Quantitative Analytical Chemistry
(QUANCHEM)

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School of Sciences
Analytical Chemistry vs. Chemical analysis.

Analytical Chemistry is the Science that studies the set of principles, laws and techniques aiming at the knowledge of the chemical composition of a sample with either a natural or synthetic nature.

Chemical analysis refers to the set of operational techniques devoted to the service of such a purpose.

Analytical Chemistry, or the art of recognizing different substances and determine their constituents, takes a prominent place in the applications of science, by enabling us to answer questions that arise when using any chemical processes for scientific or technical purposes. Its relevance has grown since the beginning of the history of chemistry, and has allowed much of the quantitative work to extend to the entire domain of science.


**Qualitative**
- Recognition and identification of the different components
- What’s?

**Quantitative**
- Determination (quantification) of the content of each of the components
- How much?

Analytical Chemistry involves the:
- identification
- determination
- separation
- of the relative amounts of the components of a given sample.

Sequential steps in chemical analysis.

Chemical or Classic:
- Qualitative analysis
- Gravimetric analysis
- Volumetric analysis (titrimetry)

Physicochemical or Instrumental:
- Spectroscopic
- Electrochemical
- Radiochemical
- Thermal...

Classical Methods vs. Instrumental Methods:

The classical methods have in common the fact that they are based on chemical reactions in equilibrium. In gravimetric analysis, quantification is done by transforming the species in an insoluble product of high purity and defined stoichiometry, which is then weighed.

In the volumetric analysis, a certain volume of either a liquid (titrimetry) or a gas (gasometry).

The classical methods are the most accurate and precise. However, they lack good sensitivity.

Instrumental methods make use of the measurement of physical or physicochemical magnitudes for the determination of the component of the sample. They are much more sensitive.
**Gravimetric Analysis**

### Chemical precipitation:

$$\text{Fe}^{3+} + 3 \text{OH}^- \rightarrow \text{Fe(OH)}_3 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3$$

### Electrodeposition:

Passage of current through the solution and weighing of the deposit formed at the cathode.

**Physicals:** weight loss upon heating

**Volatilization:** Chemicals $\text{CO}_2$ evolved from a calcite

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**Nomenclature**

A **procedure** is a set of instructions to run, in the same way, certain actions with a common series of clearly defined steps, enabling to carry out an analysis or research properly.

A **protocol** is the document that describes in detail the hypotheses to investigate, seeks objectives, outlines, design, methodology, statistical considerations, participants, schedule, organization and supervision. Here is a list of a number of items to consider in the design of the protocol:

1. Full title and acronym
2. Justification
   - Hypothesis to be verified
   - Why is it necessary or interesting to conduct the study
   - Relevant information existing about it and search methodology used
3. Usefulness of the results obtained and the field of application or generalization of these
4. Type design: randomized, observational, etc.
5. Description of treatment or phenomenon being studied
6. Calendar of study
7. What are the variables of measurement that will be studied, elementary (primary objective) and secondary
8. Method of allocation to each group (randomized, stratified by strata, etc.) as well as other mechanisms to control bias: for example, double-blind study
9. If a trial study was conducted, description and results
10. Planned sample size and justification of it
11. If a pilot study was conducted: description and results
12. Data collection procedures
13. Where appropriate number of centers that will participate in the study
14. Expected statistical analysis to be made
15. Subgroups that are expected to be studied
16. If intermediate analyses are to be effected, description of these
17. Personnel involved in the study
18. Economic analysis of the cost of the study and funding sources

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**Types of Analyses**

Considering what is being determined, the **analysis** can be:

- **Elemental**
  - Constituent elements of the unknown sample
- **Functional**
  - Functional groups
- **Immediate**
  - Group of substances integrated in the same analysis
- **Total**
  - All the elements
- **Partial**
  - Just a few components of interest

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**Quality of an Analytical method**

- **Accuracy:** Proximity of a measurement to its true value
- **Precision:** Concordance between two or more numerical results when obtained in an identical manner
- **Sensitivity:** Minimum quantity or concentration which can be determined
- **Selectivity:** Interference of a chemical species in the identification/determination of another
1. Problem identification: approach and history of the problem (objective).
2. Choice of method.
3. Obtaining a representative sample.
4. Preparation and, if appropriate, dilution of the sample.
5. Interference elimination.
6. Measuring the properties of the analyte.
7. Calculation of results.
8. Evaluation and discussion of results.

Determining factors on the choice of method:
- Concentration of the constituent
  - major: > 1%
  - minor: 1 - 0.01%
  - trace: < 0.01%
- Nature of the sample
- Precision and accuracy required
- Time available
- Cost analysis
- Possibility of destruction of the sample
- Means available

Sampling:
- Gross sample collection.
- Reducing the sample to a size suitable for the laboratory.
- Preservation and preparation of the sample in the laboratory.
Collecting marine sediments: dredges and specimens

Reduction of size of sample

Often, the initial sample to be taken to ensure adequate accuracy in the sampling is so great that it is necessary a considerable reduction in its size.

Quartered system

In the case of particulate materials, is accompanied by a corresponding decrease in particle size (use of mills, sieves, mixers ...)

Storage and preparation of samples

- Minimize changes that may occur before analysis (CO₂ absorption, hydration, water release, atmospheric oxidation, etc.)

- Normally, moisture must be removed from the sample before starting the stage of weighing or, alternatively, the water content of the sample must be determined immediately before weighing the sample.

- Obtaining of a certain amount of sample (weighed, volume)

- Dissolution of the sample
  - H₂O (cold or hot)
  - HCl diluted
  - HCl concentrated
  - HNO₃ diluted
  - HNO₃ concentrated
  - Aqua regia (3 HCl + 1 HNO₃)
Lesson 2. Fundamentals of Gravimetric Analysis

1. Classification of gravimetric methods.
2. Formation of precipitates: nucleation and crystal growth.
3. Impurification of precipitates.
4. Gravimetric analysis by chemical precipitation.
6. Gravimetric analysis by volatilization or release: Determination of water and carbon dioxide.
7. Advantages and disadvantages of organic reagents as precipitants.
8. Homogeneous precipitation.

Gravimetric Methods

Precipitation gravimetry
The analyte is separated from a solution of the sample and is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed.

Volatilization gravimetry
The analyte is separated from other constituents of the sample by converting it to a gas of known chemical composition. The mass of the gas then serves as a measure of the analyte concentration.

Properties of Precipitates and Precipitating Reagents

Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. The ideal precipitating reagent would react with the analyte to give a product that is:

- Easily filtered and washed free of contaminants
- Of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washings easily filtered and accompanying impurities may be removed by simple washing.
- Unreactive with constituents of the atmosphere
- Of known chemical composition after it is dried or, if necessary, ignited.

Properties of suspensions

- Colloidal suspensions: No tendency to settle from solution and are difficult to filter
- Crystalline suspensions: Tend to settle spontaneously and are easily filtered

Particle Size

Precipitates consisting of large particles are generally desirable for gravimetric work because:

- Are easy to filter and was free of impurities
- They are usually purer than the precipitates made up of fine particles.

Ions in solution

<table>
<thead>
<tr>
<th>Ions in solution</th>
<th>Colloidal suspension</th>
<th>Crystalline suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-8}$ cm</td>
<td>$10^{-7}$ - $10^{-4}$ cm</td>
<td>$&gt; 10^{-4}$ cm</td>
</tr>
</tbody>
</table>

Experimental Factors

Although it is true that the mechanism of the precipitate formation process is not yet fully understood, what is certain is that the PARTICLE SIZE of a precipitate is influenced by:

- precipitate solubility
- temperature
- reactant concentrations
- rate at which reactants are mixed

The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system:

$$\text{Relative Supersaturation} = \frac{Q - S}{S}$$

- Large R.S.: precipitate tends to be colloidal (small particle size)
- Small R.S.: crystalline precipitate more likely (large particle size)
Nucleation:
Process in which a few particles (as few as 4 or 5) come together to form a stable solid (generally, on the surface of suspended solid contaminants, such as dust particles)

Further precipitation may follow different pathways:
- Additional nucleation (N)
- Growth of existing nuclei (PG, crystalline growth)
- Combination of both processes

If nucleation (N) is predominant:
- Large number of small size particles
When particle growth (PG) becomes predominant:
- Smaller number of larger particles is produced

R.S. can be minimized:
- High T (S increases)
- Dilute solutions (reduces Q)
- Slow addition of the precipitating agent with good stirring (minimizes Q)

Unfortunately, many precipitates cannot be formed as crystals under practical laboratory conditions. A colloidal solid is generally formed when a precipitate has such a low solubility that $S$ remains negligible relative to $Q$, thus yielding very large R.S.

Ej.: hidrous oxides of Fe(III), Al(III) and Cr(III); heavy metal sulfides

Colloid with large amount of water:
- Gel, Hydrogel

Suspension (PG):
- Lyophobic (H$_2$O: hydrophobic); AgCl
  - $10^5$C: total loss of H$_2$O

Specific Surface Area of Colloids
- Surface area per unit mass of solid (cm$^2$ g$^{-1}$)

Crystalline precipitate: 0.1 - 0.001 cm
- m = 2g
- 30 - 300 cm$^2$ g$^{-1}$

Colloidal suspension: $10^4$ particles of $10^{-6}$ cm
- $3 \cdot 10^6$ cm$^2$ g$^{-1}$

Colloid with large amount of water:
- Gel, Hydrogel
- EMULSOID
  - Lyophilic (H$_2$O: hydrophilic); Fe, Al
- SUSPENSOID
  - Lyophobic (H$_2$O: hydrophobic); AgCl

A coagulated colloid continues to expose a large surface area to the solution from which it is formed

Process by which a colloidal suspension becomes a filterable solid.
Process by which a colloidal suspension becomes a filterable solid.

Coagulation

This phenomenon is favoured by:
• Temperature,
• Stirring, and
• Presence of electrolyte

Ostwald ripening

During digestion at elevated temperature:
Small particles tend to dissolve and reprecipitate on larger ones.
Individual particles agglomerate.
Adsorbed impurities tend to go into solution.

Coprecipitation: phenomenon by which otherwise soluble compounds are removed from solution during precipitate formation.

Four main types of coprecipitation:
• Surface adsorption (especially in colloids)
• Mixed-crystal formation
• Occlusion
• Mechanical entrapment
### Coprecipitation of AgNO₃ on AgCl

Minimizing Adsorbed Impurities on Colloids

- **Digestion**
  - Filterability greatly improves by allowing the colloid to age in the mother liquor. Water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption.

- **Washing**
  - With a solution containing a volatile electrolyte in order to avoid peptization (colloid dispersion)

  Any nonvolatile electrolyte added earlier to cause coagulation is displaced by the volatile species. Washing generally does not remove much of the primarily adsorbed ions because the attraction between these ions and the surface of the solid is too strong. Exchange occurs, however, between existing counter ions and ions in the wash liquid.

- **Reprecipitation (recrystallization)**
  - Drastic but effective way to minimize the effects of adsorption is reprecipitation, or double precipitation.

  Here, the filtered solid is redissolved and reprecipitated. The first precipitate ordinarily carries down only a fraction of the contaminant present in the original solvent. Thus, the solution containing the redissolved precipitate has a significantly lower contaminant concentration than the original, and even less adsorption occurs during the second precipitation. Reprecipitation adds substantially to the time required for an analysis.

### Mixed-Crystal Formation

Mixed-Crystal Formation

One of the ions in the crystal lattice of a solid is replaced by an ion of another element.

For this exchange to occur, it is necessary that:

- the two ions have the same charge
- their sizes differ by no more than about 5%
- the two salts must belong to the same crystal class.

For example, Hg₂PO₄ in MgNH₄PO₄, SrSO₄ in BaSO₄, and Mn₅S in CdS.
When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped, or occluded, within the growing crystal.

Mechanical entrapment occurs when crystals lie close together during growth. Here, several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.

A precipitating agent is generated in a solution of the analyte by a slow chemical reaction. CO(NH$_2$)$_2$ + 3H$_2$O $\rightleftharpoons$ CO$_2$ + 2NH$_4^+$ + 2OH$^-$

Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation.

- Marked increase in crystal size
- Improvements in purity
- Less coprecipitation
- Ignition at a lower T

In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent.

Precipitation from Homogeneous Solution

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<th>Chemical Reaction</th>
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<tr>
<td>Ba(NO$_3$)$_2$</td>
<td>BaSO$_4$</td>
<td>BaSO$_4$ $\rightleftharpoons$ Ba$^{2+}$ + SO$_4^{2-}$</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>CaCO$_3$</td>
<td>CaCO$_3$ $\rightleftharpoons$ Ca$^{2+}$ + CO$_3^{2-}$</td>
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<tr>
<td>MgSO$_4$</td>
<td>Mg(OH)$_2$</td>
<td>Mg(OH)$_2$ $\rightleftharpoons$ Mg$^{2+}$ + 2OH$^-$</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>Al(OH)$_3$</td>
<td>Al(OH)$_3$ $\rightleftharpoons$ Al$^{3+}$ + 3OH$^-$</td>
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After filtration, a gravimetric precipitate is heated until its mass becomes constant.

Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the weighing form.

The temperature required to produce a suitable weighing form varies from precipitate to precipitate.

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The temperature required to produce a suitable weighing form varies from precipitate to precipitate.
Transfer to the Filtering Support

Ignition

Common Sources of Errors

- Incomplete elimination of either H₂O or volatile electrolytes.
- Reduction of the precipitate by the C from the filter paper.
- Overignition: decomposition and obtaining of unknown products.
- Readesorption of H₂O or CO₂

Cap and use desiccator.

Precipitating Reagents

- Inorganic
  - Coordination Compounds (Chelates)
  - Organic
  - Ionic

Inorganic Precipitating Agents

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<thead>
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</tr>
</thead>
<tbody>
<tr>
<td>NH₄₂CO₂</td>
<td>Be₂O₂, Al₂(OH)₃, Fe₂O₃</td>
</tr>
<tr>
<td>H₂S</td>
<td>Zn₂S, Zn₃S₄, As₂S₃, As₂O₅, Sb₂S₃, Sb₂O₅</td>
</tr>
<tr>
<td>(NH₄)₂S</td>
<td>HgS, HgCl₂</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
<td>Mg₃(PO₄)₂</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sr, Ca, Pb, Ba(PO₄)₂</td>
</tr>
<tr>
<td>(NH₄)₂MoO₄</td>
<td>PbMoO₄</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>Cl⁻ (AgCl), Br⁻ (AgBr), I⁻ (AgI)</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>Bi₂O₃</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>BaSO₄</td>
</tr>
<tr>
<td>Mg₂PO₄, NH₄Cl</td>
<td>PO₄³⁻ (Mg₂PO₄, NH₄Cl)</td>
</tr>
</tbody>
</table>

Organic Precipitating Agents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Structure</th>
<th>Metal Precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dithizone</td>
<td>CO₁₅H₁₄N₁₀S₂</td>
<td>NH₄ in NH₄Cl or buffered HAC, pH 3 to 5 (CO₁₅H₁₄N₁₀S₂⁺)</td>
</tr>
<tr>
<td>a-Diazodichromic (sodium)</td>
<td>Cr₂O₇²⁻ + H₂O</td>
<td>Cr₂O₇²⁻ in Na₂Cr₂O₇ and sodium, H₂SO₄ and H₂S in H₂SO₄ (Cr₂O₇²⁻ + H₂S → H₂Cr₂O₇ + S)</td>
</tr>
<tr>
<td>Aminomercaptan thiol (mercury)</td>
<td>S⁻ + H₂S</td>
<td>Metal amalgam formation</td>
</tr>
<tr>
<td>Acetic anhydride (selenium)</td>
<td>C₂H₄O₂⁻ + Se⁴⁺</td>
<td>Many metals, lead for Se⁴⁺ and Hg⁰ (C₂H₄O₂⁻ + Se⁴⁺ + H₂O)</td>
</tr>
<tr>
<td>Naphthylmethylcarbazole</td>
<td>S⁻</td>
<td>Many metals from acid solutions (S⁻ + H⁺ + OH⁻)</td>
</tr>
<tr>
<td>Nitrophenylhydrazine</td>
<td>CH₁₈H₁₈N₄O₇</td>
<td>Acids like HCl, HNO₃, H₂SO₄, H₂PO₄⁻, Acetic acid solutions (CH₁₈H₁₈N₄O₇⁻ + H⁺)$^{2} + $H⁺ = CH₁₈H₁₈N₄O₇H²⁺$^{2}$</td>
</tr>
</tbody>
</table>
Organic Functional Groups that may be determined gravimetrically

Chelating Agents

- Many are insoluble in water \(\Rightarrow\) quantitative precipitation.
- High molecular weight \(\Rightarrow\) sensitivity.
- Relatively selective
- Dense and voluminous precipitates \(\Rightarrow\) manageability.

- The general low solubility may become a disadvantage, since it requires the use of an excess of reagent with the corresponding risk of contaminating the precipitate.
- Uncertainty of the chemical form after drying.
- Risk of product decomposition prior to complete drying.

Volatilization Gravimetry

- \(\text{Direct:}\)
  - Water vapor is collected on a solid desiccant, and its mass is determined from the mass gain of the desiccant.

- \(\text{Indirect:}\)
  - Loss of mass of the sample during heating (assuming that water is the only component that is volatilized).

Volatilization Gravimetry: \(\text{H}_2\text{O}\) and \(\text{CO}_2\)

- Loss of mass of the sample during heating (assuming that water is the only component that is volatilized).

Volatilization Gravimetry: \(\text{CO}_2\)

Example: Determination of \(\text{NaHCO}_3\) content of antacid tablets.

\[
\text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \uparrow \text{CO}_2 + \text{H}_2\text{O}
\]

The pure stream of \(\text{CO}_2\) in \(\text{N}_2\) passes through a weigh absorption tube containing the absorbent Ascarite (NaOH absorbed on a nonfibrous silicate), that also contains a desiccant such as CaSO_4 to prevent loss of the water produced in this latter reaction:

\[
2 \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

Volatilization Gravimetry: \(\text{S}^\text{2-}\) and \(\text{SO}_3\text{2-}\):

- \(\text{H}_2\text{S}\) and \(\text{SO}_2\) evolved from the sample after treatment with acid is collected in a suitable absorbent.

C, H in organic compounds:

- The combustion products, \(\text{CO}_2\) and \(\text{H}_2\text{O}\), are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable.

2. Titration Curves.

3. End Point Indication Systems.

4. Volumetric Calculations.

5. Volumetric Error.

Titration Curves

A titration curve is a plot of some function of the analyte or titrant concentration on the $y$ axis vs. titrant volume on the $x$ axis.

End Point Indication

1. Chemical or visual indicators
   - Colored indicators
     - Auto indicators
     - Strict sense indicators
   - Fluorescent
   - Turbidimetric
   - Adsorption

2. Physico-chemical indicators
   - Photometric
   - Electrochemical
   - Potentiometric
   - Amperometric

Volumetric Error

The equivalence point in a titration is the theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. The end point is the experimentally detected situation associated with the equivalence point. No matter how hard we try, there is always a volume difference between the theoretical equivalence point and the experimentally observed end point. That difference, expressed in volume units, is what is called the volumetric error or the titration error.
Lesson 4. Precipitation Titrations

1. Precipitation reactions in volumetric analysis.
2. Argentometric titrations.
3. Construction of the different types of titration curves.
4. Endpoint indicating systems: Mohr, Volhard and Fajans.

Introduction

Precipitation titrimetry, which is based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques. The slow rate of formation of most precipitates, however, limits the number of precipitating agents that can be used in titrations to a handful. The most widely used and important precipitating reagent, AgNO₃, which is used for the determination of the halogens, the halogen-like anions. Titrations with silver nitrate are sometimes called argentometric titrations.

Summary of adverse factors

• Lack of appropriate indicators.
• Too slow reaction rates.
• In the vicinity of the equivalence, the addition of the titrant does not provide a high supersaturation and precipitation can be very slow.
• Co-precipitation phenomena.

Argentometric Titrations: Drawbacks

50.00 mL of NaCl 0.10 M titrated with AgNO₃ 0.10 M. PS AgCl = 1.0·10⁻¹⁰
1. Start. [Cl⁻] = 10⁻¹ M
   \[ pCl = -\log (0.1) = 1.00 \]
2. Pre-equivalence. + 10 mL of AgNO₃
   \[ [\text{Cl}^-] = \frac{50.00 \text{ mL} \cdot 0.10 \text{ M}}{60.00 \text{ mL}} = 0.0833 \text{ M} \]
   \[ pCl = 0.95 \]
3. Equivalence Point. + 50 mL of AgNO₃
   \[ \text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- ; \quad \text{PS} = [\text{Ag}^+] \cdot [\text{Cl}^-] = [\text{Cl}^-]^2 = 1.0 \cdot 10^{-10} \]
   \[ [\text{Cl}^-] = 1.0 \cdot 10^{-5} \text{ M} \]
   \[ pCl = 5.00 \]
4. Post-equivalence. + 60 mL of AgNO₃
   \[ [\text{Ag}^+] = \frac{90.00 \text{ mL} \cdot 0.10 \text{ M}}{60.00 \text{ mL}} = 0.150 \text{ M} \]
   \[ pAg = 2.04 \]
   \[ pAg + pCl = pPS = 10.0 \]
   \[ pCl = 10.0 - 2.04 = 7.96 \]

Argentometric Plotting of the Titration Curve

Argentometric Plotting of the Titration Curve for Different Halogens

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Argentometric Titration: variables involved

\[ \text{Ag}^+ + X^- \rightleftharpoons \text{AgX} \quad \Delta \text{pX} \downarrow \; ; \quad \text{SP}_{1} \cdot [X][\text{Ag}] = K = \frac{1}{[\text{Ag}] [X]} \quad \Delta \text{pX} \uparrow \]

The greater the insolubility of the precipitate, the higher \( K \) and, accordingly, the better the quantitativeness.

**Effect of the concentration**

\( \Delta \text{pX} \) at the end point is a function of the concentrations of analyte and reagent.

- The lower [\( X^- \)], the larger \( pX \) in the pre-equivalence and smaller \( \Delta \text{pX} \) at the end-point.
- The lower [\( \text{Ag}^+ \)], the lower \( pX \) in the post-equivalence (\( p\text{Ag} + pX = p\text{PS} \)) and smaller \( \Delta \text{pX} \) at the end-point.

**Value of \( K \)**

\[ \Delta \text{pX} = 2 \text{ units around the equivalence point} \]

When you’ve added 49.95 mL of \( \text{Ag}^+ \):

\[ M_{5} \cdot 10^{49.95}\text{mL} (50) \cdot 0.50\text{mL} \cdot 0.1\text{M} [X] \]

\[ \text{Ag}^+ \downarrow \quad \text{AgCl} \]

\[ \Delta \text{pX} = 2 \text{ after having added 0.1 mL more: } pX = 4.3 + 2 = 6.3 \]

\[ M_{5} \cdot 10^{50.05}\text{mL} (50) \cdot 0.05\text{mL} \cdot 0.1\text{M} [\text{Ag}] \]

\[ \text{Ag}^+ \downarrow \quad \text{AgCl} \]

\[ \text{Increment of the measure around the equivalence: feasibility and appreciation of the end-point} \]

**MOHR:**

- \( \text{CrO}_4^{2-} \)
- \( \text{Ag}_2\text{CrO}_4 \) brick-red

**VOLHARD:**

- \( \text{Fe}^{3+} \)
- \( \text{Fe(SCN)}^{2-} \) red

**FAJANS:**

- Adsorption indicators

**Argentometric Titration: Indicators and Methods**

\[ \text{Cl}^- \]

\[ \text{CrO}_4^{2-} \]

\[ \text{Ag}^+ \]

\[ \Delta \text{pX} = 2 \text{ units around the equivalence point} \]

\[ \text{Ag}^+ + X^- \rightleftharpoons \text{AgX} \quad K = \frac{1}{[\text{Ag}] [X]} \quad \Delta \text{pX} \uparrow \]

When you’ve added 49.95 mL of \( \text{Ag}^+ \):

\[ [X] = 50\text{mL} 0.1\text{M} \cdot 49.95\text{mL} 0.1\text{M} \quad (50 + 49.95)\text{mL} \cdot 5 \cdot 10^{-4} \text{M} \]

\[ pX = -\log (5 \cdot 10^{-4}) = 4.3 \]

If \( \Delta \text{pX} = 2 \) after having added 0.1 mL more: \( pX = 4.3 + 2 = 6.3 \)

\[ [X] = 50\text{mL} 0.1\text{M} \cdot 50\text{mL} 0.1\text{M} \quad (50 + 50)\text{mL} \cdot 5 \cdot 10^{-4} \text{M} \]

\[ P_X = \frac{1}{2} \cdot 5 \cdot 10^{-1} \]

**Theoretical concentration of indicator would be:**

\[ [X] = 50\text{mL} 0.1\text{M} \cdot 0.02 \text{M} \]

**Argentometric Titration: The Mohr Method**

\[ \text{Na}_2\text{CrO}_4 \] can serve as an indicator for the argentometric determination of Cl-, Br-, and CN- ions by reacting with silver ion to form a brick-red silver chromate (\( \text{Ag}_2\text{CrO}_4 \)) precipitate in the equivalence-point region.

The reactions involved in the determination of Cl- and Br- (\( X^- \)) are:

**Titration reaction:**

\[ \text{Ag}^+ + X^- \rightleftharpoons \text{AgX} \quad \text{[white]} \]

**Indicator reaction:**

\[ 2\text{Ag}^+ + 2\text{OH}^- \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O} \]

\[ 2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]

The solubility of \( \text{Ag}_2\text{CrO}_4 \) is several times greater than that of \( \text{AgCl} \) or \( \text{AgBr} \).

**Argentometric Titration: The Volhard Method**

**Titration reaction:**

\[ \text{Ag}^+ + X^- \rightleftharpoons \text{AgX} \quad \text{[white]} \]

**Indicator reaction:**

\[ 2\text{Ag}^+ + 2\text{SCN}^- \rightleftharpoons \text{Ag}_2\text{SCN} \quad \text{[red]} \]

The theoretical concentration of indicator would be:

\[ [\text{SCN}^-] = \frac{P_{\text{SCN}^-}}{[\text{Ag}^+]^2} \cdot 2 \cdot 10^{-12} \]

\[ S_{\text{Ag}^+} = 7.9 \cdot 10^{-4} \text{M} \]

\[ S_{\text{Ag}^+} = 1.0 \cdot 10^{-10} \text{M} \]

**Argentometric Titration: The Fajans Method**

**Titration reaction:**

\[ \text{Ag}^+ + \text{SCN}^- \rightleftharpoons \text{AgSCN} \]

**Indicator reaction:**

\[ \text{Fe}^{3+} + 2\text{SCN}^- \rightleftharpoons \text{Fe}^{3+} + \text{SCN}^- \quad \text{[red]} \]

**Determination of \( \text{Ag}^+ \) and, indirectly, \( X^- \), in industrial samples**

**pH:**

- from 6 to 10
- pH: not critical: \( \approx 0.01 \text{ M} \)

\( pK_{\text{AgSCN}} = 2.1 - 10^{-12}; \quad S_{\text{AgSCN}} = 7.9 - 10^{-4} \text{M} \)

\( pK_{\text{Ag}_2\text{SCN}} = 1.0 - 10^{-10}; \quad S_{\text{Ag}_2\text{SCN}} = 1.0 - 10^{-10} \text{M} \)
Direct determination: Ag⁺ with SCN⁻

Risk: The precipitate that is being formed, \( \text{AgSCN} \), adsorbs Ag⁺ ions on its fresh surface and anticipates the final point.

Remedy: Vigorously shake the Erlenmeyer flask.

Indirect determination: Cl⁻

Add a well known excess of AgNO₃.

\[ \text{PS AgSCN} > \text{PS AgX} \]

Otherwise, you have to filter \( \text{AgX} \) before the titration step with SCN⁻.
Lesson 5. Acid-Base Titrations

1. Titration Curves of Strong Acids and Bases.
2. Titration Curves for Weak Acids: Choice of Indicators.
3. Titration of Diprotic Acids.
4. Elucidation of Basic Mixtures: Carbonates and Bicarbonates; Carbonates and Hydroxides. Warder and Winkler Methods.

Titration Curves of 50 mL of HCl 0.100 M with NaOH 0.100 M

1) Start: \[ V_{\text{NaOH}} = 0 \text{ mL} \]
\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]
\[ [\text{H}^+] = [\text{HCl}] = 0.100 \text{ M} ; \quad \text{pH} = -\log (0.100) = 1.00 \]

2) Pre-equivalence: \[ V_{\text{NaOH}} = 10 \text{ mL} \]
\[ [\text{H}^+] = \frac{0.100 \text{ mmol}}{0.050 \text{ mL} + 0.010 \text{ mL}} = 1.67 \times 10^{-2} \text{ M} \]
\[ \text{pH} = 1.18 \]

3) Equivalence: \[ V_{\text{NaOH}} = 50 \text{ mL} \]
\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]
\[ \text{pH} = 7 \]

4) Post-equivalence: \[ V_{\text{NaOH}} = 60 \text{ mL} \]
\[ \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \]
\[ [\text{OH}^-] = \frac{0.100 \text{ mmol}}{0.050 \text{ mL} + 0.010 \text{ mL}} = 9.1 \times 10^{-2} \text{ M} \]
\[ \text{pOH} = -\log [\text{OH}^-] = 2.04 \Rightarrow \text{pH} = 11.96 \]

Acid-Base End-Point Indication

Acidity indicators

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Color Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>Colorless to violet red</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow to blue</td>
</tr>
<tr>
<td>Methyl Red</td>
<td>Red to yellow</td>
</tr>
</tbody>
</table>

(Volume NaOH (mL))
Feasibility of Strong Acid-Strong Base Titrations

The effect of reaction completeness, $K$ value:

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$K = \frac{1}{K_w} = 10^{14}$$

Assayed concentrations

<table>
<thead>
<tr>
<th>Volume NaOH (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>10.00</td>
<td>1.18</td>
</tr>
<tr>
<td>20.00</td>
<td>1.37</td>
</tr>
<tr>
<td>25.00</td>
<td>1.48</td>
</tr>
<tr>
<td>30.00</td>
<td>1.60</td>
</tr>
<tr>
<td>40.00</td>
<td>1.95</td>
</tr>
<tr>
<td>49.00</td>
<td>3.00</td>
</tr>
<tr>
<td>49.90</td>
<td>4.00</td>
</tr>
<tr>
<td>49.95</td>
<td>4.30</td>
</tr>
<tr>
<td>50.00</td>
<td>7.00</td>
</tr>
<tr>
<td>50.05</td>
<td>9.70</td>
</tr>
<tr>
<td>51.00</td>
<td>10.00</td>
</tr>
<tr>
<td>60.00</td>
<td>11.96</td>
</tr>
<tr>
<td>70.00</td>
<td>12.23</td>
</tr>
</tbody>
</table>

Titration of a Weak Acid with a Strong Base

1) pH at the start: weak acid, $pH = f(C_a, K_a)$
2) pH in the pre-equivalence: buffer solution
3) pH at the equivalence point: hydrolysis of the formed salt
4) pH in the post-equivalence: excess added of the strong base

Titration of 50 mL of $\text{HAc}$ 0.10 M with $\text{NaOH}$ 0.10 M

1) pH at the start $V_{\text{NaOH}} = 0$ mL

Weak acid

$$\text{HAc} \rightleftharpoons H^+ + Ac^- \quad K_a = 1.75 \times 10^{-5}$$

$$[H^+]^2 = C_a \cdot K_a \quad [H^+] = 1.32 \times 10^{-3} M$$

$$\Rightarrow pH = 2.88$$

2) pH in the pre-equivalence $V_{\text{NaOH}} = 10$ mL

Buffer $\text{HAc}$/ $\text{NaAc}$

$$K_w = 1.75 \times 10^{-7} \quad pK_w = 9.26$$

$$[\text{HAc}] = \frac{[\text{HAc}]_0}{[\text{HAc}]} = \frac{4}{4.86} - 7.0 \times 10^{-5} M \Rightarrow pH = 4.16$$

3) pH in the equivalence point $V_{\text{NaOH}} = 50$ mL

Hydrolysis of the salt

$$\text{NaAc} + H_2O \rightleftharpoons HAc + NaOH$$

$$[\text{NaAc}] = \frac{[\text{NaAc}]_0}{[\text{NaAc}]} = \frac{50}{50} - 0.05 M$$

$$K_w = \frac{[\text{HAc}] \cdot [\text{OH}^-]}{[\text{Ac}^-] \cdot [H^+]} \Rightarrow [\text{OH}^-] = 1.00 \times 10^{-13}$$

4) pH in the post-equivalence $V_{\text{NaOH}} = 50.10$ mL

Hydrolysis of the salt plus excess of strong base.

$$\text{Ac}^- + OH^- \rightleftharpoons \text{HAc} + \text{OH}^-$$

$$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$$

The approximation is good because the same result can be reached using Noyes:

$$f\left(\frac{[\text{OH}^-]}{[\text{HAc}]_0} \right) \approx pH = 8.724$$

The contribution of acetate is negligible compared to the contribution of the base.

$$[\text{OH}^-] = 1.00 \times 10^{-13} M \Rightarrow pH = 10.00$$
Titration of a Weak Acid with a Strong Base: Plotting of the Curve

The following figures illustrate that as the acid becomes weaker or more dilute, the end point becomes less distinct. It is therefore not practical to titrate an acid or base when its strength is too weak or its concentration too dilute.

Titration Errors with Acid-Base Indicators

1. The pH at which the indicator changes color differs from the pH at the equivalence point. Determinate error
   Minimized by making a blank correction.

2. Originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator. Indeterminate error

Example: Calculate the % error committed in the titration of 0.01M HCl with 0.01M if the indicator changes color at: I) pH = 10 and II) pH = 5.

Suppose an initial volume of 100 mL. If the pH = 10, we are in the post-equivalence: base excess.

Suppose an initial volume of 100 mL. If the pH = 5, we are in the pre-equivalence: there remains HCl unreacted.

Example: Calculate the error in the titration of 0.5 M HAc with 0.5 M NaOH, if the indicator changes color at: i) pH = 6 and ii) pH = 9.5. Ka = 1.8·10⁻⁵

The pH in the equivalence is given by the hydrolysis of the salt, NaAc:

\[ \text{Ac} + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^- \]

If [HAc] = [OH⁻]:

\[ K_a = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}]} \]

\[ K_a = 1.00 \times 10^{-5} \]

\[ [\text{H}^+] = 1.00 \times 10^{-5} \]

\[ [\text{OH}^-] = 5.66 \times 10^{-9} \]

\[ [\text{Ac}^-] = 5.00 \times 10^{-6} \]

\[ \text{pH} = 9.07 \]

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Example: Calculate the error in the titration of 0.5 M HAc with 0.5 M NaOH, if the indicator changes color at: i) pH = 6 and ii) pH = 9.5. K_a = 1.8 × 10^{-5}

1) If pH6, we are in the pre-equivalence: buffer HAc/NaAc.

\[ K_a = 1.8 \times 10^{-5} \quad \text{[HAc][NaAc]} = K_a[HA] \]

\[ [H^+] = 10^{-5} M \quad \text{[HAc]} = 0.5 \text{ M} \times 0.5 \text{ M} \]

\[ \frac{[H^+]}{[HAc]} = \frac{10^{-5}}{0.5} = 2 \times 10^{-5} \]

Error: (94.73 - 100 mL) = -5.27 mL

2) If pH9.5, we are in the post-equivalence: excess of OH⁻.

\[ [OH^-] = 10^{-9.5} M \quad \text{[HAc]} = 0.5 \text{ M} \times 0.5 \text{ M} \]

\[ \text{pH} = 10.2 \]

Error: 0.013 mL; scarcely an error.

---

Calculation in the Titration Curves for a Diprotic Acid

50 mL of 0.10 M H₂A titrated with 0.10 M NaOH. K_a₁ = 1.00 × 10⁻³; K_a₂ = 1.00 × 10⁻⁷

1) pH at the start \( V_{NaOH} = 0 \text{ mL} \)

H₂A ⇌ H⁺ + HA⁻ \( K_{a1} = 1.00 \times 10^{-3} \)

Since \([H^+] > K_{a1} \):

\[ \text{pH} = \log_{10} \left( \frac{[H^+]}{[H_2A]} \right) = \log_{10} \left( \frac{10^{-3}}{0.1} \right) = 2.40 \]

2) pH in 1st pre-equivalence \( V_{NaOH} = 50 \text{ mL} \)

H₂A + NaOH ⇌ H⁺ + HA⁻ + Na⁺

3) pH in 1st equivalence point \( V_{NaOH} = 50 \text{ mL} \)

HA⁻ ⇌ H⁺ + A⁻

4) pH in the 2nd pre-equivalence point \( V_{NaOH} = 100 \text{ mL} \)

Hydrolysis of salt A⁻ + H₂O ⇌ AOH⁻ + H⁺

5) pH in the 2nd equivalence point \( V_{NaOH} = 110 \text{ mL} \)

Hydrolysis of salt plus base excess NaOH + Na⁺ + H₂O

6) pH in post-2nd equivalence \( V_{NaOH} = 130 \text{ mL} \)

Hydrolysis contribution is negligible compared to the contribution of the base.
The sodium, potassium and barium hydroxides avidly react with atmospheric CO₂:

\[ \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]

Do we always lose alkali ability to neutralize the acid?

1) Use of an indicator that changes color in the **acidic** zone:

\[ \text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \quad \text{No error is committed} \]

2) Use of an indicator that changes color in the **basic** zone:

\[ \text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^- \quad \text{An error is committed} \]

If you suspect an alkali standard has been carbonated, you may only use it to titrate an unknown acid when the indicator selected changes color in the acidic zone.

Analysis of Basic Mixtures: \text{CO}_3^{2-}, \text{HCO}_3^-, \text{OH}^-:

There will never be more than two of these substances together, for the third one will always be eliminated through the reaction:

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]

The analysis requires two titrations:

1. One using an indicator that changes color in the basic zone (P.T.)
2. Another using an indicator that changes color in the acidic zone (M.O.)

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K_a = 10^{-6.34} \]

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K_a = 10^{-10.36} \]

\[ \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^- \quad \text{Reactions in which the} \]

\[ \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \quad \text{titrimetric analysis relies} \]
Analysis of a Mixture of Na₂CO₃ and NaOH: Winkler Methodology

A) In one portion, the TOTAL alkalinity (CO₃²⁻ + OH⁻) is determined by titration up to color change of M.O.

B) In a second portion, the CO₃²⁻ is precipitated as BaCO₃, by adding an excess of BaCl₂. Then, the remaining OH⁻ is titrated with HCl using P.T. as indicator.

\[ V_a - V_b = [CO_3^{2-}] \]

Determination of organic N. Kjeldhal Method

1. Transformation of sample bound N into ammonium cation, NH₄⁺, by attack with hot and concentrated H₂SO₄.

2. The resulting solution is cooled, diluted and placed in a basic medium to liberate ammonia gas:

\[ NH_4^+ + OH^- \rightarrow NH_3(aq) + H_2O \quad \text{or} \quad NH_3(aq) \rightarrow NH_3(g) \]

3. The gas is distilled and collected in an acidic solution, and an acid-base titration is used to do the final quantitation.
Determination of organic N. Kjeldahl Method

CRITICAL step:

Decomposition of the sample by heating with H$_2$SO$_4$.

• C y H $\rightarrow$ CO$_2$ y H$_2$O, respectively.
• N amido and aminic $\rightarrow$ NH$_4^+$, quantitatively.
• N in groups nitro, azo and azoxy $\rightarrow$ N, $\uparrow$NO$_x$ (losses).

This loss can be avoided by trying first the sample with a reducing agent such as Na$_2$S$_2$O$_3$ or salicylic acid, which makes the N behave as amine or amide N.

Determination of inorganic N: ammonium salts

Conversion of the ammonium salt into ammonia by treatment in alkaline medium, followed by distillation and titration according to Kjeldahl.

Determination of inorganic Nitrates and Nitrites

Previous reduction to NH$_3^+$ by action of DEVARDA alloy (50% Cu, 45% Al, 5% Zn) introduced as granules into the flask containing the sample in an strongly alkaline medium. The generated NH$_3$ is distilled according to Kjeldahl.

Determination of S

Sulfur in organic and biological materials is conveniently determined by burning the sample in a stream of oxygen.

The sulfur dioxide formed during the oxidation is collected by distillation into a dilute solution of hydrogen peroxide:

$$\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$$

The H$_2$SO$_4$ is then titrated with standard base.
Lesson 6. Complexation Titrations

1. Unidentate and multidentate ligands.
2. Titrations with inorganic complexes agents: determination of cyanides.
4. Metallochromic indicators.
5. Practical applications.

Multidentate vs. Unidentate ligands

Multidentate ligands (especially with 4 and 6 donors) are preferred for titrimetry because they:
- React more completely with metal ion
- Usually react in a single step
- Provide sharper end-points

The formation of complexes with unidentate ligands generally involves the formation of 2 or more intermediate species:

\[ \text{Cu}^{2+} + n \text{A} \rightarrow \text{CuA}_n^2+ \]

Typical Inorganic Complex-Forming Titrations

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Analyte</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(NO₃)₂</td>
<td>Br⁻, Cl⁻, SCN⁻, CN⁻, thiocyanate</td>
<td>Products are neutral Hg(II) complexes; various indicators used.</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>CN⁻</td>
<td>Product is Ag(CN)₂⁻; indicator is I⁻; titrate to first turbidity of AgI.</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>CN⁻</td>
<td>Product is Na(CN)CN⁻; indicator is Ag⁺; titrate to first turbidity of AgI.</td>
</tr>
<tr>
<td>KCN</td>
<td>Cu⁺, Hg⁺², Ni⁺²</td>
<td>Products are Cu(CN)₂⁻, Hg(CN)₂⁻, and Ni(CN)₂⁻; various indicators used.</td>
</tr>
</tbody>
</table>

Unidentate ligands

Complexometry with unidentate ligand

Liebig: Determination of CN⁻ with Ag⁺

2CN⁻ + Ag⁺ → Ag(CN)₂⁻

Note: Analytical reaction: formation of insoluble complex.

End-point indication reaction

Denigès: Determination in ammoniacal medium with KI as indicator

El NH₃ prevents the anticipated precipitation of AgCN, and the first real excess of Ag⁺ causes the appearance of a yellowish white turbidity due to the formation of AgI.

Acid-Base Forms

EDTA as an ideal Multidentate ligand

- EDTA exists in up to 3 different acid-base forms depending on the solution pH.
- The most basic form (Y⁻) is the one which primarily reacts with metal ions.
Formation constants for metal-EDTA complexes

<table>
<thead>
<tr>
<th>CATION</th>
<th>$K_{MY}$</th>
<th>CATION</th>
<th>$K_{MY}$</th>
<th>pH</th>
<th>$n_{MY}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>$2.1 \times 10^7$</td>
<td>Cu⁺²</td>
<td>$6.3 \times 10^{10}$</td>
<td>2.0</td>
<td>2.70 $\times 10^{-1}$</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>$4.9 \times 10^4$</td>
<td>Zn⁺²</td>
<td>$3.2 \times 10^{16}$</td>
<td>2.5</td>
<td>7.14 $\times 10^{-11}$</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>$4.9 \times 10^8$</td>
<td>Cd⁺²</td>
<td>$2.9 \times 10^{16}$</td>
<td>3.0</td>
<td>4.00 $\times 10^{-16}$</td>
</tr>
<tr>
<td>Sr⁺²</td>
<td>$6.2 \times 10^3$</td>
<td>Pb⁺²</td>
<td>$1.1 \times 10^{16}$</td>
<td>4.0</td>
<td>2.78 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Ba⁺²</td>
<td>$6.2 \times 10^7$</td>
<td>Pb⁺²</td>
<td>$1.3 \times 10^{16}$</td>
<td>5.0</td>
<td>2.86 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Mn⁺²</td>
<td>$5.8 \times 10^7$</td>
<td>Pb⁺²</td>
<td>$1.3 \times 10^{16}$</td>
<td>6.0</td>
<td>4.55 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>$2.0 \times 10^5$</td>
<td>Fe⁺³</td>
<td>$2.9 \times 10^{16}$</td>
<td>7.0</td>
<td>1.85 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Ni⁺²</td>
<td>$4.2 \times 10^4$</td>
<td>V⁺³</td>
<td>$7.9 \times 10^{16}$</td>
<td>8.0</td>
<td>1.92 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Co⁺²</td>
<td>$2.0 \times 10^3$</td>
<td>Ni⁺³</td>
<td>$1.6 \times 10^{16}$</td>
<td>9.0</td>
<td>1.92 $\times 10^{-6}$</td>
</tr>
<tr>
<td>Zn⁺²</td>
<td>$3.2 \times 10^6$</td>
<td>Ni⁺³</td>
<td>$1.6 \times 10^{16}$</td>
<td>10.0</td>
<td>1.92 $\times 10^{-6}$</td>
</tr>
</tbody>
</table>

Calculations for the Plotting of Complexometric Titration Curves (pH vs. volume of Y⁴⁻)

1) Start $V_{EDTA} = 0 \text{ mL}$  $[\text{Ca}^{2+}] = 0.01 M$ ;  $pCa = 2.00$

2) Pre-equivalence $V_{EDTA} = 10 \text{ mL}$  $[\text{Ca}^{2+}] = 0.01 M$ ;  $pCa = 3.00$

3) Equivalence $V_{EDTA} = 50 \text{ mL}$  $[\text{Ca}^{2+}] = 0.01 M$ ;  $pCa = 5.00$

4) Post-equivalence $V_{EDTA} = 60 \text{ mL}$  $[\text{Ca}^{2+}] = 0.01 M$ ;  $pCa = 9.55$

Effect of pH

Effect of $K_{MY}$
Minimum pH for effective titrations of various metal ions with EDTA.

The points represent the pH at which the conditional formation constant, \( K_f' \), for each metal is \( 10^6 \), needed for a sharp end point.

\[ \Delta \text{pM} = 2 \text{ around the equivalence (± 0.05 mL)} \]

If the equivalence is reached for 50 mL, just one drop before:

\[ [M] = \frac{50 \text{ mL} \cdot 0.01 \text{M} - 49.95 \text{ mL} \cdot 0.01 \text{M} \cdot 5 \times 10^{-6} \text{M} \rightarrow \text{pM} = 5.3} {50 + 49.95 \text{ mL}} \]

If \( \Delta \text{pM} = 2 \), for \( \text{VEDTA} = 50.05 \text{ mL} \) (just one drop after equivalence):

\[ \text{pM} = 7.3 \Rightarrow [M] = 5 \times 10^{-6} \text{M} \]

\[ [MY^2-] = \frac{50 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-6} \text{M}} {50 + 50.05 \text{ mL}} \]

\[ [Y^-] = \frac{0.05 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-7} \text{M}} {50 + 50.05 \text{ mL}} \]

\[ K_f' = \frac{[MY^2-]}{[M][Y^-]} = \frac{5 \times 10^{-6} \times 5 \times 10^{-6}}{5 \times 10^{-7} \times 5 \times 10^{-7}} = 2 \times 10^6 \]

- Their concentration has to be kept to the minimum necessary to prevent precipitation of the analyte.
- The initial portions (pre-equivalence) of the titration curves will exhibit higher pH values the higher is the concentration of the ancillary ligand.
- Excess buffer solution may worsen unnecessarily the endpoint detection.

**Auxiliary complexing reagents**

- Eriochrome Black T (EBT)
  - Stable 1:1 Red Complexes (Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+})
  - When \( pH = 7 \):
    \[ M^{n+} + HY^{2-} \rightleftharpoons MN^{n+} + MY^{2-} \]
    - \( \Delta \text{pM} = 2 \) around the equivalence (± 0.05 mL)
    - \( \text{pM} = 7.3 \Rightarrow \text{EDTA} = 50.05 \text{ mL} \)
    - \( \text{pM} = 7.3 \Rightarrow [M] = 5 \times 10^{-6} \text{M} \)
    - \( [MY^{2-}] = \frac{50 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-6} \text{M}} {50 + 50.05 \text{ mL}} \)
    - \( [Y^-] = \frac{0.05 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-7} \text{M}} {50 + 50.05 \text{ mL}} \)
    - \( K_f' = \frac{[MY^{2-}]}{[M][Y^-]} = \frac{5 \times 10^{-6} \times 5 \times 10^{-6}}{5 \times 10^{-7} \times 5 \times 10^{-7}} = 2 \times 10^6 \)

- \( H_2O + HIn \rightleftharpoons HIn^2+ + H_2O^+ \) \( \text{pK}_{a1} = 6.3 \)

- \( H_2O + HIn \rightleftharpoons In^2+ + H_2O^+ \) \( \text{pK}_{a2} = 11.6 \)

**Metallochromic Indicators**

- Eriochrome Black T (EBT)
  - \( \Delta \text{pM} = 2 \) around the equivalence (± 0.05 mL)
  - \( \text{pM} = 7.3 \Rightarrow \text{EDTA} = 50.05 \text{ mL} \)
  - \( \text{pM} = 7.3 \Rightarrow [M] = 5 \times 10^{-6} \text{M} \)
  - \( [MY^{2-}] = \frac{50 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-6} \text{M}} {50 + 50.05 \text{ mL}} \)
  - \( [Y^-] = \frac{0.05 \text{ mL} \cdot 0.01 \text{M} - 5 \times 10^{-7} \text{M}} {50 + 50.05 \text{ mL}} \)
  - \( K_f' = \frac{[MY^{2-}]}{[M][Y^-]} = \frac{5 \times 10^{-6} \times 5 \times 10^{-6}}{5 \times 10^{-7} \times 5 \times 10^{-7}} = 2 \times 10^6 \)

**Titration of Mg^{2+} by EDT**

Eriochrome Black T Indicator

**Addition of EDTA**

Before

Near Equivalence point

After

\( \Delta \text{pM} = 2 \) around the equivalence (± 0.05 mL)
End point for the titration of hardness with EDTA using calmagite as an indicator; the indicator is:

a) red prior to the end point due to the presence of the Mg$^{2+}$-indicator complex;
b) purple at the titration’s end point; and
c) blue after the end point due to the presence of uncomplexed indicator.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH</th>
<th>Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>calmagite</td>
<td>9-11</td>
<td>Ba, Ca, Mg, Zn</td>
</tr>
<tr>
<td>Eriochrome Black T (EBT)</td>
<td>7-10.5</td>
<td>Ba, Ca, Mg, Zn</td>
</tr>
<tr>
<td>Eriochrome Blue Black B</td>
<td>8-12</td>
<td>Ca, Mg, Zn, Cu</td>
</tr>
<tr>
<td>Murexide</td>
<td>6-13</td>
<td>Ca, Ni, Cu</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>2-3</td>
<td>Fe</td>
</tr>
</tbody>
</table>

Almost all elements can be determined by EDTA titration. Some Common Techniques used in these titrations include:

a) Direct Titrations

- Analyte is buffered to appropriate pH and is titrated directly with EDTA.
- An auxiliary complexing agent may be required to prevent precipitation of metal hydroxide.

Even those cations that lack good metallocromic indicator can be titrated directly.

b) Back Titrations

Useful when the reaction of the cation with the ligand is slow or when there is not an adequate indicator.

\[ K_{MY^{2+}} < K_{MY} \]

Second metal ion must not displace analyte from EDTA.
c) Displacement titrations

Particularly useful when an adequate indicator is not available.

\[ K_{M^2+} > K_{MgY^2-} \]

\[
\begin{align*}
\text{M}2^+ + \text{an unmeasured excess of MgY}_2^- & \rightarrow \text{MY}_2^- + \text{MgY}_2^- + \text{Mg}^2+ \\
\text{Concentration of released Mg}^2+ & \text{equals } [M^+] 
\end{align*}
\]


c) Displacement titrations

It is good to recourse to indirect methods in order to determine species that do not react with EDTA.

\[ \text{Ba}^2+ + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \]

\[ \text{Ba}^2+ + \text{excess} \]

\[ \text{Pb}^2+ + \text{Ni(CN)}_3^- \rightarrow \text{CN}^- + \text{Ni(CN)}_2^+ + \text{Pb}^2+ \]

\[ K_{\text{NiY}^2-} = 10^{18.6}, \quad K_{\text{PbY}^2-} = 10^{18.0} \]

\[ \text{Pb}^2+ \text{can be easily titrated in a sample also containing Ni}^2+, \text{in spite of the close formation constants both of them exhibit with EDTA, if CN}^- \text{is used as masking agent.} \]

\[ \text{Ni}^2+, \text{Pb}^{2+} + \text{CN}^- \rightarrow \text{Ni}^2+ \text{(CN)}_2^+, \text{Pb}^{2+} \]

\[ \Delta \text{Pb}^2+ \Delta \text{Ni}^2+ \Delta \text{CN}^- \]

(d) Indirect titrations

It is good to recourse to indirect methods in order to determine species that do not react with EDTA.

\[ \text{Ba}^2+ + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \]

\[ \text{Ba}^2+ + \text{excess} \]

\[ \text{Pb}^2+ + \text{Ni(CN)}_3^- \rightarrow \text{CN}^- + \text{Ni(CN)}_2^+ + \text{Pb}^2+ \]

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\[ \text{Ni}^2+, \text{Pb}^{2+} + \text{CN}^- \rightarrow \text{Ni}^2+ \text{(CN)}_2^+, \text{Pb}^{2+} \]

\[ \Delta \text{Pb}^2+ \Delta \text{Ni}^2+ \Delta \text{CN}^- \]
Lesson 7. Oxidation-Reduction Titrations

1. Theoretical Calculations for the Titration Curves.
2. Potential at the Equivalence Point.
3. Auxiliary Oxidizing and Reduction Reagents.
4. End-Point Indicators
5. Applications with both Oxidizing and Reduction Reagents.

Redox Titration

- Based on an oxidation-reduction reaction between analyte and titrant.
- Many common analytes in chemistry, biology, environmental and materials science can be measured by redox titrations.

\[
E^\circ_{\text{Ce(IV)/Ce(III)}} = 1.44 \text{ V} \quad E^\circ_{\text{Fe(III)/Fe(II)}} = 0.68 \text{ V}
\]

\[
\text{Fe}^{3+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{2+} + \text{Ce}^{3+} \quad K = 10^{16}
\]

- Provided that the reaction be fast and reversible, the system will be in equilibrium throughout the titration.
- The electrode potentials of the two half-systems must always be identical, and equal to the potential of the system, E:

\[
E = E^\circ_{\text{Ce(IV)/Ce(III)}} - E^\circ_{\text{Fe(III)/Fe(II)}} + 0.059 \log \left[ \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right]
\]

As usual, there are three distinct regions in the titration of Fe(II) with standard Ce(IV), monitored potentiometrically with Pt and a reference electrode.

- Before the equivalence point, where the potential at Pt is dominated by the analyte redox pair.
  - Each aliquot of Ce\textsuperscript{4+} creates an equal number of moles of Ce\textsuperscript{3+} and Fe\textsuperscript{3+}
  - Excess unreacted Fe\textsuperscript{2+} remains in solution
  - Amounts of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} are known, and used to determine cell voltage.
  - Residual amount of Ce\textsuperscript{4+} is unknown

- After the equivalence point, where the potential is determined by the titrant redox pair.
  - Opposite Situation Compared to Before the Equivalence Point
  - Equal number of moles of Ce\textsuperscript{3+} and Fe\textsuperscript{3+}
  - Excess unreacted Ce\textsuperscript{4+} remains in solution
  - Amounts of Ce\textsuperscript{3+} and Ce\textsuperscript{4+} are known, and can be used to determine cell voltage.
  - Residual amount of Fe\textsuperscript{2+} is unknown

- At the equivalence point, Fe\textsuperscript{2+} has been added to react with all Fe\textsuperscript{3+}.
- Potentials for Fe\textsuperscript{2+} and Fe\textsuperscript{3+} are not known.

At the equivalence point:

\[
E_{eq} = E^\circ_{\text{Fe(II)/Fe(III)}} + \frac{0.059}{1} \log \left[ \frac{[\text{Ce}^{4+}]}{[\text{Fe}^{2+}]} \right]
\]

Adding both equations:

\[
2E_{eq} = E^\circ_{\text{Fe(II)/Fe(III)}} + E^\circ_{\text{Ce(III)/Ce(IV)}} + \frac{0.059}{1} \log \left[ \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right]
\]

According to the stoichiometry of the reaction:

\[
[\text{Fe}^{2+}] = [\text{Ce}^{4+}] \
[\text{Fe}^{3+}] = [\text{Ce}^{3+}]
\]

\[
2E_{eq} = E^\circ_{\text{Fe(II)/Fe(III)}} + E^\circ_{\text{Ce(III)/Ce(IV)}} + 0.059 \log \left[ \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right]
\]

\[
E_{eq} = \frac{E^\circ_{\text{Fe(II)/Fe(III)}} + E^\circ_{\text{Ce(III)/Ce(IV)}}}{2}
\]

If \( n_1 = n_2 \),

\[
E_{eq} = \frac{E^\circ_{\text{Fe(II)/Fe(III)}} + E^\circ_{\text{Ce(III)/Ce(IV)}}}{2}
\]
Multiplying the first by 2 and the second by 5, and adding:

\[ 3E_{eq} = 2E_{eq1} - E_{eq2} \]

According to the stochiometry of the reaction:

\[ [\text{Ce}^{4+}] = 2[\text{Sn}^{2+}]; \quad [\text{Ce}^{3+}] = 2[\text{Sn}^{4+}] \]

\[ 3E_{eq} = 2E_{eq1} - E_{eq2} \]

\[ E_{eq} = \frac{2E_{eq1} - E_{eq2}}{3} \]

For the general case:

\[ \text{Ox}_1 + a\text{ e}^- \rightleftharpoons \text{Red}_1 \quad E_1^0 \]

\[ \text{Ox}_2 + b\text{ e}^- \rightleftharpoons \text{Red}_2 \quad E_2^0 \]

It holds that:

\[ E_{eq} = \frac{aE_1^0 + bE_2^0}{a+b} \]

This general expression will be fulfilled for all cases where there is no exchange of either \( \text{OH}^- \) or \( \text{H}^+ \).

For this case we obtain:

\[ 7E_{eq} = E_{eq1} + 6E_{eq2} + 0.059\log\left(\frac{[\text{Ce}^{4+}] [\text{Cr}_2\text{O}_7^{2-}] [\text{H}^+]}{[\text{Fe}^{2+}] [\text{Cr}^{3+}]^2}\right) \]

Since in this case: \( [\text{Fe}^{2+}] = 6[\text{Cr}_2\text{O}_7^{2-}]; \quad [\text{Fe}^{3+}] = 3[\text{Cr}^{3+}] \) by replacing, the final expression is obtained:

\[ E_{eq} = \frac{E_{eq1} + 6E_{eq2} + 0.059 \log [\text{H}^+]^4}{7} \]

### 3) Equivalence \( V_{Ce^{4+}} = 25 \text{ mL} \)

\[ E_{eq} = \frac{E_{eq1} + E_{eq2}}{2} = \frac{0.680 + 1.440}{2} = 1.060 \text{ V} \]

### 4) Post-equivalence \( V_{Ce^{4+}} = 25.10 \text{ mL} \)

\[ [\text{Ce}^{4+}] = 25.00 \text{ mL}, 0.10 \text{ M} \quad \rightarrow 0.01 \text{ M} \quad 75.10 \text{ mL} \]

\[ [\text{Ce}^{3+}] = 25.10 \text{ mL}, 0.10 \text{ M} - 25.00 \text{ mL}, 0.05 \text{ M} \quad \rightarrow 0.01 \text{ M} \quad 75.10 \text{ mL} \]

\[ E = 1.440 \text{ V} - 0.059 \log \left(\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}\right) = 1.440 - 0.059 \log \left(\frac{0.01}{0.01}\right) = 1.30 \text{ V} \]

(C) 2014 Dr. J.M. Fernández
50.00 mL of 0.05 M Fe(II) with 0.02 M MnO₄⁻ in [H⁺] = 1.0 M

\[
\text{Fe}^{2+} + \text{MnO}_4^- = 8\text{H}^+ \rightarrow \text{5Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

2) Pre-equivalence

\[
V_{\text{Fe}^{2+}} = 5 \text{ mL}
\]

3) Equivalence

\[
V_{\text{Fe}^{2+}} = 25 \text{ mL}
\]

4) Post-equivalence

\[
V_{\text{Fe}^{2+}} = 25.10 \text{ mL}
\]

Were it 0.005 M Fe(II) to be titrated with 0.01 M Ce(IV), an identical curve would be obtained, because dilution does not affect the potential.

In the pre-equivalence zone, curves are just identical.

The curve for the case of Ce (IV) is symmetrical about the equivalence point due to the equimolar ratio between oxidizing and reducing reagents.

The MnO₄⁻ curve is strongly asymmetric, increasing only slightly after the equivalence point.

Potentials measured at the equivalence are obviously different (1.06 and 1.37 V).

The larger \( \Delta E \) in the equivalence for MnO₄⁻ is a manifestation of the larger value of its K in the reaction with Fe(II).
For a generic reaction:  \( \text{Ox}_1 + \text{Red}_2 \rightleftharpoons \text{Red}_1 + \text{Ox}_2 \)

where the semi-systems involved are:

\[
\begin{align*}
\text{Ox}_1 + a\; e^- & \rightleftharpoons \text{Red}_1 & E_1^0 \\
\text{Ox}_2 + b\; e^- & \rightleftharpoons \text{Red}_2 & E_2^0
\end{align*}
\]

a) we will calculate the value of \( K \) so that around equivalence \( \Delta p_{\text{Red}_2} \geq 2 \)

b) the necessary difference between the standard potential of the semi-systems to ensure that \( K \)

\[
\begin{align*}
\text{Titration of } 50.00 \text{ mL of } 0.1 \text{ M } \text{Red}_2 \text{ with } 0.1 \text{ M } \text{Ox}_1 \\
a) \quad [\text{Red}_2] = 5.0 \cdot 10^{-4} \text{ M} \\
& \quad \text{equivalent to } 50.00 \text{ mL} \\
& \quad \Delta p_{\text{Red}_2} = 4.30 \\
& \quad \text{increase of } 2 \text{ units, means that for } 50.05 \text{ mL added reagent, the } p_{\text{Red}_2} \text{ should be } 6.30.
\end{align*}
\]

\[
\begin{align*}
p_{\text{Red}_2} = 6.30 & \Rightarrow [\text{Red}_2] = 5.0 \cdot 10^{-7} \text{ M} \\
& \Rightarrow \text{equivalent to } 50.05 \text{ mL}
\end{align*}
\]

Accordingly:

\[
K = \frac{\text{In}_{\text{Red}_2} \cdot \text{In}_{\text{Ox}_1}}{\text{In}_{\text{Red}_2} \cdot \text{In}_{\text{Ox}_1}} = 10^{\frac{-0.059 E}{n}} \text{ V}^n
\]

\[
\begin{align*}
\text{Redox Indicators} \\
\text{GENERAL or "true" indicators} \\
\text{SPECIFIC indicators}
\end{align*}
\]

\[
\begin{align*}
\text{General redox indicators} & \quad \text{are those substances that change color when oxidized or reduced.} \\
& \quad \text{The change in color only depends on changes in the system's potential as titration goes.} \\
\text{In}_{\text{Red}_2} + n\; e^- & \rightleftharpoons \text{In}_{\text{Red}} \quad E = E_1^0 + 0.059 \log \left( \frac{[\text{In}_{\text{Red}_2}]}{[\text{In}_{\text{Red}}]} \right)
\end{align*}
\]

In general, a color change will be appreciated when:

\[
\begin{align*}
\left| \frac{[\text{In}_{\text{Red}_2}]}{[\text{In}_{\text{Red}}]} \right| & \leq 10 \quad \text{to} \quad \left| \frac{[\text{In}_{\text{Red}_2}]}{[\text{In}_{\text{Red}}]} \right| \leq 10 \\
& \Rightarrow E = E_1^0 + 0.059 \frac{n}{n}
\end{align*}
\]

\[
\begin{align*}
\text{Table 16-2: Redox indicators} \\
\hline
\text{Indicator} & \text{Oxidized} & \text{Reduced} & E^0 \\
\hline
\text{Phenosafranine} & Red & Colorless & 0.28 \\
\text{Indigo tetrasulfonate} & Blue & Colorless & 0.36 \\
\text{Methylene blue} & Blue & Colorless & 0.53 \\
\text{Dihydroxynaphthol} & Violet & Colorless & 0.75 \\
\text{4'-Ethoxy-2,4-diaminoazobenze} & Yellow & Red & 0.76 \\
\text{Diphenyliodole sulfonic acid} & Red-violet & Colorless & 0.85 \\
\text{Diphenylazo sulfonic acid} & Violet & Colorless & 0.87 \\
\text{Tri(2,2'-bipyridyl)iron} & Pale blue & Red & 1.129 \\
\text{Tri(1,10-phenanthroline)iron} & Pale blue & Red & 1.147 \\
\text{Tri(5-nitro-1,10-phenanthroline)iron} & Pale blue & Red & 1.25 \\
\text{Tri(2,2'-bipyridyl)nuthiunian} & Pale blue & Yellow & 1.29
\end{align*}
\]
In the presence of a strong oxidizing agent:

\[
\text{NH}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{Violet Diphenylbenzidine; } E^\circ = 0.76 \text{ V}
\]

- Diphenylamine is not very soluble in water
- Sulfonic acid derivative is used instead, with the same color changes

A starch solution with a little \(I_3^-\) or \(I^-\) behaves like a true reduct indicator, thanks to the intense blue complex that forms with the iodine (\(I_3^-\)).

In the presence of an excess of oxidizing agent, there is a high ratio \(I_3^-/I^-\) and the solution turns blue.

If, on the contrary, there is an excess of reducing agent, \(I^-\) is the prevailing species and no color is observed.

An auxiliary oxidizing and reducing reagent requires to be certain that the analyte be in a single oxidation state at the outset.

To be useful as a preoxidant or a prereductant, a reagent must:
- React quantitatively with the analyte
- React in a fast way with the analyte
- Be easily removed (it is always added in excess)

Common auxiliary prereducing reagents

- Sticks, coils, grit or powder of metals can be immersed directly in the analyte solution:
  - \(\text{Zn, Al, Cd, Pb, Ni, Cu}\)
  - \(\text{Ag (in the presence of Cl^-)}\)

After reduction is judged complete, the solid is removed manually and rinsed with \(\text{H}_2\text{O}\). The analyte solution must be filtered to remove granular or powdered forms of the metal.

Alternative:

“REDUCTOR” column packed with finely divided metal, through which the liquid containing the sample to be analyzed is passed.

Jones «reductor»

Column with amalgamated Zn packing.

\[
2 \text{Zn} + \text{Hg}^2+ \rightarrow \text{Zn}^2+ + \text{Zn(Hg)}_2
\]

Amalgamated Zn is nearly as good reducer as Zn, but inhibits the reduction of protons that originates on bare Zn:

\[
2\text{H}^+ + \text{Zn} \rightleftharpoons \uparrow \text{H}_2 + \text{Zn}^{2+}
\]

A specific indicator is a substance that reacts specifically with one of the reagents involved in the titration to produce a color.

- **SCN**: useful in the determination of Fe (III). The disappearance of the red color of the complex \(\text{Fe(SCN)}^2+\) provides an indication of the endpoint.
- **Starch**: valid for titrations involving iodine, with which it forms the dark blue complex.
Walden "reductor" uses Ag as reducing agent, which accentuates its reducing power in the presence of an anion with which it forms a sparingly soluble salt.

**Uses of the Walden Reductor and the Jones Reductor***

<table>
<thead>
<tr>
<th>Uses of the Walden Reductor and the Jones Reductor*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walden</td>
</tr>
<tr>
<td>Ag⁺ + e⁻ → Ag(0)⁺ e⁻</td>
</tr>
<tr>
<td>Fe³⁺ + e⁻ → Fe²⁻</td>
</tr>
<tr>
<td>Fe⁺ + 2e⁻ → Fe⁰</td>
</tr>
<tr>
<td>Cr²⁺ + 2e⁻ → Cr⁰</td>
</tr>
</tbody>
</table>

**Common preoxidants**

- Sodium Bismuthate \( \text{NaBiO}_3 \)
- Ammonium Peroxydisulfate \( \text{(NH}_4\text{)}_2\text{S}_2\text{O}_8 \)
- Hydrogen Peroxide \( \text{H}_2\text{O}_2 \)

\( \text{NaBiO}_3 \)

**Extremely efficient; it is able to quantitatively oxidize, in acidic media:**

- Mn(II) → MnO₄⁻  
  ✔ Available as a sparingly soluble solid; it is frequently used in a suspension under boiling for a brief time.
- Cr(III) → Cr₂O₇⁻²  
  ✔ Excess reagent is removed by filtration.

\( \text{(NH}_4\text{)}_2\text{S}_2\text{O}_8 \)

**Linus Pauling (1901-1994)**

His work in chemical bonding, X-ray crystallography, and related areas had a tremendous impact on chemistry, physics, and biology. He is the only person to receive two unshared Nobel prizes: for chemistry (1954) and for his efforts to ban nuclear weapons, the peace prize (1962).

This photo of Pauling tossing an orange into the air is symbolic of his work and importance of being able to determine concentrations of ascorbic acid at all levels in fruits and commercial vitamin preparations. Redox titrations with iodine are widely used to determine ascorbic acid.

\( \text{H}_2\text{O}_2 \)

**In acidic medium:**

- Fe(II) → Fe(III)  
  ✔ Excess reagent is eliminated by boiling:
  \[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

**In alkaline medium:**

- Cr(III) → Cr₂O₇⁻²  
- Mn(II) → MnO₂  
  ✔ Excess reagent is eliminated by boiling:
  \[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]

Reminder:

- Oxidant role: \( \text{O}_2\text{O}^2⁻ + 2\text{e}⁻ \rightarrow 2\text{O}_2 \)
- Reductant role: \( \text{O}_2 \rightarrow 2\text{e}⁻ \rightarrow \text{O}_2 \)
Most frequent oxidants: MnO₄⁻ and Ce(IV)

Powerful oxidants with similar applicability.

\[
\begin{align*}
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- & \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} & E^\circ = 1.51 \text{V}
\end{align*}
\]

From a practical viewpoint the two oxidizing agents possess comparable strength. However:

- Solutions of Ce (IV) in sulfuric are stable indefinitely, while those of MnO₄⁻ decompose slowly and require periodic re-standardization.
- The Ce (IV) does not oxidize Cl⁻, while Cl⁻ is slowly oxidized MnO₄⁻.
- There is a salt, cerium ammonium nitrate, in sufficient purity for use as a primary standard type.

Despite the above mentioned drawbacks, MnO₄⁻ is more widely used because:

- MnO₄⁻ solutions have a strong purple coloration: self-indicator.
- permanganate is much cheaper than cerium.
- solutions of Ce (IV) tend to precipitate basic salts of Ce (IV) when the medium is less than 0.1 M in strong acids.

The Preparation and Stability of Standard Solutions of MnO₄⁻

MnO₄⁻ tends to oxidize H₂O, albeit slowly:

\[
4\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + 4\text{OH}^-
\]

It is catalyzed by adverse factors:

- Light
- Heat
- Acids
- Bases
- Mn(II)
- MnO₂

Removal of MnO₂ by filtration before standardization markedly improves the stability of standard MnO₄⁻ solutions. Before filtration, the reagent solution is allowed to stand for about 24 h or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in deionized H₂O.

Paper cannot be used for filtering: use glass wool instead.

- Brown deposits involve MnO₂ formation
- Periodic re-standardization

MnO₄⁻ is standardized with:

- Sodium oxalate

\[
2\text{MnO}_4^- + 5\text{H}_2\text{C}_2\text{O}_4 + 6 \text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

- Slow kinetics at room temperature. The Mn(II) is autocatalyst.

- Iron

Weighed pure iron (99.99%) is attacked in acid, and then reduced to Fe(II).

\[
5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

- Arsenous oxide

Stable, non-hygroscopic, available in high purity.

Is dissolved in a basic medium and then in acid to titrate:

\[
5\text{HAsO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{Mn}^{2+} + 5\text{H}_2\text{AsO}_4^-\]
The Preparation and Stability of Standard Solutions of Ce(IV)

Reagents used:
- Ce(NO₃)₄·2NH₄NO₃ Primary type standard
- Ce(SO₄)₂·2(NH₄)SO₄·2H₂O
- Ce(OH)₂
- Ce(HSO₄)₄

- Ce(IV) solutions are always prepared in 0.1 M H₂SO₄ to prevent precipitation of basic salts.
- Solutions are stable over several months.
- Solutions can be boiled without suffering alteration.

Oximetry: determination of Fe in minerals

Most important iron ores:
- Hematites: Fe₂O₃
- Magnetite: Fe₃O₄
- Limonite: 2 Fe₂O₃·3H₂O

Stages of the analysis:
1. Sample dissolving
2. Reduction of iron to the divalent state
3. Titration of Fe (II) with an oxidant

1. Sample dissolving
- Complete decomposition with hot concentrated HCl
- SnCl₂ accelerates the attack, because it reduces the surface oxides of Fe (III), sparingly soluble, to more soluble Fe (II) compounds
- Silicates are very insoluble and require long treatment
- If a brown residue remains, decomposition was incomplete. It is treated with Na₂CO₃ and then with HCl in order to fully recover Fe
- If the residue is white, it is a non-interfering hydrated silica, indicating that all Fe has been dissolved

2. Reduction of iron to the divalent state
- Normally, since we are in a hydrochloric acid medium, we use SnCl₂:
  \[ \text{Sn}^{2+} + 2 \text{Fe}^{3+} \rightarrow \text{Sn}^{4+} + 2 \text{Fe}^{2+} \]
- The reduction is complete when the typical yellow color of Fe (III) hydrochloric solutions disappears
- The prereductant reagent excess is removed by adding HgCl₂:
  \[ \text{Sn}^{2+} + 2 \text{HgCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{Sn}^{4+} + 2 \text{Cl}^- \]
  - Generated Hg₂Cl₂ does not reduce the oxidizing reagent [MnO₄⁻ or Ce(IV)]
  - Presence of HgCl₂ excess is not able to re-oxidize Fe(II)

3. Titration of iron with oxidant (MnO₄⁻)
- Fe(II) induces the oxidation of Cl⁻ to Cl₂ by MnO₄⁻:
  \[ 5 \text{Fe}^{2+} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+} + 4 \text{H}_2\text{O} \]
- Fe(II) induces the oxidation of Cl⁻ to Cl₂ by MnO₄⁻
  (actually by the Mn (III) which is formed as an intermediate species)
This detrimental side reaction can be prevented:
- Physically: eliminating chlorides as HCl by evaporation in the presence of denser H₂SO₄
- Chemically: adding the Zimmermann-Reinhardt reagent that is composed of:
  - Mn (II) in a mixture of sulfuric and phosphoric acids
The presence of Mn(II) causes a decrease of the potential for semisytem

\[ \text{Mn(III)/Mn(II)} \times 0.059 \text{log}_E \]

PO₄³⁻ forms stable complexes with Mn(III), what produces an identical effect

PO₄³⁻ also complexes Fe(III), thus helping the reaction to reach completion more easily

PO₄³⁻/Fe(III) complex is colorless, thus eliminating the typical yellowish color of Fe(III) hydrochloric solutions, enabling a better observation of the end-point of the titration

3. Titration of iron with oxidant (Ce(IV))

Titration curve for the titration of 50.0 mL of 0.100 M Fe²⁺ with 0.100 M Ce⁴⁺. The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve. Because the transition for ferroin is too small to see on the scale of the x-axis—it requires only 1-2 drops of titrant—the color change is expanded to the right.

Oxidimetry: determination of Ca in limestone (CaCO₃)

Basis: precipitation of Ca²⁺ as oxalate, which is filtered, washed and dissolved in dilute acid, and then titrated with MnO₄⁻.

Excess of C₂O₄²⁻

\[ \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{iCa}_2\text{C}_2\text{O}_4 \]

\[ 2 \text{MnO}_4^- + 5 \text{H}_2\text{C}_2\text{O}_4 + 6 \text{H}^+ \rightleftharpoons 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O} \]

Less time consuming than the gravimetric determination

Oxidimetry: determination of mixtures

As with acid-base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials.

The figure shows an example of the titration curve for a mixture of Fe²⁺ and Sn²⁺ using Ce⁴⁺ as the titrant. A titration of a mixture of analytes is possible if their standard potentials or formal potentials differ by at least 200 mV.

Dichromatometry: direct determination of Fe (just the one)

\[ \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightleftharpoons 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \]

Dichromatometry: indirect determination of oxidants

Known excess of Fe(II)

\[ \text{mmol Fe}^{2+} \text{ added} = \text{mmol Fe}^{2+} \text{ consumed} + \text{mmol Fe}^{3+} \text{ free in excess} \]

Ox: NO₃⁻, ClO₃⁻, MnO₄⁻...
I₂ as oxidant: Iodimetry

Weak oxidizing agent, used for the determination of strong reducing agents.

\[ I_2 + 2e^- \rightarrow 2I^- ; \quad E^0 = 0.536 \text{ V} \]

- Its low oxidizing power may become an advantage by allowing the selective determination of a strong reducing agent in the presence of a weak one.
- It has a reversible and sensitive indicator (starch).
- Their solutions are not stable and require re-standardization.

I₂ as oxidant: Endpoint Indication

- **Self-indicator:** \([I_3^-]=5.0 \times 10^{-6} \text{ M}\) (less than 1 drop of 0.05 M reagent) gives a discernible color, provided that the sample is colorless.
- **Gain in sensitivity:** adding a few mL of either CCl₄ or HCCl₃, which turn deep purple in the presence of iodine.
- **Most common indicator:** starch.
  - The starch is irreversibly decomposed in the presence of highly concentrated solutions of iodine.
  - The addition of the indicator is delayed until near the end of the titration, when the color of \(I_3^-\) has come down from deep red to pale yellow.

I₂ as oxidant: Standardization

It may be standardized with:

- **Na₂S₂O₃**
  - very soluble in water and commercially available in primary type grade.
- **BaS₂O₃·H₂O**
  - the salt is scarcely soluble in water, but the reaction proceeds even directly with the solid:

  \[ I_2 + \text{BaS}_2\text{O}_3\cdot\text{H}_2\text{O} \triangleq \text{S}_4\text{O}_6^{2-} + \text{Ba}^{2+} + 2\text{I}^- \]

I₂ as oxidant: Application Conditions

Iodine titrations must always be carried out in a **neutral or acid** medium, because in a **basic media** the following processes take place:

\[ I_2 + \text{OH}^- \triangleq 1O^- + I^- + H^+; \quad 3I^- \triangleq IO_3^- + 2I^- \]

Reductimetry: reductants as titrant reagents

- **Standard solutions of most reductants tend to react with atmospheric oxygen.**
- **Accordingly, reductants are seldom used for the direct titration** of oxidizing analytes.
  - Indirect methods are used instead.
- **Most common reductants:** Fe(II) and I⁻.
Fe as reductant

- Mohr's salt: Fe(NH₄)₂(SO₄)₂·6H₂O
- Desper's salt: FeC₂H₄(NH₃)₂(SO₄)₂·4H₂O

Fe(II) easily oxidizable in air
- It is preserved in 0.5 M H₂SO₄ acid medium

Fe as reductant: practical applications

- Determination of Cr(VI), Mo(VI), NO₃⁻, ClO₃⁻, ClO₄⁻ as reductant

I⁻ as reductant

\[ 2I⁻ \rightleftharpoons I₂ + 2e⁻ \]

- The strong color of the reaction product prevents the use of endpoint visual indicators.
- Unstable, it gets oxidized in the air

Indirect determinations

- Iodometry: an oxidizing analyte is added to excess iodide (KI) to produce iodine (I₂), which is then titrated with standard thiosulfate solution (Na₂S₂O₃) in neutral or slightly acidic medium.

Iodometry: the I₂ - S₂O₃²⁻ reaction

\[ I₂ + 2S₂O₃²⁻ \rightleftharpoons 2I⁻ + S₄O₆²⁻ \]

- Reaction is no longer quantitative at pH > 7
- At pH > 7 hypoiodite is generated, which is capable of oxidizing thiosulfate to sulfate:
  \[ IO⁻ + 2OH⁻ \rightleftharpoons I⁻ + H₂O + 2OH⁻ \]
- When I₂ 0.05 M, pH < 6.5
- When I₂ 0.005 M, pH < 5
- The starch must be added at the end of the titration, to avoid its decomposition by prolonged contact with iodine.

S₂O₃²⁻ solutions

- Stable in air
- They show a tendency to decomposition:
  \[ S₂O₃²⁻ + H⁺ \rightleftharpoons HSO₃⁻ + S(0) \]
- The rate of this decomposition reaction depends on:
  - pH
  - Presence of microorganisms (metabolize the transformation of S₂O₃²⁻ to SO₃²⁻, SO₄²⁻ and S(0))
- Work in sterile conditions, and / or in the presence of bactericides.
- Concentration of the solution
- Presence of Cu(II)
- Exposure to sunlight

S₂O₃²⁻ solutions: standardization

They are standardized against KIO₃, as a primary type standard.

The KIO₃ once weighed, is dissolved in water containing an excess of KI. Upon acidification, the formation of I₂ takes place instantaneously:

\[ IO⁻ + 5I⁻ + 6H⁺ \rightleftharpoons 3I₂ + 3H₂O \]

The S₂O₃²⁻ is then titrated against this \( \text{in situ} \) liberated I₂:

\[ I₂ + 2S₂O₃²⁻ \rightleftharpoons 2I⁻ + S₄O₆²⁻ \]

1 mol I₂ = 3 mol I⁻ = 6 mol S₂O₃²⁻

- \( \text{CrO}_3 \) + 6I⁻ + 14H⁺ \rightleftharpoons 2Cr³⁺ + 3I₂ + 7H₂O
- \( \text{BrO}_3 \) + 6I⁻ + 6H⁺ \rightleftharpoons Br⁻ + 3I₂ + 3H₂O

Iodometric determination of Cu in minerals and alloys

Example: Brass (Sn, Pb, Cu, Zn)

- Attack and dissolution with HNO₃:
  - metals with maximum oxidation state.
  \[ 2\text{Cu}^{2+} + 4I⁻ \rightleftharpoons 2\text{CuI(s)} + I₂ \]
- Interferences: Fe, As, Sb

Alternative: you work in a pH 3.5 HNH₄F₂/HF buffered medium.
  - \( \text{FeF}_3 \) is formed: decrease of the Fe(III)/Fe(II) potential
  - As and Sb are not able to oxidize I⁻, contrary to what they do in strong acidic conditions.
Iodometric determination of O₂ dissolved in H₂O: WINKLER

1) Precipitation of Mn(OH)₂ in basic medium
2) Oxidation to Mn(OH)₃ by the dissolved O₂.
3) Mn(OH)₃ oxidizes I⁻ to I₂ in acidic medium
4) The stoichiometrically generated I₂ is titrated with S₂O₃²⁻.

\[ \text{Mn(OH)}_2 + 2\text{I}^- + 2\text{OH}^- \rightarrow \text{Mn(OH)}_3 + \text{I}_2 + 2\text{H}_2\text{O} \]

\[ 4\text{Mn(OH)}_3 + \text{O}_2 + 4\text{H}_2\text{O} \rightarrow 4\text{MnO(OH)}_2 + 4\text{OH}^- \]

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \]

Iodometric determination of total Chlorine residual

Endpoint for the determination of the total chlorine residual.
(a) Acidifying the sample and adding KI forms a brown solution of I₃⁻.
(b) Titrating with Na₂S₂O₃ converts I₃⁻ to I⁻ with the solution fading to a pale yellow color as we approach the end point.
(c) Adding starch forms the deep purple starch–I₃⁻ complex.
(d) As the titration continues, the end point is a sharp transition from a purple to a colorless solution.

The change in color from (c) to (d) typically takes 1–2 drops of titrant.

1. KBrO₃
   Determination of olefinic groups and certain aromatic functional groups.

2. HIO₄
   Selective reaction with groups

3. Karl Fischer reagent
   Determination of H₂O

1. KBrO₃: Indirect applications

Analyte, Red₂

\[ \text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O} \]

\[ \text{E}^- = 1.44 \text{ V} \]

- Primary type standard substance.
- Stable indefinitely.
- Precursor of Br₂:

\[ \text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \]

- Reactions with Br₂: slow kinetics.
- Few direct applications: As(III), Sb(III), Fe(II)

\[ \rightarrow \text{Indirect titrations are preferred instead.} \]

1. KBrO₃: Substitution reactions

Indirect titration

Sufficiently rapid reaction: Direct titration

Example: Determination of Al

\[ \text{Al}^{3+} + 3\text{HOC}_2\text{H}_3\text{N}^- \rightarrow \text{Al(OCH}_2\text{H}_2\text{N})_3 + 3\text{H}^+ \]

\[ \text{Al(OCH}_2\text{H}_2\text{N})_3 + \text{H}_2\text{O} \rightarrow 3\text{HOC}_2\text{H}_3\text{N} + \text{Al}^{3+} \]

\[ 3\text{HOC}_2\text{H}_3\text{N} + 6\text{Br}_2 \rightarrow 3\text{HOC}_2\text{H}_3\text{NBr}_2 + 6\text{HBr} \]

\[ \text{BrO}_3^- (\text{standard}) + \text{Br}_2 \]

1 mol Al³⁺ = 3 mol HQ = 6 mol Br₂
These reactions involve the opening of the olefinic double bond.

**Example: Determination of ascorbic acid**

- Positive assays are indicated by the appearance of a yellowish white color due to the precipitate of silver iodate when the assay is made in the presence of silver.
- Non-adjacent groups are not oxidized.

**2. HIO₄ Selectivity of Malaprade reaction**

- Primary and secondary α-hydroxamines undergo Malaprade reaction, contrary to α-diamines that do not suffer any reaction. The C atom containing an amino group, loses ammonia (or a substituted amine if the compound was a secondary amine) and the alcohol moiety is converted to an aldehyde.
- Ammonia is distilled from the reaction mixture, which is already in a basic medium, and quantified by a neutralization reaction.
Possible selective determination of the four $\alpha$-hydroxylamines present in proteins:

- Serine
- Threonine
- $\beta$-Hydroxyglutamic acid
- Hydroxylysine

3. Karl-Fischer reagent

Mixture, dissolved in CH$_3$OH, of:

- I$_2$ : C$_6$H$_5$N : SO$_2$
  - 1 : 10 : 3

It is carried out in a methylic medium:

- $\text{N}_2\text{SO}_4 + \text{CH}_3\text{OH} \rightarrow \text{NHSO}_4\text{H}$
Lesson 8. Potentiometry, Electrogravimetry and Coulometry

1. Indicator electrodes: classification.
2. Glass membrane electrode: potentiometric measurement of pH.
3. Coulometric titrations.
4. Electrogravimetry.

**Indicator electrodes**

- **Metallic**
  - Inert redox
  - First kind
  - Second kind
  - Third kind

- **Membrane**
  - Non-crystalline
    - Glass
    - Liquid membrane
  - Crystalline
    - Monocrystal
    - Polycrystal

**Inert redox electrode**

Metallic electrode, good conductor, which responds to the redox potential of another system in which it only intervenes as physical carrier.

Materials such as Pt, Au, Pd and C can be used to monitor redox systems.

**First kind electrode**

Attackable metal electrode immersed in a solution of its own ions.

- The pure metal electrode is in direct equilibrium with its own cation in the solution.
- The electrode potential is a measure of the activity (concentration) of its ions in solution.

\[
E = E^{\circ} - \frac{0.059}{n} \log a_{\text{ion}} = E^{\circ} - 0.059 \log a_{\text{ion}}
\]

**Second kind electrode**

Attackable metal electrode immersed in a solution which - besides its own ions - contains an anion with which can form a relatively stable compound (sparingly soluble salt or stable complex).

\[
\text{Ag}^+ + e^- \rightarrow \text{Ag}^{0}, E^\circ = 0.792 \text{V}
\]

\[
\text{AgCl}_s = \text{Ag}^{0} + \text{Cl}^- \quad E^\circ_{\text{AgCl}} = 0.199 \text{V}
\]

\[
\text{AgCl}_s = \text{Ag}^{0} + \text{Cl}^- \quad E^\circ_{\text{AgCl}} = 0.199 \text{V}
\]

If the anion concentration is kept constant, then the electrode potential remains constant.

- Excellent reference electrodes!

![Image](image_url)
Electrodes of the second kind have displaced the use of NHE as reference electrode.

The ideal reference electrode has a potential that is:
- accurately known,
- constant,
- and completely insensitive to the composition of the analyte solution.

In addition, this electrode should be:
- rugged,
- easy to assemble, and
- should maintain a constant potential while passing minimal currents.

Problems with the Reference Electrode

- Blockage of the junction causes an increase in the electrodes’ impedance, which in turn makes the measurement more susceptible to noise pick-up. High impedances should be avoided where possible in electrochemical measurements.
- Blockage and/or contamination of the junction can result in a variable junction potential, which in turn causes a variability in electrode response. The junction potential results from a separation of charge due to the different mobility of anions and cations and can be as large as 20 mV.

Problems with the Ag/AgCl electrode can often be traced to the presence of soluble AgCl.

- AgCl is sparingly soluble in highly concentrated chloride solutions due to formation of the silver–chloride complex:
  \[
  \text{AgCl}_{\text{solid}} + \text{Cl}^- \rightleftharpoons \text{AgCl}_{\text{aq}}
  \]
- If the reference electrode is stored in water and solutions of low chloride activity, AgCl solid will form and lead to the junction blocking.
- The AgCl can decompose to Ag₂O which is a black/purple colored deposit.
- For this reason it is best to store the electrode in 3M KCl solution.
- Blockage of the junction can also take place due to precipitation of KCl.
- This problem can occur at low temperature and if the electrode is stored in air.
- For this reason the use of saturated KCl as the internal filling solution should be avoided. Better to use 3M KCl.
Second kind electrode

\[ \text{HgY}^{2-} + 2e^- \rightleftharpoons \text{Hg} + \text{Y}^{4-} \]

\[ E = 0.210 \, \text{V} - \frac{0.059 \log[	ext{HgY}^{2-}]}{2} \]

\[ K_{\text{HgY}} = 6.3 \times 10^{-22} \]

\[ E = K \times \frac{0.059}{2} \log[\text{Y}^{4-}] \]

They are responsive to the concentration of a cation that is not part of their constituents.

Third kind electrode

\[ \text{Hg}^{2+} / \text{HgY}^{2-} / \text{CaY}^{2-} / \text{Ca}^{2+} / \]

\[ E^* = 0.210 \, \text{V} - \frac{0.059 \log[	ext{HgY}^{2-}]}{2} \]

\[ \text{E}^* = 0.210 \, \text{V} - \frac{0.059 \log[	ext{Ca}^{2+}]}{2} \]

They are responsive to the concentration of a cation that is not part of their constituents.

Membrane indicator electrodes

- Non-crystalline
- Glass

Properties of membranes

The inherent sensitivity and selectivity of the membranes are due to:

- Minimal solubility
- Some electrical conductivity (small): migration of singly charged ions within the membrane.
- Selective reactivity with the analyte:
  - Ion exchange
  - Crystallization
  - Complexation
**Glass electrode**

\[ \text{S.C.E.} / [H^+] = a_1 / \text{GLASS MEMBRANE} / [H^+] = a_2, [Cl^-] = 1.0 \text{ M, AgCl\textsubscript{sat'd}/Ag} \]

External reference electrode

\[ E_{SCE} = E_1 = E_2 = E_{Ag/AgCl} \]

Boundary potential

**External reference solution**

**Internal reference solution**

**Schematic diagram of the structure of glass, which consists of an amorphous network of SiO\textsubscript{2} tetrahedra connected through their oxygen atoms.**

**Hygroscopicity:**

50 mg H\textsubscript{2}O/cm\textsuperscript{3} glass

108 \text{ \Omega} \text{ \Delta} Na\textsuperscript{+}

**Na\textsuperscript{+} provides conductivity**

**Hydration of the membrane**

\[ \text{H}^+ \text{ + Na}^+R^- \Leftrightarrow \text{Na}^+ \text{ + H}^+R^- \]

**Charge accumulation across the membrane: source of potential**

\[ \text{H}^+ \text{ + R}^- \Leftrightarrow \text{H}^+ \text{ + R}^- \]

**Reference electrodes potentials:**

\[ E_{SCE}, E_{Ag/AgCl} \]

**Liquid junction potential:**

\[ E_j \]

**Asymmetry potential:**

\[ E_{assy} \]

**Boundary potential:**

\[ E_b = E_1 - E_2 = 0.059 \log a_1 - 0.059 \log a_2 = 0.059 \log a_1 + L' = -0.059 \text{ pH} \]

**The pH is determined by the boundary potential**

developed on both sides of the glass membrane.

**Corning 0015:** 22% Na\textsubscript{2}O; 6% CaO; 72% SiO\textsubscript{2}
E_{ind(glass electrode)} = E_{Ag/AgCl} + E_{wasy} + E_0

E_{ind(glass electrode)} = E_{Ag/AgCl} + E_{sat} + L' + 0.059 \log a_1

E_{ind(glass electrode)} = L + 0.059 \log a_1

E_{ind} = L - 0.059 \text{pH}

\Delta E_{cell} = E_{ind} - E_{SCE(Ext'l Ref.)} = L - 0.059 \text{pH} - M = N - 0.059 \text{pH}

H^+ + R^- + B^+ \xleftarrow{\text{Trans}} B^+ + R^- + H^+

K = \frac{a_i b_i}{a_i b_i}

b_i = b_i \cdot K

\frac{a_i}{a_i} = b_i

When $a_H$ is very small, the glass electrode senses other cations. The solution appears more acidic than it really is.
In very acid solutions, the activity of water is less than unity (it solvates the proton). The \( a_w \) is decreased, and the pH reading is increased. High concentrations of dissolved salts or adding a nonaqueous solvent does the same.

### Glass Electrode

- **Glass electrode:** 
  \[ E = \text{L} + 0.059 \log a_{w} \]

- **In general, for any ion selective electrode:** 
  \[ E = \text{const} + \frac{0.059}{z} \log a_i \]

### In the presence of interfering ions:

\[ E = \text{const} + \frac{0.059}{z} \log \left( a_i + K_{i,j} a_j^{z_a} + K_{i,j} a_j^{z_b} + \ldots \right) \]

Where:
- \( K_{i,j} \) is the selectivity coefficient for the determination of \( i \) in the presence of interfering \( j \)
- \( z_i \) is the charge of the principal ion \( i \)
- \( a_i, a_j \) are charges of interfering ions \( j, k \)

### Method A

A selective glass membrane electrode for \( K^+ \) ion immersed in a solution with \( a_{w} = 1.05 \times 10^{-4} \) M gave a potential reading of 0.528 V. That same electrode immersed in a solution composed of \( a_{w} = 2.50 \times 10^{-4} \) M and \( a_{w} = 1.70 \times 10^{-4} \) M showed a potential of 0.602 V. Calculate the selectivity coefficient \( K_{K,Li} \) for this electrode.

\[ E = \text{const} + 0.059 \log a_{w} \]

\[ 0.528 \text{ V} = \text{const} + 0.059 \log (1.05 \times 10^{-4} \text{ M}) \]

\[ \text{const} = 0.528 \text{ V} - 0.059 \log (1.05 \times 10^{-4}) = 0.762 \text{ V} \]

Once you know the value of const., we can solve for the value of the selectivity coefficient:

\[ 0.602 \text{ V} = 0.762 \text{ V} + 0.059 \log (2.5 \times 10^{-4} + K_{K,Li} \times 1.70 \times 10^{-4}) \]

\[ \Rightarrow K_{K,Li} = 10 \]

### Method B: Fixed Interference Calibration Curve

The calibration curve for \( A \) is prepared in the presence of fixed activity of interfering ion. The intersection is where the electrode responds equally to both ions.

### Electroanalytical Methods

Two main electroanalytical methods based on electrolytic oxidation or reduction of an analyte for sufficient period to assure quantitative conversion to new oxidation state:

1. **Constant-Current Coulometry**
2. **Electrogravimetry**

In the first, quantity of electricity needed to complete the electrolysis serves as measure of amount of analyte present. Total charge, \( Q \), in coulombs passed during electrolysis is related, according to Faraday’s law, to the absolute amount of analyte:

\[ Q = n F N \]

Where:
- \( n \) is number of mol of analyte
- \( F \) is Faraday’s constant = 96485 C mol\(^{-1}\)
- \( N \) is number of mol of analyte
- \( \text{Coulomb} = C \cdot \text{Ampere} \cdot \text{second} = A \cdot s \)

For electrogravimetry, product of electrolysis is weighed as a deposit on one of the electrodes.
The current is kept constant until an indicator signals completion of the analytical reaction. The quantity of electricity required to attain the end point is calculated from the magnitude of the current and the time of its passage. Controlled-current coulometry, also known as coulometric titrimetry.

When called coulometric titration, electrons serve as the titrant.

Controlled-current coulometry has two advantages over controlled-potential coulometry:

First, using a constant current leads to more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled current coulometry is less than 10 min, as opposed to approximately 30-60 min for controlled-potential coulometry.

Second, with a constant current the total charge is simply the product of current and time. A method for integrating the current-time curve, therefore, is not necessary.

Other necessary instrumental components for controlled-current coulometry is an accurate clock (a digital clock provides accurate measurement of time, with errors of ±0.1 ms) for measuring the electrolysis time, \( t_e \), and a switch for starting and stopping the electrolysis.

In an electrogravimetric analysis, the analyte is quantitatively deposited as a solid on the cathode or anode.

- The mass of the electrode directly measures the amount of analyte.
- Not always practical, because numerous materials can be reduced or oxidized and still not plated out on an electrode.

In practice, there may be other electroactive species that interfere by co-deposition with the desired analyte.

- Even the solvent (water) is electroactive, since it decomposes to \( H_2 + \frac{1}{2} O_2 \) at a sufficiently high voltage.
- Although these gases are liberated from the solution, their presence at the electrode surface interferes with deposition of solids.
- Because of these complications, control of the electrode potential is an important feature of a successful electrogravimetric analysis.

Some metals can be deposited as metal complexes e.g., Ag, Cd, Au.

Some metals are deposited as oxides on the anode e.g., Pb\(^{2+}\) as PbO\(_2\) and Mn\(^{2+}\) as MnO\(_2\)
Lesson 9: Photometric endpoint indication

2. Deduction of Beer’s Law.
4. Titration with photometric indication.

Analytical chemistry is the science that identifies the components of a sample (qualitative analysis) and which determines the relative amounts of each of them (quantitative analysis). Usually, requires a prior separation of the analyte of interest.

Classical methods: wet chemistry (titration, gravimetry and systematic qualitative analysis)

Instrumental Methods: exploit the physical properties of the analyte to obtain both qualitative and quantitative information

Spectroscopy: studies the interaction of the electrical field component of electromagnetic radiation with matter by means of phenomena such as absorption, emission and scattering of light.
Beer’s law applies to a medium containing more than one kind of absorbing species. Provided there is no interaction among the various species, the total absorbance for a multicomponent system is given by:

\[ A_{\text{total}} = A_1 + A_2 + \ldots + A_n \]

\[ = b_c_1 \varepsilon_c_1 + b_c_2 \varepsilon_c_2 + \ldots + b_c_n \varepsilon_c_n \]

where, the subscripts refer to absorbing components 1, 2, ..., n.

The molar absorptivities of compounds X and Y were measured with pure samples of each.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( X )</th>
<th>( Y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>272</td>
<td>16440</td>
<td>3870</td>
</tr>
<tr>
<td>327</td>
<td>3990</td>
<td>6420</td>
</tr>
</tbody>
</table>

A mixture of compounds X and Y in a 1.000 cm cell has an absorbance of 0.957 at 272 nm and 0.559 at 327 nm. Find the concentrations of X and Y in the mixture.
A (analyte) + T (titrant) → P (product)

\[ [Y] \epsilon + [CuY] \epsilon \rightarrow [Cu] \epsilon \]

\[ \text{Abs} = \varepsilon_{450}^{\text{Cu}^{2+}} [\text{Cu}^{2+}] + \varepsilon_{450}^{\text{Y}^4-} [\text{Y}^4-] + \varepsilon_{450}^{\text{CuY}^2-} [\text{CuY}^2-] \]

\begin{align*}
\varepsilon_{450}^{\text{Cu}^{2+}} & = 500 \text{ Lmol}^{-1} \text{ cm}^{-1} \\
\varepsilon_{450}^{\text{Y}^4-} & = 100 \text{ Lmol}^{-1} \text{ cm}^{-1} \\
\varepsilon_{450}^{\text{CuY}^2-} & = 50 \text{ Lmol}^{-1} \text{ cm}^{-1} 
\end{align*}