The GOUY Method

Perhaps the simplest technique for measuring the magnetic susceptibility of metal complexes is the Gouy Method. From a classical description of magnetism, Lenz's Law (around 1834) can be written as

\[
\frac{B}{H} = 1 + 4\pi \frac{I}{H}
\]

or

\[
\frac{B}{H} = 1 + 4\pi \kappa \label{1}
\]

where

- \( B/H \) is called the magnetic permeability of the material and
- \( \kappa \) is the magnetic susceptibility per unit volume, \((I/H)\).

The determination of a magnetic susceptibility depends on the measurement of \( B/H \). Experimentally the Gouy method involves measuring the force on the sample by a magnetic field and is dependent on the tendency of a sample to concentrate a magnetic field within itself.

At any given point, \( dx \), of the sample, the force is given by:

\[
dF = \mu^o H \kappa dV \frac{dH}{dx} \label{2}
\]

where

- \( \mu^o \) is the permeability of a vacuum (=1 when using c.g.s. units)
- \( H \) is the magnitude of the magnetic field at point, \( dx \),
- \( dV \) is the volume of the sample at point \( dx \),
- \( \kappa \) is the magnetic susceptibility per unit volume.

The sample is uniformly packed into a glass tube (Gouy tube) each end of which is at a constant field strength. This is attained by using a tube that is packed to a certain height (say 10 cm) and the tube is suspended between the poles of a magnet such that the bottom of the sample is in the center of the field (a region where a uniform field strength can be readily obtained) whilst the top of the sample is out of the field, i.e. \( H=0 \). By integrating the above equation, the total force on the sample can be given as:

\[
F = \frac{1}{2} \mu^o A \kappa (H^2-H^o^2) \label{3}
\]

and since \( (H^o =0) \) at the top of the sample then

\[
F = \frac{1}{2} \mu^o A \kappa H^2 \label{4}
\]

where \( (A/\) is the cross sectional area of the sample.
The force is measured by the apparent change in mass when the magnetic field is switched on, or
\[ F = g \delta w = \frac{1}{2} \mu^o A \kappa H^2 \] where \( \delta w \) is the apparent change in mass, and \( g \) is the acceleration due to gravity.

An allowance needs to be made for the tube, since it will have its own magnetic properties as a result of the air within the tube (which is displaced from the tube when the sample is introduced) and also from the materials used in its construction. Equation \ref{5} becomes:
\[ g \delta w' = \frac{1}{2} A \mu^o (\kappa-\kappa') H^2 \]

where
- \( \delta w' = \delta w + \delta \)
- \( \delta \) is a constant allowing for the magnetic properties of the empty tube
- \( \kappa' \) is the volume susceptibility of the displaced air.

This leads to:
\[ \kappa = \frac{(2g\delta w')}{(\mu^o AH^2)} + \kappa' \]

Converting from volume susceptibility to gram susceptibility \( (\chi_g) \) leads to:
\[ \chi_g = \frac{\kappa}{\rho} = \frac{\kappa}{V/W} \]

where \( \rho \) is the density of the sample so that
\[ \chi_g = \frac{\beta \delta w'}{W} + \frac{\kappa'V}{W} \]
or
\[ \chi_g = \frac{\alpha + \beta \delta w'}{W} \]

where
- \( \alpha \) is a constant allowing for the air displaced by the sample,
- \( \beta \) is a constant that is dependent on the field strength, \( =2gV/(\mu^o AH^2) \)
- \( W \) is the weight of the sample used.

Written more simply then:
\[ \chi_{g\text{cal}} = \frac{\beta \delta w'}{W_{\text{cal}}} + \frac{\alpha}{(W_{\text{cal}})} \]

the last expression is usually negligible.

\( \beta \) is then obtained and from this
\[ \chi_g \text{sam} = \beta \delta w' / W_{\text{sam}} + \alpha/W_{\text{sam}} \]

the \( \chi_g \) sample can be obtained, again the factor for the susceptibility of air is usually negligible.

To accurately determine the gram magnetic susceptibility of a sample, it is necessary to predetermine the value of the constants \( \alpha, \beta \) and \( \delta \). Since these constants are dependent on the amount of sample placed in the tube, the tube itself and the magnetic field strength, it should be emphasized that each experimenter must determine these constants for their particular configuration. That is, results obtained with one tube are not transferable to other Gouy tubes.

The field strength is determined by the current supplied to the electromagnet. In order to ensure a constant magnetic field strength from one measurement to the next, always set the current to the same value. Note that the magnet may display hysteresis effects so that if you do go beyond the 5 Amp value it may take some time to reestablish itself, after you have decreased the power.

**Determination of the Constants**

Select a tube and piece of nichrome wire to make an assembly which will allow the tube to be suspended from the analytical balance so that the bottom of the tube is aligned halfway between the polefaces of the magnet and the top of the sample is above the magnet and hence subject to essentially zero field, \( H=0 \).

1) \( \delta \), delta

Adjust the zero setting on the balance, then suspend the empty tube from the balance and weigh it (\( W_1 \)). Set the field to the required strength and reweigh the tube (\( W_2 \)). The force on the tube, \( \delta \), therefore is:

\[ \delta = W_2 - W_1 \]

this will normally be negative since the tubes are generally diamagnetic and pushed out of the field, ie. weigh less.

2) \( \alpha \), alpha

Fill the tube to the required height with water and weigh it (check the zero first), this will give \( W_3 \). Assuming the density of
water at this temperature is 1.00 g cm$^{-3}$ this gives the volume of water (and also that of the sample).

vol. = (W3-W1)/1.00 where the weight changes should be expressed in g.

\[ \alpha = \kappa' \cdot V \]

\[ \alpha = 0.029 \times (W3-W1) \text{ in } 10^{-6} \text{ c.g.s. units,} \]

where 0.029 is the volume susceptibility of air /cm$^3$. For strongly paramagnetic samples this correction is generally insignificant.

3) beta, $\beta$

The determination of $\beta$ requires the use of a compound whose magnetic properties have been well established. Common calibrants include HgCo(SCN)$_4$ and [Ni(en)$_3$]S$_2$O$_3$. Since the magnetic properties are often temperature dependent, the susceptibility of the calibrant must be calculated for the temperature at which the sample is measured.

Record the temperature, $T_1$. Fill the tube to the required height with the calibrant (in this case either HgCo(SCN)$_4$ or [Ni(en)$_3$]S$_2$O$_3$ and weigh it with the field off (W4) and with the field on (W5).

For HgCo(SCN)$_4$ the following relationship can be used:

\[ \chi_g = \frac{4985}{(T+10)} \text{ in } 10^{-6} \text{ c.g.s units at temperature } T, \]

while the corresponding relationship for [Ni(en)$_3$]S$_2$O$_3$ is:

\[ \chi_g = \frac{3172}{T} \text{ in } 10^{-6} \text{ c.g.s units at temperature } T \]

Using this $\chi_g$ then

\[ \beta = (\chi_g W - \alpha) / \delta W' \]

where $\delta W' = (W_5 - W_4) - \delta$ in mg

and $W = (W_4 - W_1)$ in g

**Determination of the Magnetic Susceptibility of your sample**

Once $\alpha$ and $\beta$ are known, then $\chi_m'$ can be determined for the sample in question. Fill the tube to the required height with your sample and weigh it with the field off (W6) and with the field on (W7). From this calculate:

\[ \chi_g = (\alpha + \beta \delta W') / W \]

where $\delta W' = (W_7 - W_6) - \delta$ in mg

and $W = (W_6 - W_1)$ in g

To convert from $\chi_g$ to $\chi_m$ the molar mass must be accurately known, since:
\[ \chi_m = \chi_g \times \text{R.M.M.} \]

The final correction is for the diamagnetism of the sample

\[ \chi'_m = \chi_m + \chi_{\text{dia}} \]

where \( \chi_{\text{dia}} \) is the susceptibility arising from the diamagnetic properties of the electron pairs (and therefore not a property of the unpaired electrons) and must be allowed for. The values for \( \chi_{\text{dia}} \) have been well documented (Pascal's constants) for different atoms and ions and a selection of them are tabulated.

To summarize, the overall procedure is:

- Weigh the empty tube - magnet off/on W1/W2
- Weigh the tube with water - magnet off W3
- Weigh the tube with calibrant - magnet off/on W4/W5
- Weigh the tube with your sample - magnet off/on W6/W7
- Record the temperature(s) of calibrant/sample T1/T2 in K
- Calculate the Molar Mass of your sample M.M.
- Estimate the total diamagnetic correction for your sample D.C.

Calculate the magnetic moment using:

\[ \delta = (W_2 - W_1) \text{ in mg} \]

\[ \alpha = 0.029 \times (W_3 - W_1) \text{ in } 10^{-6} \text{ c.g.s. units} \]

\[ \beta = \frac{[(\chi_m(\text{Calibrant})) (W_4 - W_1) - \alpha]}{[(W_5 - W_4) - \delta}] \text{ at temperature } T_1 \]

\[ \chi_m \{\text{Sample}\} = \frac{[\alpha + \beta ((W_7 - W_6) - \delta)]}{(W_6 - W_1)} \text{ at temperature } T_2 \]

\[ \chi'_m = \chi_m \times \text{R.M.M.} + \chi_{\text{dia}} \]

also \[ \chi'_m = \mu^* \mu^B_2 \text{ N}/3k. \mu_{\text{eff}}^2/T \]

where \( \mu_B \) is the Bohr Magneton, N is Avogadro's number and k is the Boltzmann constant. Hence,

\[ \mu_{\text{eff}} = \sqrt{(3k/\mu^* \mu^B_2 N). \sqrt{(\chi'_m T_2) \text{ B.M.}}} \]

or \[ \mu_{\text{eff}} = 2.828 \sqrt{(\chi'_m T_2 \times 10^{-6})} \text{ at temperature } T_2 \]

where the \( 10^{-6} \) that has been ignored in these expressions is finally included.

(Determination of the magnetic moment using the Gouy method has been simplified by the use of an on-line template or spreadsheet.)

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