Slides About Magnetic Susceptibility
Instructor Notes to Accompany the Slides

Short description on magnetism:
The behavior of any magnetic material is dependent on the presence of unpaired electrons and how they interact with each other. To be more precise, any moving electrical charge with spin and orbital angular momentum generates a magnetic field in a system. The quantitative measurement of the magnetic response of a material to an applied magnetic field is known as susceptibility (χ). The magnetic materials are broadly classified into two categories, which are dia- and paramagnetic materials. Diamagnetism arises from the interaction of paired electrons with a magnetic field (repelled by the magnetic fields) whereas paramagnetism comes from the presence of unpaired electrons in the system (attracted by the magnetic field). The type of spin-coupling of adjacent spin pairs, further categorizes the paramagnetic materials. For example, ferromagnetic ordering is achieved when the spins are aligned parallel (↑↑) and antiferromagnetic ordering is the result of antiparallel (↑↓) spin alignment of the spin pair. The commonly known ferromagnetic solids are the materials made of iron, cobalt, nickel and several rare earth metals and their alloys.

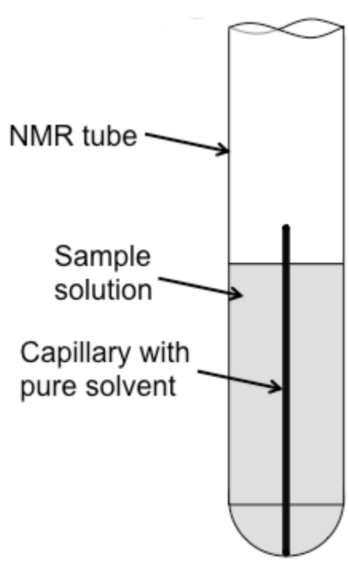

Figure 1. Coaxial capillary and NMR Tube for Evans Method.

Evans Method
In the determination of magnetic susceptibility of a paramagnetic compound in solution, ^{1}H NMR is a powerful tool. This method was first developed by Evans (Evans, D. F. *J. Chem. Soc.* **1959**, 2003). In the basic protocol of this method, a sealed capillary containing pure deuterated NMR solvent is placed in a regular NMR tube with a solution of the paramagnetic compound in the same NMR solvent (Figure 1). A ^{1}H NMR spectrum is then collected. The NMR solvent in the outer NMR tube remains in the diamagnetic region, giving a peak to be used as a reference. While the NMR solvent in the capillary will give a shifted peak due to the bulk paramagnetic behavior of the sample solution in the magnetic field. This shift relative to the reference peak can then be measured and used to calculate the magnetic susceptibility.

Both calculation formulas are shown below:

$$\chi_M = \frac{3}{4\pi}\frac{\Delta\nu}{\nu_0}\frac{1000}{c} + \chi_0 - \chi_D \qquad \text{Eq. 1}$$

χ_M = total molar susceptibility

$\Delta\nu$ – paramagnetic shift of the solvent (Hz)

ν_0 – frequency of the NMR spectrometer (Hz)

c – concentration of the metal complex, L/mole

χ_0 – solvent susceptibility = χ_g (gram susceptibility of solvent from *CRC handbook*) × molecular weight of the metal complex

χ_D – diamagnetic correction for the metal complex (Carlin, R. L. In Magnetochemistry; Springer-Verlog: New York, 1986, p3)

$$\mu = 2.84 \times \sqrt{\frac{\chi_M \times T}{n}} \qquad \text{Eq. 2}$$

χ_M – total molar susceptibility

T – temperature of measurement (K)

n – number of paramagnetic metal centers

Figure 2. SQUID Instrumentation, Courtesy of Professor George Christou.

SQUID Method

SQUID magnetometer is one of the most effective and sensitive ways of measuring magnetic properties. Super conductive quantum interference device (SQUID) is comprised of two superconductors separated by thin insulating layers to form two parallel Josephson junctions which is designed to measure magnetic moment even for an extremely small magnetic response generated by the compound. The picture of the above magnetometer is MPMS-XL-SQUID suscpetometer from Professor George Christou's laboratory at University of Florida which is equipped with a 7 T magnet and operating in the 1.8-300 K range. Samples are embedded in solid eicosane to prevent torqueing. The raw data from the instrument was processed to achieve molar paramagnetic susceptibility (χ_M). Employing the χ_M in the following equation, the spin ground state (S) for any complex can be obtained.

Every electron has a magnetic moment of s = ½, now depending on the interaction among the unpaired electrons the total magnetic moment for the system needs to be measured in order to understand the overall magnetic response for the system. The following equation is largely used to measure the overall spin state of the system (or any metal complex).

$$\chi_M T = g^2 S(S+1)/8$$

where g is a constant (Landé factor) which is usually 2 for transition metals. *S* stands for the total spin state.

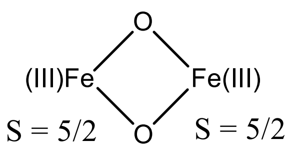

Figure 3. Iron Complex.

Example Problem
For example, Fe(III) has five unpaired electrons which add up to spin state 5/2 for a single iron center, however, for a dinuclear Iron complex, the overall magnetic response depends on the interaction between the two iron centers. The SQUID magnetometer provides the X_M which rationalizes the interaction between the iron center which could be either ferromagnetic or antiferromagnetic. See the following figure to understand how to rationalize the overall spin state for a binuclear iron complex.

Magnetic Susceptibility Balance
Calculating the magnetic susceptibility from the output of the balance is very straight forward using the following relationship:

$\chi_g = CL(R - Ro)/ 10^9$ m

C = Calibration constant for balance

L = Length of sample (cm units)

m = mass of sample in grams

R = balance reading for sample in tube

R_o = balance reading for empty tube

Useful Resources
1. Jiles, D. *Introduction to Magnetism and Magnetic Materials*; Chapman & Hall; New York, 1991.
2. Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.
3. Smart, L. M., E. *Solid State Chemistry*; Chapman & Hall: New York, 1993.
4. Calculating magnetic susceptibility.
http://www.sherwood-scientific.com/msb/msbindex.html (accessed July 17, 2014).