Method of determination of magnetic susceptibility in chemistry

Method	Principle	Sample State	Common Information
Gouy Balance	Measures the force on a sample in an inhomogeneous magnetic field.	Solid or Liquid	**Qualitative/Quantitative:** Molar susceptibility (χ_m)
Evans Method (NMR)	Measures the shift in an NMR signal due to the sample's magnetic susceptibility.	Solution	**Quantitative:** Molar susceptibility (χ_m) and magnetic moment ($\mu_e$ff)
Faraday Balance	Similar to Gouy, but measures force on a very small sample.	Solid	**Quantitative:** Highly accurate χ_m and its temperature dependence.
SQUID Magnetometry	Measures the magnetic moment via quantum interference in a superconducting loop.	Solid, Liquid, Film	**Quantitative:** Most sensitive method; full χ vs. T, M vs. H data.

1. The Gouy Balance (Classical Method)

This is one of the oldest and most demonstrative methods, excellent for teaching the principles of magnetism.

- **Principle:** A sample, suspended from a balance, is placed in a magnetic field that is **strong at one end and weak at the other** (an inhomogeneous field). The force (F) on the sample is measured.
  - A **paramagnetic** sample ($\chi > 0$) is **pulled into** the strong field region, increasing the measured weight.
  - A **diamagnetic** sample ($\chi < 0$) is **pushed out of** the strong field region, decreasing the measured weight.
- **Procedure:**
  1. The sample is packed into a cylindrical Gouy tube.
  2. The tube is suspended from an analytical balance, with the bottom of the tube positioned between the poles of a strong magnet.
  3. The weight of the sample is measured with the magnet **off (W_0)** and then **on (W)**.
  4. The force is the difference: $\Delta W = W - W_0$.
- **Calculation:**
  The magnetic susceptibility is related to the force by:
  $$\Delta W = (1/2)(\chi - \chi_a) A \mu_0 H^2$$
  Where:
  - ΔW is the change in mass (converted to force).
  - χ is the susceptibility of the sample.
  - χ_a is the susceptibility of the air (or atmosphere) displaced.
  - A is the cross-sectional area of the sample tube.
  - μ_0 is the permeability of free space.
  - H is the magnetic field strength.

  By calibrating with a standard substance of known susceptibility (e.g., water, $[Ni(en)_3]S_2O_3$), the field strength and tube constant can be accounted for, allowing for the calculation of the sample's χ.

- **Advantages:** Simple concept, relatively inexpensive, good for demonstrations.
- **Disadvantages:** Requires a large amount of sample, less accurate than modern methods, not ideal for temperature-dependent studies.

2. The Evans Method (NMR Method)

This is an extremely popular method in synthetic chemistry labs because it is rapid and uses standard equipment.

- **Principle:** A paramagnetic substance has a different magnetic susceptibility than the solvent. This difference creates a small, non-uniform magnetic field inside the NMR tube, which causes a measurable shift in the NMR resonance frequency of the solvent peaks.
- **Procedure:**
    1. Prepare an NMR sample with your paramagnetic compound dissolved in a deuterated solvent (e.g., $CDCl_3$) with a trace of TMS (internal standard).
    2. Using a **coaxial insert** (a very thin NMR tube), place a reference solution (the pure deuterated solvent with TMS) inside the main NMR tube.
    3. Run a simple ^{1}H NMR spectrum. You will see two sets of solvent peaks: one from the inner reference solution and one from the outer solution containing your paramagnetic compound.
    4. Measure the difference in the chemical shift (Δf in Hz) between the two solvent peaks.
- **Calculation:**
  The molar magnetic susceptibility (χ_m) can be calculated using the formula:
  $\boldsymbol{\chi_m = (3\Delta f) / (4\pi f m) + \chi_0 + (\chi_0 - \chi_i)(d/D)}$
  For most practical purposes, a simplified version is used:
  $\boldsymbol{\chi_m = (3\Delta f) / (2\pi f m) + \chi_0}$
  Where:
    - Δf is the frequency difference (in Hz).
    - f is the NMR operating frequency (in Hz, e.g., 400 MHz).
    - m is the molality of the solution (mol/kg).
    - χ_0 is the mass susceptibility of the solvent (a known constant).

- (The d/D terms account for the geometry of the coaxial insert and are often negligible).

From χ_m, the effective magnetic moment ($\mu_e$ff) can be calculated using the Curie law: **$\mu_e$ff = 2.828 √(χ_m T)**

- **Advantages:** Fast, requires very little sample, works on standard NMR spectrometers, provides data in solution state.
- **Disadvantages:** Less accurate for very weakly paramagnetic or diamagnetic samples; requires the compound to be soluble.

3. SQUID Magnetometry (Modern Gold Standard)

A Superconducting Quantum Interference Device (SQUID) is the most sensitive and powerful method available.

- **Principle:** The sample is moved through a set of detection coils in a stable, high magnetic field generated by a superconducting magnet. This movement induces a current in the coils. The SQUID sensor, a highly sensitive quantum device, measures this current, which is directly proportional to the magnetic moment of the sample.
- **Procedure:**
    1. A small, precisely weighed sample (a few milligrams) is loaded into a capsule and attached to a sample rod.
    2. The rod is inserted into the magnet, which is cooled by liquid helium (typically to 1.8 - 400 K).
    3. The instrument is programmed to perform two primary types of measurements:

M vs. H (Magnetization vs. Field): The magnetic field (H) is varied at a constant temperature, and the magnetization (M) is measured. This produces a hysteresis loop for ferromagnets or a straight line for paramagnets.

χ vs. T (Susceptibility vs. Temperature): The temperature is varied while applying a constant magnetic field (e.g., 0.1 T), and the susceptibility (χ = M/H) is measured. **This is the most important experiment for chemists.**

Data Output and Interpretation:

The instrument outputs raw data for magnetic moment (emu). This is converted to molar susceptibility (χ_m) and then to effective magnetic moment ($\mu_e$ff).

- A plot of **1/χ vs. T** is created.
- The data is fitted to the **Curie-Weiss Law: $\chi = C / (T - \theta)$**.
- From the slope (1/C), the **$\mu_e$ff** is calculated, revealing the number of unpaired electrons.
- From the x-intercept, the **Weiss constant (θ)** is determined, revealing magnetic interactions (ferromagnetic if $\theta > 0$, antiferromagnetic if $\theta < 0$).

- **Advantages:** Extremely sensitive, works on very small samples, provides data over a wide range of temperatures and magnetic fields, the definitive method for advanced magnetochemistry (SMMs, SCMs, etc.).
- **Disadvantages:** Very expensive, not a routine benchtop instrument, requires expert operation and data analysis.