

CALIBRATION METHODS

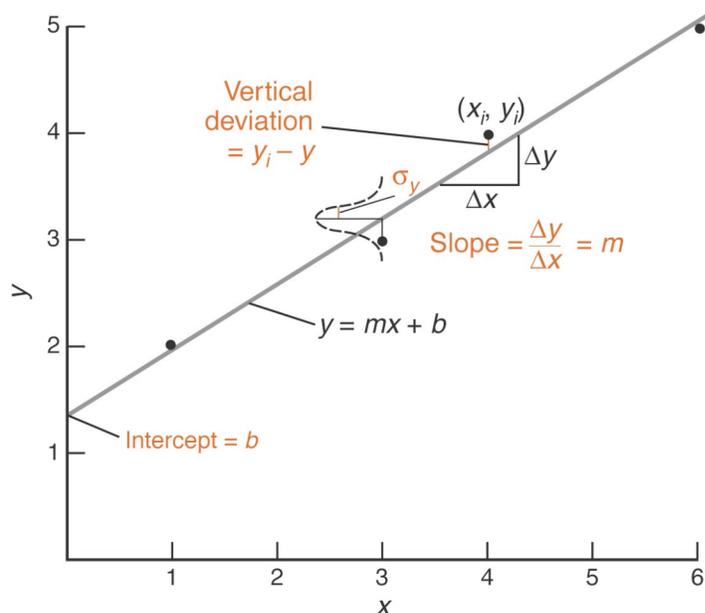
Most of the analytical techniques require a graph showing the analytical response as a function of the known quantity if the analyte present: **calibration curve**. Basic steps are involved into preparation of the calibration curve:

1. Prepare set of solutions (**standard samples**) with the known content of the analyte. Usually serial dilutions are made. Also, prepare one more sample with no analyte present (sample diluent): **blank**.
2. Analyze standard samples and blank, and record results.
3. Subtract value obtained for the **blank** from every **standard sample**: to obtain **corrected** value.
4. Make graph of **corrected** values as function of concentration of the analyte.
5. Use least-square procedure to obtain linear regression line.

$$y = kx + b$$

where **y** is the signal from the measurement
x is the corresponding concentration of the analyte

6. PC does it for you if you use Excel.



8. Graphically or algebraically determine the concentration of the analyte present in the unknown sample:

$$x_{unk} = \frac{y - b}{k}$$

GRAVIMETRIC METHODS OF ANALYSIS

I. Introduction

- A. Gravimetric methods are methods that depend upon measuring mass (i.e., gravity).
- B. There are two major types of gravimetric methods:

1. Precipitation methods: The species to be determined is precipitated by a reagent that yields a sparingly soluble product (or a product of known composition, or a product that can be converted to one of known composition).
 2. Volatilization methods: The analyte (or its decomposition products) are volatilized at a suitable temperature. The volatilized species are collected and weighed directly or weighed by difference.
- C. Both methods usually report the analytes as a weight percent:

$$\%A = \frac{\text{weight } A}{\text{weight of sample}} \times 100\%$$

II. Precipitation Methods

A. Properties of precipitates and precipitating agents.

1. The ideal precipitating agent is one that reacts with one and only one analyte to produce a solid that is:
 - a. Sparingly soluble (i.e., not lost during filtration and washing).
 - b. Readily filterable and washes free of contaminants (i.e., not a gelatinous mess).
 - c. Unreactive to the atmosphere.
 - d. Of known composition (or can be converted to something of known composition).
2. Precipitates with large particle size work best for filtration and washing.
3. Colloidal suspensions (precipitates with particle sizes of 1-100 nanometers) are undesirable.
 - a. The particles do not settle out.
 - b. Filtration is difficult due to plugging of pores in the filter, or passing through the filter.
4. Precipitate size can be controlled (to some extent) by the conditions used to cause precipitation.

B. Mechanism of precipitate formation.

1. Two steps are involved in precipitation:
 - a. Nucleation: Formation in a supersaturated solution of the smallest precipitate particles capable of spontaneous growth.
 - b. Particle Growth: Deposition of ions/molecules on the surface of the solid, nucleated particles.
2. In general, particle size is governed by the number of nuclei formed:
 - a. Large supersaturation leads to more nuclei (and smaller particle size) and often produce colloids.
 - b. Dilute solutions lead to fewer nuclei, more deposition on the fewer nuclei and larger crystals.

3. Spontaneous nucleation is rare. Usually, you must induce nucleation to provide a site to attract and hold ions/molecules by...

- a. Scratching the side of the container.
- b. Adding seed crystals.

4. Other experimental factors controlling precipitate size include...

- a. Diffusion of ions/molecules to the surface of the growing crystal. This is affected by stirring, temperature, the nature of the ions/molecules, and concentration (low concentration is usually best).
- b. Deposition on the surface of the crystal. This is affected by concentration, impurities on the surface of the crystal, growth characteristics of the crystal and pH (if pH-dependent).

C. When first formed, precipitates usually exist as colloidal particles.

D. The colloidal particles need to coagulate to increase the particle size.

E. Coagulation is accomplished by:

1. Heating.
2. Stirring.
3. Adding electrolytes to negate surface charges.

F. Peptization should be avoided. (Peptization is the process by which a coagulated precipitate is returned to its colloidal state.) Peptization can be caused by...

1. Washing away electrolytes responsible for coagulation.
2. Washing away colloidal pieces of the precipitate.

G. Peptization can be minimized by washing a precipitate with a solution of an electrolyte that is volatilized during an ensuing drying step.

H. The bottom line on precipitation is:

1. Colloids are best precipitated from hot, stirred, dilute solutions.
2. Filterability is improved if the coagulated colloid is digested (heated for over an hour) in the mother liquid. (Digestion expels water from the crystal, producing a denser, better filtering precipitate.)

III. Problems Encountered With Obtaining A Pure Precipitate.

A. Co-precipitation is the major problem.

1. Co-precipitation is the precipitation of an otherwise soluble substance along with the insoluble material.
2. Co-precipitation may happen simultaneously or following the first precipitation.

B. There are several mechanisms of co-precipitation. These include...

1. Surface adsorption.
2. Mechanical entrapment. Two crystals grow together and trap a species in the space between them.
3. Occlusion. An ion and its counter ion are trapped in a pocket of a rapidly growing crystal (i.e., the crystal grows around them).
4. Post precipitation. The precipitate causes a localized high concentration of unwanted species.

C. Co-precipitation is reduced by:

1. Using dilute solutions.
2. Rapid filtration.
3. Removing undesired ions *before* precipitation.

IV. Drying and Ignition of Precipitates.

A. Drying removes the solvent(s) of the mother liquid from which the precipitate was formed.

B. Ignition converts the precipitate to a known composition called the *weighing form*.

C. Drying/ignition is not as simple as heating in an oven at 100°C to get rid of water. Consider calcium oxalate (CaC_2O_4):

1. Around 200°C, calcium oxalate exists as the hydrate $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.
2. Around 400°C, calcium oxalate exists as CaC_2O_4 .
3. Around 700°C, calcium oxalate exists is converted to CaCO_3 .
4. Above 1,000°C, calcium carbonate is converted to CaO .

D. Each compound has different drying/ignition behavior which must be determined on a case by case basis.

V. Typical Gravimetric Determinations.

A. Determination of chloride ion by precipitation with silver ion to form AgCl .

B. Determination of sulfate ion by precipitation with barium ion to form BaSO_4 .

C. Determination of nickel(II) ion by precipitation with dimethylglyoxime to form the $\text{Ni}(\text{DMG})_2$ precipitate, a brilliant red-colored precipitate.

1. DMG precipitates Pd(II) as a yellow precipitate.
2. DMG also precipitates Bi(II) as a colorless precipitate.

D. 8-Hydroxyquinoline chelation of magnesium(II) (and other) ions in a pH-dependent precipitation.

E. Sodium tetraphenylboron forms salt-like precipitates with potassium or ammonium ion in cold, mineral acid solutions.

1. Sodium tetraphenylboron is selective, but not specific for potassium and ammonium ion.
2. Mercury(II), Ruthenium(II) and Cesium(I) interfere.